MIGRATION OF ADDITIVES FROM THERMOPLASTIC POLYMERS

by

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Summary

A homologous series of ultra-violet stabilisers containing 2-hydroxybenzophenone(HBP) moiety as a uv absorbing chromophore with varying alkyl chain lengths and sizes were prepared by known chemical synthesis. The strong absorbance of the HBP chromophore was utilized to evaluate the concentration of these stabilisers in low density polyethylene films and in relevant solvents by ultra-violet/visible spectroscopy. Intrinsic diffusion coefficients, equilibrium solubilities, volatilities from LDPE films and volatility of pure stabilisers were studied over a temperature range of 5-100°C. The effects of structure, molecular weight and temperature on the above parameters were investigated and the results were analysed on the basis of theoretical models published in the literature.

It has been found that an increase in alkyl chain lengths does not change the diffusion coefficients to a significant level, while attachment of polar or branched alkyl groups change their value considerably. An Arrhenius type of relationship for the temperature dependence of diffusion coefficients seems to be valid only for a narrow temperature range, and therefore extrapolation of data from one temperature to another leads to a considerable error. The evidence showed that increase in additive solubility in the polymer is favoured by lower heat of fusions and melting points of additives. This implies the validity of simple regular solution theory to provide an adequate basis for understanding the solubility of additives in polymers.

The volatility of stabilisers from low density polyethylene films showed that time-dependent loss rate of an additive from a polymer can be expressed in terms of a first-order kinetic equation. In addition, the rate of loss of stabilisers were discussed in relation to its diffusion, solubility and volatility and found that all these factors may contribute to the additive loss, although one may be a rate determining factor.

Stabiliser migration from LDPE into various solvents and food simulants were studied at temperatures 5, 23, 40 and 70°C; from the plots of rate of migration verses square root time, characteristic diffusion coefficients were obtained by using the solution of Fick's diffusion equations. It was shown that the rate of migration depends primarily on partition coefficients between solvent and the polymer of the additive and also on the swelling action of the contacting media. Characteristic diffusion coefficients were found to approach to intrinsic values in non swelling solvents, whereas in the case of highly swollen polymer samples, the former may be orders of magnitude greater than the latter.

KEY WORDS:- Diffusion Coefficients, Equilibrium Solubility,
Volatilisation, Migration, Food-simulants

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To my parents and my wife Dilina

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List of Abbreviations

LDPE	Low Density Polyethylene
HDPE	High Density Polyethylene
PP	Polypropylene
HBP	hydroxy benzophenone
HOBP	hydroxy octoxybenzophenone
BHT	buta hydroxytoluene
uv/vis	ultra-violet/visible
I.D.C.	Intrinsic Diffusion Coefficient
C.D.C.	Characteristic Diffusion Coefficient
m. pt	Melting point

List of Chemical Names

Plastanox 2246	2,2'-Methylene-bis(4-methyl-6-butylphenol
Topanol CA	1,1,3-Tris(2'-methyl-4'-hydroxy-5'-t-butyl-phenyl)butane
Irganox 1010	pentaerythrityl-tetrakis(3,5-di-t-butyl-4-hydroxyphenylpropinate)
Cyasorb UV531	2-hydroxy-4-methoxybenzopenone

CHAPTER ONE

INTRODUCTION AND LITERATURE SURVEY

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GENERAL INTRODUCTION AND LITERATURE SURVEY

1.1 Introduction

The versatility, cheapness and ease of processing of polymeric materials has led to their extensive use in a vast array of industrial and domestic applications. Among these polymeric meterials, polyolefins are used extensively in food packaging and in domestic appliances. This fact is clearly apparent from the large consumption of polyolefins in various household applications by Western European countries during the past three years (Table 1.1)[1].

LDPE	1985	1986	1987
Blow moulded products	96	91	92
Films, sheeting	2858	3240	3420
Injection moulded prod.	256	275	280
Others	383	797	830
Total	3593	4403	4622

(Table 1.1 continued)

HDPE	1985	1986	1987
Blow moulded products	757	841	942
Films and sheeting	247	273	312
Injection moulded products	493	531	602
Others	322	374	419
Total	1819	2019	2275

PP	1985	1986	1987
Films	284	342	396
Moulded & extruded prod.	1070	1236	1395
Spun and film fibers	684	705	770
Total	2038	2283	2561

Table 1.1. Consumption of polyolefins in Western European countries[1]. (in 1000 metric tons)

Of the three types of polyolefins, low density polyethylene (LDPE) is the more popular choice for producing films, sheets and household products and majority of these are being used for food packaging and this trend is ever increasing[1].

Polyolefins are susceptible to oxidative degradation, primarily during processing and subsequently in exposure to uv light[2]. Furthermore, the desired processing conditions and end requirements of the product cannot be achieved by using the pure polymer alone. Therefore polymers need to be modified to an acceptable requirements and this can be resolved in two ways.

(a) By modification of the polymer structure, so that the polymer is more resistant to degradation[3], eg. from polyethylene to polytetrafluoro ethylene or poly-p-phenylene,

or

(b) by incorporation of chemical additives[2,4] that inhibit the degradation process and give a satisfactory end product.

The first approach is not, in general, a workable solution due to cost constraints. In addition, the differences in mechanical properties and processing characteristics of modified polymers limit the applicability of this method. Therefore, the second approach is widely adopted in commercial practice as a means of achieving stabilisation and the required mechanical properties.

At present, a variety of low molecular weigh additives are being used in the processing of polymers[2,4]. These are mainly, melt stabilisers, light stabilisers, antioxidants, uv absorbers, lubricants and plasticisers.

These low molecular additives often possess high mobility in polymeric materials and are readily lost from the polymer products[5,6]. These losses are important, since they determine the amount of additive retained in the polymer during its life span and consequently its utility in its desired function. For example, Hawkins et al.[7], Temchin et al.[8], Bair[9] and more recently Moisan and Lever[10] have shown that typical stabilising additives are lost from polyethylene films, at rates which are significant relative to the lifetime of the polymer. Similar conclusion have been observed for loss of phenolic and amine antioxidants from rubbers[11,12]. In addition, if the product is destined for use as a packaging material for foodstuffs, although the polymers are generally considered to be inert, polymer additives may have the potential to migrate into contacting foodstuffs and will contaminate them, thus possibly causing tainting or toxicological problem and health hazards[13,14]. Therefore, in either case loss of additive from polymers causes undesired effects and this has been recognised over the years and led to the discovery of additives with minimal loss[2]. There are now strict legal controls[13,14,15] governing the limits of migration levels of additives into foodstuffs. The aim of these is to ensure that no harmful additives migrate into foodstuffs thus preventing possible health risks to the consumers.

Although the loss of additives from polymers has been investigated over the years, the mechanistic understanding of additive loss has been studied only recently[6]. It has been proposed that the loss of an additive is controlled either by the rate of its loss from the surface, by its rate of diffusion through the bulk to reach the surface or by a combination of both processes. The rate of loss of an additive from a polymer surface can be predicted from volatility (or solvent solubility, if the polymer is in contact with a solvent) of the pure additive and its solubility in the polymer. The rate of migration of the additive to the surface, on the other hand, is controlled by its rate of diffusion in the bulk polymer[6]. Therefore, this theory suggests, that additive loss from a polymer depends upon additive volatility, diffusion and solubility in polymer and in contacting media[6]. Most of the previous studies on loss mechanisms have been concerned with only one or two of the above factors. For example, in 1961, Angert et al.[12] pointed out that rate of loss of an additive and its concentration near the polymer surface might both be expected to depend on the diffusion rate of the additive and on its volatility. Their studies concluded that volatility was the most important factor determining the rate of additive loss. On the other hand, several workers[16,17] interpreted the loss of additive as a diffusion controlled process, ignoring the possible effects of solubility and volatility. By contrast, some other workers[18,19,20] correlated the loss of additive from polymers with the volatilities of the pure compound without considering the possible effects of diffusion and solubility, while others[[21] considered compatibility as the important factor which determine additive loss. More recently, Moisan[10], studied the outdoor ageing of low density polyethylene and found an emperical relationship between the induction time of LDPE films and the ratio of (solubility^2 /diffusion) for a series of phenolic antioxidants. Billingham et al.[6] used available literature data to predict the loss times of additives from polymers in terms of solubility, volatility and diffusivity.

There are several studies concerned with additive solubility, volatility, diffusivity and extractability [5]. These quantities were measured at relatively high temperatures and due to the different experimental procedures, large discrepancies were observed between the values obtain by different workers[5,6]. In addition, there are no instances in the literature, where these parameters were measured together using the same compound by the same worker. For example, Westlake and Johnson[22,23] have measured the solubility of 2,4-dihydroxy and 2-hydroxy-4-octoxy benzophenone in low density polyethylene and polypropylene over a narrow temperature range and also determine the appropriate diffusion coefficients. The same molecules have been studied by Cicchetti and co-workers[24,25], whose values for diffusion coefficients vary by several factors from those of Westlake and Johnson[22,23]. The volatilities of these stabilisers were not studied by either of the groups, although Schmitt and Hirt[26] quoted a value of 6.2×10^{-10} cm^2/sec for the volatility of 2,2'-dihydroxy-4-methoxy benzophenone at 25°C. Roe et al.[27] believed that the solubility of phenolic antioxidant in polyethylene can be estimated from its measured solubilities in low molecular hydrocarbon solvents and thereby applying regular solution theory. Allara and White[28] reached similar conclusions about the solubility of copper carboxylate in hydrocarbons. Recent studies by Billingham and co-workers[29] showed that regular solution theory cannot be applied to estimate the solubilities of phenolic additives in polymers from their measured solubilities in alkane solvents. This is evident in the values obtained for the solubility of high molecular weight phenol(pentaerythrityl-tetrakis(3,5-di-t-butyl-4-hydroxyphenylpropionate), Irganox 1010), which is 0.245w/w at 70°C compared to the 0.07% w/w obtained by Roe and co-workers[27]. Furthermore, Billingham and Calvert[6] in their mathematical model for additive loss have pointed out that it is unreliable to extrapolate high temperature data to room temperature with any certainty. They further emphasised the necessity of a proper study of these quantities by the same worker to obtain a reliable data base for additive loss mechanism. Unfortunately, no studies have been reported in which the same worker has studied the above parameters in the same system at low temperatures.

Migration tests have been designed to measure the additive loss from food packaging materials in order to apply legal limits for the amount of additive loss. Since food materials are generally too complex in nature, for analytical purposes, these tests are often being carried out in simulants and solvents. It is expected that, the study of the migration of additives into those simulants would give comparable results to that of foodstuffs. In reality, this is far from simple and there are inconsistencies about the types of simulants and the conditions to be used[30,31]. For instance, it was shown[32] that water is a poor simulant for milk, since it considerably underestimates the likely migration level, whilst fatty simulants overestimate the migration[33]. Solvents such as heptane are totally unsuitable as replacements for fatty foods as they cause unrealistically rapid migration[34]. Most migration tests have been carried out using radio-active additives and this is a costly operation. Simpler analytical methods are needed. Furthermore, it is of paramount importance to understand the additive loss behaviour at low temperatures, which may be completely different from that at high temperature. Furthermore, some solvents may swell the polymer, so that the polymer matrix may be modified due to the solvent uptake and therefore the bulk diffusion coefficient may be completely different from the unswollen polymer. Though, some data are available in the literature, showing that there is a significant difference[34] in properties between the swollen polymer and dry polymer, there is virtually no data available in literature where both parameters were measured together by the same worker.

The design of additives to minimise loss has been given a great deal of attention over the last few years[6]. Some workers have suggested that the binding of additives to the polymer matrix is one probable solution to minimise additive loss[35]. Though, this seems to have an interesting prospect, the cost factor needs to be carefully considered. On the other hand, design of an additive to minimise loss requires more fundamental informations about additive structure to its loss.

1.2 Diffusion in Polymers

Diffusion of molecules in polymers is a phenomenon which deals with the mobility of additives within the polymer matrix. Therefore it plays an important role in both evaporation and leaching of additives from polymers. By recognising this, diffusion of high and low molecular weight materials in polymers has received great attention over the years. In this section some of the important findings in diffusion of high molecular weight materials will be summarised.

The basic mathematical theory of the diffusion process has been published by Crank[36] and it deals with the mathematical description of general diffusion processes in terms of the differential equations. The diffusion of small molecules such as gases, water and solvents in polymers has been studied in great detail and is extensively reviewed[37,38]. More recently Luston[5], Billingham and Calvert[6], Moisan[39] and Flyn[40] have reviewed the existing data available on diffusion of stabilising additives in polymers together with providing some new data.

1.2.1 Mathematical Description of Diffusion

The analogy between heat transfer and the diffusion process was recognized by Fick, who first put diffusion in a quantitative manner by adopting the mathematical equations of heat conduction derived by Fourier[41]. According to this theory, rate of mass transfer per unit area, F, of diffusing substances in an isotropic media is proportional to the concentration gradient measured normal to the section:

$$F = -D\,\partial C/\partial x \qquad 1.1$$

where D is called the diffusion coefficient, C is the concentration and x is the space co-ordinate measured normal to the section. Equation 1.1 is known as Fick's first law and can only be applied to diffusion in the steady state conditions where the concentration does not vary with time.

Fick's second law of diffusion describes the non-steady state and it has several forms; for one-dimensional diffusion it can be written as:

$$\partial C/\partial t = D\,\partial^2 C/\partial x^2 \qquad 1.2$$

or for three dimensional diffusion:

$$\partial C/\partial t = D\left\{\partial^2 C/\partial x^2 + \partial^2 C/\partial y^2 + \partial^2 C/\partial z^2\right\} \qquad 1.3$$

Any problem concerning concentration-independent diffusion can be tackled by solving these differential equations with an appropriate boundary conditions. Solution of these equations for different boundary conditions, as well as the mathematics of concentration-dependent diffusion, has been given by Crank[36]. Systems whose diffusion characteristics can be described by the above equations are said to follow "Fickian" diffusion. The concentration of stabilisers in polymers are usually very low and it is expected, and found in practice, that the diffusion of polymer stabilisers is Fickian and consequently the diffusion coefficient is independent of concentration[6].

The temperature-dependence of the diffusion coefficient (D) can be expressed by an Arrhenius type equation:

$$D = D_o \exp(-E_d/RT) \qquad 1.4$$

Where E_d is the activation energy and D_o is known as the pre-exponential factor or the frequency factor. For a "Fickian" diffusion, E_d is constant over a wide range of temperatures and the plot of log D versus (1/T) is linear[5].

1.2.2 Diffusion of High Molecular Weight Additives in Polymers

The theoretical and experimental aspects of diffusion of high molecular weight additives has been reviewed [5,6,39,40]. The diffusion coefficients were found to depend on temperature, polymer melting region, glass transition temperature, morphology, crystallinity, orientation, structure and diffusant structure, molecular weight, size and melting point.

The dependence of the above factors on diffusion is discussed in the following sections.

1.2.3 Temperature Dependence of Diffusion

The temperature dependence of the diffusion coefficient and the relation between penetrant size and activation energy of diffusion are explained by free-volume theories [43]. These free-volume theories are based on the ability of the polymer to create diffusion channels or holes through which penetrant molecule can move from one site to another. According to these theories, the activation energy (E_d), depends on properties of the polymer and its proportional to the molar volume of the diffusant and pre exponential factor (D_o) is usually predicted to depend upon the square of the diffusant diameter. The low molecular penetrants have smaller molecule sizes than the average "hole" size in the polymer, therefore, the diffusion occurs by local activated jumps from one hole to another unoccupied hole and the activation energy involved takes into account a few monomer segments near the penetrant. On the other hand, when the size of the penetrant molecule is larger than the average hole size, a much larger number of polymer segments must rearrange to allow the penetrant to pass through. Therefore, the activation energy will be dependent on temperature for large penetrant molecules, while it is constant over a wide range of temperature for small penetrants[42]. The dependence of the diffusion coefficient on temperature, which increases with increasing temperature, is also consistent with the "hole" theory, since increasing temperature will increase the segmental mobility of the polymer, thus creating more holes available for the penetrant.

A new free volume theory was recently developed to predict the temperature, molecular weight and concentration dependence of mutual diffusion coefficients in polymer-solvent systems[43]. However, it was found that the predicted values were significantly higher than the experimentally determined values[44]. Therefore, as a result of this shortcomming, modification of the theory have been introduced[45]. In addition, a theory based on the statistical thermodynamics of chain packing for diffusion of simple penetrants in semi-crystalline polymers[46] and another theory predicting activation energies of diffusion directly from the temperature of diffusion for gases in elastomers has recently been proposed[47].

The influence of melting region of polymer for the diffusion of gases and alkane solvents in natural rubber [48] and polyethylene[49,50] was studied. It was shown, that there is a discontinuity of Arrhenius plots of diffusion coefficients in the melting region of the polymer. Similar, discontinuity of Arrhenius plots was also shown to occur at the glass transition temperature of polymers[51]. Therefore, these evidence suggests that temperature dependent diffusion follows an Arrhenius type equation, provided that there is no phase transition in the polymer. However, Moisan[39], has pointed out that, if there is a phase transition in the diffusant, the Arrhenius plots will be discontinuous at the melting point of the diffusant. As a result of this, two different activation energies were found above and below the melting point of the diffusant, but no comment about the significance of this change in relation to activation energy of the diffusion process was made.

1.2.4 Influence of the Polymer Structure on Diffusion in Polymers

Diffusion of stabilisers in polymers involves the migration of individual large molecules through a tangled mass of polymer chains and therefore it involves a co-operative movement of the polymer chains. Consequently, factors which reduces the ability of the polymer chain to move may be expected to decrease the diffusion coefficient. Therefore, in general, diffusion in polymers decreases with increasing the number of polar and methyl groups attached to the polymer backbone[51,52]. Methyl groups impair the flexibility of the chain resulting in lower diffusion coefficients and greater activation energy of the diffusion process. Similarly, polar side groups cause an increase in the cohesive energy of the polymer which manifests itself by an increase in the activation energy of diffusion. Unsaturated bonds pendent to the polymer chain have a similar lowering effect on diffusivity while unsaturation in the backbone of the polymer has an opposite effect[53,54]

1.2.5 Effect of Crystallinity and Morphology on Diffusion in Crystalline Polymers

It has been shown[55] that the diffusion of gases in a series of polyethylene films varied with crystallinity, x as:

$$D = D_o(1-x)^n \qquad 1.5$$

The value (n) was found to be 1.25 for branched polyethylene and 1.88 for linear polyethylene. This was also shown to be the case for diffusion of stabilisers in polyethylene, for example, Moisan[39] has shown that the diffusion coefficient of 2,2'-methylene-bis-(4-methyl-6-t-butyl phenol) (Plastnox 2246) decreased steadily with increasing density of a series of low density polyethylene samples, implying a decrease in diffusion coefficient with increasing crystallinity. However, the same worker observed that, except at lower temperatures, the diffusion of Irganox. 1076(hindered phenol) is higher in an annealed polymer (high crystallinity and density) than in a quenched(low crystallinity and density) sample. Furthermore, Lowell and Mccrum[56] showed that in a series of samples crystallised at different cooling rates diffusivity decreases as density (crystallinity) increases. However, if all the samples are annealed to the same density (same crystallinity) their diffusivities will increase and the samples which had the higher diffusion before annealing have higher diffusivities after annealing. Similar observation of irregularity between diffusion and crystallinity were also reported[57]. For example, Klein and Brisco[57] found that diffusion of both dodecyl dodecanoate and docosyl docosanoate was found to be slower in rapidly cooled linear polyethylene than slowly cooled samples; a more crystalline material. In other words all these observations show that not only the crystallinity but also the polymer morphology plays an important role in diffusion. Influence of both these factors on diffusion in polymers has been theoretically presented by Peterlin[58]. Crystalline homopolymers were described as a two component system with amorphous and crystalline regions and concluded that the diffusion of penetrant of low molecular weights proceeds almost exclusively through the amorphous component of the semicrystalline polymer. By considering the diffusion contribution of the crystalline phase, the effective diffusion coefficient(D), is given by $D = D_a\Psi/\beta$ where D_a is the diffusion coefficient for the completely amorphous system, Ψ is the geometric impedance factor accounting for the reduction in diffusion due to the necessity of the molecules to bypass the crystallites and move through the amorphous region, and β is the blocking factor[58]. The factor Ψ/β describes the reduction of permeability below that of a homogeneous medium with diffusion coefficient D_a. It is caused by the distortion of the lines of diffusion flow as a result of the presence of impermeable crystal lamellae dispersed throughout the polymer solid. Michaels et al.[59] have developed a similar expression for the modification of the diffusion coefficient for semi-crystalline polymers.

The crystallinity of a polymer not only depends on cooling rates of the polymer melt but also on its molecular orientations as well as on its thermal and mechanical history. The rapidly cooled samples will yield large number of disordered crystals whereas slowly cooled samples give large highly ordered crystals. Annealing also results in an increase in the degree of crystallinity and a highly ordered crystallites. In the light of this, a new theoretical model for the diffusion of long molecules in semicrystalline polymers was put forward[60] and recently this was experimently confirmed[57].

The effect of mechanical history of the polymer on diffusion was demonstrated by Preston and Pal[61], who observed that there is a reduction in the rate of dye absorption in viscose rayons with an increasing elongation of the fibres. Similar observations in nylon were found and shown that the diffusion coefficient decreases with increasing draw ratio of the polymer[62,63]. In addition, it was found[39], the rate of diffusion of Irgnox 1076 parallel to the orientation direction in low density polyethylene samples, fell with increase in orientation, whereas the rate of diffusion perpendicular to the orientation direction increases.

1.2.6 Influence of the Diffusant Agent on Diffusion

The properties and the structure of the diffusant can affect the diffusion rates in many ways. The effect of molecular weight(M) on diffusion of phenolic antioxidants in LDPE was shown in the following mathematical form[27]:

$$D = (3.46\times10^{-5})\ M^{-1.33} \qquad 1.6$$

In spite of above assertion, this relationship seems to be valid only for a given type of polymer and the diffusant. Therefore, a more general equation can be written as follows:

$$D = K \times M^{-\alpha} \qquad 1.7$$

Where K and α are constants and depend on the polymer, its properties and the properties of the diffusant. According to literature, equation 1.7 holds for diffusion of esters of 3,3'-thiodipropionic acid and 2-hydroxy-4-n-alkoxybenzophenones in isotactic polyethylene[24] and in some 2-hydroxy-4-n-alkoxybenzophenones in PP, HDPE and LDPE[25]. The relationship between diffusion coefficients of paraffins was investigated[50,64-68] and found that it decreases with increasing length of the molecule. Furthermore, diffusion rate is affected not only by the length and molecular weight but also by its steric structure. Cyclisation and branching of the diffusant reduces the diffusion coefficient and therefore attempts were made to correlate the diffusion coefficient to the diffusant molecular volume[69-73]. Park[72,73] expressed the dependence of the diffusion coefficient on molar volume of halogenated methane to the following equation:

$$D = K\exp(\beta V_M) \qquad 1.8$$

where K and β are constants and V_M is the molar volume of the diffusant. For halogenated paraffins, the correlation given in the form of:

$$D = K\exp(AV_M + Bd) \qquad 1.9$$

Where d is the molecular diameter and A, B, are constants.

The polar properties of the diffusant reduces the diffusion due to inter molecular attractions. These intermolecular attractions create a resistance to seperate individual molecules and consequently increases the activation energy of the diffusion[54].

1.2.7 Experimental Evaluation of Diffusion Coefficients

Most of the experimental work in the literature on diffusion of high molecular weight additives have generally been carried out with polymer stabilisers. The most common experimental technique used in these studies is the radio-tracing technique. In this context, radioactively labelled (^{14}C isotope) compounds are allowed to diffuse into one side of a polymer disc and either the increase in the counting rate of particles is monitored on the other side by means of a Geiger-Muller tube [22,23,74-79] or thin slices from the disc are cut on a lathe and the radioactivity of the slice is measured with a liquid scintillator[24,25]. The solution of the Fick's second law equation with appropriate boundary conditions yields the diffusion coefficients while the solubilities of lablled additives can also be evaluated from the equilibrium counting. In principle this method is sufficiently sensitive to allow measurements with a precision of ±10% at additive concentrations of 0.1%. However in practice, results from different workers in the same systems were found to vary by factor of two or three. The drawback of this method is the necessity to synthesise the required stabilisers involving the use of radio-isotopes, which can be costly. Moreover, the handling of these radio active chemicals can be problematic. Spectroscopic methods have also been used to measure diffusion coefficients. For example Klein and Brisco[57] measured the concentration profiles for diffusion of esters by means of infra-red spectroscopy and Andress and Rohl[78] applied a similar method to phenolics using uv spectroscopy.

Roe et al.[27] obtain the concentration profiles by using stack of polymer films, embedded in between the additive source. The concentration of these individual films were made by measuring the autoxidation induction periods. Similar stack method employed by Moisan[79,80] who used uv and infra-red spectroscopy to monitor the diffusion of phenolics and thiodipropionate esters.

Recently more sophisticated experimental techniques have been applied to measure diffusion coefficients of low molecular weight additives. Krassowski[81] used neutron activation analysis followed by autoradiography to show inhomogenity of pigments in polystyrene and Joks[82,83] used a similar approach to monitor diffusion of water in polyesters. Rothwell[84] have used nmr imaging to monitor penetration of epoxy resins and Berliner et al.[85] used esr imaging to monitor permeation of liquids in polystyrene and polycarbonate. Allara and White[28] used Rutherford back scattering spectroscopy to monitor diffusion of copper carboxylates in polyethylene and Mills[86] used same technique to investigate the diffusion of chlorine-containing diffusants in poly(methyl methacrylate). Unfortunately non of these methods has been applied to diffusion of polymer stabilisers in spite of the fact that they may be potentially applicable. Billingham and Calvert[87] have shown that the diffusion profiles of uv absorbers in polymers can be measured by ultra-violet microscopy.

This has great advantages, since the magnifying power of the UV microscope allows the concentration profilies of the diffusion to be defined in small diffusion distances. The shortcoming is that this method can apply only to uv absorbing classes of stabilisers.

1.3 Solubility of Additives in Polymers

Solubility of additives in polymers is an important phenomenon since it determines the amount of additive present in the polymer as a homogeneous equilibrium solution. Though the permeability of gases in polymers, which is the product of the diffusion coefficient and the solubility has been extensively studied[37,88], less is known about the solubility of stabilisers in polymers. In this study we are mainly concerned with the extraction of additives by foodstuffs from the polymer packaging materials, and in the absence of swelling, the extraction is principally determined by the partition coefficient of the additive defined as the ratio of the solubility of an additive in the polymer to its solubility in the contacting media. It has also been shown[89,90] that the partition coefficient plays an important role in the loss of a drug through plastic capsules which are designed to control the drug release to necessary requirements.

1.3.1 Theories of Solubility

The solubility of a crystalline additive in a polymer matrix is defined as the concentration of the additive in equilibrium with the polymer at a given temperature and pressure. Therefore, the solubility depends both upon the interactions of the additive with the polymer and upon the physical state of the pure additive. This implies that various crystal forms of the additive can have different solubilities and an amorphous additive can have a totally different solubility from its crystalline form. It is now established[28,91] that soluble additives dissolve only in the amorphous region of polyolefins so that measured solubilities require correction for crystallinity.

1.3.2 Mathematical Analysis of Solubility

The method used for analysing the thermodynamics of solution has been the use of regular solution theory and this was first applied to polymers by Gee[92] and latter by Roe and co-workers[27]. Furthermore Billingham and co-workers[29] have recently reviewed the application of this regular solution theory to polymers together with new experimental details. The following sections summarises this theory.

The solubility of a crystalline additive in contact with a polymer surface is determined by the condition that the (negative) free energy of mixing of liquid additive at the required temperature is equal to the (positive) free energy necessary to convert the crystalline additive into liquid at that temperature[92]. The free energy of fusion $(\Delta G_F)$of a crystalline solid at given temperature T is given by:

$$\Delta G_F = \Delta H_F - T\Delta S_F \qquad 1.10$$

and since $\Delta S_F = \Delta H_F / T_M$, where T_M is the melting point of the crystalline additive, it follows that,

$$\Delta G_F = \Delta H_F(1 - T/T_M) \qquad 1.11$$

ΔH_F is the heat of fusion of the crystalline additive.

The Flory-Huggins theory[93] of mixing of liquids with polymers suggests that the partial molar free energy of mixing(ΔG_M) can be related to the volume fractions of liquid and polymer by the following expression:

$$\Delta G_M = RT[\ln \varnothing_1 - (1 - V_1/V_2)\varnothing_2 + \chi \varnothing_2^2] \qquad 1.12$$

where V_1 and V_2 are the molar volumes of additive and polymer respectively and χ is the solute-solvent interaction parameter. The first two terms in equation

1.12 represent the geometric entropy of mixing, arising because the mixture is more disordered than the individual components. The third term χ represents the non-ideality of mixing due to interactions between the components. The definition of solubility requires that $\Delta G_F = \Delta G_M$, setting $\Phi_2 = 1$ for the very low solubility of additives in polymers and it can be written as;

$$-\ln \varnothing = \Delta H_F/R \; [1/T - 1/T_m] + [1 - V_1/V_2] + \chi \qquad 1.13$$

The temperature dependence of solubility can be predicted from the heat of fusion of the additive as contained in the first term of the equation 1.13, if χ is temperature independent.

For the case of an additive which is above its melting point, the equilibrium condition is defined by the condition that ΔG_F in equation 1.11 is equal to zero, since the energy of fusion ΔH_F vanishes. Therefore, setting $\Phi_2 = 1$, the equation 1.12 becomes

$$-\ln \varnothing = [1 - V_1/V_2] + \chi \qquad 1.14$$

This suggests that if χ is temperature independent, solubility is constant above the melting point of the additive or in other words solubility is independent of temperature.

Since the molar volumes of polymers are very high the term $(1-V_1/V_2)$ in equation 1.13 is approximately equal to one. This implies that the effect of molar volume of the additive on its solubility is expected to be significant for low molecular weight solvents and much less for polymers. Therefore, rewriting the equation 1.13 in the approximate form for polymers gives:*

$$-\ln \emptyset = A + 1 + \chi \qquad 1.15$$

where,

$$A = \Delta H_F/R\ [1/T - 1/T_M] \qquad 1.16$$

The dependence of solubility on temperature can also be derived from equation 1.13 as

$$-\partial \ln \emptyset / \partial(1/T) = \Delta H_F/R + \partial\chi/\partial(1/T) \qquad 1.17$$

So that it can be expressed by the well known Arrhenius type equation:

$$\ln \emptyset = \ln S_o - \Delta H_s/RT \qquad 1.18$$

where ΔH_s is the molar heat of solution and S_o is a constant.

*** unpublished theoretical analysis of solubility, with permission of Dr. N. C. Billingham, Sussex University, Brighton, U. K.**

If X is temperature independent, by comparing equation 1.17 with 1.18, it can be seen that the heat of fusion of the additive should be equal to the molar heat of solution below the melting point of the additive. i.e.

$$\Delta Hs = [-R\,\partial \ln 0/\partial (1/T)] \qquad 1.19$$

Roe and co-workers[27] have shown that the equation 1.13 accurately predicts the variation of solubility with solvent and temperature for phenolic antioxidants in hydrocarbons and polyethylene. Allara et al.[28] claimed that this could be used to predict the solubility of copper salts in polyolefins. In contrast, Billingham and co-workers[29] have shown that solubilities measured at high temperatures or in alkane solvents cannot be used to estimate their solubilities in polymers at room temperature. Furthermore, these workers could not find a simple correlation when regular solution theory was applied to predict the dependence of solubility on either temperature or the molar volume of the solvent.

1.3.3 Factors Affecting the Solubility of Stabilisers in Polymers

As mentioned earlier there are very few data available in the literature for the solubility of additives in polymers. An excellent review of the early studies on solubility is given by Billingham and Calvert[6] and further new data has been given and discussed by Moisan[39]. In the following discussion, some of the more important findings of the solubility is highlighted.

Roe and Co-workers[27] who measured the solubility of two phenolic antioxidants in low density polyethylene and in linear -C8, -C16 and -C28 hydrocarbons at temperatures around 65°C. The solubilities in hydrocarbons were determined by visual observation of the disappearance of solid material on heating. The values for the polymer were estimated by extrapolating diffusion profiles obtained in a stack of polymer films sandwiched between two thick films containing of a large excess of additive. They assumed that equation 1.13 is temperature dependent but is independent of solvent volume for a particular additive and obtained a good fit with experimental data. However, the solubility values extrapolated to room temperature were extremely low because temperature dependence of solubility was dominated by the large heat of fusion of the crystalline material. Allara et al.[28] used similar method to predict the solubility of copper salts in polyethylene at 90°C by extrapolating the solubility data obtained from n-alkanes and found a good agreement between the measured and the predicted solubility.

There are few other early instances where the solubilities for antioxidant and light stabilisers in polyethylene were measured in the literature. Feldshtein and Kuzminski[94] obtained the solubility of two phenolic antioxidants at 22°C by using polymer stack method. Their values are much higher than the values predicting from the Roe et al.[27] data. Johnson and Westlake [22,23] used the multi-film stack method with radio chemical assay to determine the solubilities of benzophenone light stabilisers in polyethylene and data is reported for 2,4 dihydroxy benzophenone and 2-hydroxy-4-octoxy benzophenone.

In recent years, the solubilities of phenolic antioxidants in hydrocarbons and polyolefins have been studied and discussed by Billingham et al.[6,29] and a similar treatment has also been discussed by Moisan[39]. The former studied the solubility in an equilibrium state whereas the latter obtained it by extrapolating diffusion profiles. The data obtained by these two groups are generally in agreement with each other and with the more limited data in literature. Billingham et al.[95] has confirmed that additives dissolve only in the amorphous phase of the polyolefine and are rejected from the crystal during cooling from the polymer melt. Therefore the solubility of an additive is independent of precise morphology (which is not true for highly orientated samples) then it will be inversely proportional to the crystallinity of the polymer and therefore correction of solubility is needed for crystallinity[95]. Moisan[79] has shown that the solubilities and the heats of solution of the additives in low density polyethylene are dependent not only on the chemical structure of the polymer but also on its thermal treatment, density and the morphology. Thus both the solubility and the heat of solution of phenolic antioxidants fall with increasing density of the polymer and the solubility of Irganox 1076 in polyethylene fell by almost a factor of five if the polymer was stretched to a draw ratio of greater than 8.

1.3.4 Experimental Methods of Evaluation of Equilibrium Solubility of Stabilisers in Polymers

The determination of equilibrium solubility in polymers requires some method of establishing the equilibrium between the polymer sample and the additive. This has been achieved in various ways, the most popular one being the equilibrium method. The analytical method of analysing concentration depends on the additive type, for example, some phenolics and uv stabilisers are good ultra-violet light absorbers and can be determined easily by either uv spectroscopy or uv microscopy. Similarly for other types of additives ir spectroscopy, radio-tracer technique and gas chromatography have been commonly used.

Westlake and Johnson[22,23] determined the solubilities of ultra-violet stabilisers such as 2,4-dihydroxy benzophenone and 2-hydroxy-4-octoxy benzophenones in polyethylene and polypropylene using a radio-active tracer technique from their diffusion studies. Roe et al.[27] studied the diffusion and solubility of two phenolic antioxidants in low density polyethylene using polymer stack method and the concentrations of the additives in the polymer were evaluated by thermogravimetry which relies on the ability of the additives to supress oxidation reactions.

Guillet[96] has shown that it is possible to measure the solubility of low molecular weight additives in polymers from their retention times in a gas chromatography column with the polymer as the liquid phase. Though, this method has experimently been used for simple solutes[97], there are several practical shortcomings for the applications to stabilisers. This method requires excessively high column temperatures to elute typical antioxidants at a reasonable rate. Furthermore, the application of HPLC methods requires thin films of polymer in order to minimise diffusion effects.

As mentioned above the most popular method of measuring the solubility of additives involve establishing equilibrium saturation between the additive and the polymer. Frank et al.[98] dispersed the solute in the polymer, then heated the sample slowly and used the disappearance of turbidity to determine the temperature at which all the additive dissolved. The drawback of this method is that it can only be used if the polymer is optically clear which in turn restricts its use in polyolefins to atactic polypropylene or to temperatures above the melting point of the polymer. Equilibrium method also used by Kuck[99,100], who prepared films of polypropylene containing Irganox 1010 at concentrations well above the saturation solubility and allowed them to equilibriate at a series of temperatures. The supersaturated additive precipitates on the film surface and its residual concentration was measured from its oxidation induction periods. This method seems closest to the reality of polymer use but was complicated by the fact that as the temperature was lowered, the selected additive tends to separate from the polymer as a glass rather than a crystal which has a higher solubility. Consequently the plot obtained for logrimethic solubility against reciprocal of absolute temperature was a complex one. Similar observations were also made by Scott et al.[101] for the solubilities of dithiocarbamates in polypropylene.

A much more reliable method of establishing the equilibrium between the polymer and the additive has been demonstrated by Billingham and co-workers[29]. They have used similar method to that of Feldshtein and

Kuzminskii[94] and later by Roe et al.[27] for the establishment of equilibrium between the polymer and the additive. They prepared a stack of polymer films around 100 µm thick and these films were interleaved with the powdered additive. The stack was maintained under a gentle pressure with a clamp and under the required temperature to establish the equilibrium between the film and the additive. Subsequently films were removed from the stack and the surface was washed with a cold solvent. Afterwards, the concentration of these films were determined by known analytical techniques. For example, the concentrations of uv stabilisers were determined by ultra-violet spectroscopy. Furthermore they also assess the uniformity of the distribution of the additive in the polymer by exposing to the ultra-violet microscopy. Though there are minor draw backs, such as removing all the traces of crystalline solid which has grounded to the film surface and that the experiments needed much longer times, this method could be regarded as most satisfactory way of measuring the true equilibrium solubility of additives in polymers.

A new approach to measure the equilibrium solubility has been presented by Moisan[39]. The experimental set up was similar to the above one but instead of pure additives he used a thick film of polymer containing a high concentration of additive. After some time the stack was stripped apart and then by analysing the concentration of individual films, concentration profiles were obtained with respect to distance. Equilibrium solubility was obtained by mathematically extrapolating this diffusion process to infinite times. The advantage of this procedure is the shorter experimental time, since this method does not involve equilibriation. But the question remains whether the extrapolation of an essentially kinetic situation to obtain an equilibrium property is a sensible approach.

1.4 Volatility of Additives From Polymers

Volatilisation of an additive from a polymer surface is another form of physical loss of an additives from polymers. The study of additive loss from a polymer surface is important because the effectiveness of an additive is entirely dependant upon its ability to remain in the polymer. Volatilisation of an additive causes its depletion in the polymer matrix and this may result in total degradation of polymer products This kind of consideration has led to the development of additives with low volatility such as Irganox 1076, Irganox 1010 and UV-531 in the place of more volatile butalated hydroxy toluene(BHT) and 2,4-dihydroxy benzophenone(DHP). In this section present knowledge of volatilisation loss of an additive is summerised.

1.4.1 Additive Loss Mechanism

Billingham and Calvert[6] proposed a theory, whereby the loss of additives from a polymer can be divided into two categories depending on the additive solubility in the polymer.

1. If a polymer contains an additive at a concentration below its equilibrium solubility, then the initial loss of the additive takes place by its evaporation from the surface of the polymer. This causes the depletion of the additive on the surface and consequently the setting up of a concentration gradient across the polymer matrix. Further loss can only occur by diffusion of the additive along this concentration gradient, to replenish the surface from the bulk. The above workers developed a mathematical model to take into account the effect of both of these factors together with equilibrium solubility. According to their model, which is based on the mathematics of heat transfer processes, the rate of removal of the additive from unit surface area of the polymer(V) can be related to the volatility of the pure additive(V_o) by the following equations:

$$V = V_o.C_s/S = H.C_s \qquad 1.20$$

where C_s is the concentration of the additive at the polymer surface and S is the saturation solubility. They assigned, $H(=V_o/S)$, as the surface loss parameter and used it to describe the mathematical modelling of the loss procedure together with the intrinsic diffusion coefficient of the additive in the bulk of the polymer.

2. If the polymer is supersaturated or in contact with a solvent, then the additive may be lost from the surface layers by blooming or leaching. The effect of blooming is to fix the concentration of the additive at the polymer surface to its saturation solubility value so only the excess can be removed by this mechanism. The loss is essentially by diffusion driven by the concentration gradient in the sample and in this case the bulk additive diffusion rate controls additive loss until the concentration of the additive falls below S, where case 1 applies.

   The effect of leaching is that the concentration of the polymer sample at the surface becomes zero, so all the additives can be removed by this mechanism.

1.4.2 Studies of Volatilisation Loss Process

Two excellent reviews covering the recent literature together with the detailed discussions of additive loss were published[5,6]. It is apparent, that studies of volatilisation loss of an additive can be divided into two main categories:

1. study of the volatilisation of a pure additive and its use to estimate or forcast the loss of the stabiliser from the polymer

2. direct study of volatilisation of stabiliser from the polymer.

The correlation of pure additive volatility to that from the polymer has to be done with care since the latter depends on its equilibrium solubility in the polymer. This is because, the vapour pressure exerted by the additive above a saturation solution in the polymer is identical to that of the pure additive, while the vapour pressure above any subsaturated solution is the value for saturation multiplied by the fraction of saturation solubility. Moreover, this type of study may also ignore the involvement of diffusion of the additive in the polymer. For example, Durmis et al.[18,19] and Scott et al.[20] have correlated the loss of additives from polyolefins with the volatilities of the pure compounds without considering the possible involvement of diffusion and additive solubility. On the other hand, most studies based on the second approach tend to consider loss mechanism as a diffusion controlled process and thereby ignoring the possible involvements of volatility and solubility of the pure stabiliser. Evidence for this comes from the work of Smith[16], who interpreted the loss of additive from neoprene as a diffusion controlled process and Olson and Webb[17] have similarly interpreted the loss of uv stabilisers from polycarbonates.

Early work showing the involvement of diffusion and volatility of stabilisers on the loss process were shown by Angert et al.[12], for the loss of phenyl-β-naphthylamine from rubber. It was concluded that the volatility was dominant in the loss of additives from rubber. Furthermore, Moisan and Lever[10] showed that there is an emperical relationship between the induction time and the ratio S^2/D for a series of phenolic antioxidants in low density polyethylene, implying the importance of solubility and diffusion on additive loss. The influence of additive volatility, solubility and diffusivity on additive loss was demonstrated recently by Billingham and Calvert[6]. They used literature available diffusion, volatility and equilibrium solubility data to estimate the additive loss time from polymers. In spite of experimental and extrapolation uncertaincies this is the only study that relates additive loss to the above parameters.

1.4.3. Factors Influencing Loss of Additives by Volatilisation

As discussed in the above section, the loss of an additive from a polymer depends on its diffusion, equilibrium solubility and the volatility of the pure stabiliser. Factors affecting diffusion and solubility have been considered in sections 1.2 and 1.3 of this Chapter. Therefore in this section the factors that affect the pure additive volatility will be discussed. The influence of structure, molecular weight and other properties of the stabiliser on its volatility have been the subject of many papers and have been summarised[5,6,39]. The volatility of a pure stabiliser depends on the surface area of the sample and not on the total amount of stabiliser used[8] and the dependence of the loss time is linear corresponding to zero reaction order[8,20]. The effect of temperature on stabiliser volatility has been treated in several papers. Arrhenius type relationships were ascertained for the thermally activated volatility[8,10,12,104]. Other workers[20] have found a linear dependence of the logarithm of volatility on temperature. The significant of the slope of these plots was not discussed. However, Schmitt and Hirt[26] obtained a Clausius - Clapeyron type relationship for the dependence of vapour pressure on temperature for several uv stabilisers and showed that there is a change in slope of the plots at the melting point of the stabiliser and calculated the latent heats of sublimation, fusion and vapourisation from the gradient of these plots. This study is a model of its kind and it is unfortunate that most other workers have used temperature above the melting points of the stabilisers for their studies and consequently did not observe any changes in the activation energies from their plots. Therefore the extrapolation of these data to other temperatures was not possible due to changes in the activation energies below melting point of the additive.

The influence of polymer sample shape on stabiliser volatility was investigated by Angert et al.[12], Temchin et al.[8] and found that the rate of evaporation of the stabiliser from rubber[12] and from polyethylene[8] was inversely proportional to the thickness of the sample and directly proportional to its surface area. A similar effect of the thickness of sheets was also observed[105]. In contrast to pure stabilisers, the kinetic curves expressing the volatile loss of additives from polymers were found to be first-order [5,8,12]. However, the loss of additives with very low vapour pressures cannot be described by an equation of first-order[8]. For these additives, the rate of evaporation is less rapid than the rate of diffusion of the stabiliser to the surface. The concentration of the stabiliser in the surface layer therefore increases and the rate of diffusion decreases so that the loss of stabiliser no longer follows first-order kinetics. However, these workers did not comment on its relationship to the volatility of pure additive or to any other form of kinetic equation.

1.4.4 Experimental Methods of Volatility Estimation.

The volatility of an additive causes a decrease in its concentration in the polymer, thus impairing its stability. Simultaneously, the concentration of the stabiliser in the surrounding space increases. Possible ways of determining the volatility of additives were based in the following experimental procedures[5]:

1. Weight decrease of the pure stabiliser or stabilised polymer,
2. determination of the stabiliser vapourised,
3. determination of the concentration of stabiliser in a polymer after volatilisation,
4. estimation of decrease in stability of the polymer.

The most popular choice was the weight decrease method but the values available are not comparable due to the variations in the experimental conditions used[8,20,104,105]. This is because volatilisation loss is a kinetic quantity which is sensitive to the experimental procedures. The determination of the stabiliser vapourised was quantitatively determined by ultra-violet spectroscopy[106,107] or colorimetry[12]. The concentration of the stabiliser remaining in the polymer was determined by UV spectroscopy[18] or gas chromatography[19].

Hawkins et al.[108] and Bair et al.[9] regarded the decrease in stability as a manifestation of the volatility of stabilisers in polymers and showed that the life time of the polymer is comparable with its volatilisation loss and determined the volatilisation loss from their induction times.

1.5 Loss of Additives From Polymers into Food Materials

Since polymers are being increasingly used as packaging materials for foodstuffs, the loss of additives from polymers into food materials is a significant problem. Therefore, the use of additives in food packaging is subject to legislation or other strong legal control procedures[15,109], whose purpose is to ensure that no toxilogically harmful materials will migrate into food with associated health risk to the consumers. Therefore, migration of additives into food materials has received great attention in recent years and in this section, current knowledge of migration phenomena is reviewed.

1.5.1 Mechanism of Migration

When a polymer is in close contact with a solid, or with a highly viscous, non penetrating substance additives may transfer from one phase to another until an equilibrium is reached. This equilibrium is governed by the partition coefficient of the additives over the polymer and the contacting material. The mathematical equations describing this type of migration are fully given in literature[36,110].

A second case is apparent when a well stirred liquid continuously removes the additive from the surface of a polymer, without actually penetrating into the polymer. In this instance, the concentration of the additive in the polymer may eventually become zero. Again, mathematics of this has been dealt with in some details in literature[36].

A completely different situation arises when an extracting solvent migrates into the polymer and simultaneously additive diffuse outward. In this case three important parameters govern the rate of migration:

1. The diffusion coefficient of the penetrating solvent in the polymer(D_s). Usually, D_s is strongly dependent on the concentration of the solvent in the polymer(C_{ps}).

2. The maximum possible concentration of the penetrating solvent in the polymer(C_{so}). C_{so} has a finite value, since otherwise the solvent would be ineffective as an extracting solvent.

3. The diffusion coefficient of the additive in the swollen polymer (D_p). This may be significantly different from the intrinsic values because of the modification of the polymer matrix caused by solvent penetration.

When D_p is strongly dependent on the concentration of the solvent, the effect will be that once a region in the polymer has been opened up by the penetrating solvent molecules, ingress of more solvent is highly facilitated. As a result, the polymer may be divided into an essentially unswollen region and a highly swollen region separated by an easily detectable solvent front. According to the theory, varified experimently by several workers[111,112],the penetration depth of this front(b), is proportional to square root of the time of contact (t). Furthermore, the rate of progress of the solvent front is also proportional to square root of the maximum value of D_s, and increases with increasing value of C_{ps}. It has been derived and experimently confirmed[113] that the total rate of solvent uptake is proportional to square of time (t) or simply $A\sqrt{t}$. Where A is dependent on D_s and C_{ps}. Therefore, the rate of extraction of additives is dependent on the diffusion coefficient of the additive in swollen polymer (D_p) and on the value of A which is the value that determines the rate of progress of the solvent front into the polymer. If the diffusion coefficient of the additive in the unswollen polymer is assumed to be negligible, two cases are possible.

1. $D_p << A$. Here the extraction of the additive in the polymer always takes place in the fully swollen region, since the additive extraction front at any time lagging behind the penetration solvent front. In this case rate of extraction depends on the diffusion coefficient of the additive in the swollen polymer(D_p).

2. $D_p > = A$. In this case extraction of additive proceeds faster than ingress of extraction solvent. The polymer is divided into two regions, swollen and unswollen. The solvent boundary is moving at a rate of $A\sqrt{t}$ into the polymer. Therefore, the rate of extraction depends on the ratio A/D_p.

1.5.2 Migration Experiments and Food Simulants

It would be ideal if the amount of additives extracted into foodstuffs could be determined when it is in contact with the polymer under normal conditions of practice. However in reality, because of the heterogeneous nature of the foodstuffs, great analytical difficulties are involved in the determination of migrated additives. Therefore natural migration must be simulated in model tests to determine the amount of additives extracted. However, the results of such migration tests are only valid if the conditions under which polymeric material are in contact with the food in pratice are simulated in model tests sufficiently exactly. It is therefore necessary to define temperatures and contact times that are closely related to those utilised in practice. Moreover, contact media(food simulant) must be used which are comparable with the different foodstuffs regarding their behaviour towards packaging material.

In the view of above observations , the Council of the European Communities in 1982 has laid down the basic rules necessary for testing of the polymeric material when it come into contact with foodstuffs[114]. According to these rules the following food simulants are recommended for all food packaging materials.

1. distilled water or water of equivalent quality (A)
2. 3% acetic acid (w/v) in aqueous solution (B)
3. 15% ethanol (v/v) in aqueous solution (C)
4. rectified olive oil, synthetic triglycerides or sunflower oil. (D)

The relevant test conditions are

1. Contact time: $t > 24$ hours		
1.1.	$T < 5^\circ$C	10 days at 5°C
1.2	$5^\circ\text{C} < T < 40^\circ$C	10 days at 40°C
2. Contact time: two hrs $< t < 24$ hrs		
2.1	$T < 5^\circ$C	24 hrs at 5°C
2.2	$5^\circ\text{C} < T < 40^\circ$C	24 hrs at 40°C
2.3	$T > 40^\circ$C	In accordance with national laws
3. Contact time: $t < 2$ hrs		
3.1	$T < 5^\circ$C	2 hrs at 5°C
3.2	$5^\circ\text{C} < T < 40^\circ$C	2 hrs at 40°C
3.3	$40^\circ\text{C} < T < 70^\circ$C	2 hrs at 70°C
3.4	$70^\circ\text{C} < T < 100^\circ$C	1 hrs at 100°C
3.5	$100^\circ\text{C} < T > 121^\circ$C	30 min at 121°C
3.6	$T > 121^\circ$C	In accordance with national laws.

The simulants A, B and C have been widely accepted nationally and internationally as a suitable food simulants for packaging materials for non fat-releasing foodstuffs. By contrast, there are completely different regulations or recommendations in different countries regarding the simulation of additive migration into fatty foods. The fat simulants used are mainly organic solvents, such as n-heptane[115,116], ethanol[117], diethyl ether[117] and parafin oil[118]. Though these substances do not present any analytical difficulties for analyses, their chemical nature is completely different from fatty foods and are unsuitable as fat-simulants[119]. Consequently, a synthetic, analytically pure triglyceride mixture, known as HB 307 which has a fatty acid and triglyceride distribution similar to that of coconut oil has been proposed as a universally applicable simulant for edible oils and fat-containing foodstuffs[119]. However, though it seems to be a reasonably suitable simulant for some fatty foods, it presents substantial problems in analysis[120] and a good simulant for fatty foods has yet to be found[120].

1.5.3 Studies of Migration of Additives in Food and Food Simulants.

A detailed and broad review of the current knowledge of the migration behaviour of additives in foodstuffs has been published by Shepherd[14]. The migration of polymeric additives into actual foods other than vegetable oils has been studied only infrequently [120-123]. The most extensive work that has been carried out in this area is concerned with the migration of BHT from HDPE into variety of foods[121]. The analysis was performed by using radio tracer technique involving the preparation of ^{14}C labled additives with associated handling difficulties. Figge[123] has emphasised an experiment to find a suitable simulant for fatty foods and has carried out migration tests using radio active additives into variety of oils and food materials. This is the most extensive work done on this area and the findings show that in general, where simulants are chosen to represent the individual foodstuffs, results are comparable to those obtained in actual pratice [30,31,120,123]. However, it is essential that simulants do adequately reflect the chemical and physical nature of the food materials of all types and give an accurate estimation of true migration. This has been highlighted by Haesen[32], who found that when water was used as a simulant for milk, it under-estimated migration levels, whilst fat simulants overestimate migration. Furthermore solvents such as heptane are totally unsuitable as simulants for fatty foods since they cause unrealistically rapid migration[15]. These observations show the difficulties in obtaining a successful simulant for fatty foods. Therefore, efforts have been made to find a suitable mixture that could simulate fatty foods and methanol/tetrahydrofuran mixtures as fat simulants represents an interesting approach[17].

1.5.4 Effect of Extractant Properties on Migration

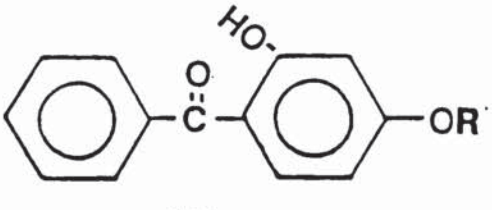
The physical form of an extractant plays an important role in migration. Migration into a solid extractant will be limited by a formation of a layer on the polymer surface, containing a high level of additives, thereby reducing the concentration gradient across the bulk polymer which the driving force for migration. Therfore under these conditions distribution of the migrant in the extractant may strongly influence the total amount of migration[124].

The chemical nature of the extractant is also important, for instance, the migration of BHT into water is restricted because of the very low solubility of BHT in water[126]. However, in certain circumstances, the extent of migration can exceed solubility limits. For example, plasticiser transfer from PVC film into stirred water yield unexpected high values and this was thought to be due to the co-migration of other additives in the films such as glycerol mono-oleate or polyethylene oxide[121].

The other significant feature of the extractant is its ability to penetrate into polymers. Some low molecular weight components of food such as triglyceride or terpenes are capable of penetrating into the polymer materials and thereby increase the migration rates substantially. The resistance of the polymer to such penetration is dependant upon the chemical and physical nature of the polymer. Furthermore, this penetration of extractant is usually accompanied by swelling of the polymer, consequently, the changes in the inter-macromolecular dimensions and free volume leads to a rapid migration. Not all polymers swell, but in all cases where a polymer is penetrated by an oil, diffusion coefficients in the mixed phase may be increased by several orders of magnitudes[126].

1.6 Scope and Objects of Present Work

The above discussion reveals the importances of physical parameters such as solubility, volatility, diffusion and solvent solubilities of additives in their loss from polymers. The purpose of the present study is to gain a further insight into the relationship between the above parameters to the loss of an additive from a polymer, preferably at low temperatures, by a more systematic approach. Furthermore, a complete study of the additive loss mechanism is also needed for additive design purposes. Therefore in this study, a homologous series of benzophenone type stabilisers(I), with varying alkyl chain lengths were prepared by using established chemical methods.



(I)

This type of additive was selected because of its versatility to structural changes. In addition, the strong uv/vis absorbances of these compounds can be used to monitor, the concentrations of additives in the polymer through uv spectroscopy. The diffusion coefficients, solubility and volatility of above series in low density polyethylene were studied by using a reliable experiment method in the temperature range 5-100°C. Individual parameters were obtained from the above studies were to be analysed by using existing theories and models.

The same homologous series was intended to be used in migration tests which would indicate the loss behaviour of additives in contact with various solvents of differing swelling powers and additive solubilities. It was expected these studies would yield extraction capabilities of such solvents towards various structural properties and physical quantities of additives. Correlation of these data together with above determined data should yield a descriptive understanding of additive loss mechanism from polymers.

CHAPTER TWO

GENERAL EXPERIMENTAL TECHNIQUES

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2.1 Materials, Sources and Purification Methods

The purification of the reagents used in the present work were substantially based on the methods described by Weissberger[127]. The literature values were quoted either from the "handbook of Chemistry and Physics"[128] or the "Dictionary of Organic Compounds"[129].

(a) Low Density Polyethylene - Unstabilised additive free low density polyethylene in granular form (Grade D 572) was supplied by British Petrolium Limited (Grangemouth) and stored in a freezer at -23°C.

(b) 2,4-dihydroxybenzophenone- 99% pure, was supplied by Aldrich Chemical Company and this was recrystallised with ethanol/water to give light yellow crystals of melting point 145.5°C.

(c) 2-hydroxy-4-octoxy benzophenone- This is commercially known as Cyasorb UV-531, was supplied by American Cynamid Company. This was recrystallised several times with ethanol/water mixture to give light yellow crystals of m.pt 42-44°C.

(d) Thioglycollic acid- Supplied by Aldrich Chemical Company and used without further purification. m.pt. -16°C. b.pt. 96°C.

(e) Alkyl Bromides- The following were supplied by Aldrich Chemical Company used without further purifications.

Ethyl bromide
n-butyl bromide
t-butyl bromide
n-octyl bromide
n-dodecyl bromide
n-octadecyl bromide

(f) Ethanol- Denutrated spectroscopic grade was used for all uv-spectrographic analysis, was supplied by Aldrich Chemical Company.

(g) Heptane- 99.8% HPLC grade was supplied by Aldrich Chemical Company.

(h) Olive oil- Was supplied by Aldrich Chemical Company, stored in a dark cupboard.

(i) Glacial acetic acid- 99.8% pure was supplied by Aldrich Chemical Company.

(j) Glycerol trioleate- Was supplied by BDH Chemical Comapny.

(k) Toluene- Supplied by the chemical stores of the Chemistry Department of Aston University. Distillised twice and dried over anhydrous magnisium sulphate.

(l) Ethylene chlorohydrine- Was supplied by Aldrich Chemical Company and used without further purification.

(m) General Solvents- All other general solvent used, were distilled few times before usage.

2.2. Incorporation of Additives and Processing of Polymers.

2.2.1 Preparation of Concentrated Stabiliser Master-batches

Stabilisers were mixed with LDPE at a concentration 7.5% w/w in a RAPRA torque rheometer[132] at temperature of 160°C for 7 minutes. The screw speed was 60 rpm and the processing was carried out in a closed mixer. On completion of processing, the polymer sample was rapidly removed and quenched in cold water to prevent further thermal oxidation. These samples were stored in sealed bags in a freezer at -23°C.

2.2.2 Preparation of Diluted Stabiliser Batches

The concentrations of the masterbatches were analysed by extracting it into spectroscopic grade ethanol and then by uv-vis spectroscopy. These values were used to calculate the concentrations required in the dilution batches. Afterwords, the diluted polymer samples were obtained by mixing with pure polymer and processing for further 5 minutes following the same procedure as above.

2.3 Preparation of Polymer Films

The films were obtained by compression moulding of processed LDPE using polished stainless steel moulds. The moulds were thoroughly cleaned before used to ensure a smooth surfaces and a special grade of cellophane paper was used to prevent the film sticking to the plates. 5 g of raw or processed polymer was found to produce films of thickness 0.025 cm(250µm). The weighed amount of the polymer film was placed between the two plates and inserted into an electric press whose platens were maintained at 160±2°C. After initial heating of 2 minutes and subsequently subjecting the sample to a pressure of 85 kg/cm^2 for further two minutes, the platens were cooled to about 40°C by running cold water while maintaining the full pressure. The mould were then removed from the press and the films obtained were stored in a freezer at -23°C. Typical infra-red and uv/vis spectra obtained for the raw and processed polymer are given in Figures 2.1, 2.2 and 2.3. This shows that no carbonyl or other oxidation products appear during the processing and pressing of polymer films. The concentration of the stabiliser was evaluated by uv/vis spectroscopy and this showed that, especially for low molecular weight compounds, the concentration found are less than those expected. Therefore, the ratio of pure polymer to master - batches were adjusted to give the required final concentration in the films.

Films of thickness 0.25 cm were prepared from the master-batches using a similar mould but with a larger cavity.

2.4 Solvent Extraction of Polymer Films

Hot soxhlet extraction with spectroscopic grade ethanol was used for solvent extraction of stabilisers from polymer films. It was found that a maximum of six hours extraction was sufficient to remove any stabiliser present in the polymer films.

2.5 Ultra-violet/visible Spectroscopy

The ultra-violet/visible spectroscopic studies of the stabiliser-containing LDPE polymer films and in solutions were carried out by using a computer controlled Beckman DU-7 high speed uv/vis spectrophotometer. For

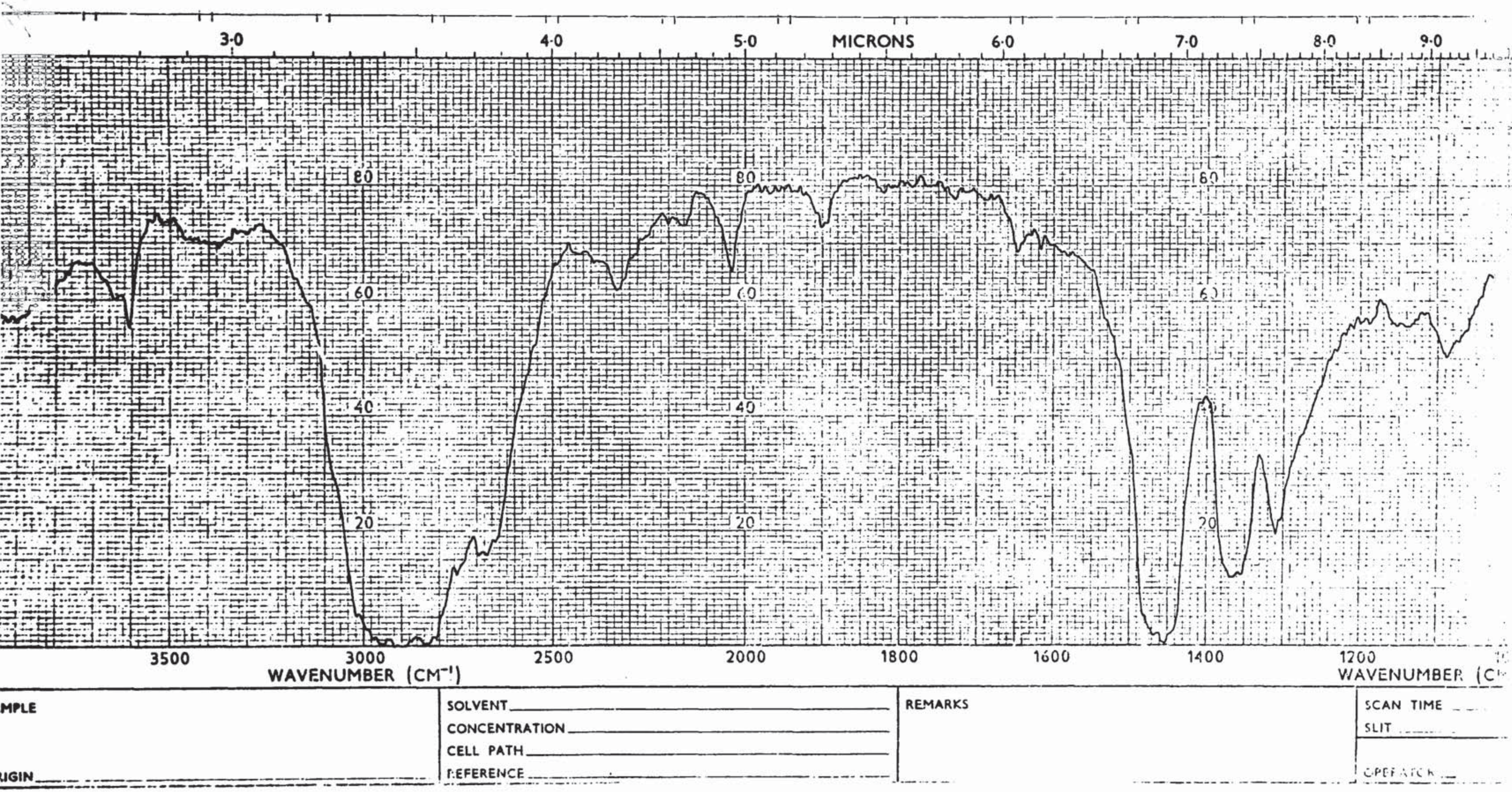


Figure 2.1:- Typical Infra-red spectrum of additive free LDPE polymer film.

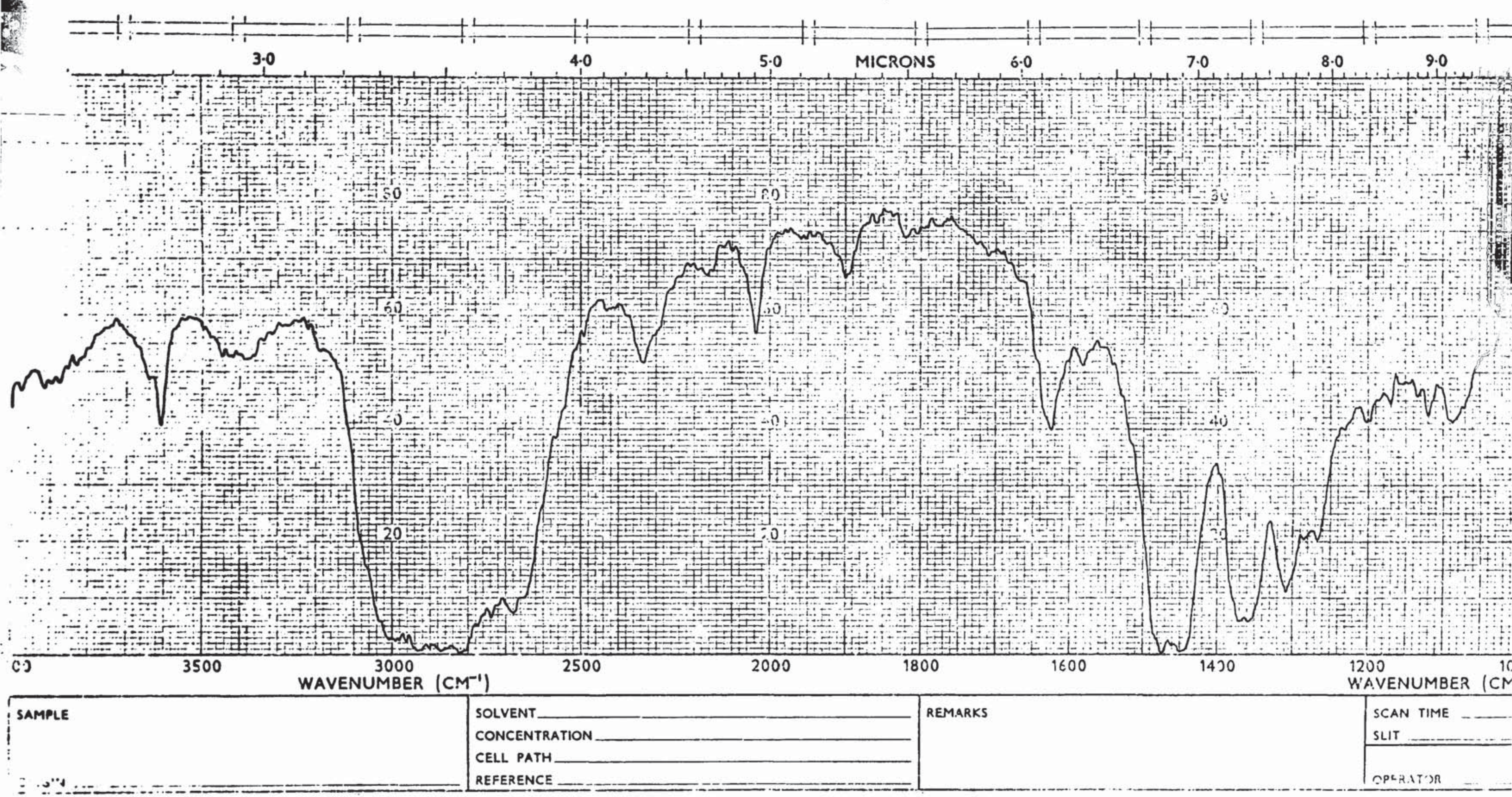


Figure 2.2:-Infra-red spectrum of LDPE polymer film processed with 2-hydroxy-4-octyloxy benzophenone.

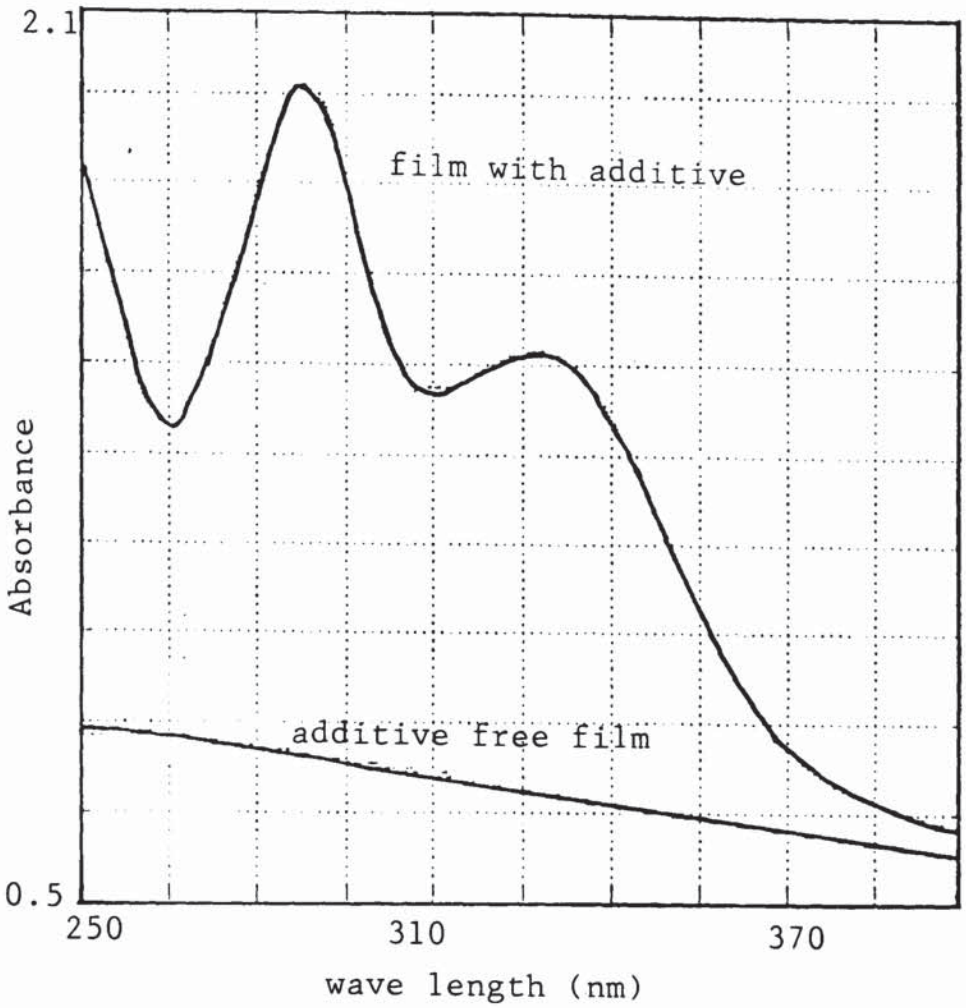


Figure 2.3:- Typical uv spectrum of additive free LDPE film and a film containing an additive.

polymer films, air was used as a reference background and polymer films were directly exposed to the ultraviolet/visible beam. For solutions, the spectra were obtained using quartz cells of 10.0 mm path length with pure solvent as the reference solvent. The spectra were recorded in the region 250-350 nm using scan speed of 120 nm/min. Typical spectra obtained for stabilisers are given in Figure 2.3. There are two high intensity uv/vis absorbing peaks of stabilisers were observed, one around 285 nm region and other in 330 nm reigon. The band in the region of 285 nm was the more strong among two and therefore used for concentration evaluations. This Beckman DU-7 high speed uv/vis spectrophotometer is equipped with a mini computer to store or perform calculations such as net absorbances (see Figure 2.4) using a required base line and these facilities were used to evaluate concentrations of the additive as shown in section 2.6.

2.6 Concentration Determination of Polymer Films

In all concentration determinations, the following form of Beer-Lambert equation was used[133]:

$$A = \mathrm{Log}\ I_0/I = \epsilon c l \qquad 2.1$$

where A = absorbance or optical density(Net absorbance)

I_0 = intensity of the incident light

I = intensity of the transmitted light

ϵ = extinction coefficient

c = concentration of the absorbing group

l = path lengh of the light within the sample

Equation 2.1 was used to calculate the concentrations of the stabiliser in the polymer films as follows:

Equation 2.1 suggests that for a given thickness absorbance is proportional to the concentration in the film. A typical net absorbances versus concentration plot can be seen in figure 2.5. It can be seen from the plots that the concentration in the polymer films follow Beer-Lamberts equation. However, absorbances above 2.0 did not give a straight line relationship and the absorbances are much lower than the conentration predicted and were therefore not used in this study. In such cases an extraction procedure was used. These plots were used to evaluate the concentration of stabiliser in polymer films. In either case, this method allows the sensitive determination of stabiliser concentrations of upto 5μg/cm^3).

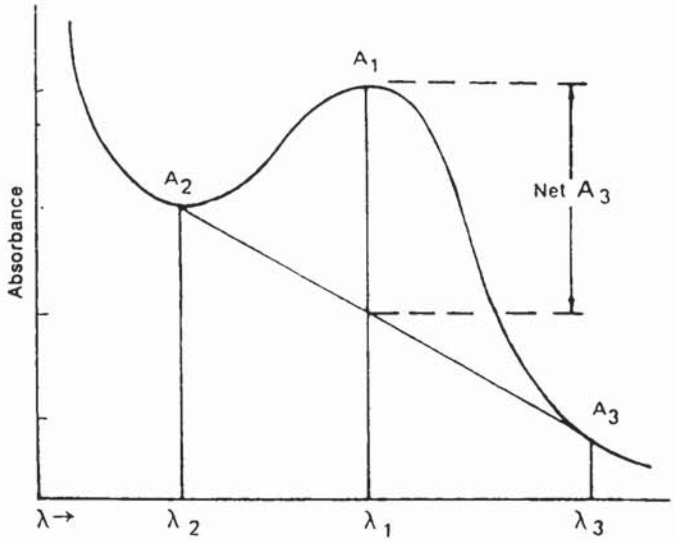


Figure 1.2 Net A3 Calculation

The calculations are performed as follows:

$$\text{Result} = \left[A_1 - A_3 - \left(A_2 - A_3\right)\left(\frac{\lambda_1 - \lambda_2}{\lambda_3 - \lambda_2}\right) \right] \times (\text{Factor})$$

Where

A_{1samp}, A_{2samp}, and A_{3samp} = Absorbance of sample at λ_1, λ_2, and λ_3, respectively.

λ_1, λ_2, and λ_3 = First, second, and third wavelength values entered by user.

Factor = Entered predetermined factor.

Figure 2.4:- net absorbance calculation of the uv spectrum.

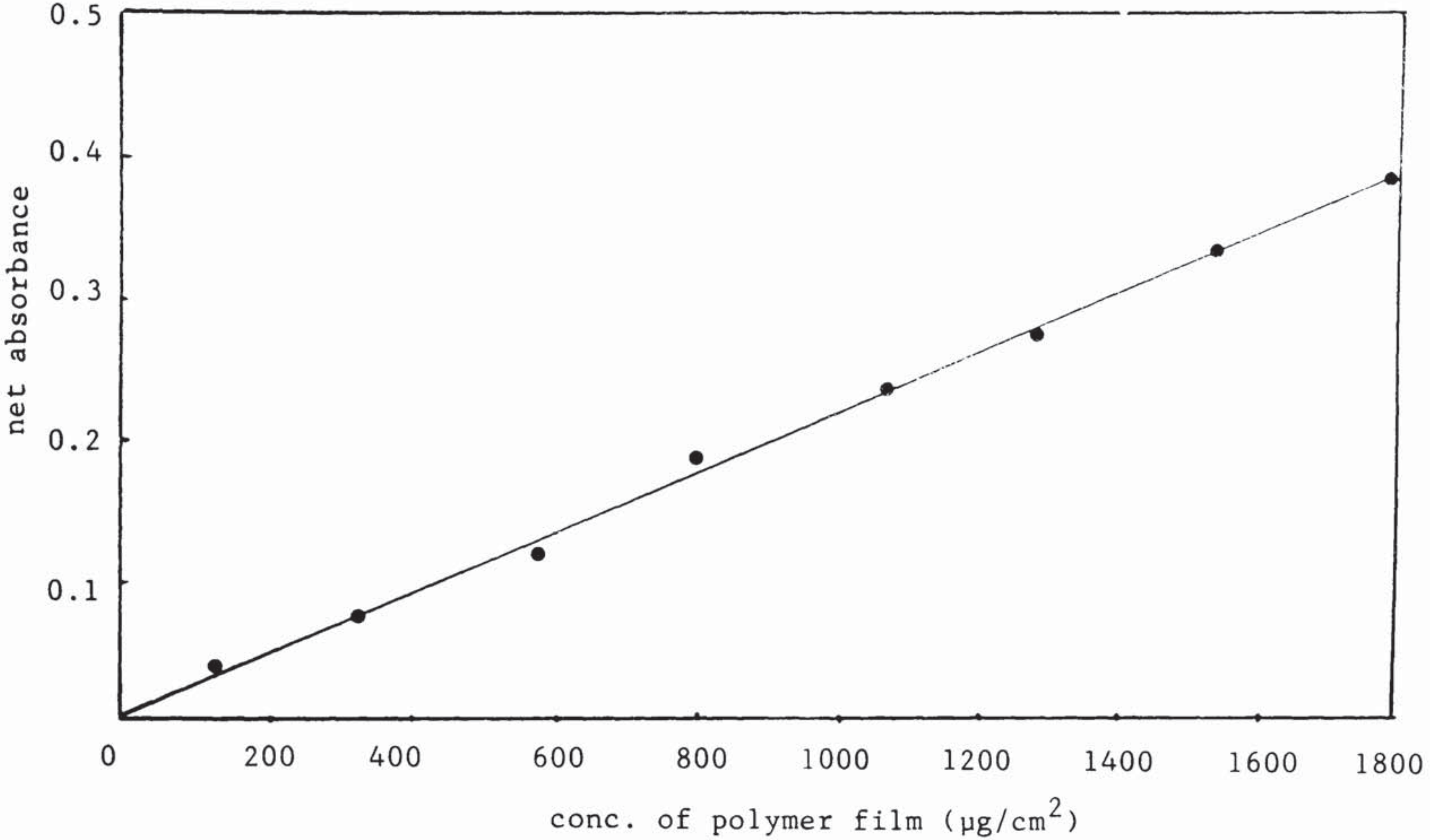
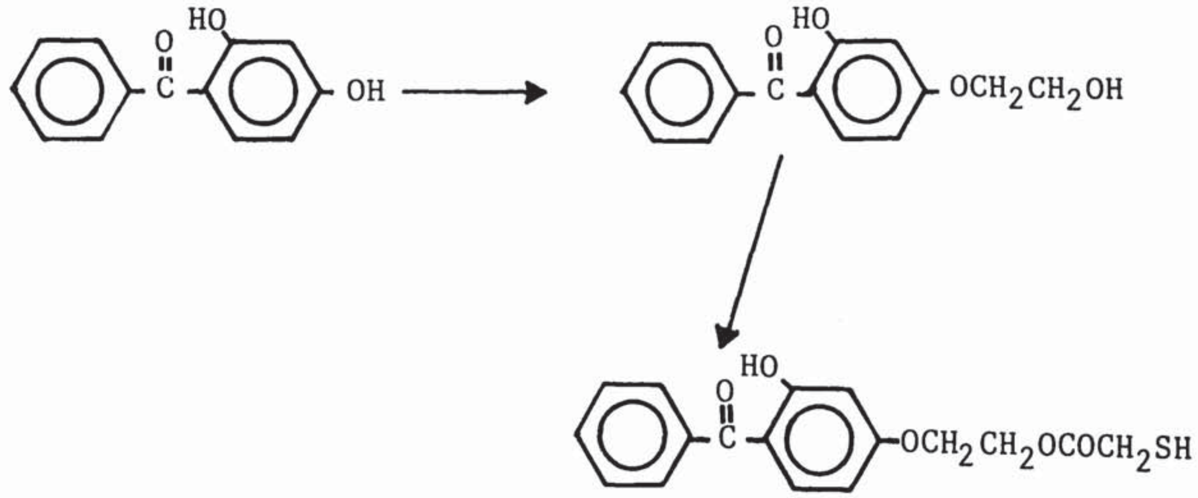


Figure 2.5. net absorbances verses concentration of the films(0.025cm) of LDPE containing satbiliser 4-benzoyl-3-hydroxyphenyl ethoxy glycollate

2.7 Synthesis and Characterisations of Stabilisers

2.7.1 Synthesis of 4-benzoyl-3-hydroxyphenyl ethoxy thioglycollate

The following two-stage reactions were carried out in the synthesis of the compound[130]:



Preparation of 2-hydroxy-4-(β-hydroxy ethoxy)benzophenone

21.4 g (0.1 m) of 2,4-dihydroxy benzophenone and 4.0 g (0.1 m) of sodium hydroxide were dissolved in 125 ml of distilled water. 8.1 g (0.1 m) of ethylene chlorohydrin was then added all at once to the above solution and was left to stir for 4 hours at 90-95°C and then 125 ml of distilled water at 95°C was added. The solution was allowed to stand overnight with stirring at room temperature. The next day, the precipitate obtained was washed several times with distilled water and mechanical stirring continuted further 24 hours. A light brownish powder was obtained. This was recrystallised with acetone/water and dried in a vaccum oven. The yield was found to be 60% and the melting point was 92°C.

Infra-red data

Phenolic hydroxyl and alcoholic hydroxyl - 3500-3100 cm^{-1}
Benzophenone carbonyl - 1630 cm^{-1}
Aliphatic CH_2 - 2920 cm^{-1}

NMR data

Aromatic protons - 2.3-2.5 τ (multiplet)
Phenolic protons - 2.2 τ (singlet)
Alcoholic hydroxyl proton - 4.0 τ
Methylenic protons - 6.5-6.7 τ (multiplet)

Reaction of 2-hydroxy-4(β-hydroxy ethoxy)benzophenone with thioglycollic acid

---

25.8 g(0.1 m) of 2-hydroxy-4(β-hydroxyethoxy)benzophenone and 10.0 g (0.109 m) of thioglycollic acid were dissolved on 200 ml of dry toluene contained in a flask fitted with a Dean and Stark apparatus and a condensor. A few drops of conc. sulphuric acid was added to the mixture and it was refluxed under nitrogen until no further water was collected in the apparatus (5-6 hours). The solution was washed until neutral with sodium bicarbonate solution, distilled water and dried over anhydrous MgSo$_4$. The toluene was then removed by rotary evaporation under reduced pressure to give a brownish viscous liquid, which solidifies slowly in a refrigerator to give yellow-crystals. Melting point 52-53°C. The typical infra-red spectrum of this compound can be seen in Figure 2.6.

Infra red data

Hydrogen bonded phenolic OH - 2400-3200 cm^{-1}
Ester carbonyl group - 1740 cm^{-1}
Mercapton group (-SH) - 2560 cm^{-1}

NMR data

Aromatic Proton - 2.3-2.6τ
Methylene protons - 6.2-6.5τ
Phenolic proton - 2.2τ
Thiol - 7.2τ
3 Aromatic proton - 3.2-3.7τ

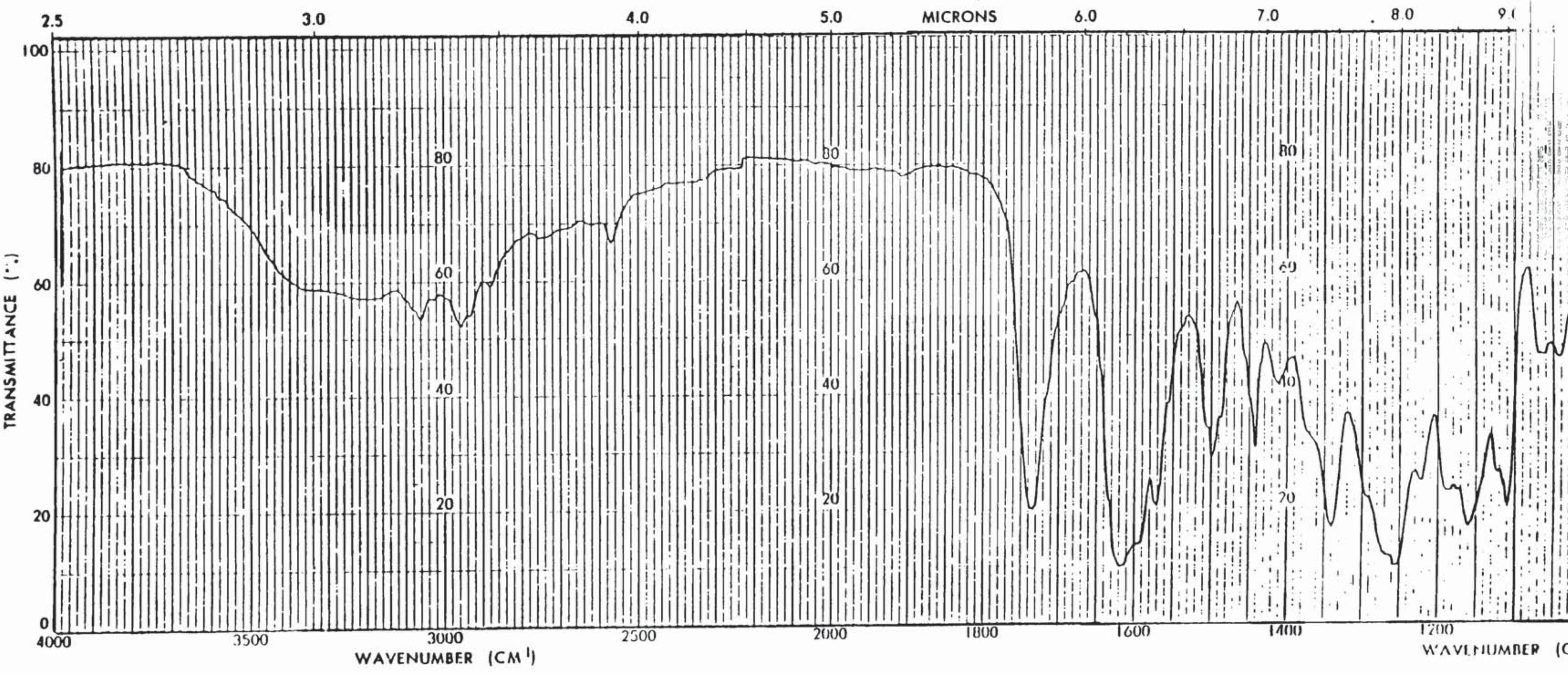
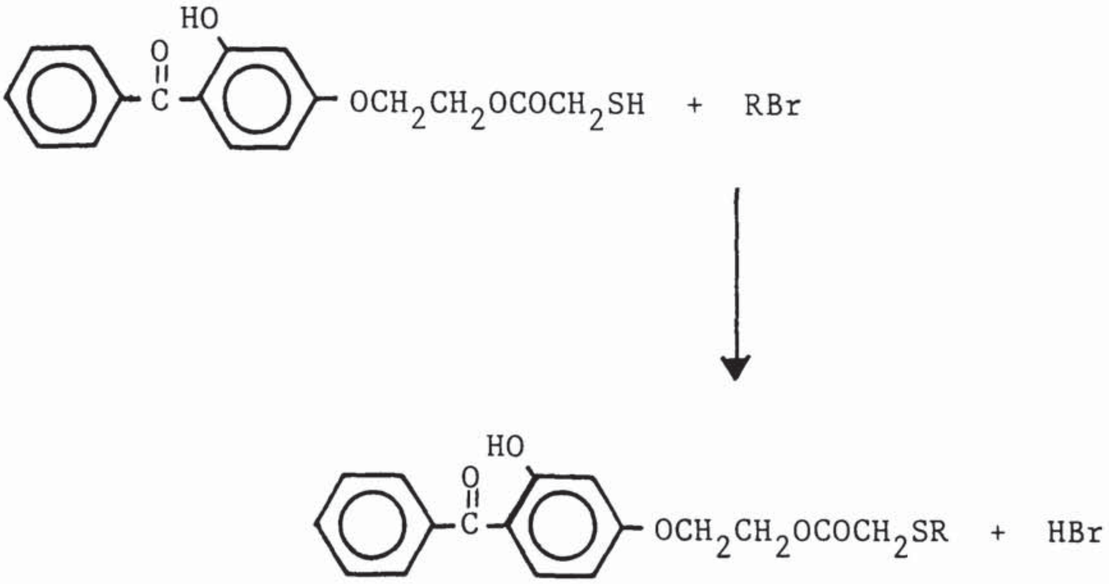


Figure 2.6:- Infra-red spectrum of 4-benzoyl-3-hydroxyphenyl ethoxy thioglycollate

2.7.2 Preparation of 4-benzoyl-3-hydroxy-phenylethoxy Alkyl thioglycollate

This was prepared according to the following rection[131]:



0.1 m of 4-benzoyl-3-hydroxylphenylethoxy thioglycollate and 0.1 m of alkyl bromide were dissolved in 200 ml of dry toluene. The solution was gently stirred and the temperature was gradually increased to 35°C. Tiny bubbles of HBr were escaped from the solution. The reaction was stopped until no more gas was evolved. The solution was then poured into ice-cool water and the organic phase was extracted with ether. This was dried over calcium sulphate for 24 hours after which the solvent was evaporated to give the required product. The absence of extraneous band in the infra-red spectrum showed the compound to be satisfactory pure and no further purification was made.

The following alkyl bromides were used to produce the stabilisers of the benzophenone series:

(1) ethyl bromide
(2) n-and t-butyl bromide
(3) n-octyl bromide
(4) dodecyl bromide
(5) octadecyl bromide

A typical infra-red and uv/vis spectrum of the stabiliser series is given in Figures 2.7 and 2.8 for the octoxy derivative.

Table 2.1 presents the stabilisers synthesised from the above methods and the commercial stabilisers used in this study together with their code names. These code names were used throughout the following Chapters of this thesis.

2.8 Measurement of Heat of Fusion and Crystallinity

The crystallinity of the polymer samples were measured by differential scanning calorimetry (DSC). A Perkin-Elmer DSC-2 instrument was used. In this instrument a sample and a reference holder are heated (or cooled) at a

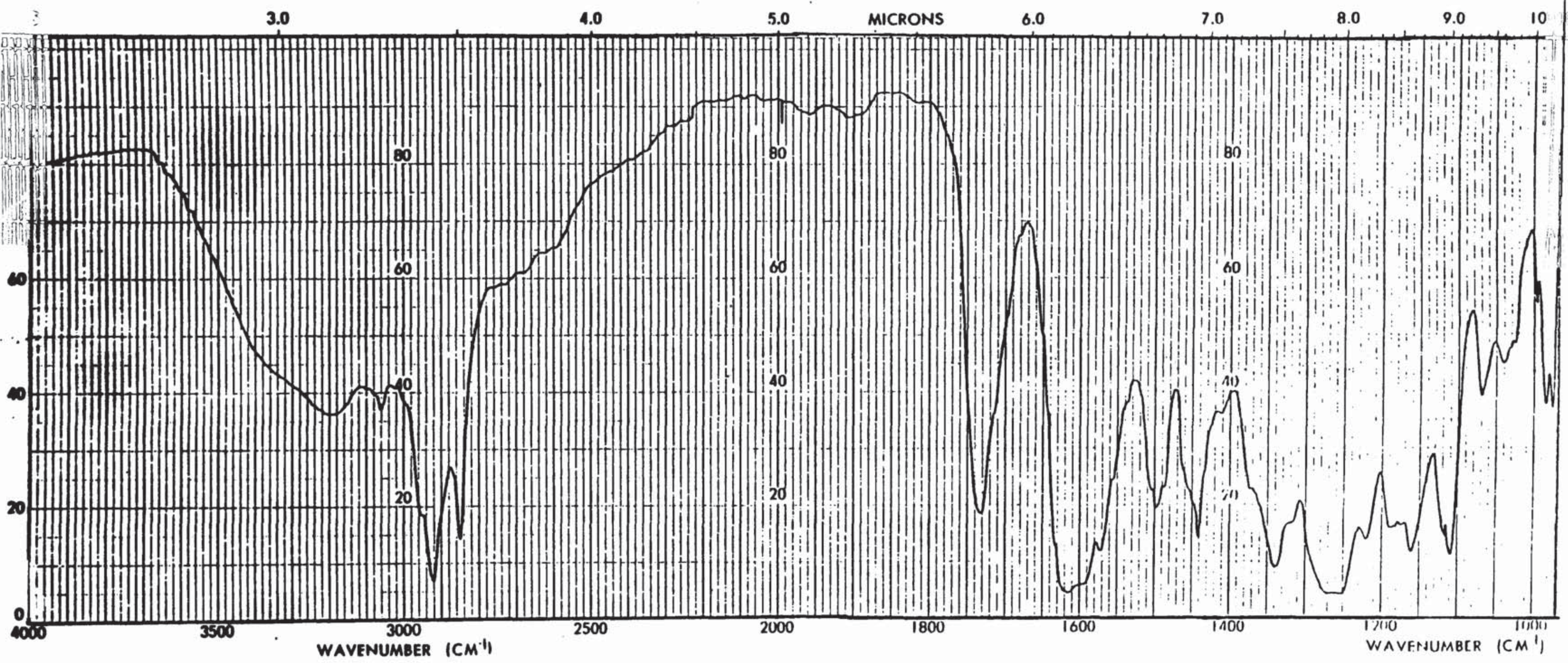


Figure 2.7:- Infra-red spectrum of 4-benzoyl-3-hydroxyphenyl ethoxy octadecyl glycollate

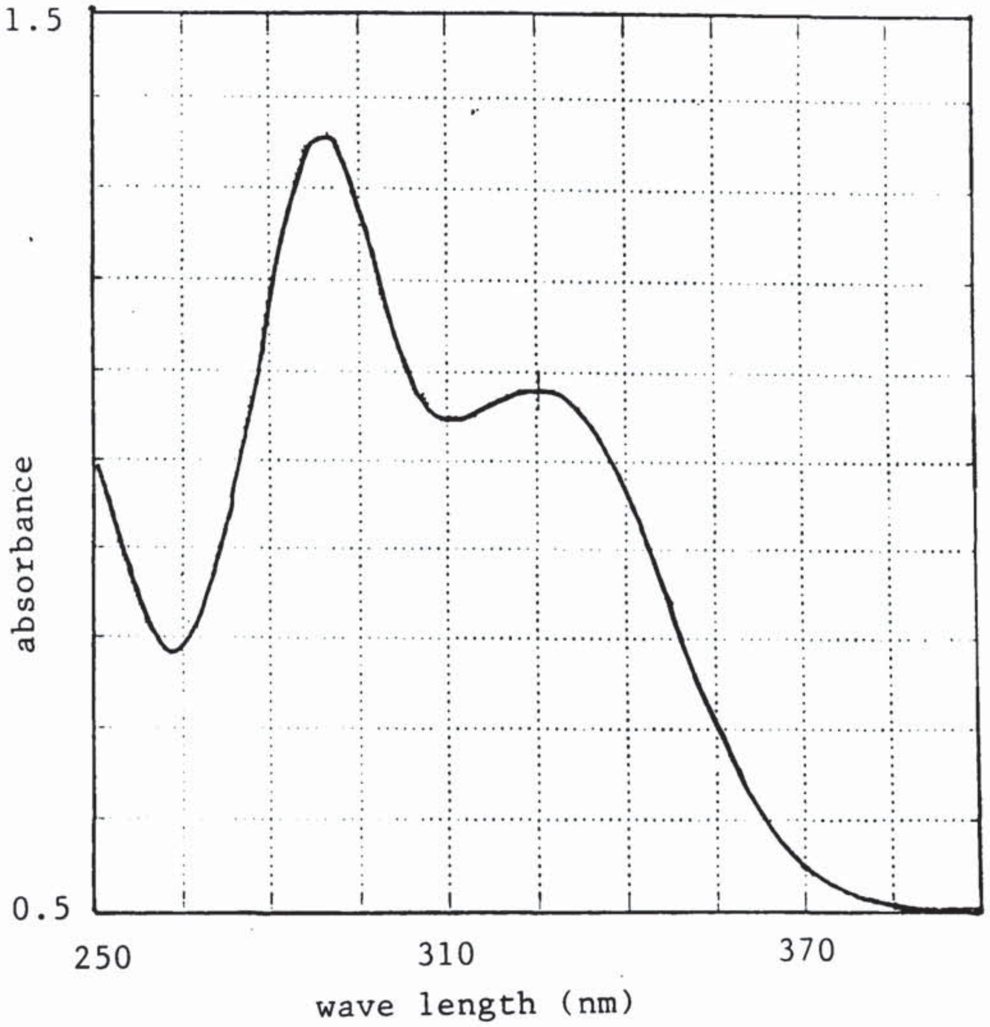


Figure 2.8- Typical uv spectrum of the stabiliser series respresented by 4-benzoyl-3-hydroxyphenyl ethoxy glycolate.(in ethanol).

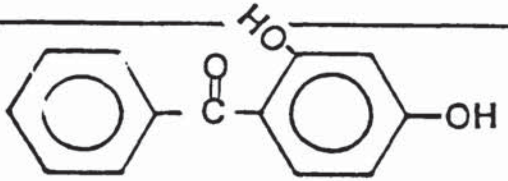
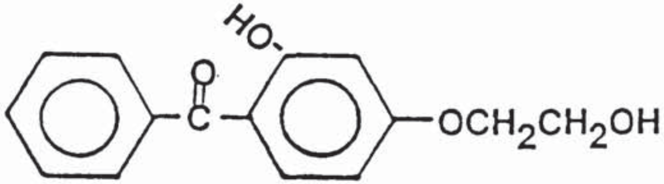
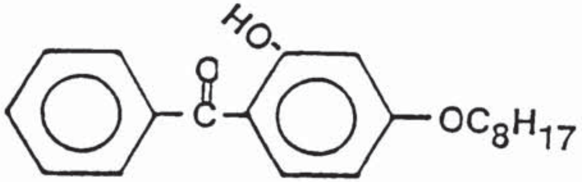
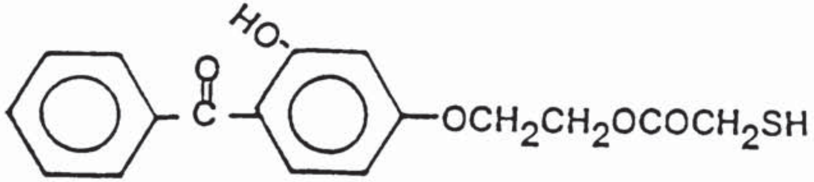
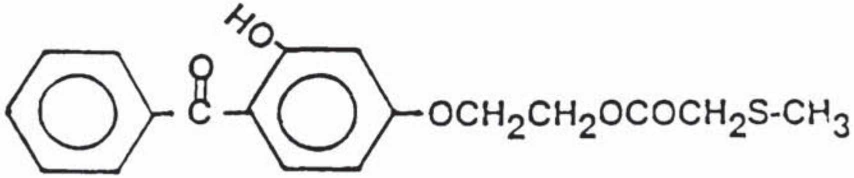
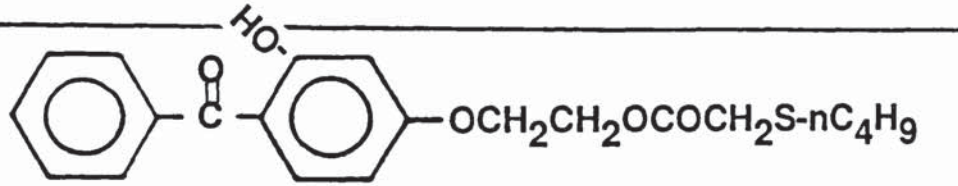
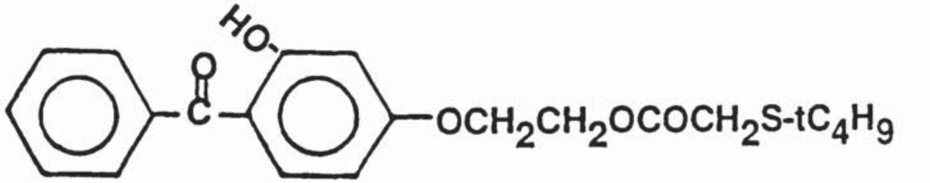
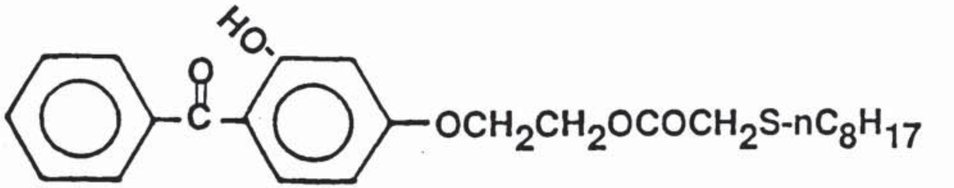
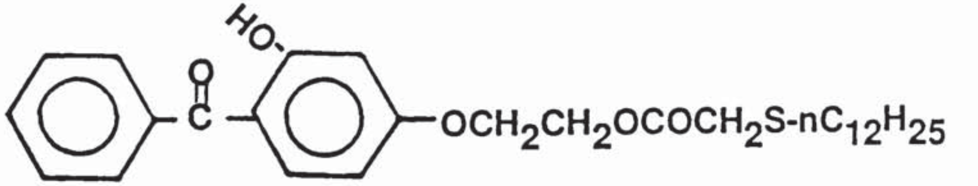
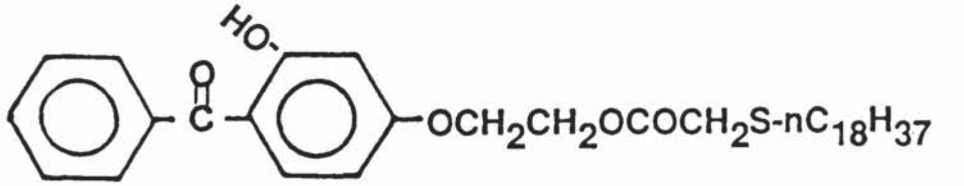
stabiliser	code name	mol.wt
	UV-OH	214.22
	UV-C2OH	258.27
	UV-nC8	326.25
	UVS-H	332.37
	UVS-C1	346.40

Table 2.1 List of stabilizers used in the present study together with their code names

(Table 2.1 continued)

stabiliser	code name	mol.wt
	UVS-nC4	388.47
	UVS-tC4	388.47
	UVS-nC8	444.58
	UVS-nC12	550.68
	UVS-nC18	584.84

constant rate. The difference in the power requirement of the sample relative to the reference, which is equivalent to the rate of energy absorption or evolution of the sample, to keep the temperatures of the holders equal to each other is recorded as output. About 10 mg of polymer was weighed accurately in an aluminium DSC pan and sealed. The sealed pan was placed in the sample chamber of the instrument with an empty pan in the reference chamber. The melting thermogram was recorded by programming the DSC upwords from 320 K at a rate 10 K/min, through the melting range of the polymer. A typical melting thermogram is shown in Figure 2.9. The melting thermogram of an indium standard of known weight was also recorded. The areas between the melting peak and base line were measured by planimeter for the sample and the indium standard. The enthalpy of fusion of low density polyethylene was determined from the following relationship.

$$\Delta H_{sample} = \Delta H_{ind} \times \frac{W_{ind}}{W_{sam}} \times \frac{R_{sam}}{R_{ind}} \times \frac{S_{ind}}{S_{sam}} \times \frac{A_{sam}}{A_{ind}} \qquad 2.2$$

where W, R, S and A are weight, range, chart speed and area between the peaks for indium and sample respectively. ΔH_{ind} is the heat fusion of pure indium metal equal to 28.4 $J/g.^{-1}$.

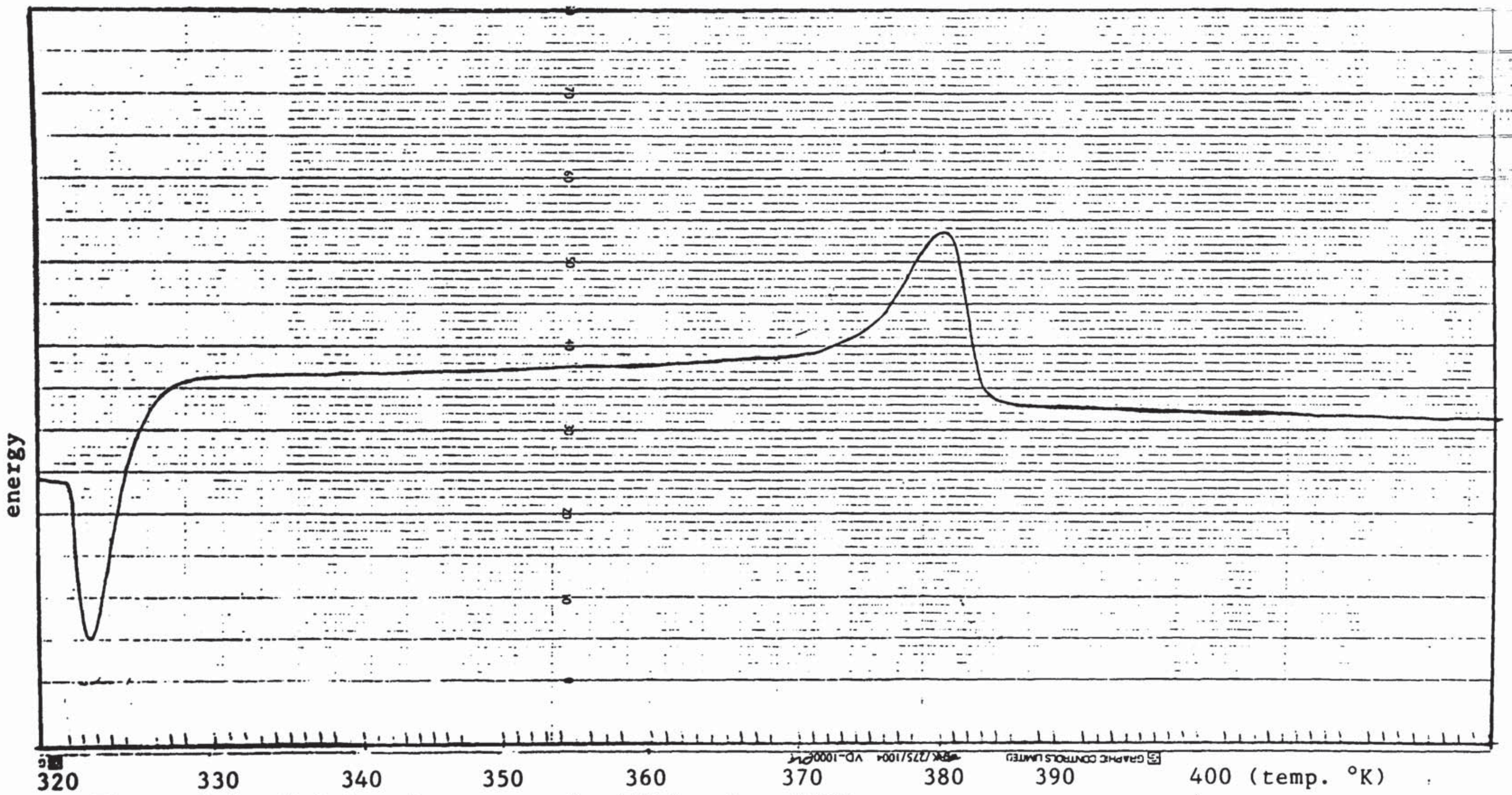


Figure 2.9:- Melting thermogram of additive free LDPE

% crystallinity of LDPE samples were calculated from the following relationship:

$$\% \text{ crystallinity} = \frac{\Delta H_f}{\Delta H_f^{100}} \times 100 \qquad 2.3$$

ΔH_f is the heat of fusion of LDPE used in this study and was evaluated as 66.5 J/g^{-1}. ΔH_f^{100} is the enthalpy of fusion of 100% crystalline LDPE. Since 100% crystalline LDPE was not available, literature values were used[134]. This is quoted as 293 J/g^{-1} of polymer and using this value the cryatallinity of the polymer sample is 22.69. However, density of the LDPE polymer sample was found to be 0.921g/cm^3 suggesting that the crystallinity may be in the region of 47%.

The Heat of fusion of pure stabilisers were determined in a similar way and used in Chapter four.

CHAPTER THREE

DIFFUSION OF STABILISERS IN LOW DENSITY POLYETHYLENE

CHAPTER THREE

DIFFUSION OF STABILISERS IN LOW DENSITY POLYETHYLENE

Intrinsic diffusion coefficients of the stabiliser series (given in Table 2.1) were determined in low density polyethylene over a temperature range 5-100°C. In this chapter the theoretical analysis and the experimental procedure for determination of diffusion coefficients are described. Furthermore, The results obtained will be compared with available literature data and will be discussed in terms of existing theories.

3.1 Mathematical Approach and Experimental Technique for the Evaluation of Intrinsic Diffusion Coefficients.

3.1.1 Mathematical Approach

Evaluation of diffusion coefficients for a semi-infinite medium can be achieved by solving Fick's second law differential diffusion equation[36]:

$$\partial C/\partial t = D\, \partial^2 C/\partial x^2 \qquad 3.1$$

A polymer sheet with a known thickness can be taken as a semi-infinite medium if the diffusant is deposited on one face and is not allowed to reach the other face. If both faces of the polymer sheet are exposed to the diffusant, it will still behave as a semi-infinite medium upto about 60% of the total diffusant taken[37]. Therefore, the principle underlying the experimental technique to the solution of the above equation is to establish a concentration profile of a diffusant within the polymer matrix under the above condition with time.

In cases where a solid is bounded by two parallel surfaces which are very large in area compared to the distance between the two surfaces, solution to Fick's equation(3.1) can be obtained. The solution is similar to the case of diffusion into plane sheet where all the diffusion substances enter through the plane faces and a negligible amount enter through the edges[36]. Figure 3.1A shows the initial setting up of concentration profile of diffusant within the diffusion substrate, while Figure 3.1B shows the concentration profile after time t.

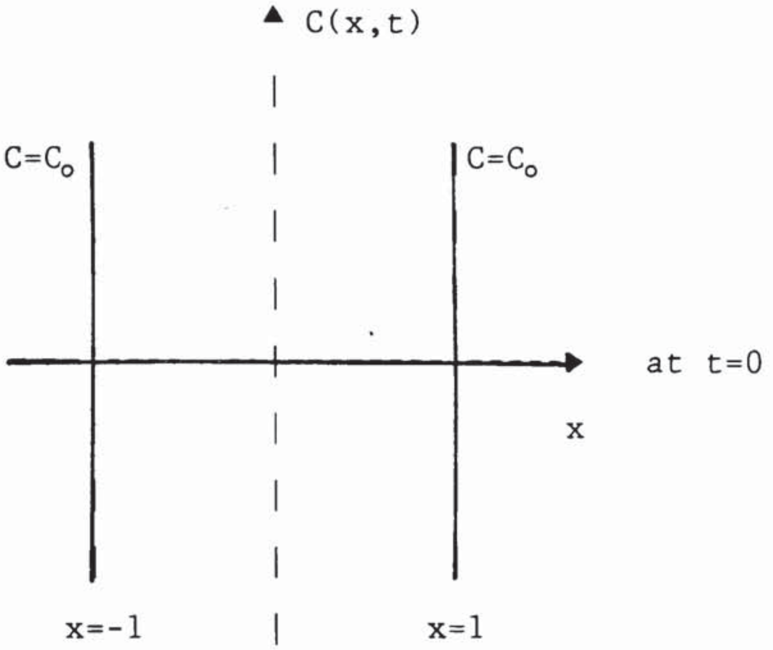


Figure 3.1A Initial concentrations and boundary conditions for the set up of the concentration profile of diffusant within the polymer matrix

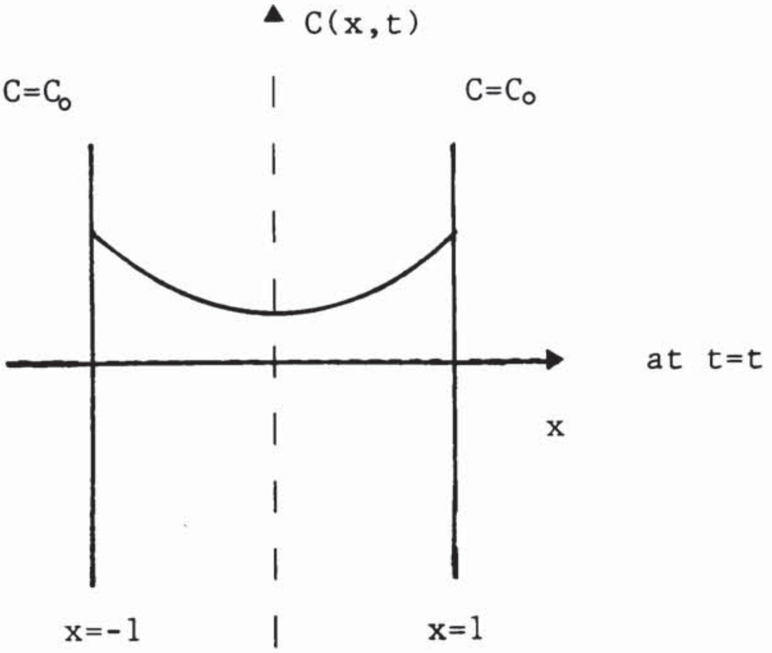


Figure 3.1B Setting up of a concentration profile of diffusant after time t.

The boundary conditions are:

$$C(x,t) = C_o \;, \quad -l > x > l,\; t > 0 \qquad 3.2$$

$$= 0 \;, \quad x = 0 \;,\; t > 0 \qquad 3.3$$

the initial condition is:

$$C(x,0) = 0 \;, \quad -l < x < l, \quad t = 0 \qquad 3.4$$

Equation 3.3 expresses the condition that there is no diffusion across the central plane of the sheet.

The solution of the diffusion equation 3.1 which satisfies the above conditions is given by Crank[36] (Chapter 2, eq. 2.54 and 2.67). For small values of time, the solutions are given as two standard series:

$$C(x,t) = C_o\sum_{n=0}^{\infty}(-1)^n\mathbf{erfc}(2n+1)l-x/2\sqrt{(Dt)}+C_o\sum_{n=0}^{\infty}(-1)^n\mathbf{erfc}(2n+1)l+x/2\sqrt{(Dt)} \qquad 3.5$$

$$C(x,t) = C_o - 4C_o\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\;\mathbf{exp}(-D(2n+1)^2\pi^2t/4l^2\;\mathbf{cos}\frac{(2n+1)}{2l}\pi x/2l \qquad 3.6$$

where erfc Z = 1-erf Z, and erf Z is the error function. D is the diffusion coefficient, C(x) is the concentration of the diffusant at x distance from the centre of the solid at time t, C_o is the surface concentration and considered to be a constant throughout the experiment.

The series 3.5 and 3.6 converges rapidly for large values of t. If the value of $Dt/l^2 = 1$, the concentration at the centre of the solid is given by $C(0,t) = 0.8920C_o$, and $Dt/l^2 = 0.25$ the value is $0.3145C_o$. Consequently the accuracy of the estimation of D is best when Dt/l^2 is close 0.25. Furthermore, the validity of series 3.5 and 3.6 for the experimental procedures lies on three assumptions[36,37].

(a) Polymer film of known thickness can be taken as a semi-infinite medium.

(b) Diffusion is essentially one dimensional and only perpendicular to the plane of the sheet.

(c) The value of diffusion coefficient remains essentially constant over the period of the measurement.

Out of these two series, series 3.5 which is easy to solve, was used to obtain theoretical concentration profiles (similar to that given by Crank[36]) with the aid of a basic computer program.

The series 3.6 can be redefined as:

$$C(x,t)/C_0 = 1 - 4/\pi \sum_{n=1} (-1)^n \exp\{-(2n+1)^2\pi^2 K/4\} \cos\{(2n+1)\pi x/2l\} \qquad 3{\cdot}6a$$

where,

$$K = Dt/l^2 \qquad 3{\cdot}7$$

For a given value of K, $C(x,t)/C_o$ can be evaluated from equation 3.6. Therefore, plots of $C(x,t)/C_o$ against x/l were obtained for a number of K values and these are shown in Figure 3.2.

3.1.2 Experimental Procedure

The experimental set up used in the present work for the establishment of concentration profiles of diffusant within the polymer matrix is shown in Figure 3.3. The diffusion device is similar to the one used by Roe and co-workers[27]. Twenty two compression moulded films of low density polyethylene containing no additives, having thickness of 250 μm and diameter of 5 cm were prepared according to the method described in Chapter 2 (section 2.3). These films were stacked in the centre of the diffusion device. Two thicker sheets (5 cm in diameter and is 3 mm in thick) were made from the same LDPE but

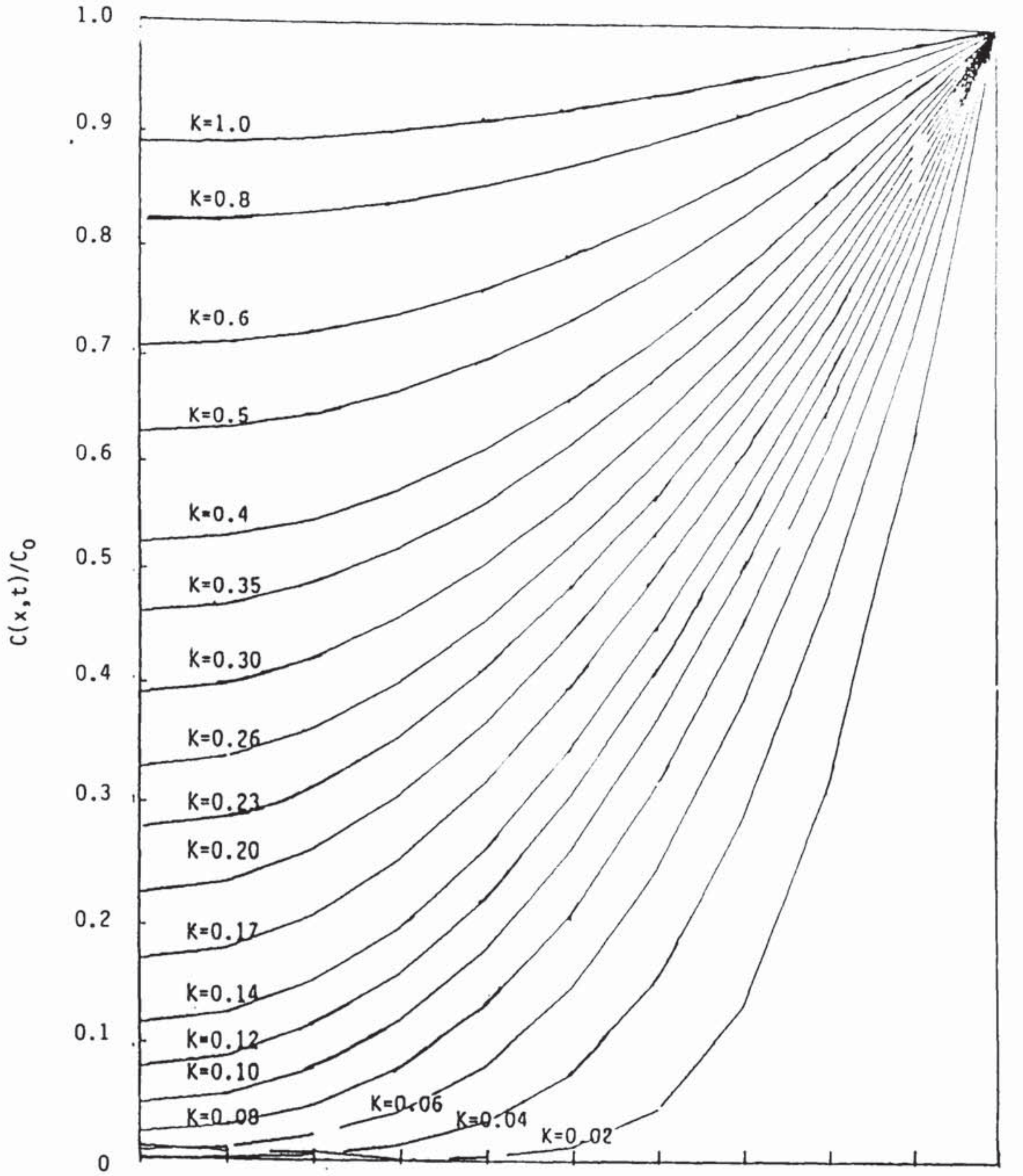


Figure 3.2 Solutions of diffusion equation

x is the position coordinate from the centre of the stack; l is half the total thickness of the stack; C(x,t) is the concentration at position x at time t; C_0 is the equilibrium solubility. The profiles are obtained for different values of K indicated, where $K = Dt/l^2$.

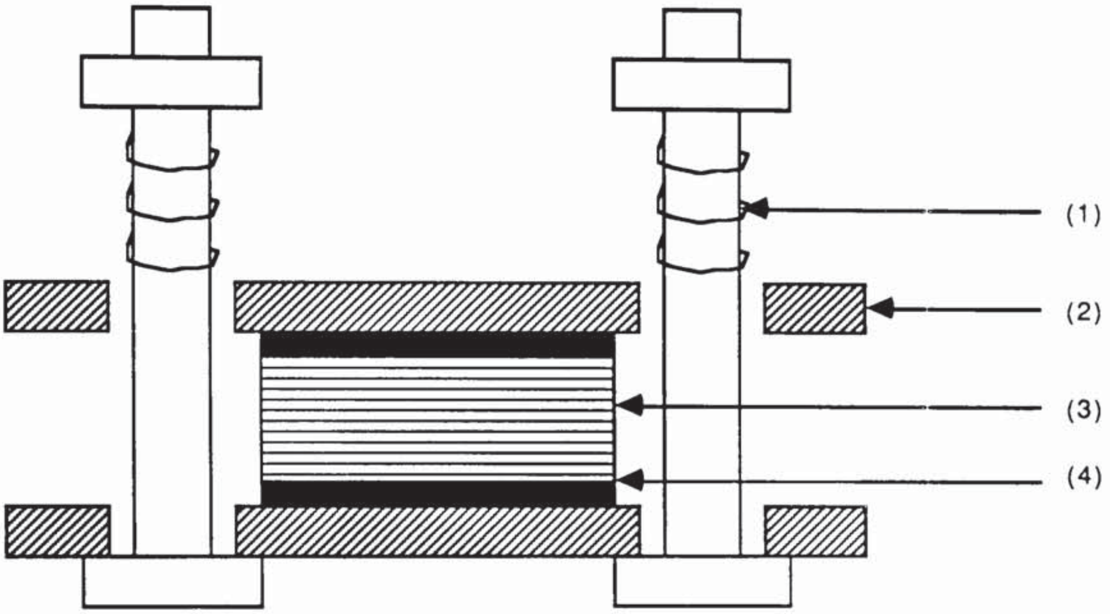


Figure 3.3 Schematic illustration of diffusion cell:

(1) bolts and nuts with compression springs;

(2) aluminium plates;

(3) stack of LDPE films, each 250μm and 5cm in diameter;

(4) LDPE sheets, 3000μm thick and containing excess additives.

contain excess weight of the additive(5-7% w/w) under examination were placed one above and one below the stack to serve as reservoir of additive as well as to maintain the surface concentration at a constant value. Subsequently, the assembly was clamped between two polished aluminium plates (thickness of 5 mm) and pressure to the device was applied through six bolts fitted with compression spring sleeves. The whole device was then placed in a vacuum oven for a period of time at the required temperature. At temperatures below 23°C, 100 μm films were used in the stack to reduce longer experimental times.

At the end of the run, the LDPE films were peeled apart and the concentration of each individual film was determined, by using a Beckman DU-7 ultra-violet/visible computing spectrophotometer according to the method given in Section 2.6(Chapter 2). Afterwards, the concentration profiles of stabilisers were created as a function of position after a fixed length of time. These experimental profiles were then compared with the theoretical curves obtained from equation 3.6 (Figure 3.3) and the K values of the best fit curve was selected with the aid of a basic computer program. The K value of this best fit curve was used to calculate the diffusion coefficients(D) from equation 3.7. As mentioned in section 3.1.1 the sensitivity for the determination of D is best when K is in the vicinity of 0.25±5. Therefore initial experiments were conducted to obtain the approximate values of D and this has been used as a guide line to establish the diffusion times to give value of K in the region of 0.25±0.5. Typical experimentally obtained concentration profiles are shown in Figure 3.4 for 2,4-dihydroxy benzophenone at 70°C.

The above experiment technique was used to obtain diffusion coefficients for all the stabilisers in Table 2.1 at a temperature range of 40-100°C. Prior to these experiments, all the additive free films were kept for one hour at 100°C under nitrogen to acquire a uniform morphological structures throughout the temperature range. To improve the precision of analysis, for temperatures above 40°C, diffusion experiments were carried out at three different times for the same temperature and fitted by a single diffusion coefficient value within an experimental error of 20%.

The experiments at 5°C and 23°C were carried out using 100 μm films. Refrigerator was used for diffusion experiments at 5°C and a temperature variation of ±3°C was observed. Furthermore, the K values obtained were lower (>0.008). Therefore, some theoretical uncertainties might creep into those diffusion coefficients values. In addition, the D values were obtained only from a single diffusion experiment.

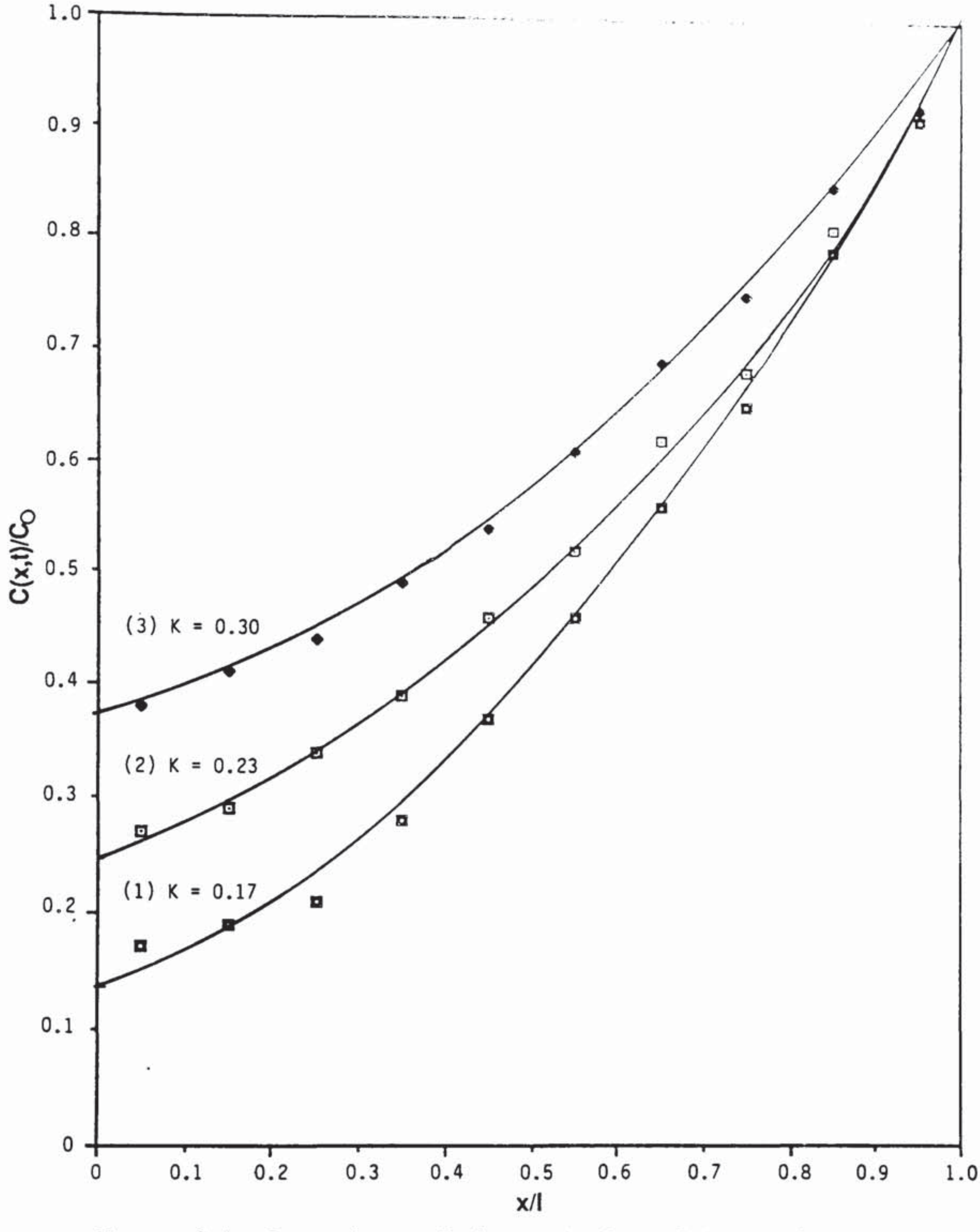


Figure 3.4 Comparison of theoretical profiles with experimentally obtained concentration profiles for UV-OH at 70°C. Points represents the experimental data, solid curves are theoretically calculated values for:

(1) after 150 hours $D = 1.97 \times 10^{-8}$

(2) after 240 hours $D = 1.78 \times 10^{-8}$

(3) after 360 hours $D = 1.45 \times 10^{-8}$

A variation in thickness of the compressed films was observed (in this case 25µm , 10%), this is unavoidable because of the experimental difficulties of pressing films with uniform thicknesses.

Although the polymer films in the stack were compressed under pressure of the springs, gaps might still exist between the contacting films which can offer resistance to the diffusion of additives. To examine the possibilities of such an effect, a control experiment, in which five 1000µm films were used in place of 250µm films while maintaining the overhall thickness of stack similar to the standard procedures, ran concurrently with the standard experiments. These concentration profiles are given in Figure 3.5. It can be seen that, results obtained from the control experiments were identical to that obtain from standard methods within an experimental error of 20%. This suggests that the pressure exerted from compression springs were sufficient for the additives to be transported readily through the polymer stack without any resistance from the surfaces of the contacting films.

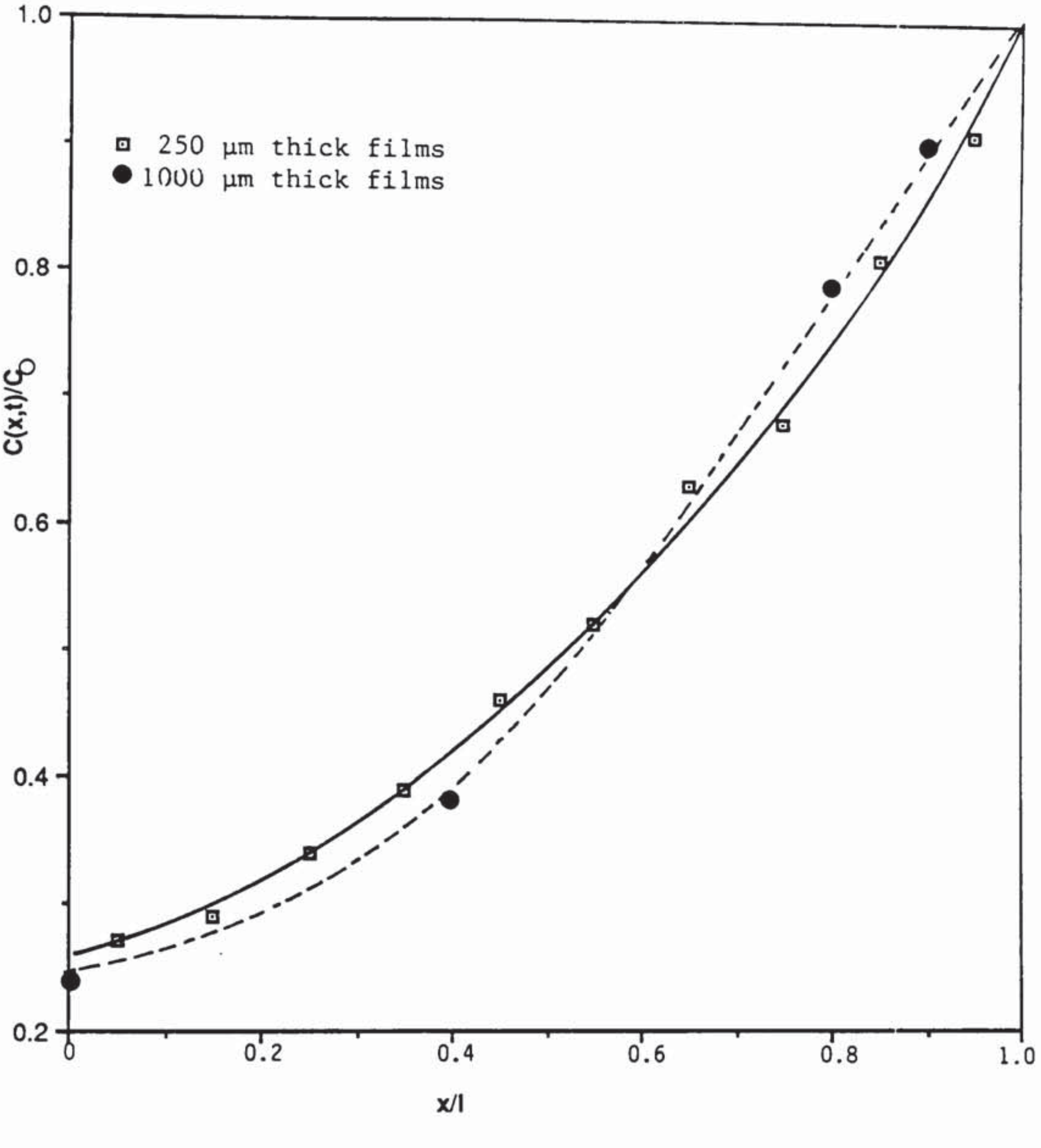


Figure 3.5 Comparison of standard experimental profiles (solid curve) with profiles obtained from 1000 µm films (dotted line) for UVS-nC8 at 70°C

3.2 Results and Discussion

3.2.1 Intrinsic Diffusion Coefficients

Table 3.1 presents the diffusion coefficients of stabilisers (given in Table 2.1) in low density polyethylene over the temperature range 5-100°C. The values given for the temperature range 40-100°C are the arithmetic means of diffusion coefficients calculated from at least three experiments at three different times agreed with each other within an experimental error of ±20%. These errors were quoted as standard deviations in Table 3.1.

The most popular analytical technique selected for measurement of concentration profiles of stabilisers in polymers is the radio-tracer methods[22-25], which is sufficiently sensitive to allow measurements with a precision of ±10% at additive concentrations below 0.1% w/w. In this study errors were some what larger than the above techniques, but considering difficulties in maintaining uniform polymer films with same crystallinity and morphology, these errors can be considered satisfactory.

Intrinsic diffusion coefficients of benzophenone-type uv stabilisers have been evaluated in the literature in low density polyethylene but only over a very narrow

	DIFFUSION COEFFICIENTS(cm^2/sec)				
Tem. K	UV-OH	UV-C2OH	UV-nC8	UVS-H	UVS-C1
278	2.44×10^{-11}	2.43×10^{-11}	6.03×10^{-11}	6.34×10^{-12}	1.02×10^{-11}
296	2.71×10^{-10}	2.38×10^{-10}	5.08×10^{-10}	7.08×10^{-11}	8.74×10^{-11}
313	$1.45 \pm .15 \times 10^{-9}$	$1.33 \pm .13 \times 10^{-9}$	$3.51 \pm .36 \times 10^{-9}$	$5.67 \pm .23 \times 10^{-10}$	$6.10 \pm .46 \times 10^{-10}$
323	$3.34 \pm .45 \times 10^{-9}$	$3.62 \pm .19 \times 10^{-9}$	$1.12 \pm .32 \times 10^{-8}$	$1.34 \pm .41 \times 10^{-9}$	$1.94 \pm .19 \times 10^{-9}$
333	$9.08 \pm .56 \times 10^{-9}$	$8.48 \pm .32 \times 10^{-9}$	$1.83 \pm .29 \times 10^{-8}$	$3.93 \pm .24 \times 10^{-9}$	$5.05 \pm .50 \times 10^{-9}$
343	$1.72 \pm .27 \times 10^{-8}$	$1.41 \pm .23 \times 10^{-8}$	$2.96 \pm .34 \times 10^{-8}$	$7.35 \pm .49 \times 10^{-9}$	$7.93 \pm .80 \times 10^{-9}$
353	$2.27 \pm .37 \times 10^{-8}$	$2.35 \pm .17 \times 10^{-8}$	$4.52 \pm .43 \times 10^{-8}$	$1.32 \pm .76 \times 10^{-8}$	$1.50 \pm .23 \times 10^{-8}$
363	$3.85 \pm .59 \times 10^{-8}$	$3.20 \pm .39 \times 10^{-8}$	$7.93 \pm .63 \times 10^{-8}$	$2.09 \pm .63 \times 10^{-8}$	$2.49 \pm .45 \times 10^{-8}$
373	$6.20 \pm .51 \times 10^{-8}$	$5.50 \pm .69 \times 10^{-8}$	$9.59 \pm .62 \times 10^{-8}$	$2.85 \pm .81 \times 10^{-8}$	$3.39 \pm .69 \times 10^{-8}$

Table 3.1 Diffusion coefficients of stabilisers (see Table 2.1 for chemical structures)

	Diffusion coefficients(cm^2/sec)				
Tem. K	UVS-nC4	UVS-tC4	UVS-nC8	UVS-nC12	UVS-nC18
278	2.16 x 10^{-12}	6.42 x 10^{-13}	5.63 x 10^{-12}	3.47 x 10^{-12}	2.21 x 10^{-12}
296	2.06 x 10^{-11}	9.25 x 10^{-12}	5.26 x 10^{-11}	3.31 x 10^{-11}	2.01 x 10^{-11}
313	1.78±.39 x 10^{-10}	7.68±.28 x 10^{-11}	3.36±.36 x 10^{-10}	1.80±.26 x 10^{-10}	1.21±.36 x 10^{-10}
323	6.09±.20 x 10^{-10}	2.38±.62 x 10^{-11}	6.87±.22 x 10^{-10}	4.57±.41 x 10^{-10}	2.89±.29 x 10^{-10}
333	1.42±.42 x 10^{-9}	5.73±.38 x 10^{-10}	9.14±.42 x 10^{-10}	9.50±.29 x 10^{-10}	6.42±.50 x 10^{-10}
343	2.84±.72 x 10^{-9}	1.47±.63 x 10^{-9}	2.86±.51 x 10^{-9}	1.78±.31 x 10^{-9}	1.28±.51 x 10^{-9}
353	5.48±.62 x 10^{-9}	2.94±.45 x 10^{-9}	4.85±.80 x 10^{-9}	2.97±.72 x 10^{-9}	2.05±.63 x 10^{-9}
363	8.01±.29 x 10^{-9}	4.17±.41 x 10^{-9}	6.34±.67 x 10^{-9}	4.15±.61 x 10^{-9}	2.77±.75 x 10^{-9}
373	1.36±.71 x 10^{-8}	7.87±.69 x 10^{-9}	1.07±.52 x 10^{-8}	6.70±.81 x 10^{-9}	3.94±.69 x 10^{-9}

Table 3./(ctd) Diffusion coefficients of stabilisers

temperature range[22-25,78,79]. Westlake and Johnson [22,23] studied the diffusion of 2,4-dihydroxybenzophenone and 2-hydroxy-4-octoxybenzophenone (Cyasorb UV531) in LDPE at temperature range of 44 and 75°C. Cicchetti et al.[25] determined the diffusion coefficients of many ultra-violet stabilisers in LDPE between 70 and 90°C. In both studies radio-active stabilisers were used and the concentrations were analysed by using radiotracer techniques. The former measured the rate of diffusion of the radio-active benzophenones by depositing a thin layer of stabiliser on one side of a polymer disc and then by monitoring the counting rate at the initially stabiliser-free surface by means of a Gieger-Muller tube. The latter workers allowed the radio-active additive to diffuse into one end of a rod of polymer and then by sectioning it into slices, radio-activity of those slices were measured in a liquid scintillator. Moisan[78,79] used polymer stack method together with infra-red and uv spectroscopy to evaluate diffusion coefficients of many thermal and photo stabilisers in LDPE. Table 3.2 compares diffusion coefficients values obtained for 2,4-dihydroxybenzophenone from the above studies together with the values obtained in this work (note that Cicchetti et al. values are given for 4-hydroxy-4-methoxybenzophenone). Since the above literature data were available for a limited temperature range, these values were extrapolated to other temperatures by assuming that temperature dependence of diffusion

	DIFFUSION COEFFICIENTS(cm^2/sec)		
Tem. °K	Present data	Westlake and Johnson [22]	Cicchetti et al* [24]
278	2.44×10^{-11}	5.19×10^{-11}	6.93×10^{-10}
296	2.71×10^{-10}	3.90×10^{-10}	5.58×10^{-9}
313	1.45×10^{-9}	2.12×10^{-9}	7.88×10^{-9}
323	3.34×10^{-9}	5.27×10^{-9}	1.43×10^{-8}
333	9.08×10^{-9}	1.24×10^{-8}	2.51×10^{-8}
343	1.72×10^{-8}	2.79×10^{-8}	4.27×10^{-8}
353	2.27×10^{-8}	5.97×10^{-8}	7.03×10^{-8}
363	3.85×10^{-8}	1.28×10^{-7}	1.13×10^{-7}
373	6.20×10^{-8}	2.42×10^{-7}	1.76×10^{-7}

Table 3.2. Comparison of diffusion data from the present study with literature data for UV-OH in LDPE

* data obtained for 2-hydroxy-4-methoxy benzophenone

N.B. Data were extrapolated where it is necessary as discussed in Section 3.2.1.

coefficients follow an Arrhenius type relationship and the relevant activation energies remained constant over the temperature range of interest. This extrapolation can be seen in Figure 3.6 where the values of log D was plotted against 1/T(absolute temperature K).

It can be seen from Table 3.2 and Figure 3.6, that the values obtained in this study are generally lower than the data given in literature for 2,4 dihydroxybenzophenone. However, there seems to be a reasonable agreement over the temperature range 40-70°C with the values given by Westlake and Johnson[22]. The values of Cicchetti et al.[25] are much higher at lower temperatures (which is expected because of the reduction in the inter molecular hydrogen bonding of the methoxy derivative) but comparatively lower than that of Westlake and Johnson[22] at high temperatures (over 80°C). Considering that the values obtain by Westlake and Johnson were measured at a temperature range 44-75°C while those of Cicchetti et al. were obtained at 70-80°C, the agreement of the present results with values given by both workers at relevant temperatures were quite remarkable.

Similarly, the comparison of diffusion coefficients of 2-hydroxy-4-octoxybezophenone by the above three studies together with Moisan[78,79] is given in Table 3.3(Fig.3.7).

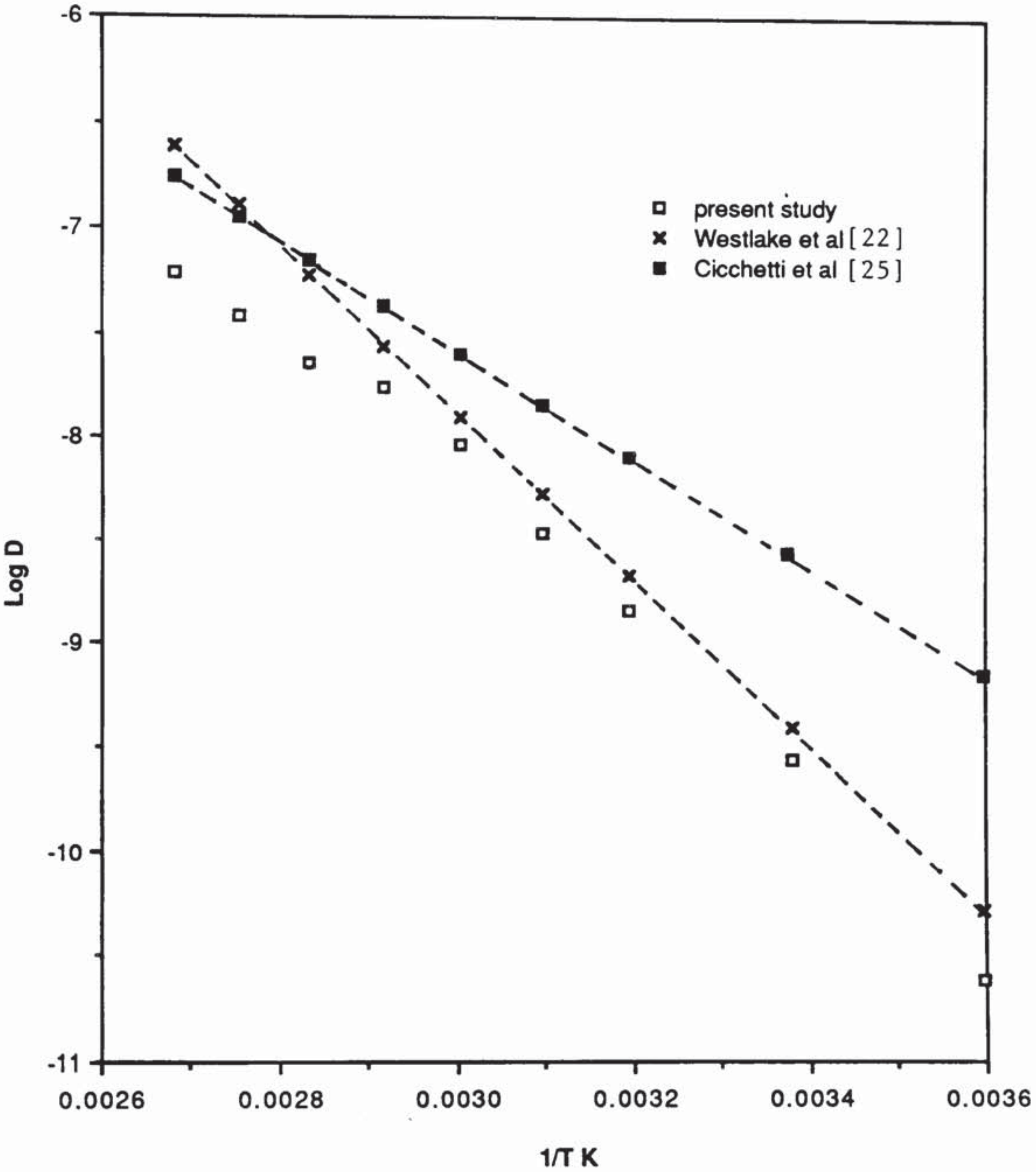


Figure 3.6 Comparison of diffusion coefficient data of this study with, that of Westlake and Johnson [22] and Cicchetti et al.[25] for UV-OH

Diffusion coefficients(cm^2/sec)				
Tem. K	Present data	Westlake and Johnson [23]	Cicchetti et al. [25]	Moisan [39]
278	6.03×10^{-11}	1.64×10^{-10}	1.99×10^{-10}	1.31×10^{-10}
296	5.08×10^{-10}	1.04×10^{-9}	8.81×10^{-10}	1.20×10^{-10}
313	3.51×10^{-9}	4.93×10^{-9}	3.07×10^{-9}	7.71×10^{-9}
323	1.12×10^{-8}	1.14×10^{-8}	6.01×10^{-9}	2.10×10^{-8}
333	1.83×10^{-8}	2.50×10^{-8}	1.13×10^{-8}	5.39×10^{-8}
343	2.96×10^{-8}	5.25×10^{-8}	2.05×10^{-8}	1.31×10^{-7}
353	4.52×10^{-8}	1.06×10^{-7}	3.60×10^{-8}	3.02×10^{-7}
363	7.93×10^{-8}	2.04×10^{-7}	6.10×10^{-8}	6.67×10^{-7}
373	9.59×10^{-8}	3.81×10^{-7}	1.01×10^{-7}	1.41×10^{-6}

Table 3.3. Comparison of diffusion data from the present study with literature data for UV-nC8 in LDPE

N.B. Data were extrapolated where it is necessary as discussed in Section 3.2.1.

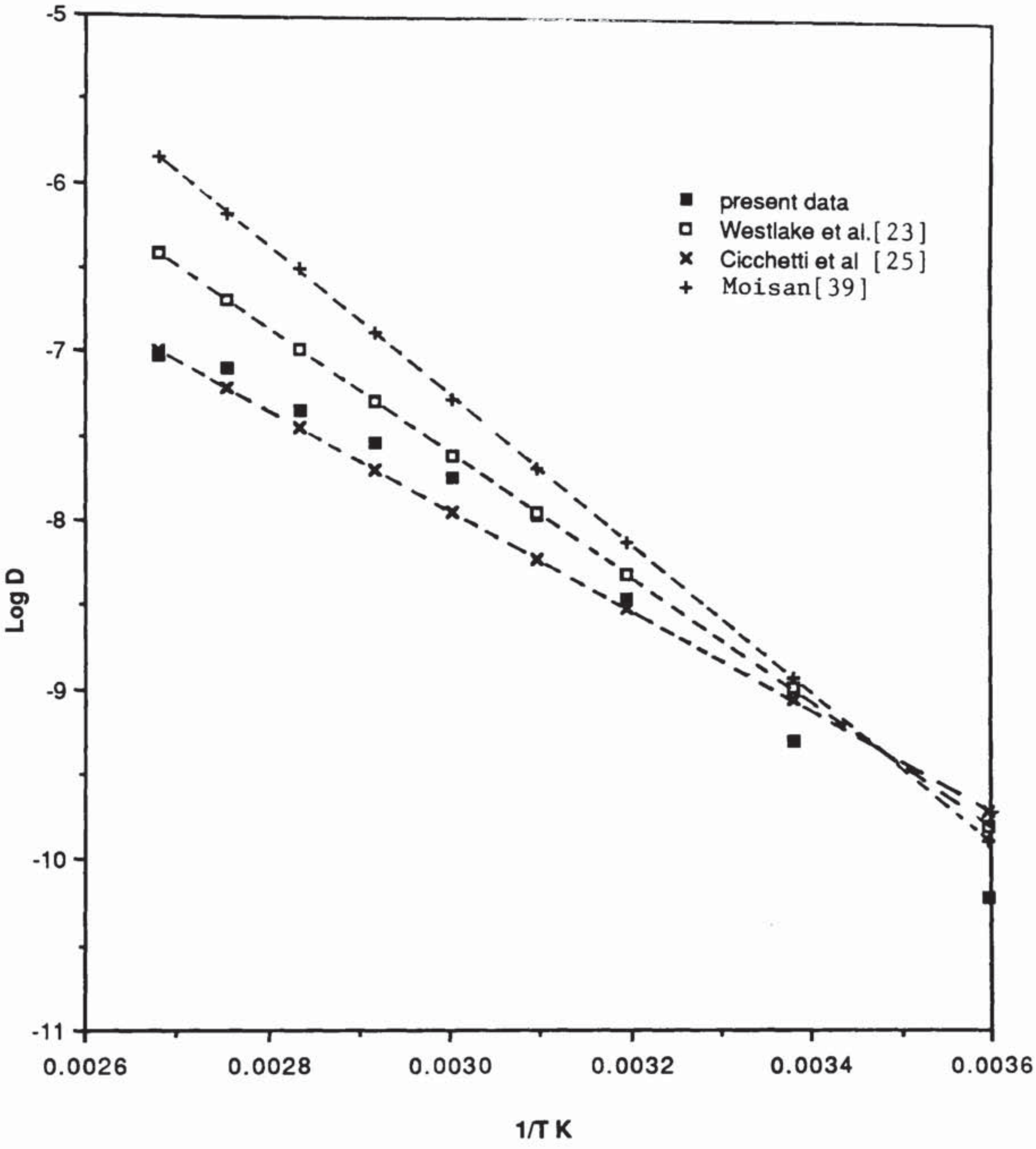


Figure 3.7 Comparison of diffusion data obtained in this study, with that of Westlake and Johnson[22], Moisan[39], Cicchetti et al.[25] for UV-nC8 in LDPE

It can be seen from Table 3.3, the values given by Moisan[78,79], Westlake and Johnson[23] are significantly higher than that of given by Cicchetti et al.[24], whereas the values from this study lies in between. Furthermore, diffusion coefficients obtained in this study at 50°C are similar to the value given by Westlake and Johnson[23] and Moisan[78,79] whereas values obtained above 70°C are closer to the one given by Cicchetti et al.[24]. Therefore, these observations further confirm that the data given in the literature are valid only in the temperature range of study and extrapolation to other temperatures is unreliable.

The differences in diffusion coefficient values obtained by the above workers were further evident when a comparison of the values for 2-hydroxy-4-octoxy benzophenone(Cyasorb UV531) in isotactic polypropylene was made(Table 3.4). The values obtained by Westlake and Johnson[23] at a temperature range 44-75°C are considerably higher than the values given by Cicchetti et al.[25] at a temperature range 80-110°C. These deviations suggest, the variation in results from different laboratories were mainly due to the temperature studied and the nature of the polymer rather than the experimental technique. Comparing present data and the data obtained by Moisan[78,79] with that obtained from radio-tracer technique, it is reasonable to assume that spectroscopic determination of diffusion coefficients

	Diffusion coefficients(cm²/sec)	
Tem.°K	Westlake and Johnson[23]	Cicchetti et al.[25]
278	8.62×10^{-13}	4.25×10^{-13}
296	1.16×10^{-11}	4.21×10^{-12}
313	1.13×10^{-10}	2.88×10^{-11}
323	3.34×10^{-10}	8.12×10^{-11}
333	1.01×10^{-9}	2.15×10^{-10}
343	2.86×10^{-9}	5.38×10^{-10}
353	7.63×10^{-9}	1.28×10^{-9}
363	1.93×10^{-8}	2.90×10^{-9}
373	4.64×10^{-8}	6.28×10^{-9}

Table 3.4. Comparison of literature data for UV-nC8 in isotactic poly propylene.

N.B. Data were extrapolated where it is necessary as discussed in Section 3.2.1.

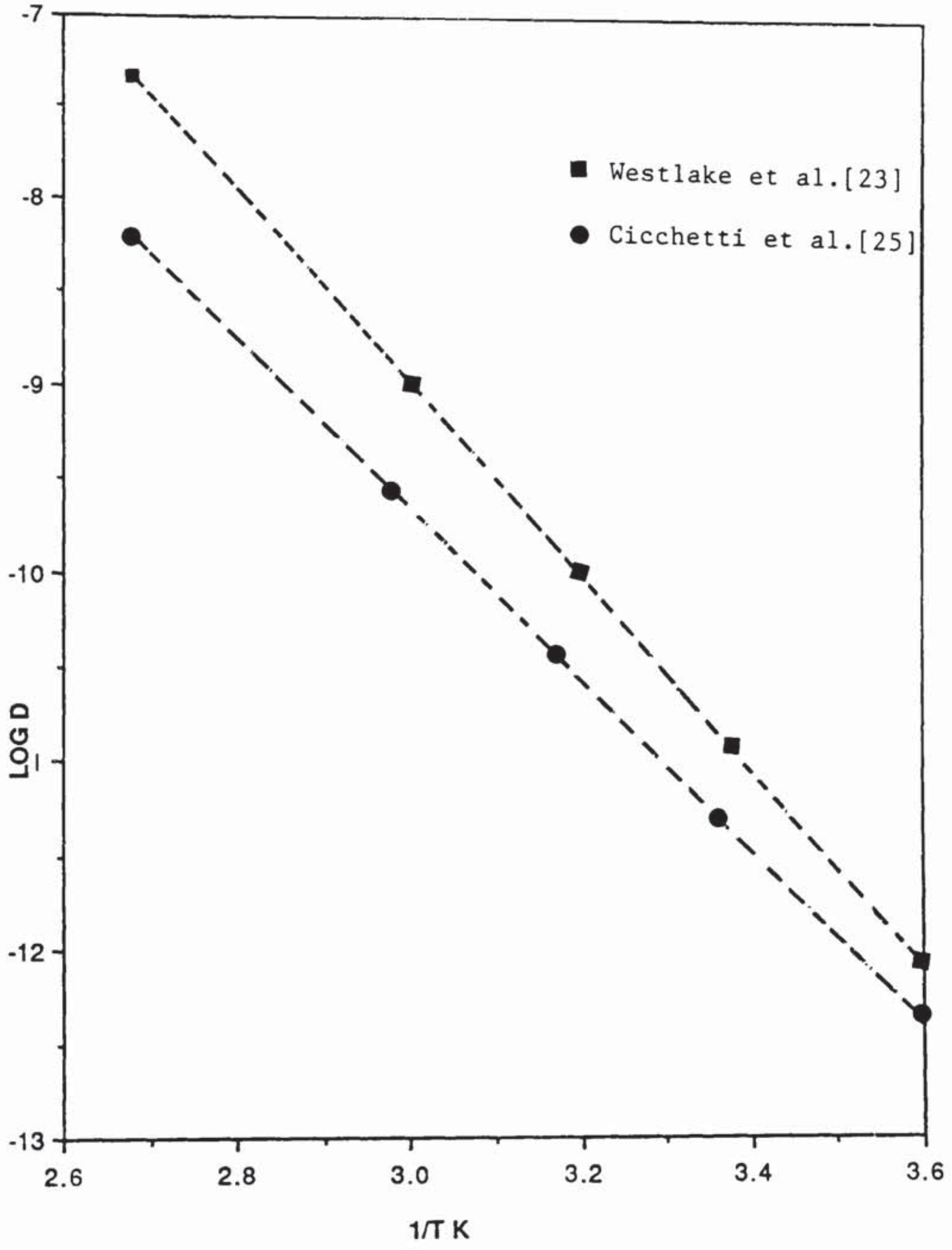


Figure 3.8 Comparison of diffusion coefficients data of Westlake et al. [23] and that of Cicchetti et al.[25] for UV-nC8 in isotactic polypropylene

are as effective as radio-tracer studies. However, it should be born in mind that any attempts to compare the various diffusion data must take into account the physical properties and morphology of the polymer. It has been shown that (Chapter 1, Section 1.2.5) thermal history, crystallinity, size of the spherulites, annealing and transcrystallinity all have considerable effect on the diffusion rates. Slower cooling rates from the melt produced higher crystallinity and higher diffusion coefficients in polyethylene[57]. However, further studies[56,57,39] on diffusion suggest that morphology of the polymer sample is more influential on diffusion coefficients than crystallinity. It was also observed that transcrystallinity at the surfaces increased the diffusion coefficients by a factor of 2.5 in polypropylene[135]. From these observations, it is evident that the morphology is more important on diffusion than crystallinity. Therefore, it is reasonable to assume that the differences in the diffusion coefficients obtained by different groups may be due the variations of morphological properties of the sample used. Unfortunately, the lack of data on morphology of the polymers used in those diffusion studies do not enable us to assess the differences in more details.

3.2.2. Temperature Dependence of Diffusion Coefficients

The diffusion of stabilisers in semi-crystalline polymers is an activated process and therefore the temperature dependence of diffusion coefficients can be represented by an Arrhenius type equation:

$$D = D_o \exp(-E_d/RT) \qquad 3.8$$

where E_d is the activation energy and D_o is the frequency factor. This equation can be simplified to:

$$\text{Log } D = \text{Log } D_o - E_d/2.303\text{x}RT \qquad 3.9$$

The experimental plots of Log D verses 1/T K are given in Figures 3.9A-D, for compounds UV-OH, UV-C8, UVS-H, UVS-Cl, UVS-nC4, UVS-tC4 and UVS-nC8, UVS-nC18 respectively. Similar plots were obtained for other stabilisers. It is apparent from these figures that the plots are not linear but tend to deviate from linearity as the temperature increases. In other words, with increasing temperature diffusion coefficients take lower values than expected from their values at low temperatures. The similarity in the deviations of all the plots suggests, that this deviation is not due to the physical state of the stabiliser but more due to behaviour of the polymer itself. This contrasts the observations made by Moisan[78,79] and Rudy and Rubtsove[136]. They found a

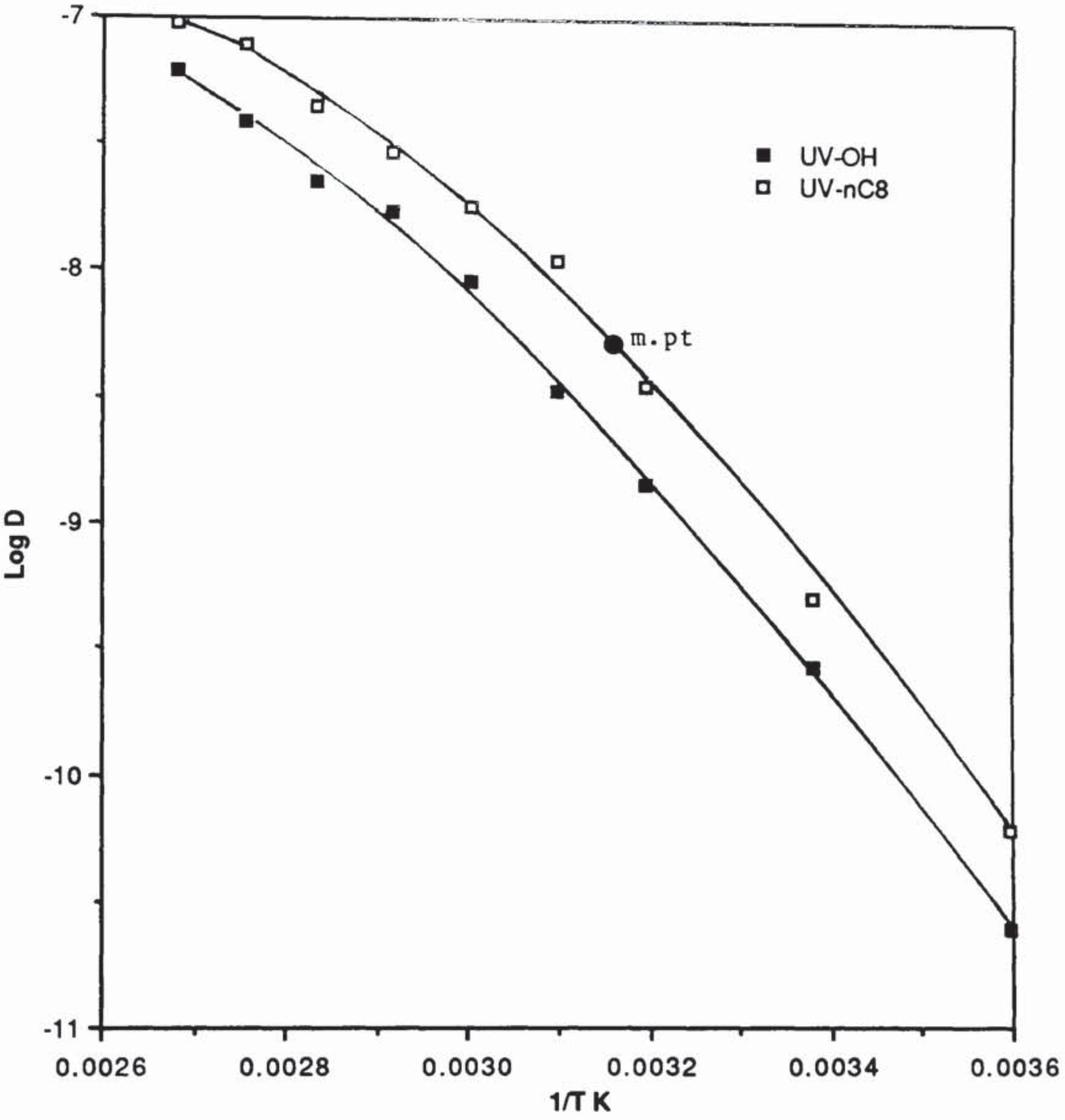


Figure 3.9A Arrhenius plots of diffusion coefficients of UV-OH and UV-nC8 in LDPE

m.pt UV-OH is 145.5°C

m.pt UV-nC8 is 43°C

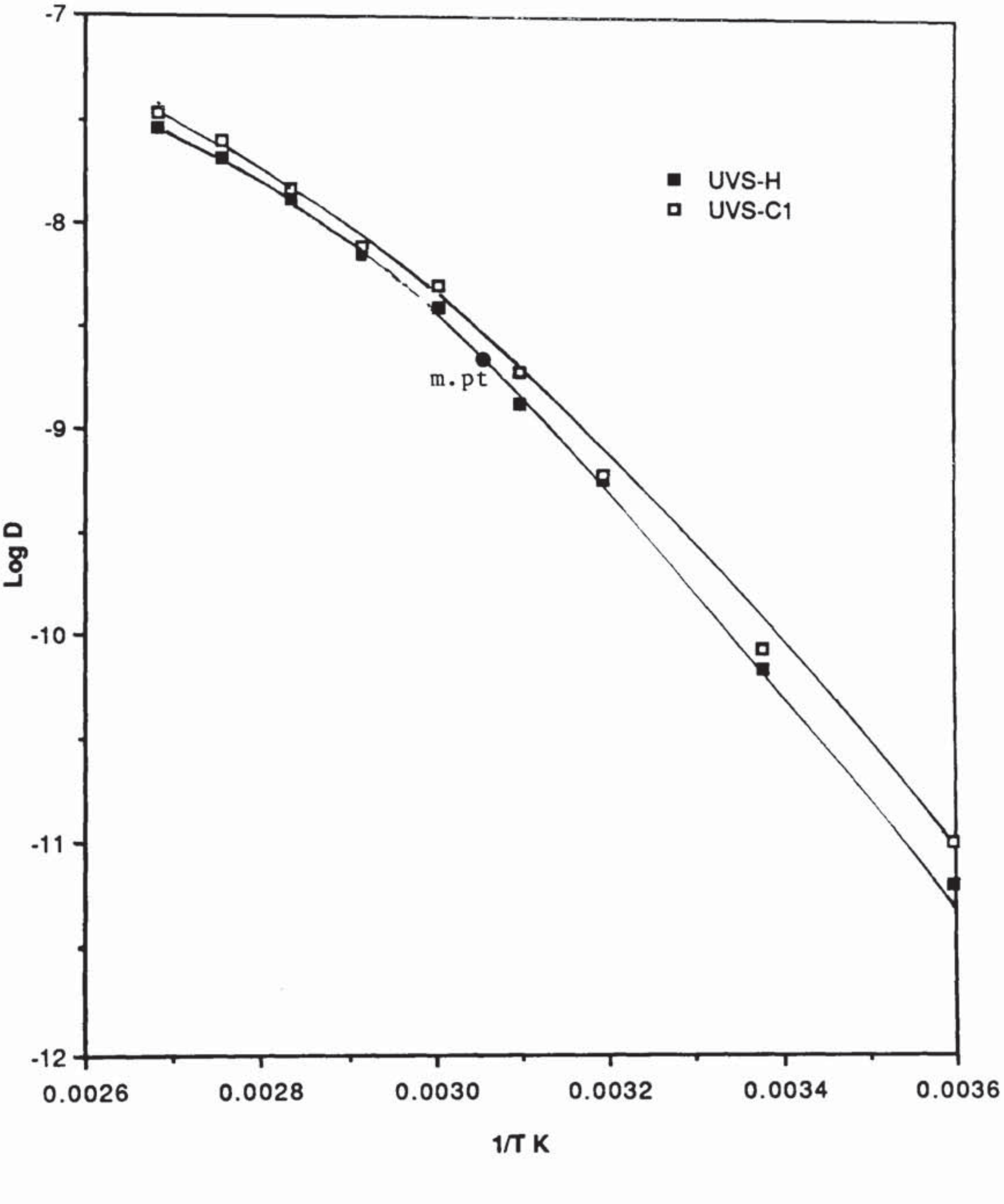


Figure 3.9B Arrhenius plots of diffusion coefficients of UVS-H and UVS-Cl in LDPE

m.pt UVS-H is 53.5°C

UVS-Cl is a liquid in this temperature range.

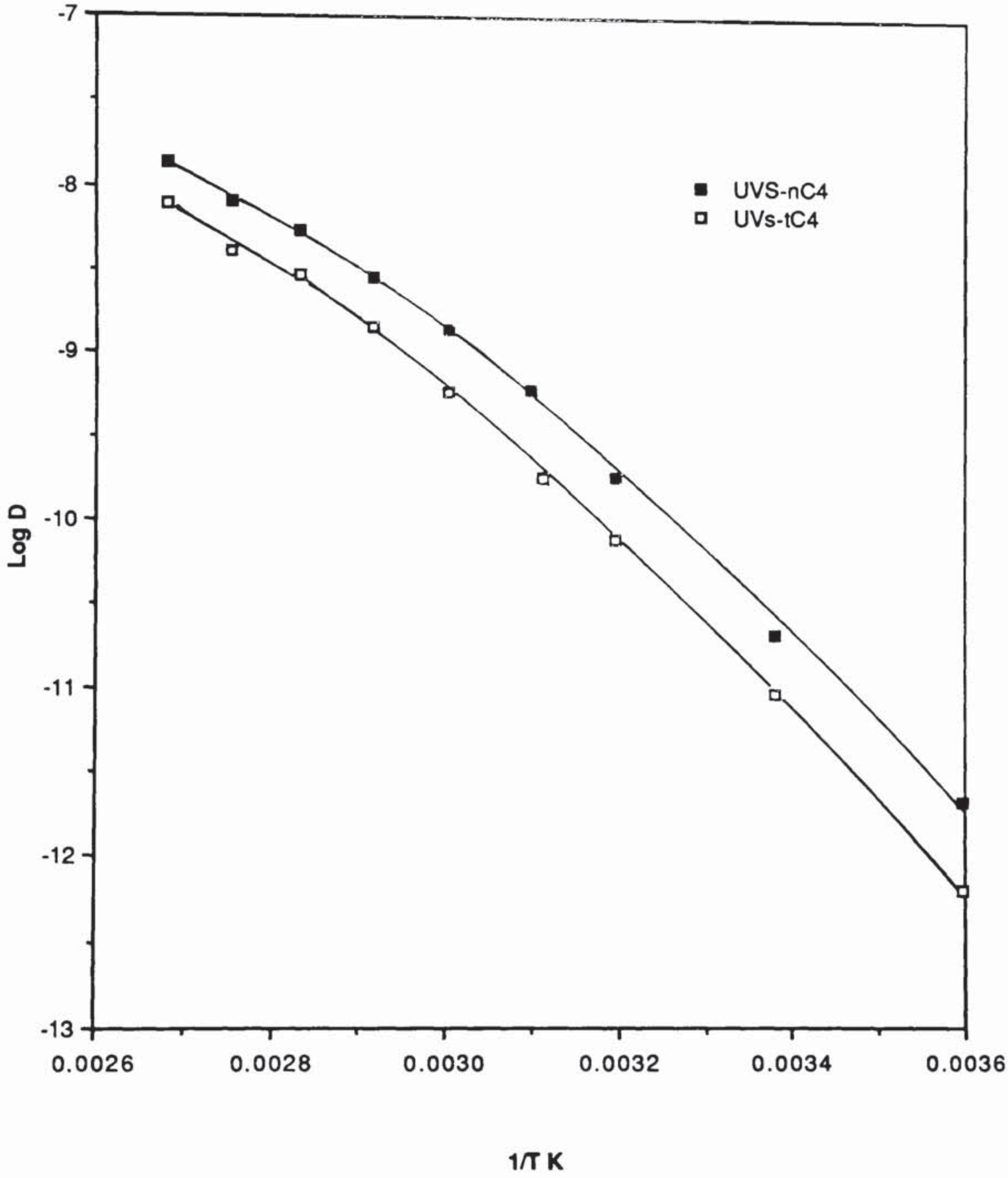


Figure 3.9C Arrhenius plots of diffusion coefficients of UVS-nC4 and UVS-tC4 in LDPE
(Both are liquids in this temperature range)

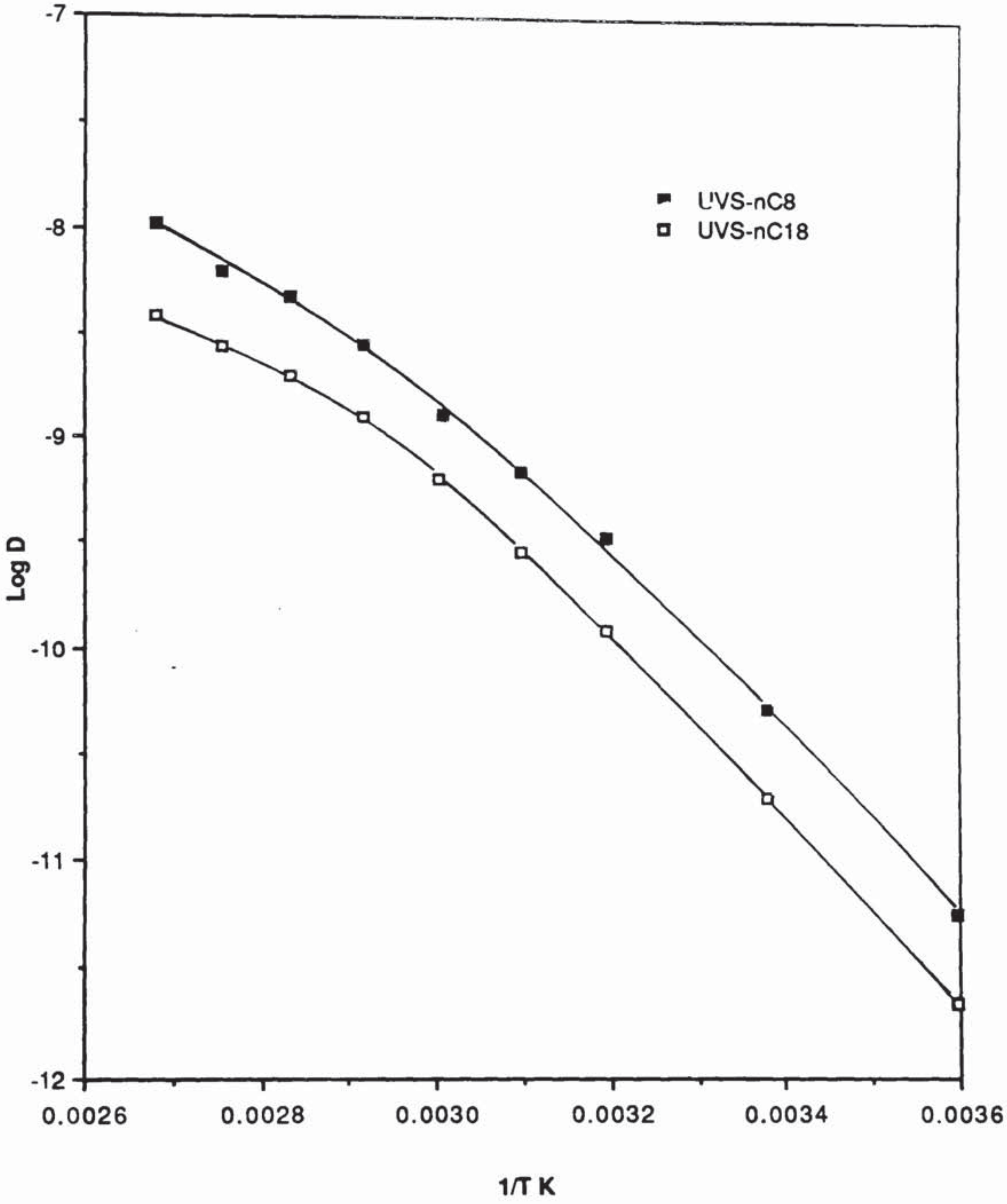


Figure 3.9D Arrhenius plots of diffusion coefficients of UVS-nC8 and UVS-nC18 in LDPE

(Both are liquids in this temperature range) discontinuity of the Arrhenius plots occur above the melting point of the stabiliser. Moisan[39,78,79] attributed, this change in the slopes of Arrhenius plots near the melting point of the additive, to its physical form but did not comment about the significance of these two different slopes. It was argued that the diffusant behaves as a rigid sphere below the melting point of the additive and hence it is less flexible. On the other hand, above the melting point the diffusant, acquires a greater flexibility and is able to diffuse more easily. This seems to be an unrealistic explanation, considering the fact that diffusion and melting are two entirely different processes. The melting point of a crystalline additive is defined as the difference in free-energy between the crystal and the liquid phase, whereas diffusion is an interaction between the polymer and an isolated molecule of the additive which cannot be aware of whether its interaction with other additive molecules would or would not lead to crystallisation. Therefore, these changes in slopes may be either artefact of the experiments or that the temperature at which the change in slope was observed is only fortuitously around the melting point of the additive. Furthermore, it seems more likely that this may have been the result of the morphological changes of the polymer during the experiments or the monotonous deviation of diffusion coefficients from linearity as observed in this study.

Since these Arrhenius plots were not linear, they were divided into three narrow temperature regions, 5-40°C, 40-70°C and 70-100°C. Least square method of regression analysis was then used to find the best fit line for these three regions and one for the entire temperature range. Table 3.5 presents the activation energies and pre-exponential factors calculated from the above best fit lines. These activation energy values (Table 3.5) clearly show a reverse relationship with temperature. This suggests that activation energies are dependent on temperature for these stabilisers. This contrasts the temperature independence of activation energies of small molecules[42]. At this point, one should bear in mind that activation energy calculations are sensitive to experimental errors in diffusion coefficient data and comparison of these values has to be done with care.

Comparison of activation energies obtained from the present study together with that given by Westlake and Johnson[22,23], Cicchetti et al.[24] and Moisan[39], for stabilisers UV-OH and UV-nC8 in LDPE are shown in Table 3.6. There is a remarkably good agreement between the values given by Westlake and Johnson and data obtained in this study in the same temperature range(44-75°C), whereas the values given by Cicchetti et al. in a temperature range 70-90°C are in close agreement with the values calculated at 70-100°C. The activation energy values obtained by Moisan[39] were higher than the others

	Activation Energy (kJ/mol)							
Tem. range	278-373°K		278-313°K		313-343°K		343-373°K	
Stab.	E_d	$\mathrm{Log}D_0$	E_d	$\mathrm{Log}D_0$	E_d	$\mathrm{Log}D_0$	E_d	$\mathrm{Log}\ D_0$
UV-OH	70.61	2.85	84.67	5.32	75.25	7.67	46.42	-0.73
UV-C2OH	69.83	2.69	82.89	4.97	71.08	3.02	46.70	-0.74
UV-nC8	68.25	2.55	77.23	4.29	71.01	0.01	43.63	-0.88
UVS-H	77.70	3.58	92.88	6.24	78.33	3.82	48.30	-0.76
UVS-C1	75.67	3.32	84.51	4.87	77.60	3.79	51.85	-0.18
UVS-nC4	80.85	3.66	91.06	5.42	82.01	3.98	54.14	-0.29
UVS-tC4	85.76	4.10	99.01	6.41	86.98	4.41	57.27	-0.10
UVS-nC8	67.64	1.63	84.57	4.66	65.47	0.42	44.30	-1.79
UVS-nC12	68.44	1.58	81.79	3.92	68.05	1.63	45.88	-1.76
UVS-nC18	68.78	1.45	82.81	3.90	70.39	1.83	39.15	-2.92

Table 3.5 Activation energy(E_d) and Log D_0 of stabiliser series.

N.B. Data obtained by least square method of regression analysis.

	Present study				Westlake and Johnson [22,23]	Cicchetti et al. [24]	Moisan [39]
	Temperature range						
	278-373°K	278-313°K	313-343°K	343-373°K	313-348°K	343-363°K	323°K
UV-nC8	68.25	77.23	71.01	43.63	70.39	56.57	84.80
UV-OH	70.61	84.67	75.25	46.42	76.68	74.16	-

Table 3.6 Comparison of activation energy data obtained in this study together with literature available data

and this may be due to the low temperatures (≈50°C) used for diffusion experiments. This evidence confirms further, that activation energies are temperature dependent and consequently the Arrhenius plots are valid only for a very narrow temperature range. Therefore extrapolating diffusion data can lead to enormous uncertainties.

3.2.3 Factors Affecting Diffusion Coefficients

Not only the substrate affects diffusion of additives in polymers, but the properties and structure of the diffusant also play a role. One of the factors that affect the diffusion coefficient is shown to be the molecular weight of the diffusant[27,57,64-66].

Figure 3.10 shows the relationship between Diffusion coefficients and the molecular weight of the stabiliser series at temperatures 5, 40, 70 and 100°C. The scatter of data in Figure 3.10 reveals that, although there is a general tendency for the diffusion coefficient to decrease with increasing molecular weight, no direct relationship can be obtained. It seems that the diffusion coefficient is more dependent on the structure and shape of the additive rather than on its molecular weight. However, there seems to be a linearity between the diffusion coefficients and the length of the alkyl chain for stabilisers UVS-nC(X), X=1,4,8,12,18 (Figure

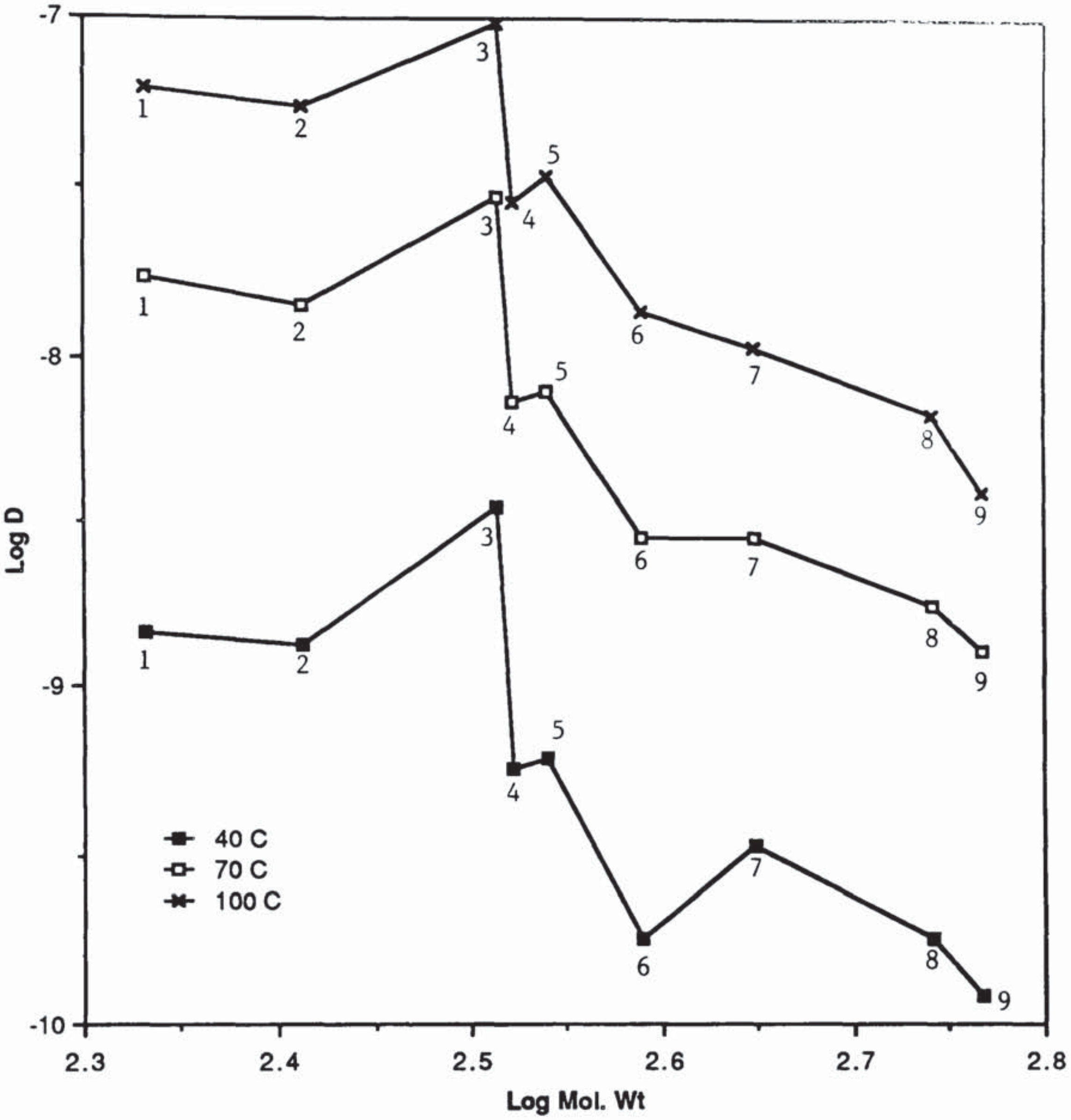


Figure 3.10 Plots of log molecular weight verses log diffusion coefficients of stabilisers at 40, 70 and 100°C

1. UV-OH 2. UV-C2OH 3. UV-nC8 4. UVS-H

5. UVS-nC1 6. UVS-nC4 7. UVS-nC8 8. UVS-nC12

9. UVS-nC18

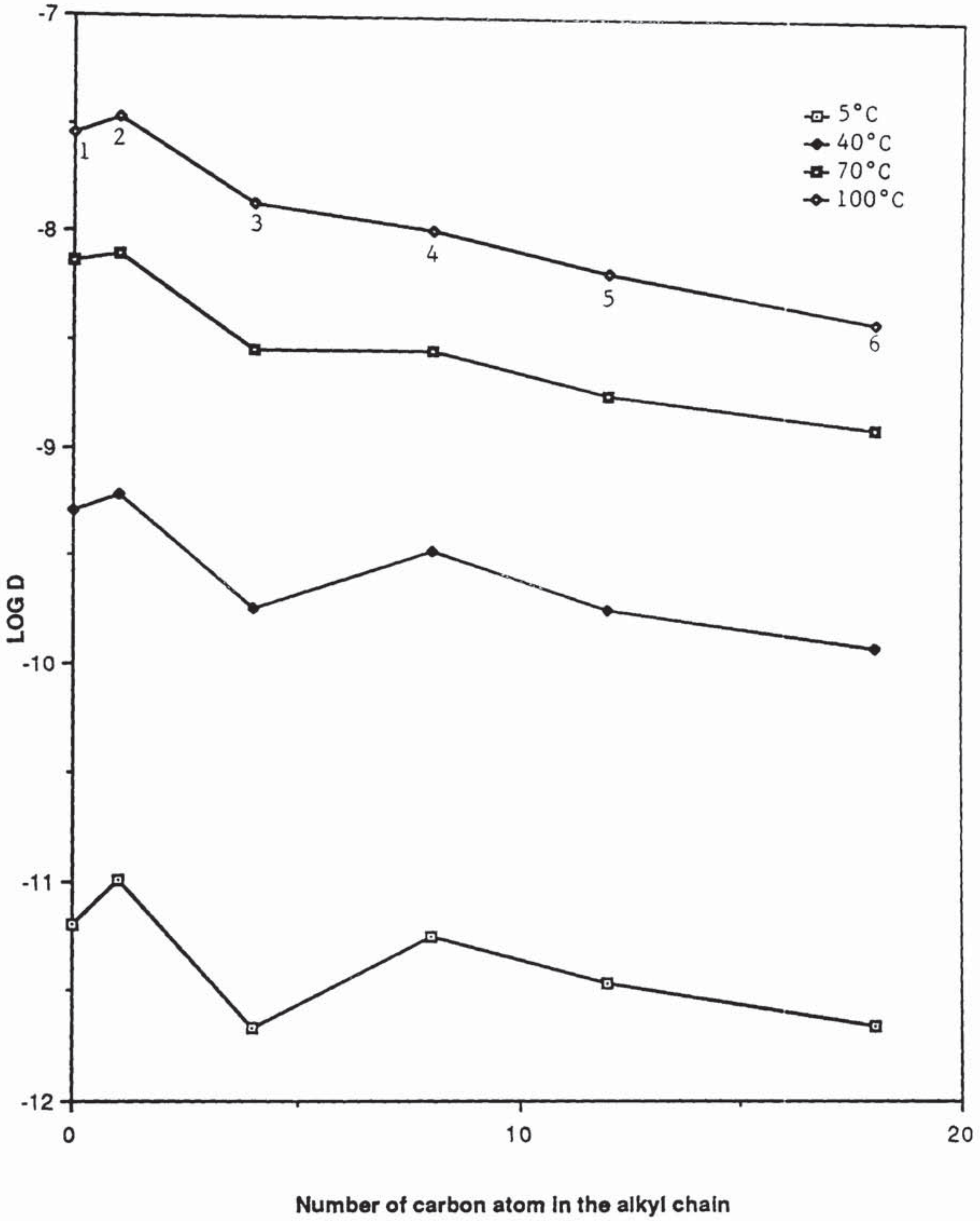


Figure 3.11 Plots of number of carbon atoms in the alkyl chain of the UVS-nC(X) series verses log diffusion coefficients at temperatures 5, 40, 70 and 100°C.
1. UVS-H 2. UVS-nC1 3. UVS-nC4 4. UVS-nC8
5. UVS-nC12 6. UVS-nC18

3.11), diffusion coefficients decrease with increasing length of the alkyl chain. Similar observations were made by Prager and co-workers[64-65], for the diffusion of paraffins in polymers.

Attempts were made in the literature to correlate the diffusion coefficients(D) of a diffusant to its molecular weight(M) in the form of the following equation[27, 137]

$$D = KM^{-\alpha} \qquad 3.10$$

Where K and α are constants. The plots of Log D verses LOG M for UVS-nC(X), (X=1,4,8,12,18) stabiliser series can be seen in Figure 3.12 for temperatures 40, 70 and 100°C. There seems a reasonable correlation between the molecular weight and the diffusion coefficients except at high temperatures rather than the low temperatures.

Another interesting observation is the difference in diffusion coefficients of UVS-nC4 and UVS-tC4. Despite their similar molecular weights, the difference in diffusion coefficient of n- and t-butyl group suggests that diffusion coefficients depends more on the cross sectional area of the molecule rather than its length. For example at 100°C, changing the alkyl chain of UVS-nC1 to UVS-nC4, the percentage decrease in the diffusion coefficient is 250%, while changing from UVS-C1 to UVS-tC4, this change is 430%. Similarly, moving from

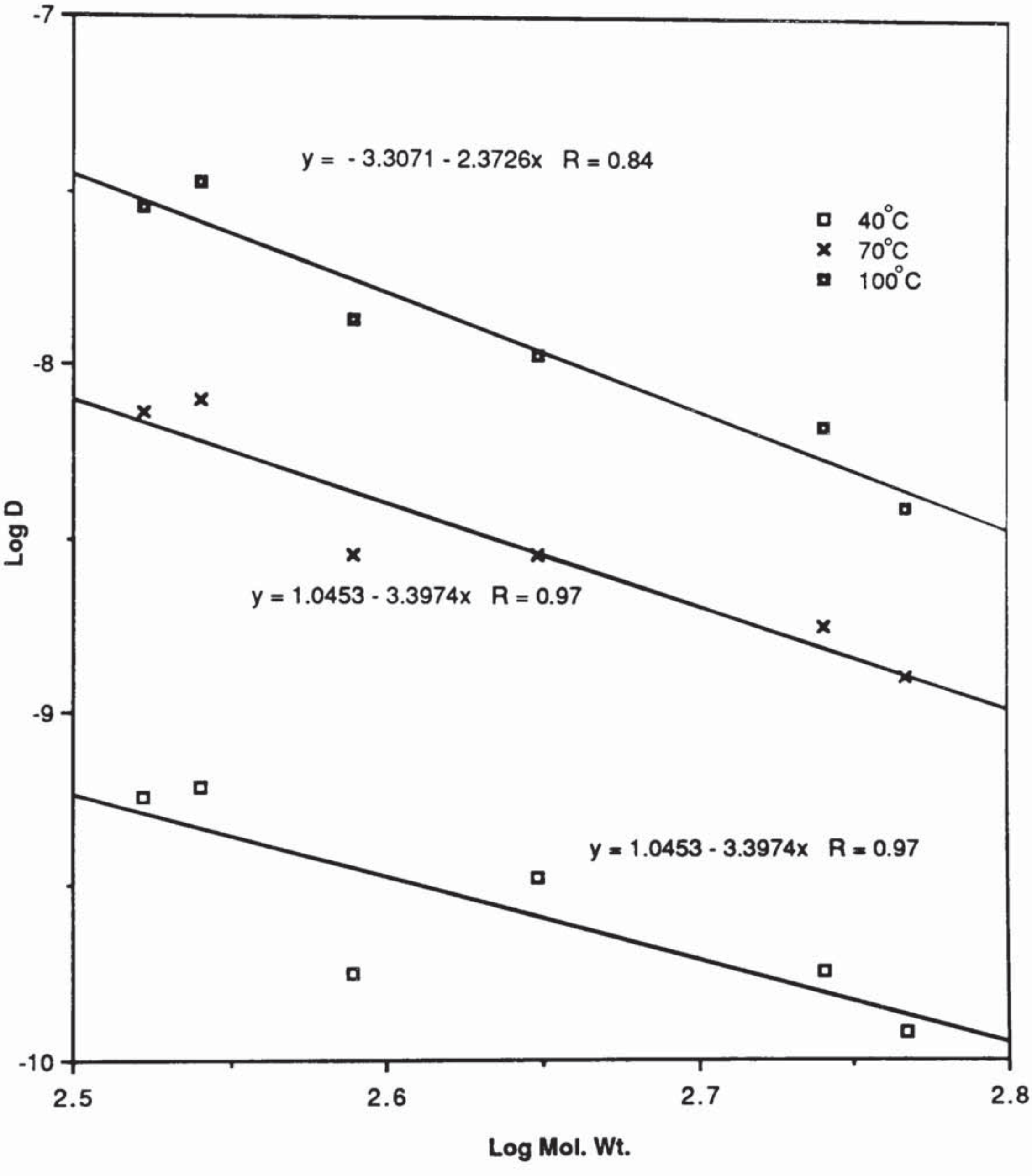


Figure 3.12 Plots of log molecular weight of stabilisers verses log diffusion coefficients of the UVS-nC(X), X = 0, 1, 4, 8, 12, 18 of stabilisers at 40, 70 and 100°C.

UVS-nC4 to UVS-nC8 is associated with a decrease of 127% and from UVS-nC4 to UVS-tC4, decrease by 172%. This shows that diffusion coefficients can be reduced to a significant level by increasing its cross sectional area rather than the length of the diffusant. Similar effect of branching of additives on diffusion was demonstrated by Prager and Long[64] for the diffusion of different alkanes in polyisobutylene (see Table 3.7).

Hydrocarbon	$D \times 10^{-10}$ cm^2/sec
n-propane	4.81
n-butane	3.24
isobutane	1.45
n-pentane	2.64
isopentane	1.32
neopentane	0.62

Table 3.7. The effect of the diffusant size on the diffusion of hydrocarbons in polyisobutylene

The work described here and the above table[64] confirm that the bulk has a greater influence on diffusion than the length at a comparable molecular weight of the diffusant. Therefore, attempts to correlate the diffusion coefficients with molecular volumes but not with the length or molecular weight of diffusants were made[70].

The above effect can be explained by "hole" theory[43]. The activation energy of diffusion corresponds to the energy required to push the polymer molecule far enough apart to form a "hole" (free volume), and therefore added energy is required to the diffusant to jump into a hole[43]. Therefore, the larger the size of the diffusant molecule, the larger the hole needed for the diffusion to take place and this results in low diffusion coefficients. Furthermore, Barrer and co-workers[138] and Prager et al.[64,65] have shown that diffusion coefficients of n-paraffins in polymer do not change above a certain length of the molecule. This confirms that the diffusion takes place preferentially along the greatest length of the molecule. The present results also suggest that increase in the alkyl length of the stabiliser has little effect on diffusion coefficients.

The results obtained for the diffusion coefficients (Table 3.1) suggests that, diffusion rate is affected not only by the molecular weight and molecular dimensions but also by its chemical structure. The effect of hydrogen bonding on diffusion rate is clear in the case of compounds UV-OH and UV-nC8. According to the "hole" theory, higher diffusion coefficient is expected for the smaller UV-OH than UV-nC8, however results obtained show the reverse trend. Similarly, increase in diffusion rate in UVS-Cl compared to that of UVS-H is due the reduction of the hydrogen bonding of the former compound. The polar properties of the diffusant also affects the diffusion rate. For example, UV-nC8 and UVS-H have similar molecular weights but have different functional groups attached to the benzophenone moiety. The UV-nC8 contains non polar octyl hydrocarbon group while UVS-H has polar thio-ester group (Table 2.1). The diffusion coefficients of these two additives are varied by factor of four, the high diffusion coefficients of the less polar analogue is obvious. Similarly, polar properties of the diffusant was attributed for the difference of diffusion rates of 1,1-dichloroethane and 1,2-dichloroethane[54], though both have identical molecular weights and composition, the latter diffuse slowly owing to the polar nature of the molecule. This effect can be explained by considering the interaction between the diffusants in a non polar polymer. These interactions manifest themselves by an apparently higher molecular weight or volume arising from aggregations of molecules through their intermolecular attractions or hydrogen bondings.

3.2.4 Factors Affecting Activation Energies of Diffusion

Activation energy of diffusant can be considered as the energy barrier that has to be overcome for the diffusion of molecules in polymers to occur. Therefore, it depends on the nature of the polymer and the diffusant and factors which decrease activation energies may decrease the diffusion rate of the molecule in the polymer.

In this study activation energies are obtained in three different temperature regions and these values can be seen in Table 3.5. It is apparent from these figures that activation energy decreases when the temperature increases. Figure 3.13 shows the dependence of activation energy on molecular weight and because of the scatter of the data points (Figure 3.13), no definite pattern can be obtained. However, considering that the activation energy calculations are very sensitive to experimental errors, only approximated observations can be made. Activation energies are usually discussed in terms of free volume theories[43,44,46]. According to this theories, activation energy depends upon the polymer and it is proportional to the molar volume of the diffusant[43]. Figure 3.14 shows activation energies of diffusants containing n-alkyl group(except for t- an n-butyl). It seems that the activation energies are independent on the number of carbon atoms in the alkyl chain(except for

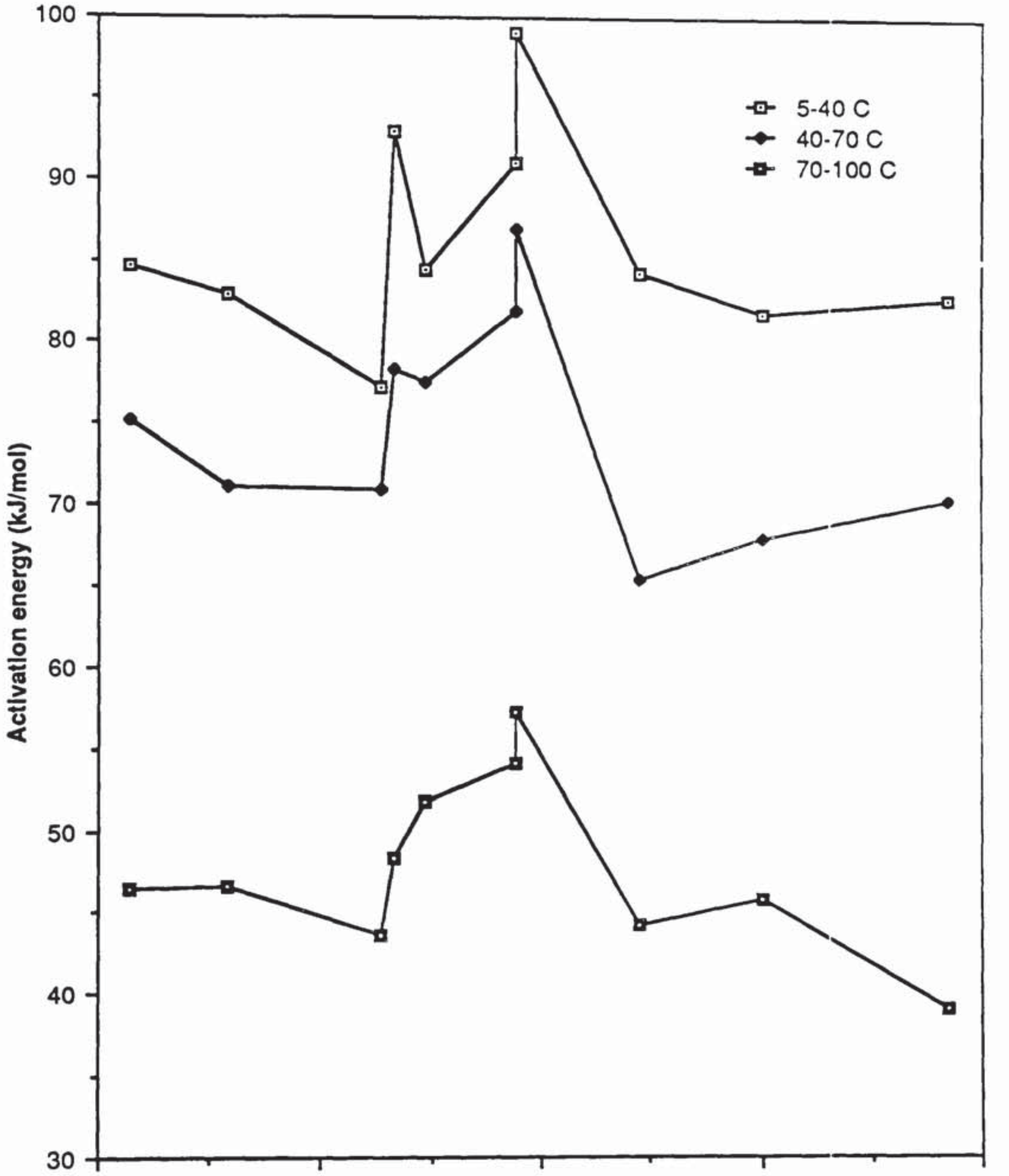


Figure 3.13 Plots of molecular weight of stabilisers verses activation energy calculated for three narrow temperature range

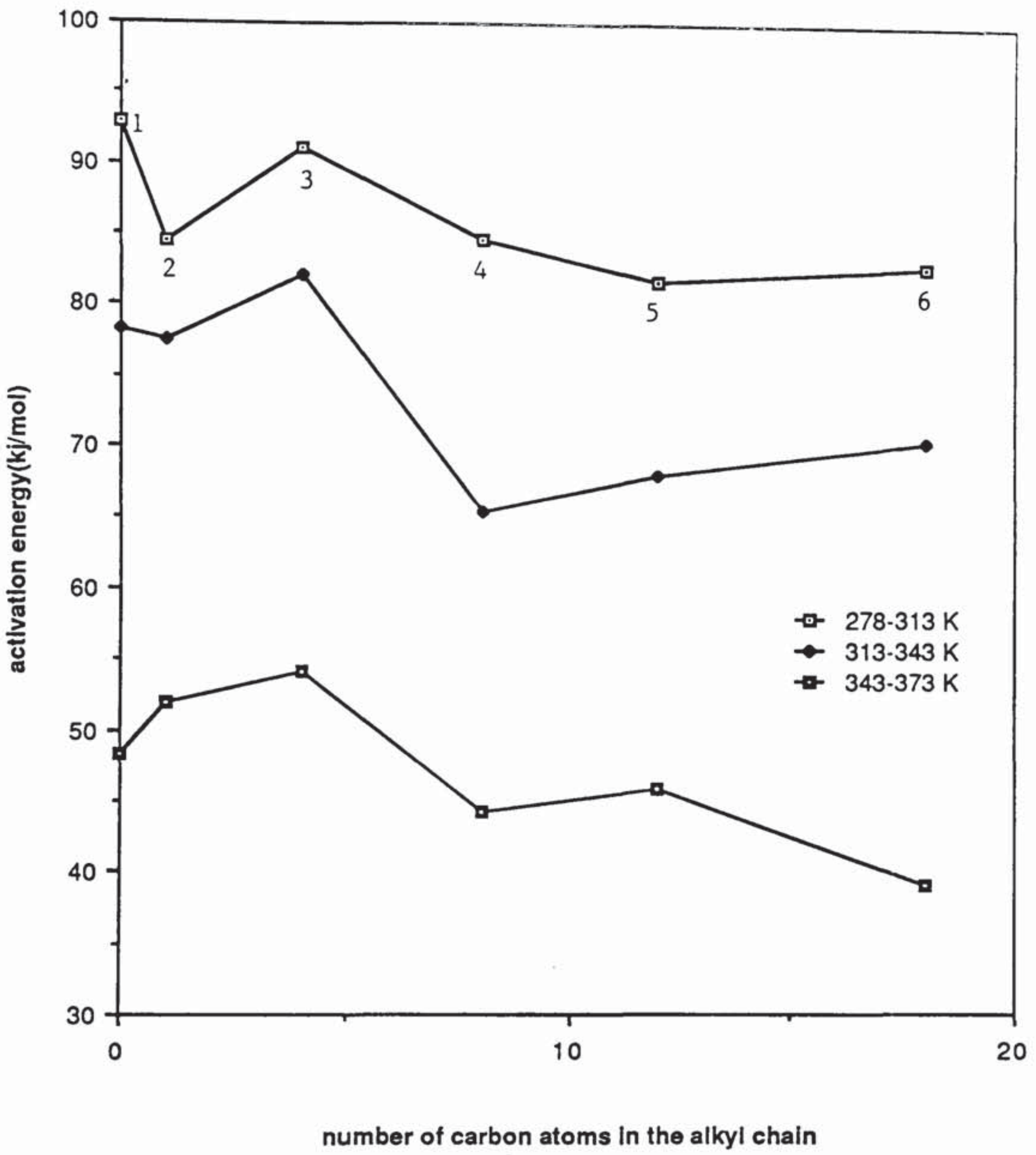


Figure 3.14 Dependence of activation energy on the the number of carbon atoms in the alkyl chains of UVS-nC(X) series at three narrow temperature range

1. UVS-H 2. UVS-C1 3. UVS-nC4 4. UVS-nC8 5. UVS-nC12 6. UVS-nC18

n-butyl) implying that activation energies are independent of molecular weight for a particular classes of compounds.

Similar observation of independence of activation energy on molecular weight for a homologous series was shown by DeGennes[138]. An alternative approach to the "hole" theory was suggested and treats the diffusion of long, flexible molecule as a 'reptation' process, analogous to the snake in the forest. This approach leads to the prediction of the independence of activation energy on molecular weight. However, in this study, it was observed that the above relation is valid only for a homologous series of additives.

The introduction of polar groups, that are capable of forming intermolecular hydrogen bonds and branched side groups has pronounced effect on activation energy. All these factors decrease the activation energies considerably and can be explained in terms of the free volume theories[43].

3.3 Conclusions

1. Polymer stack method, together with uv/vis spectroscopy prove to be a successfull technique for evaluation of diffusion coefficients of hydroxybenzophenone in low density polyethylene. The diffusion coefficients yielded were subject to 20% of experimental error and this can be considered as satisfactory when compared with 10% error observed in highly sophisticated radio-tracer evaluations.

2. The diffusion coefficient obtained in this study are agreed well with those previously reported in literature for similar compounds over a narrow temperature ranges.

3. The temperature dependence of diffusion coefficient follows an Arrhenius type equation only for a narrow temperature range.

4. As temperature increases diffusion coefficients take lower values than expect from extrapolating from low temperature measurements. This may be due to the morphological changes occur in the polymer films during the experiments.

5. Diffusion coefficients were found to depend more on the chemical structure of the diffusant rather than

their molecular weights. Groups that increase the diameter of the molecule decrease the diffusion subtantially, while increasing in chain length has little effect on its value.

6. For stabilisers, if only change of the structure is by a linear alkyl group, the dependence of molecular weight on diffusion coefficient can be established. At high temperature, the relationship is more pronounced than at low temperature.

7. Additive melting point does not have a significant effect on temperature dependence Arrhenius plots of diffusion coefficients. This contrasts, some observations made in the literature.

8. As the diffusion temperature increases, the activation energies take lower values. Activation energies does not have significant effect when the chain lengh of the additive increase, while attachment of polar or groups that are capable of forming hydrogen bonding may increase it value considerably.

CHAPTER FOUR

SOLUBILITY OF STABILISERS IN LOW DENSITY POLYETHYLENE

CHAPTER FOUR

SOLUBILITY OF STABILISERS IN LOW DENSITY POLYETHYLENE

Equilibrium solubilities of the stabiliser series (given in Table 2.1) were determined in low density polyethylene over a temperature range 5-100°C. In this Chapter experimental procedure for the determination of solubilities will be discussed. The results obtained will be analysed in terms of regular solution theory. In addition detail structural analysis of solubility data in low density polyethylene will be presented.

4.1 Theoretical Approach to the Experimental Determination of Equilibrium Solubility

The solubility of an additive in a polymer is determined by the free energy change associated with the transfer of the additive from its equilibrium state as a pure material into the polymer matrix. Therefore measurements of solubilities of additives in polymers require a true equilibrium to be established between the additive and the polymer. Various experimental approaches used for the achievement of this equilibrium are discussed in Chapter 1(Section 1.3.3) and it seems that most methods of measuring solubilities were equilibrium methods. These procedures involve establishing saturation equilibrium between the additive and the polymer, and subsequently by measuring the additive concentration in the polymer. In this study similar approach for the evaluation of solubilities were used.

4.1.1 Experimental Procedure for the Evaluation of Equilibrium Solubility

The experimental set up for evaluating equilibrium solubility for stabilisers is shown in Figure 4.1. The construction of the solubility cell was similar to the diffusion cell (see Chapter 3, Section 3.1.2) and the experimental procedure was similiar to that used by Feldshtein and Kuzminskii[94] and later by Billingham and co-workers[29]. Three compression moulded films of low density polyethylene without any additives, having thickness of 250 μm and 5 cm diameter were stacked together and this was held in between two thicker films about 3000μm thick and having the same diameter, but containing about 5-7% w/w of the stabiliser. In order to avoid any physical contamination between the bloomed additive on the surface of the thicker film with additive free films, two further films of thickness 100μm but containing no additives were placed above and below the three film stack of additive free films. This eliminates the cleaning of the surface of the films during and after the experiments. Altogether five such units were assembled and placed in between two aluminium plates of the solubility cell. Pressure to the device was applied

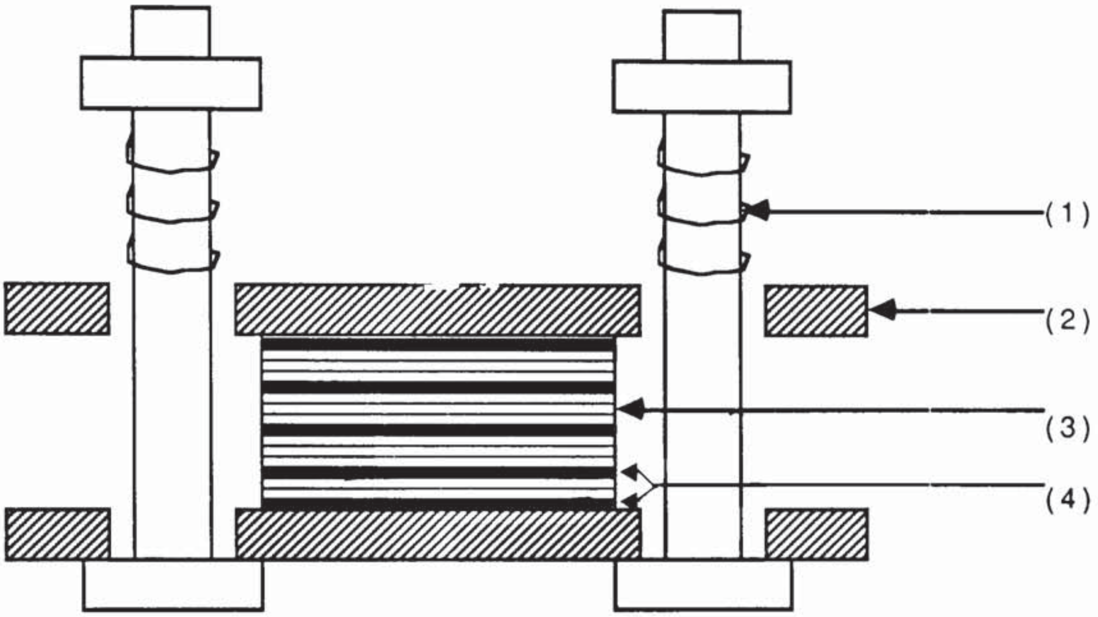


Figure 4.1 Schematic illustration of solubility cell:

(1) bolts and nuts with compression springs;

(2) aluminium plates;

(3) stack of LDPE films, each 250μm and 5cm in diameter

(4) LDPE sheets, containing excess additives.

through six bolts fitted with compression springs. Afterwords, the whole device was placed in a vacuum oven (except at 5°C where the stack was kept in a refrigerator) at the required temperature. The establishments of the equilibrium and therefore the length of time of the experiment was followed by periodical determination of the concentration of the additive in the films.

The experiments were terminated when the concentrations of the three films in a unit were attained to the same constant value. The initial results obtained were the concentration profiles with time. Such profiles are given in Figure 4.2 for 2-hydroxy-4-octoxy benzophenone. Similar equilibrium curves were obtained for all the stabilisers in the series. Afterwards by using such profiles, the maximum attainable concentration in the films were evaluated. The average of these values have been calculated and taken as its equilibrium solubility.

The equilibrium data at 5°C and 23°C were obtained by using films of thickness 100μm, this is in order to curtail the lengthy experimental times. All the additive free films were equilibration at 100°C for one hour under N_2 prior to the experiment in order to achieve the similar morphological structure of all the polymer films used in this study.

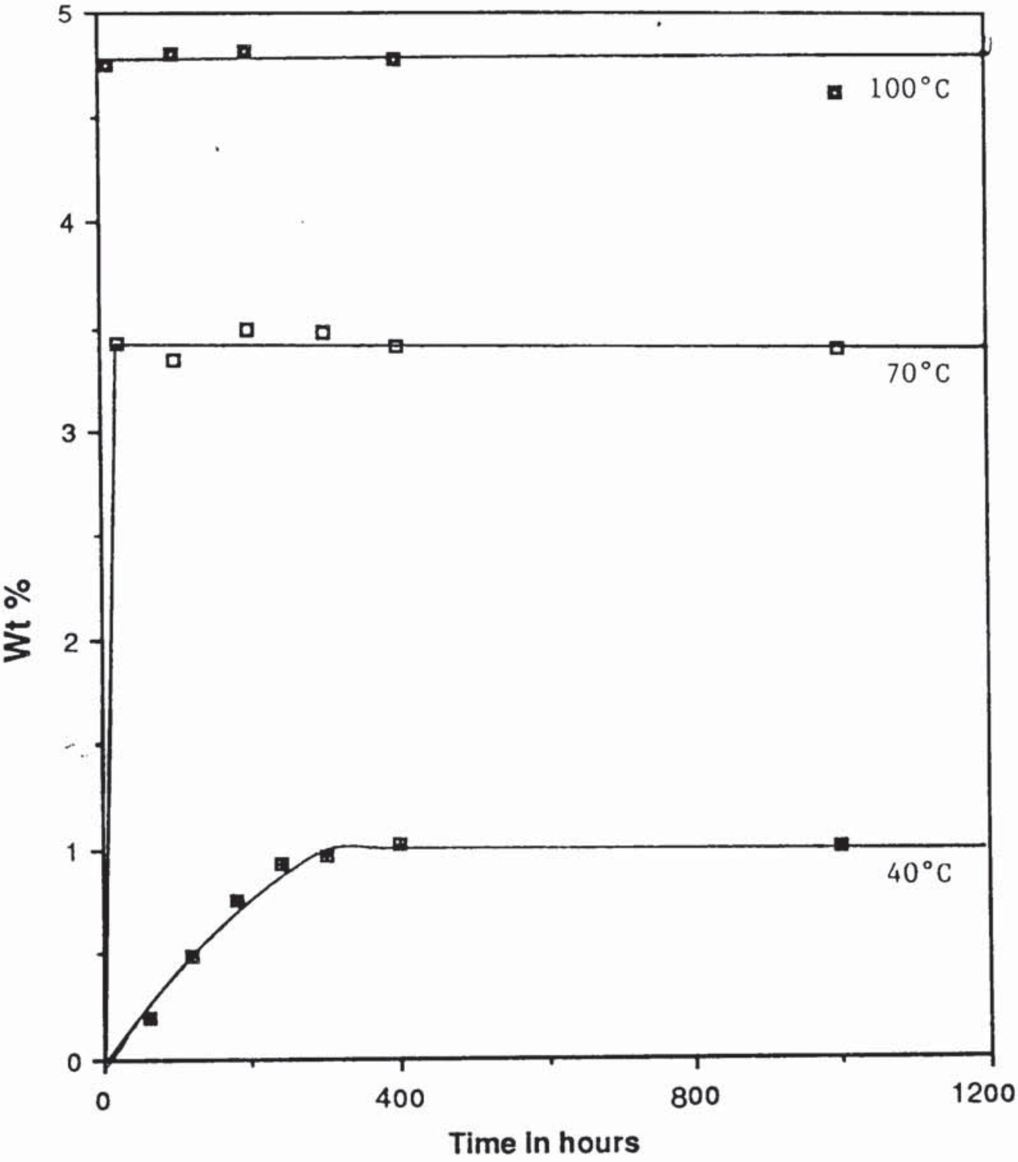


Figure 4.2 % weight uptake of UV-nC8 by LDPE films during solubility experiment (Figure 4.1), at temperatures 40°C, 70°C and 100°C

4.2 Results and Discussion

4.2.1 Equilibrium Solubility

Table 4.1 presents the solubilities of the stabiliser series given in Table 2.1, determined over the temperature range between 5-100°C. This data has not been corrected for crystallinity. The experimental error found in those experiments were in the region of ±20% and these may be due to:

1. possible variation of the thickness of the film,
2. though the films were processed under the same condition, variations may exist between the crystallinity of the films.

There is very little data available in the literature for solubility of stabilisers in polymers and the solubility of hydroxybenzophenone type stabilisers in LDPE presents no exception. Early studies on solubilities of this type of additives were carried out by Johnson and Westlake[22,23]. From their diffusion studies they were able to estimate the equilibrium solubilities of 2,4-dihydroxy-benzophenone and 2-hydroxy-4-octoxybenzophenone in low and high density polyethylene and polypropylene. The equilibrium solubility values for above two stabilisers in LDPE at

Temp. K	UV-OH	UV-C2OH	UV-nC8	UVS-SH	UVS-Cl
278	0.00079	0.0021	0.070	0.0085	0.120
296	0.0032	0.0180	0.297	0.039	0.282
313	0.0181	0.0421	1.03	0.120	0.404
323	0.0306	0.113	1.93	0.285	0.509
333	0.0759	0.0224	2.36	0.600	0.746
343	0.159	0.299	3.05	0.725	0.885
353	0.273	0.492	3.44	0.890	1.080
363	0.382	0.698	4.26	1.060	1.263
373	0.725	1.43	4.80	1.420	1.800

Table 4.1 Solubility of stabilisers given in Table 2.1(values given as wt% and not corrected for crystallinity).

Temp.K	UVS-nC4	UVS-tC4	UVS-nC8	UVS-nC12	UVS-nC18
278	0.074	0.048	0.270	0.235	0.225
296	0.152	0.112	0.435	0.405	0.410
313	0.245	0.205	0.670	0.725	0.660
323	0.357	0.293	0.875	0.985	0.890
333	0.440	0.380	1.085	1.030	0.125
343	0.535	0.450	1.235	1.475	1.375
353	0.613	0.532	1.485	1.630	1.560
363	0.693	0.640	1.660	1.780	1.790
373	0.820	0.780	1.925	2.075	2.125

Table 4.1 (continued)

75°C are 0.09 wt% and 1.4 wt% respectively. These values are considerably lower than the values obtained from this study which is 0.159 wt% for 2,4-dihydroxybenzophenone and 3.05 wt% for 2-hydroxy-4-octoxybenzophenone at 70°C. In their study, Johnson and Westlake[22] reported that the extraction technique employed for 2,4-dihydroxybenzophenone was not feasible for 2-hydroxy-4-octoxybenzophenone and estimated the solubility of the latter by using the result obtained from 2,4 dihydroxybenzophenone. In addition extraction procedures were carried out with polymer films containing additives immersed in water and by measuring the extracted amount of additive in water by radio-tracer method, until it reaches to an equilibrium value. In the light of studies reported in Chapter 5 of this thesis, it seems that diffusion of water into the polymer film may have modified the bulk polymer leading to the extraction of more additive from the polymer and consequently the equilibriation obtained may have yielded lower values. Since 2,4-dihydroxybenzophenone is relatively more soluble in water than 2-hydroxy-4-octoxy benzophenone, the solubility value obtained for the former was lower than it should be, consequently the estimated solubility of the latter may have yielded a lower value.

Though, this seems to be the reason for the low solubility values obtained by above workers[23], there are no other data available on LDPE for similar stabilisers in the literature to confirm the above arguments. Recently, Ruddy and Rubtstove[136] have indicated that they have measured solubilities of some benzophenone stabilisers in LDPE, unfortunately their data were not available at the time of this presentation.

The comparison of dynamic methods and the equilibrium methods for determining the equilibrium solubility can be established by following the work presented by Roe et al.[27], Moisan[39] and Billingham and co-workers[29]. The first two workers obtained the solubility values by extrapolating their diffusion data and the latter by using the equilibrium method. The values given by the above three workers for the solubility of Topanol CA in LDPE are presented in Table 4.2. This Table shows that values obtained by Moisan[39] and Billingham and co-workers[29] were identical for Topanol CA. However, this is not true for the case of Irganox 1010 where the results obtained by the above three workers differ quite substantially. Moisan[39] has attributed this discrepancy to the different methods used. It was argued that the large antioxidant molecule modifies the amorphous phase of the polymer sufficiently and as consequence of this, when solubility is measured by the equilibrium method this modification is sufficient to yield higher values of solubility. Though, Moisan[39,79,80] has given some data to support this conclusion, he does not recognize the fact that Irganox

Additive	Solubility at 25°C (wt%)	Solubility at 70°C (wt%)	References
Toponol CA	0.009	0.12	Billingham and co-workers[29]
	0.011	0.125	Moisan[39]
Irganox 1010	0.00006*	0.012*	Roe et al.[27]
		0.026	"
	0.020	0.24	Billingham and co-workers[29]
	0.003	0.14	Moisan[39]

Table 4.2 Equilibrium solubilities of phenolic stabilisers given in the literature for LDPE

* values were from extrapolating solubilities obtained from model solvents; they only concern a totally amorphous material

1010 can have several different crystalline forms depending on the condition of its preparation. Since the physical form of an additive has an influence on solubility[29], it can be believed that this might be the reason for the difference in solubility. Furthermore, Billingham and co-workers[29] have shown that there is no apparent effect of morphology on solubility. Anyhow there is not enough evidence in the literature to indicate which of the methods is the more reliable way of determining equilibrium solubility. But in principle that it will be less satisfactory to extrapolate from an essentially kinetic situation to establish an equilibrium property and it seems that the equilibrium method is more realistic, if it can reasonably be used.

4.2.2 Temperature Dependence of Equilibrium Solubility

In Chapter 1(Section 1.3.2), the temperature dependence of solubility on the basis of the regular solution theory shown in form of the following equation:

$$-\ln \varnothing = \Delta H_F/R\ [1/T - 1/T_m] + [1 - V_1/V_2] + \chi \qquad 4.1$$

If χ is temperature independent, then the temperature-dependence of solubility can be predicted from the heat of fusion of the additive (ΔH_F), as contained in the first term of the right-hand side of equation 4.1. This factor term assigned as the A value of the additive and is given in equation 4.2:

$$A = \Delta H_F/RT[1/T - 1/T_m] \qquad 4.2$$

In addition partial differentiation of equation 4.1 with respect to the reciprocal of absolute temperature gives,

$$-\partial \ln \O / \partial(1/T) = \Delta H_F/R + \partial\chi/\partial(1/T) \qquad 4.3$$

and by comparing the above equation with well known Arrhenius type equation $\ln \O = \ln S_o - \Delta H_s/RT$ (eq. 4.4) equation 4.5 can be obtained:

$$\Delta Hs = [-R\, \partial \ln\O/\partial(1/T)] \qquad 4.5$$

where ΔH_s is the molar heat of solution of the additive. This shows that if χ is temperature independent, the heat of fusion of the additive should be equal to the molar heat of solution below the melting point of the additive. Above the melting, the heat of fusion term in equation 4.3 vanishes and the solubility will become temperature independent.

The validity of the above hypothesis has been tested by plotting logrimethic solubility against 1/T and this can be seen in Figure 4.3A, B, C and D for stabilisers UV-OH, UV-nC8, UVS-H, UVS-nC4, UVS-tC4 and UVS-Cl, UVS-C18 respectively. These plots clearly show that the equilibrium solubilities of the stabilisers are temperature dependent above the melting point of the polymer, showing that λ cannot be temperature independent. Nevertheless, the Arrhenius plots are discontinuous near the melting point of the stabiliser suggesting there is at least a qualitative justification for the use of equation 4.1. Under the above circumstances, the temperature dependence solubility of an additive below the melting point of the polymer can be predicted from the values obtained above the melting point of the stabiliser if the molar heat of fusion of the stabiliser is known. From theory it can be written:

$$\Delta H_1 + \Delta H_F = \Delta H_2 \qquad 4.6$$

where ΔH_1 and ΔH_2 are the molar heat of solutions of the additive above and below the melting point of the additive respectively, and ΔH_F is the heat of fusion of the additive. The relevant heat of solution data for the stabiliser series were obtained by fitting a least square regression line to a each set of data and calculating from the gradient of this line. The heat of solution values obtained above and below the melting point of the additive is presented in Table 4.3. According to the above equation, the difference between heat of solution

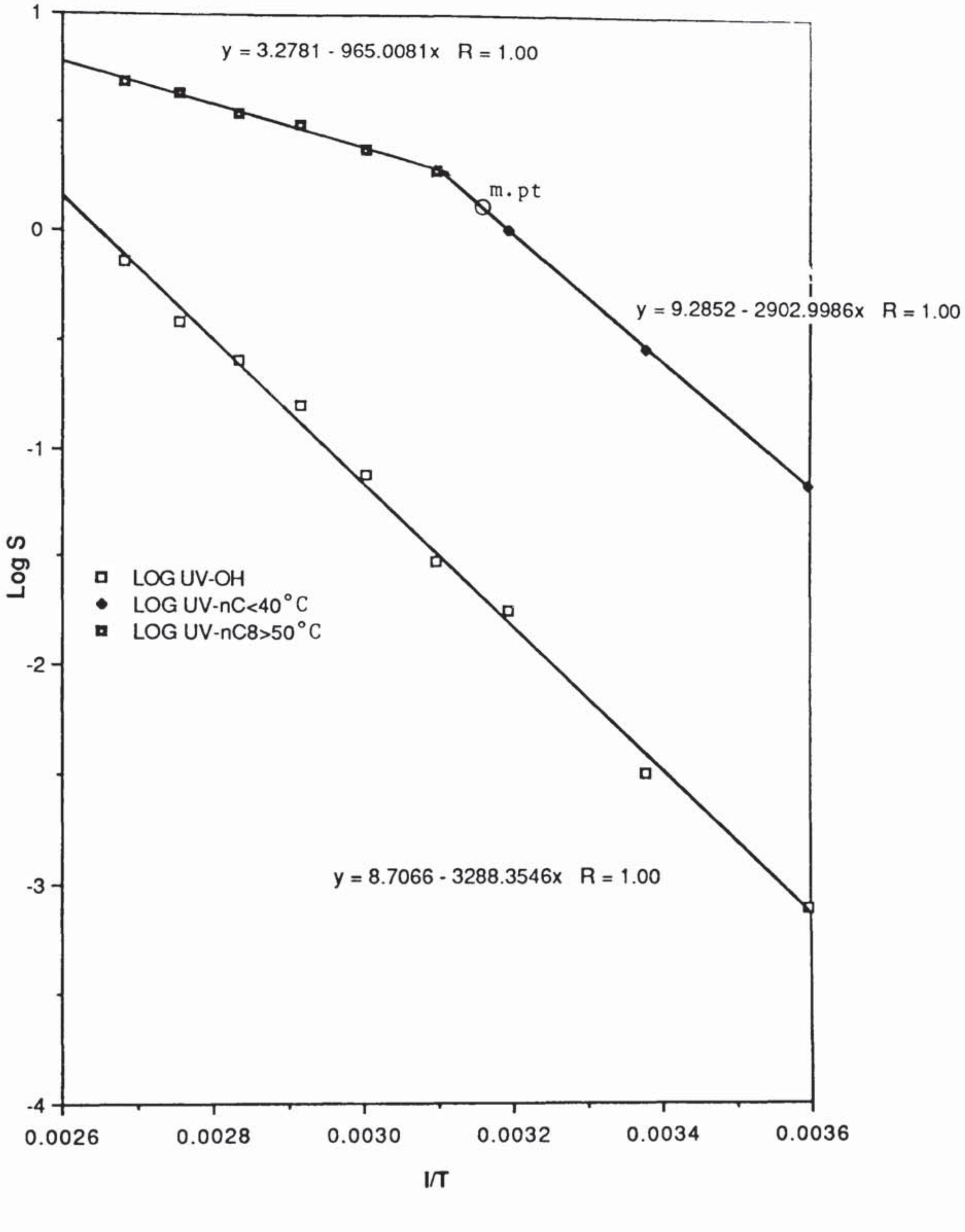


Figure 4.3A Plots of log solubility verses l/T for stabilisers UV-OH and UV-nC8 in LDPE. The plot of UV-nC8 shows the discontinuity of the plot above melting point of UV-nC8 (43.5°C)

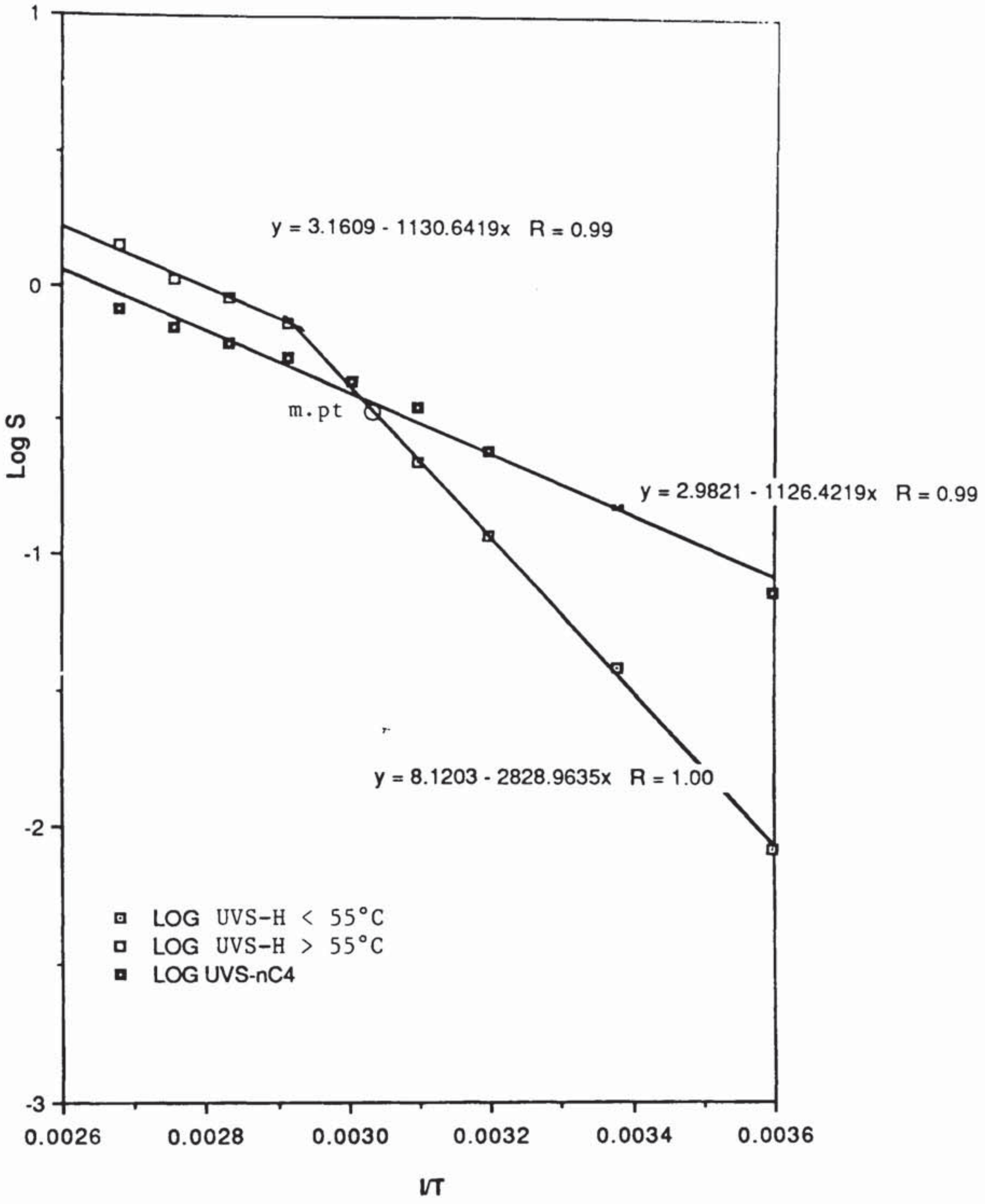


Figure 4.3B Plots of log solubility verses l/T for stabilisers UVS-H and UVS-nC4 in LDPE. The plot of UVS-H shows the discontinuity of the plot above melting point of UVS-H (54°C)

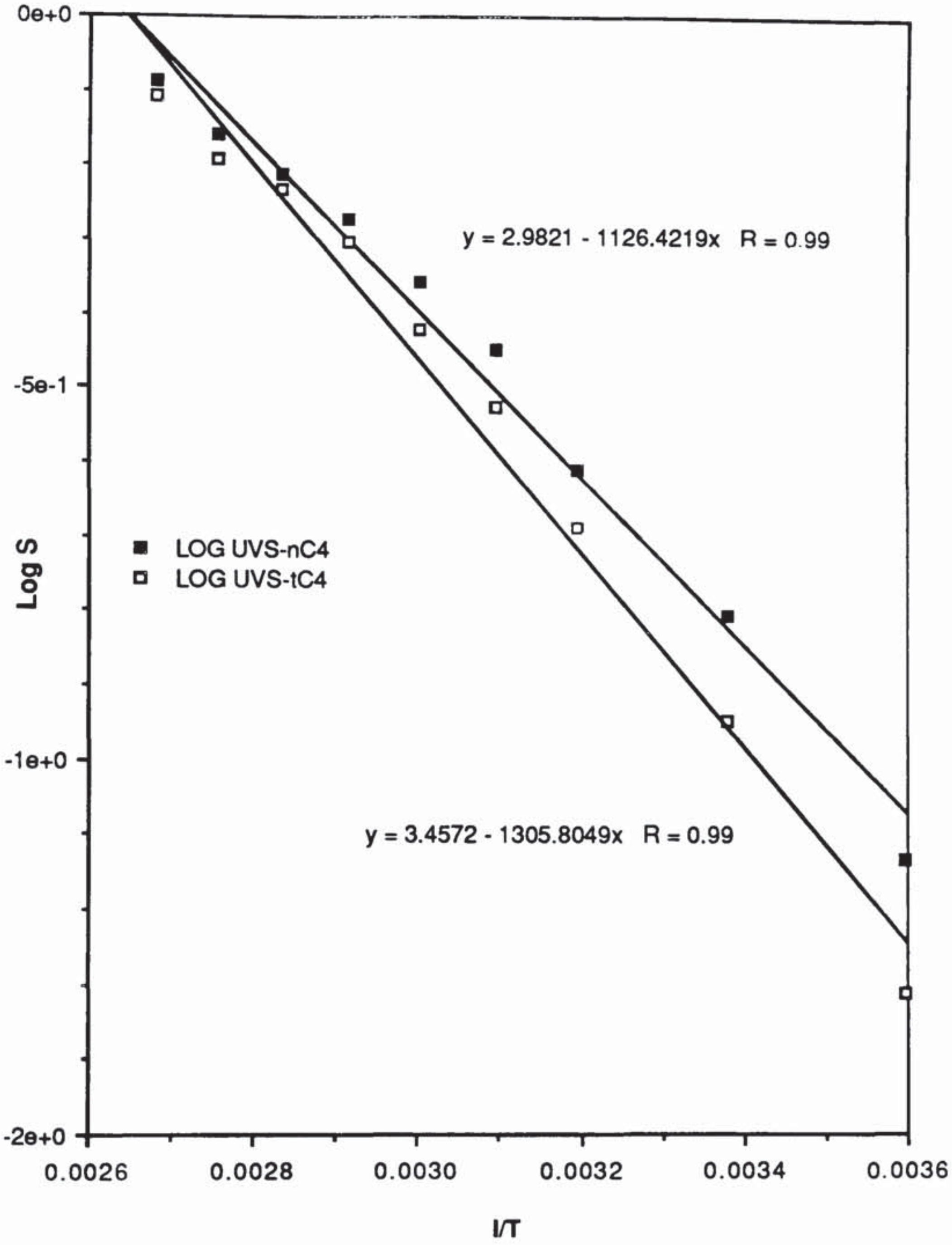


Figure 4.3C Plots of log solubility verses 1/T for stabilisers UVS-nC4 and UVS-tC4 in LDPE.

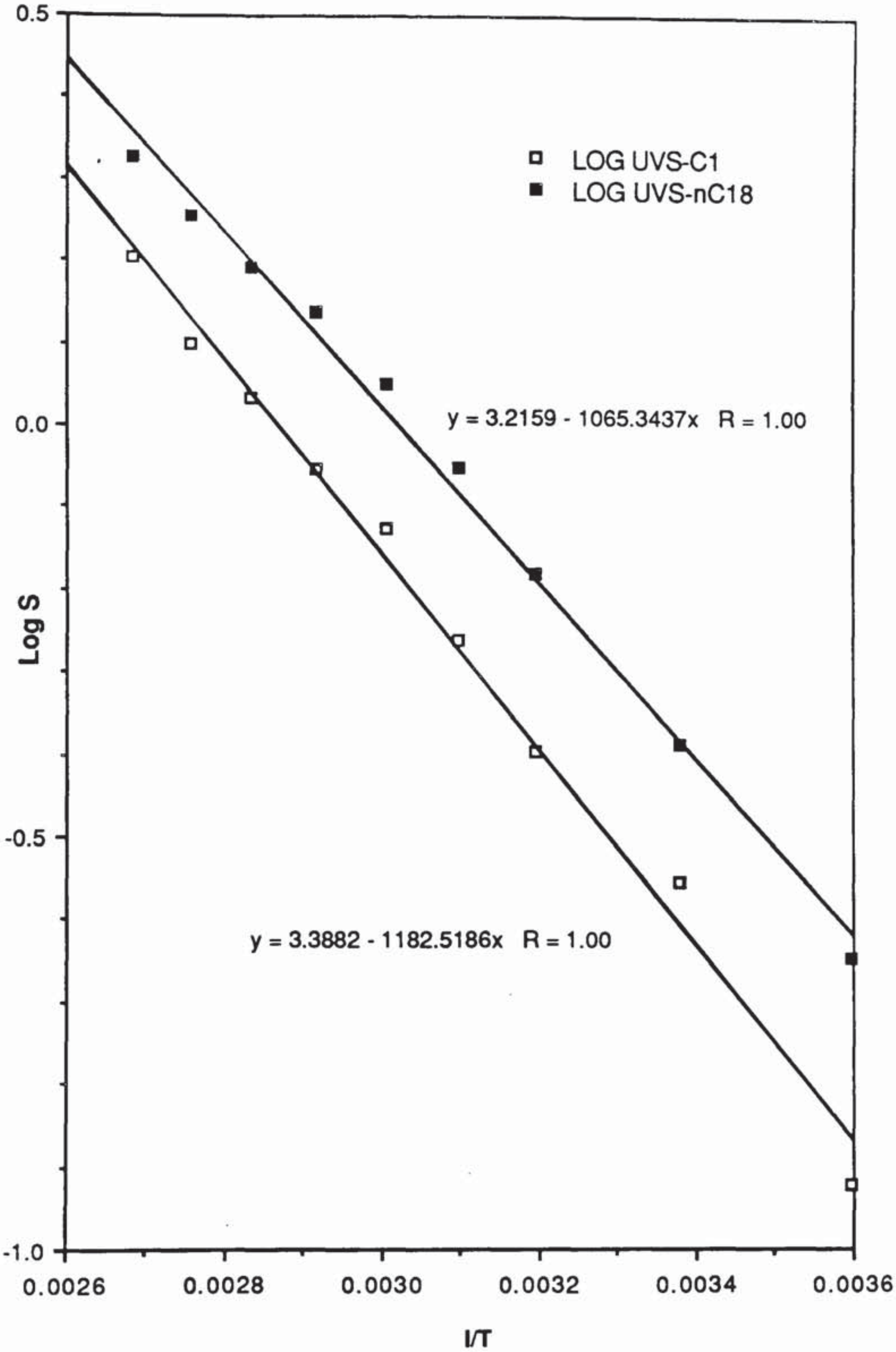


Figure 4.3D Plots of log solubility verses 1/T for stabilisers UVS-C1 and UVS-nC18 in LDPE.

above and below the melting point of the polymer should be equal to the heat of fusion of the additive. The relevant data can be seen in Table 4.3. Considering the fact that the calculation of heat of solutions are very sensitive to experimental errors, there seems to be a fair agreement between them. Further evidence to the discontinuity of the Arrhenius plots near the melting point of the additive was given by Moisan[39,79,80], for solubilities of hexadecanone-3, methyl stearate, stearic acid and Irganox 1076 in LDPE, and Ruddy and Rubtstove [136], for solubilities of benzophenone type stabilisers in LDPE. Both workers have observed discontinuities of Arrhenius plots of solubility just above the melting point of the additive. These observations together with the results obtained from this study suggest that equation 4.1 can be used, at least as a basis for understanding the factors that affect the equilibrium solubilities of additives in polymers.

4.2.3 Influence of Inherent Properties of the Stabiliser on its Equilibrium Solubility

The equation 4.1 can be written as,*

$$-\ln \phi = A + [1 - V_1/V_2] + \chi \qquad 4.7$$

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* unpublished theoretical analysis of solubility, with permission of Dr. N. C. Billingham, Sussex University, Brighton, U. K.

Stabilisers	Heat of above T kJ/mol	solution below T kJ/mol	Difference kJ/mol	Heat of fusion kJ/mol
UV-OH	-	62.96	-	11.17
UV-C2OH	-	57.25		15.14
UV-nC8	18.47	55.58	37.11	36.12
UVS-H	21.64	54.16	32.52	24.35
UVS-C1	23.14	-		
UVS-nC4	21.57	-		
UVS-tC4	25.00	-		
UVS-nC8	18.03	-		
UVS-nC12	20.06	-		
UVS-nC18	20.05	-		

Table 4.3 Heat of solution data obtained from the gradients of Arrhenius type plots given in Figures 4.3A and 4.3B.(Heat of fusion data obtained from DSC measurements as discussed in Chapter 2 (Sec. 2.8)

where A is given by

$$A = \Delta H_F/RT[1/T - 1/T_m] \tag{4.8}$$

The above relationship suggests some predictions about additive solubility:

1. The solubility of the additive in a polymer is determined by four factors.

    a. Heat of fusion of the additive, which determine the value of A,
    b. Melting point of the additive, which also influence the value of A,
    c. Molar volume of the additive,
    d. Free energy of interaction(χ) of the additive with the polymer.

2. It is apparent from the value of A, for a given temperature, that it is an entirely a intrinsic property of the additive. Therefore, the value of A can be regarded as the contribution made to solubility from the nature of the additive itself. This suggests that any inherent property that increases the value of A will decrease the solubility.

3. Since the molar volumes of the polymers are very high, the term $(1-V_1/V_2)$ is very close to 1. Therefore, the effect of molar volume of the additive on its solubility is expected to be significant for low molecular weight solvents but much less for polymers.

4. The χ factor represents the non ideality of the solution due to interaction between the polymer and the additive and this can be regarded as a measure of compatibility between the additive and the polymer in the true thermodynamic sense. Although the term 'compatibility' is widely used to describe the solubility of the additive in the polymers, it can properly be related to value of χ.

Therefore, in order to investigate the validity of the above predictions, the parameters governing equation 4.7 have been evaluated and these are given in Table 4.4. The temperatures 23°C and 70°C are taken deliberately to represent the values of solubilities above and below the melting point of the additives. The heats of fusion of additives are calculated from DSC measurements as given in Chapter 2(see Section 2.8). The plots of log Solubility verses the values of A and χ can be seen in Figures 4.4A and 4.4B for stabilisers UV-OH, UV-C2OH, UV-nC8 and UVS-H respectively. It is apparent from these figures, that decreasing the values of A, increases the

Stabiliser	M.pt	ΔH_F kJ/mol	A at 70°C	χ at 70°C	Solubility at 70°C	A at 23°C	χ at 23°C	Solubility at 23°C
UV-OH	145°C	11.17	0.70	4.25	0.258	1.32	8.03	0.0032
UV-C2OH	92°C	15.14	0.32	4.13	0.429	1.16	4.16	0.180
UV-nC8	43°C	36.12	0(-1.04)	2.36	3.44	0.81	4.01	0.297
UVS-H	54°C	24.35	0(-.41)	3.72	0.890	0.97	5.87	0.039

Table 4.4 Intrinsic properties of four stabilisers (The negative values given for A represents the values obtained above the melting point of the additive and therefore meaningless. The solubility values used in the calculations were corrected for crystallinity.)

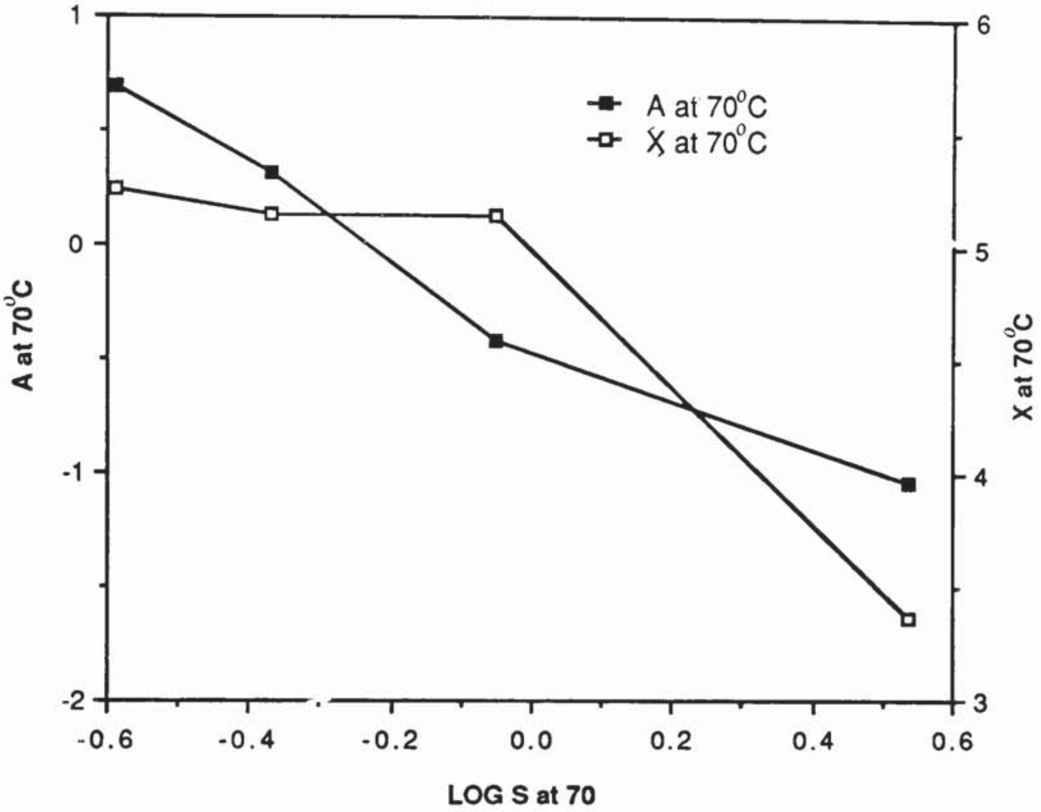


Figure 4.4A

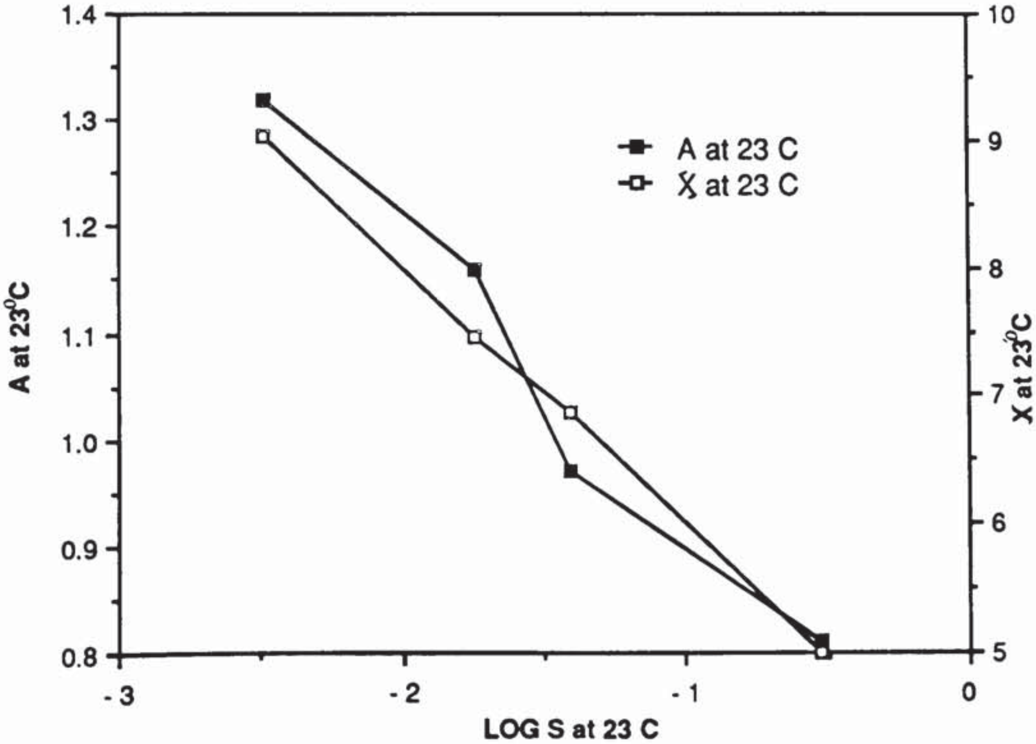


Figure 4.4B Dependence of equilibrium solubility of stabilisers on the value of A and X

solubility but the effect of χ not always follow the same trend. At 70°C, though the values of χ remain constant for UV-OH, UV-C2OH and UVS-H, their solubilities differ substantially. Since χ represents the compatibility of the additive with the polymer, this suggests that compatibility and solubility cannot always be interrelated. For these additives, the value of A on solubility is seems more dominant than compatibility. For example, UVS-H has got the highest interaction parameter (χ) at both temperatures and therefore in terms of compatibility this additive is expected to have a lower solubility among others. In contrast, this has got the second highest solubility among the rest of the additives, and this is by virtue of the low value of A. The effect of reducing both the parameters can be clearly seen for the stabiliser UV-nC8. This stabiliser has the lowest A and χ values, the net result being an increase in solubility by a factor of 13 when compared with the corresponding value for UV-OH. Data suggesting the similar observations also can be extracted from literature for phenolic antioxidants in polypropylene [29]. Table 4.5 gives the values of solubilities of BHT, Plastanox 2246 and Irganox 1010 together with their A and values at 25°C. According to this Table Irganox 1010 has the lowest value of χ and the highest value of A. On the other hand Plastanox 2246 has much lower value for A, but comparatively similar value for χ as Irganox 1010. The net result being a 15 times increase in

Additive	M.pt°C	A at 25°C	χ at 25°C	Solubility at 25°C(wt%)
BHT	71	1.0	2.7	0.44
Plastanox 2246	130	2.6	1.7	1.03
Irganox 1010	123	5.5	1.4	0.73

Table 4.5 Solubility properties of some phenolic antioxidants in Poly propylene

(Data adapted from the reference 29)

solubility of Plastanox 2246 compared to Irgnox 1010. BHT has the lowest A value and the highest χ value and this results in a six fold increase in solubility when compared with that of Irganox 1010.

The above observations reveal two important factors:

1. The solubility of an additive in polymer can be predicted qualitatively if not quantitatively on the basis of the equation 4.1,
2. The true compatibility of an additive(χ) in a polymer cannot be used as a prediction of solubility. Less compatible additives can have higher solubilities in polymers by virtue of their lower melting point and/or a lower heat of fusions.

4.2.4 Factors Affecting Equilibrium Solubility of Additives in Polymers

Figure 4.5 presents the plots of log solubility verses molecular weight of the stabilisers for the stabiliser series given in Table 2.1. As can be seen from Figure 4.5, no definite relationship can be obtained. A pattern is more obvious when the number of carbon atoms in the alkyl chain is plotted against solubility in the UVS-nC(X), n=0,1,4,8,12,18, series (Figure 4.6). Though the substitution of hydrogen by methyl in UVS-H

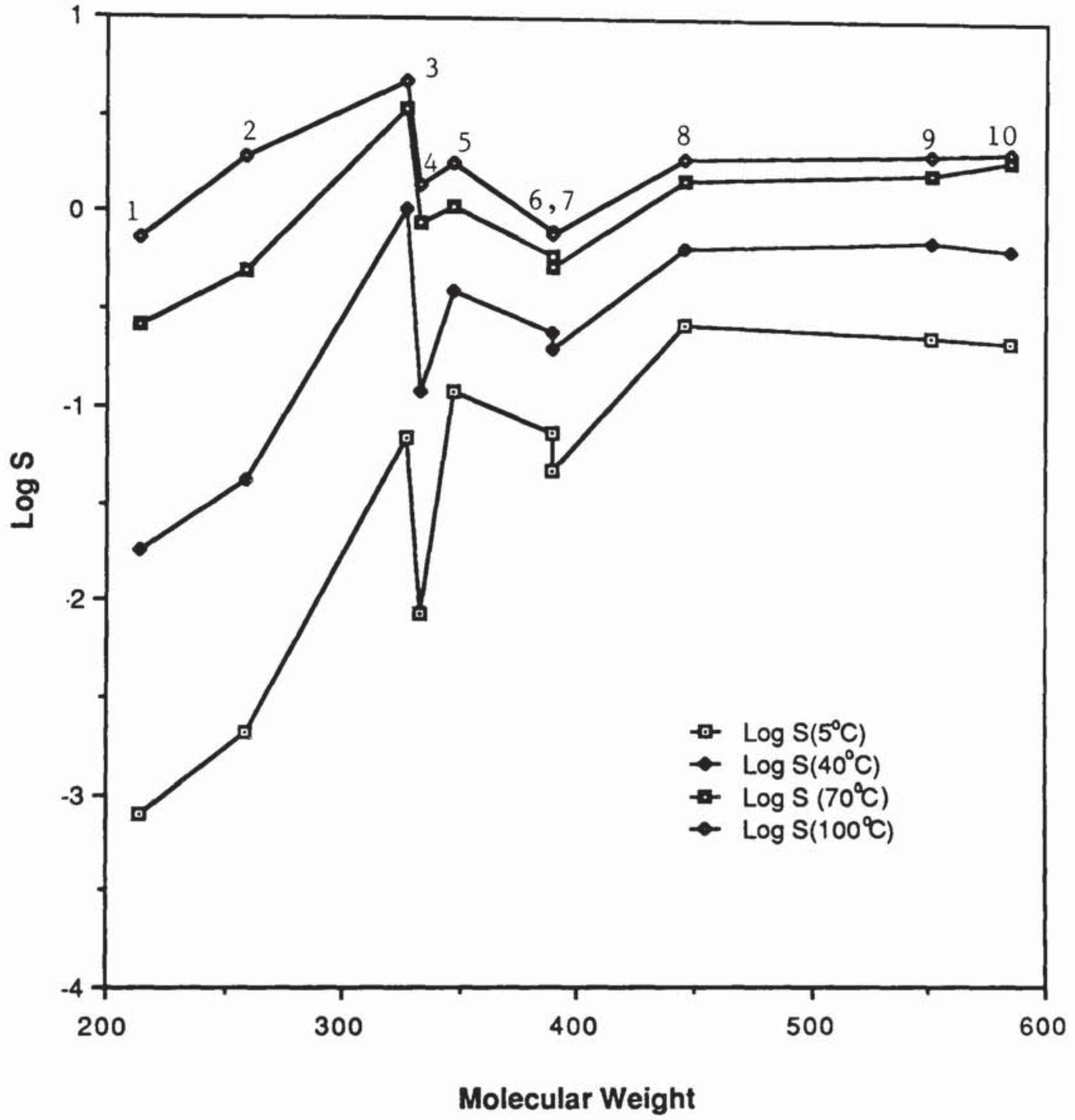
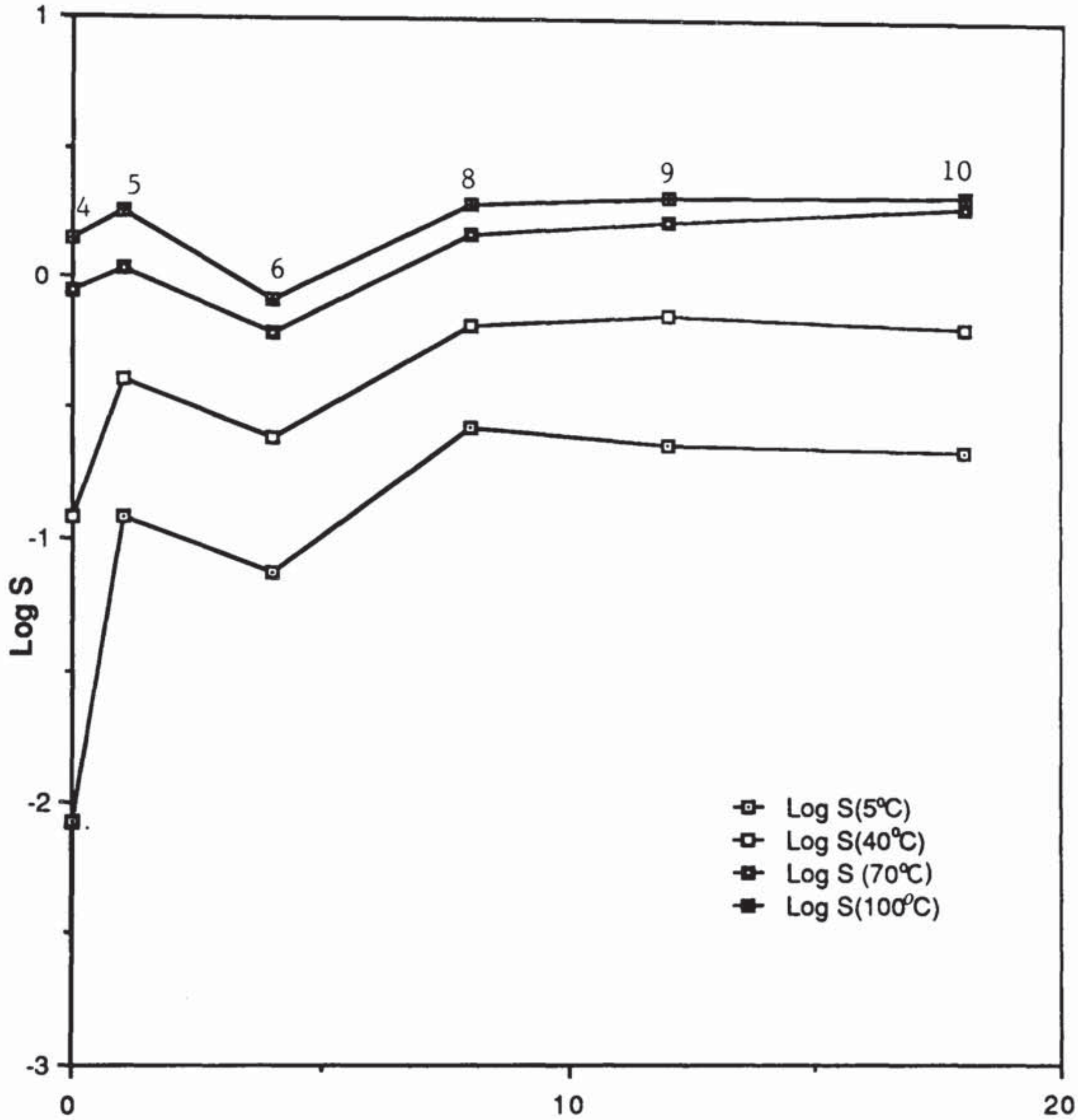


Figure 4.5 Plots of molecular weight of stabilisers verses log of equilibrium solubilities.

1. UV-OH 2. UV-C2OH 3. UV-nC8 4. UVS-H

5. UVS-Cl 6. UVS-nC4 7. UVS-tC4 8. UVS-nC8

9. UVS-nC12 10. UVS-nC18



number of carbon atoms in the alkyl chain

Figure 4.6 Dependence of additive solubility on the number of carbon atoms in the alkyl chain of UVS-nC(X) series.

4. UVS-H 5. UVS-C1 6. UVS-nC4 8. UVS-nC8 9. UVS-nC12 10. UVS-nC18

substantially increases the solubility of UVS-Cl below the melting point of UVS-H(54°C), not much difference in solubility can be observed above the melting point of the stabilisers (with the exception of UVS-nC4) within the rest of the series. In addition, this further shows that changing the length of the carbon from C8 to C18 has virtually no effect on solubility. The influence of increasing the chain length of stabiliser is to decrease the melting point which leads to an increase in solubility. On the other hand, it increases the heat of fusion of the additive due to the high entropy of fusion associated with freeing the motion of the long alkyl groups on melting, which resulted in decrease in solubility. Therefore, the net result which affects the value of A could be negligible and this has reflected in the experimental values of solubility which remains unchanged.

The structural properties of the stabiliser is itself manifest from its physical parameters such as heat of fusion, melting point and interaction parameter(χ). The effect of hydrogen bonding is to increase the melting point which leads to a lower solubility. Similar observations are true for the polarity of the stabiliser but this is not so pronounced as in the case of hydrogen bonding. The changing of the n-butyl (UVS-nC4) to t-butyl(UVS-tC4) does not have a significant effect on solubility at high temperatures. The only possible explanation to this behaviour is that both stabilisers have similar molar volumes, which does not influence the values of A and χ .

4.3 Conclusions

1. A simple regular solution theory provides an adequate basis for understanding the solubility of a homologous series additives in polymers. But as literature data suggest , it may not possible to make quantitative predictions on solubility from the measurements on model solvents due to large non-idealities present in the polymer when compared to the solvents.

2. The solubility of an additive is influenced by its inherent properties and by its interaction with the polymer. In some cases the effect of heat of fusion and melting point of additive on the solubility is more influential than compatibility(χ). Increasing solubility is favoured by a lower heat of fusion and a lower melting point of the additive and groups which give favourable interaction with the polymer(χ).

3. True compatibility(χ) as opposed to the common use of the name can be misleading when it related to solubility. Highly compatible additives may not be highly soluble in the polymer.

4. The dependence of additive molecular weight on solubility is a complex one. However, change in the alkyl chain length after a certain limit has no effect on solubility.

CHAPTER FIVE

MIGRATION OF STABILISERS FROM LOW DENSITY POLYETHYLENE FILMS INTO SOLVENTS AND FOOD SIMULANTS

CHAPTER FIVE

MIGRATION OF STABILISERS FROM LOW DENSITY POLYETHYLENE INTO SOLVENTS AND FOOD SIMULANTS

The loss of stabilisers from low density polyethylene films into various solvents and food simulants was investigated at temperatures 5°, 23°, 40° and 70°C. In this Chapter experimental procedure for the determination of stabiliser loss together with the analysis of migration data in terms of Fick's equations is discussed. The loss mechanisms are interpreted in relevant to characteristic diffusion coefficients and partition coefficients. Furthermore, the stabiliser and extractant effects on loss procedure will be presented.

5.1. Migration tests

Migration tests are designed to investigate the additive loss from polymers into food materials. Since food materials are complex in nature these tests are normally carried out in simple solvents in order to facilitate analytical techniques. There are no definite mathematical theories has been discussed in the literature for these migration tests. However, several attempts are being made for the modelling of the loss procedures using Fick's diffusion equations.

5.1.1 Experimental Procedure

Low density polyethylene films of additive concentrations 0.1% w/w(1000µg/cm^3) with thickness of 250µm were prepared according to the method described in Chapter 2, Section. 2.2. These films were kept at 100°C for 15 minutes under nitrogen in an oven and the surfaces were cleaned to remove any bloomed additives present on the surface with cold ethanol. The initial concentration of additives in the test films were determined from uv/vis spectroscopy by extraction. For all the other test samples, the initial net uv absorbances were recorded in the region of 250-350 nm of their uv spectra prior to the migration tests. Migration tests with solvents/simulants were conducted in 100 ml flasks with liquid volume of 100 cm^3. The required temperatures was achieved via a thermostatically controlled water baths except at 5°C where the tests were carried out in a refrigerator.

After the solvent has achieved the required temperature, test films were fully immersed in the liquid, exposing both sides to the medium. The total exposure area of the test coupon to the solvent medium was 18 cm^2, giving solvent volume to surface area ratio of 5.5. As time elapsed, films were removed and the solvent present on the surface of the polymer films were absorbed into cotton wools and subsequently, the uv/vis absorbances of these films were recorded in the Beckman DU-7 high speed uv/vis spectrophotometer. Simultaneously, the solvent absorbances were also monitored except 3% acetic acid, olive oil and glycerol trioleate. Since ultra-violet cut off points for olive oil and glycerol trioleate was in the region of 290 nm, the solvent spectra determination was not possible. However, uv spectrum of the films did not show any signs of solvent absorption, this may suggest that the removal of the solvent from the test films was successfull. Migration tests on all the stabilisers were performed for the following solvents and simulants under the given test conditions:

Simulants

1. distilled water
2. 3% aqueous acetic acid
3. absolute ethyl alcohol
4. 50% aqueous ethyl alcohol
5. olive oil
6. glycerol trioleate
7. heptane

Test Conditions

i. 6 months at 5°C
ii. 10 days at 23°C and 40°C
iii. 5 hours at 70°C.

For a given temperature, stabiliser and a solvent, three tests were performed simultaneously in order to determine the reproducibility of the results.

5.2 Results and Discussion

5.2.1 Migration Test Results

Migration tests have been carried out for all the stabilisers listed in Table 2.1 at temperature 5°, 23°, 40° and 70°C. Initial data obtained were the concentration changes in the film with respect to the time of contact of the test coupon in the liquid medium. Three simultaneous migration tests carried out for the same stabiliser for the same temperature showed a variation of about ±20%. This can be considered as the experimental error and this may be due to the following factors.

i. Variation in the initial concentration of the additive in the polymer films. The variation of 10% of the initial concentration of the additive in the film was observed,

2. Variation of the thickness of the film. Though the films were pressed to give thickness of 0.25mm, the resulting sheet thickness were varied between 0.25±0.05mm,

3. Though the test films were prepared under the same conditions, variations can exist in the morphology

or crystallinity of the polymer film.

Since the initial concentrations of the stabilisers were difficult to maintain to the required values, concentration changes were normalised to an initial value of 1000μg/cm^3 (≈0.1% w/w) assuming that the migration time was proportional to the initial concentration. All the simulants and solvents used were liquid at all temperatures except olive oil which become a solid at 5°C.

5.2.2 Analysis of Migration Data

5.2.2.1 Theory

The time-concentration data obtained from the migration tests can be analysed by visualising the migration behaviour of such a process. This type of migration can be regarded as a diffusion of an additive in a plane sheet immersed in an infinite medium, since the solvent volume to film ratio is high (5.5). This assumes that there is no concentration gradient of the additive across the solvent media and that no equilibrium exists between the stabiliser in the film and the solvent. Under such circumstances two limiting cases of interest are possible.

1. The simulants or solvents can penetrate into the film until it is saturated with the solvent. The penetration of the solvent may modify the resulting mobility of the stabiliser in the polymer depending on the ability of the solvent to swell the polymer film. There is evidence to indicate[30] that the penetration of the solvent occurs as a Fickian wave with a rate proportional to the square root of the contact time. As Knibbe[34] and Rudolph [140,141] have shown, for Fickian penetration of the simulant/solvent, the migrant has a characteristic diffusivity, which is independent of time, position, and concentration of either migrant or penetrant. This characteristic diffusivity may, however, significantly differ from intrinsic diffusivity of the migrant in the penetrant-free polymer. Therefore, for the purpose of theoretical analysis it is assumed that stabilisers have an effective diffusion coefficient in the polymer which does not vary with the migration time but is a function of temperature and possibly of the simulant/solvent used.

2. The additive starts migrating out from the film into the solvent. In this case the initial loss takes place by the dissolution of the additive on the surface of the film by solvent. If this rate of dissolution is high or, in other words, the stabiliser is fairly soluble in the liquid, then the

surface concentration of the film becomes zero and this will set up a concentration gradient of the stabiliser within the polymer matrix. This concentration gradient then becomes the driving force for the stabiliser mobility and allows more and more additive to migrate to the surface of the film and subsequently to migrate into the solvent, by dissolution. If the solvent/simulant behaves as an infinite sink for the stabilisers, this procedure will proceed until all the stabiliser in the polymer has migrated into the solvent. Therefore, for highly simplified situation, where the stabiliser has a constant diffusivity (D_p) in the polymer and there is no external mass transfer resistance effects or equilibrium partitioning, the solution of Fick's second law leads to an expression for the total stabiliser lost to the solvent/simulant per unit area M_t, at time t[36].

$$M_t = LC_{po}\left\{1-2\sum_{n=1}^{\alpha}\exp(q_n{}^2\Psi)/q_n{}^2\right\} \qquad 5.1$$

with

$q_n = (2n-1)\pi/2$

$\Psi = D_p t/L^2$

L is the half-thickness of the test coupon for the two sided migration used in this study. C_{po} is the initial stabiliser concentration of the test coupon, assumed to be constant over the plaque thickness.

For cases in which the dimensionless group $D_p t/L^2$ is very small (<<1), eq 5.1 reduces to a simpler form:

$$M_t = 2C_{po}\sqrt{(D_p t/\pi)} \qquad 5.2$$

In other words eq. 5.2 is applicable when the stabiliser concentration in the middle plane has not changed significantly from its initial value. This equation shows that the stabiliser migration per unit area is proportional to the square root of time. Therefore, the concentration-time data obtained from migration tests were analysed form the use of equation 5.2, by plotting the stabiliser extracted per unit area against square root of the migration time. Furthermore, equation 5.2 also yields the characteristic diffusion coefficient of the stabiliser, (which could also be determined) from the gradient of these plots.

5.2.3 Migration Plots and Characteristic Diffusion Coefficients

The typical migration results obtained from the model tests may be classified into several categories according to the solvent behaviour towards the polymer and the additive in the polymer matrix, namely:

1. the solvent does not swell the polymer to a significant degree,
2 the polymer is in contact with a highly swelling solvent
3. an intermediate case between highly and poor swollen behaviour
4. low rate of dissolution of stabiliser in the solvent.

In the following section the behaviour of stabilisers will be discussed for some cases of interest with reference to the above four classifications.

1. UV-OH (2,4 dihydroxy benzophenone)

Results of the four migration tests carried out at 5°, 23°, 40° and 70°C are shown graphically in Figures 5.1A-D where the UV-OH extracted per unit area is plotted as a function of square root of time. As can be seen from these figures, except at 5°C the typical migration pattern obtained in the order of decreasing migration rate as follows:

Heptane >>> Olive oil > Glycerol trioleate > Ethanol > 50 % ethanol > 3% acetic acid = water

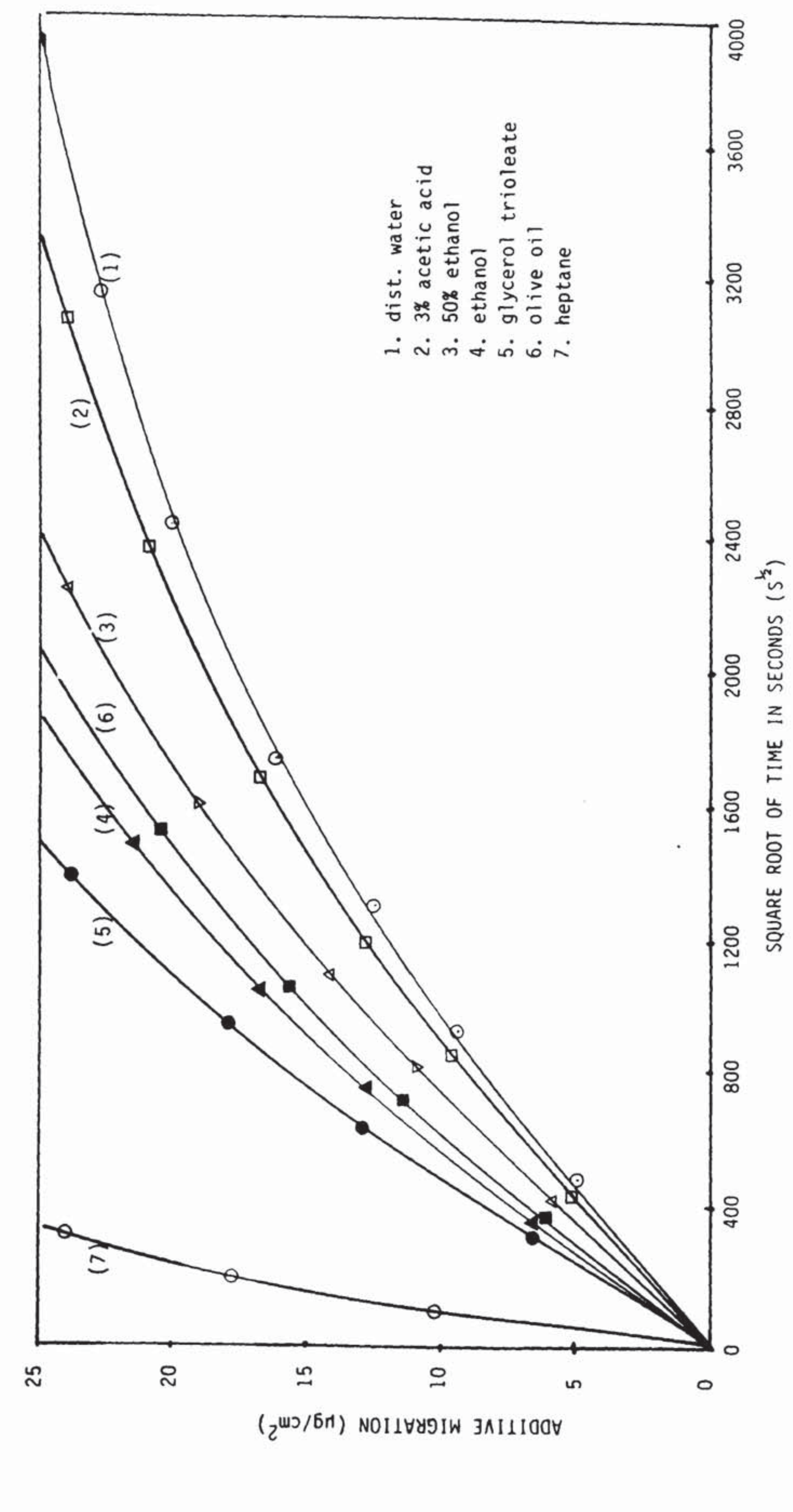


Figure 5.1A Migration of UV-OH from LDPE films into various solvents at 5°C.

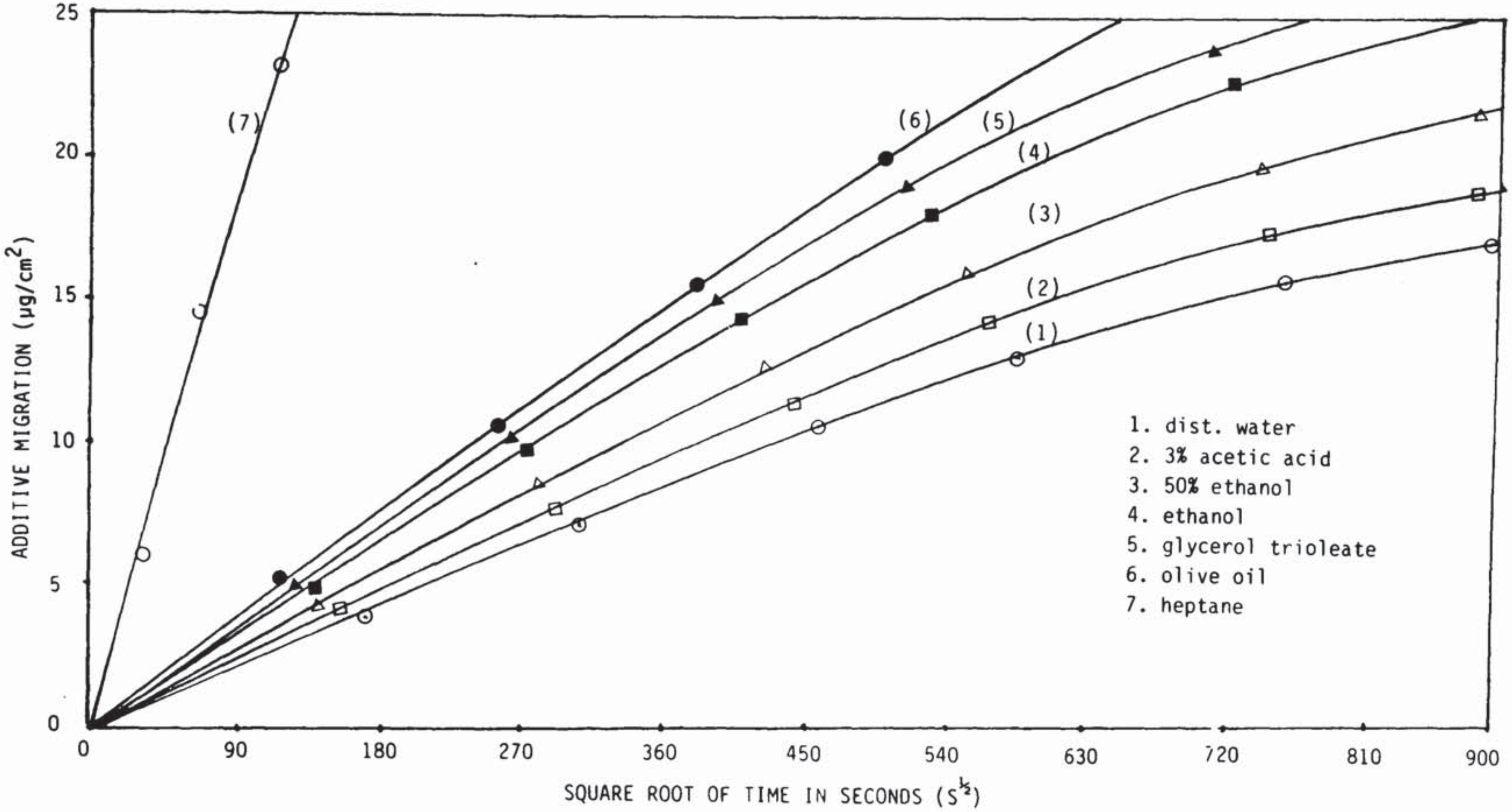


Figure 5.1B Migration of UV-OH from LDPE films intovarious solvents at 23°C.

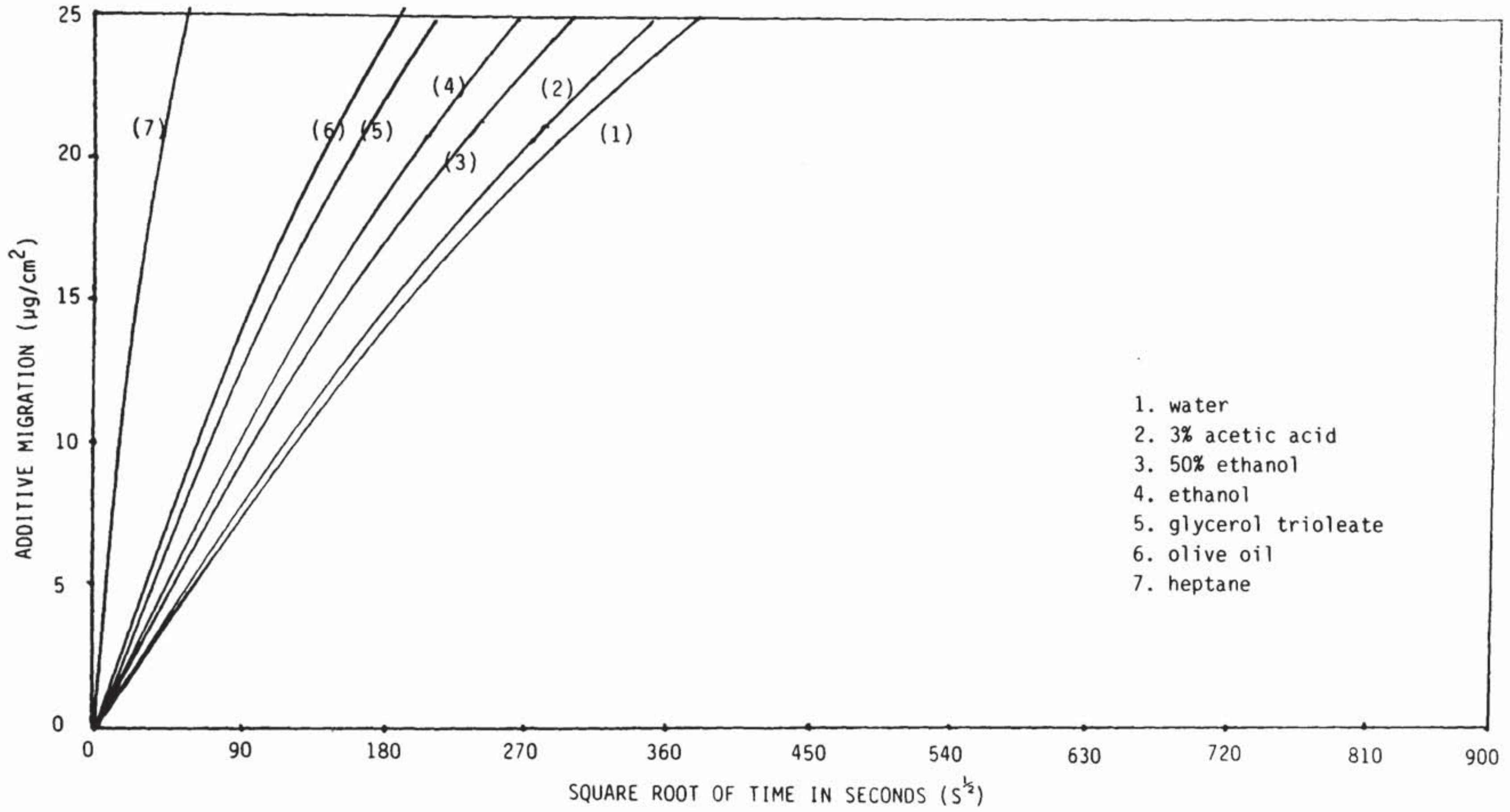


Figure 5.1C Migration of UV-OH from LDPE films into various solvents at 40°C.

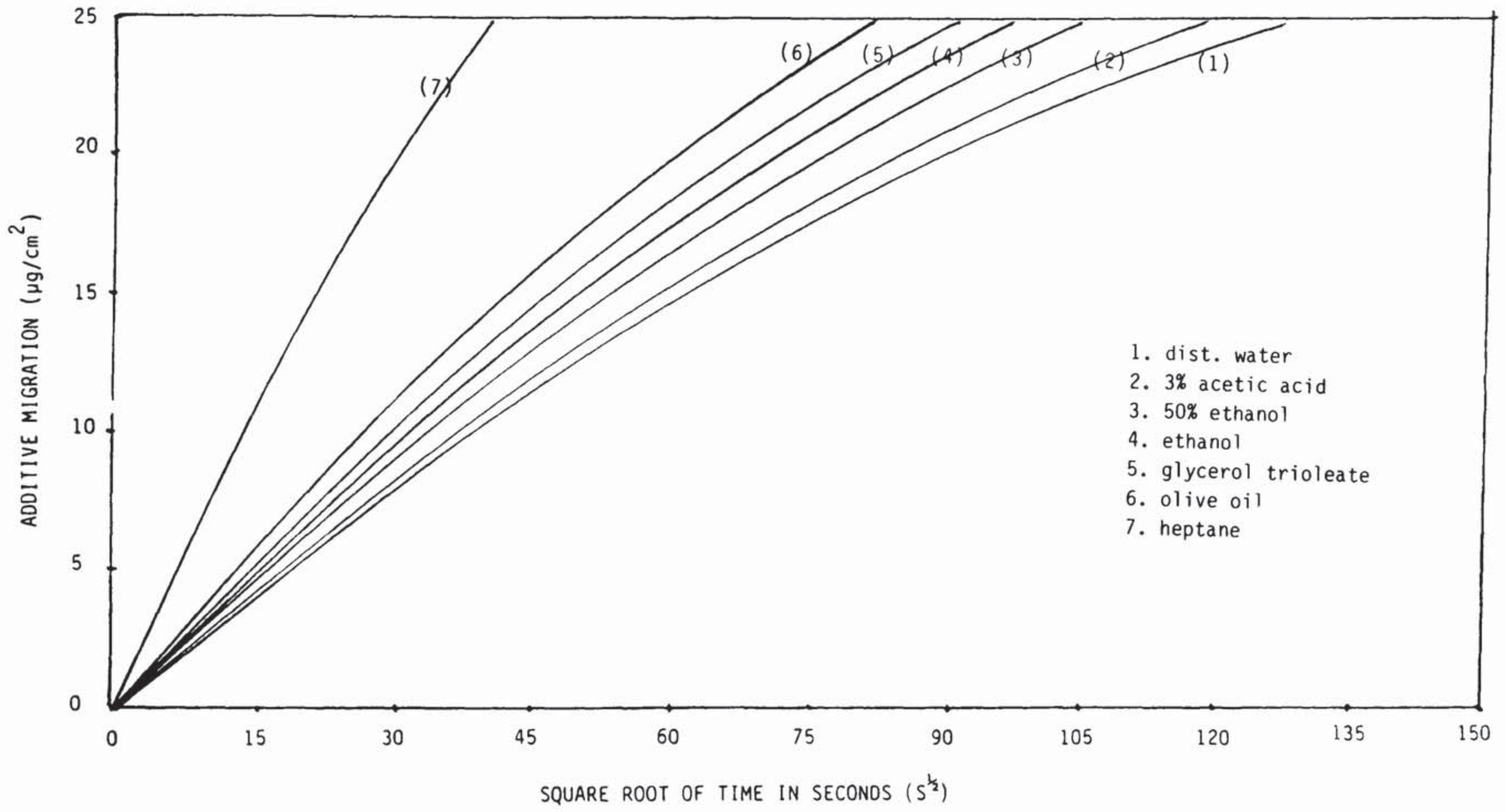


Figure 5.1D Migration of UV-OH from LDPE films into various solvents at 70°C.

At 5°C, the migration into olive oil is relatively less rapid when compared with other solvents at elevated temperatures. This may be due to the solid nature of the olive oil at this temperature, where it could result in the lower rate of removal of the additive from the surface of the film.

Figures 5.1 A-D also show that up to about 50% (ie 12.5 $\mu g/cm^2$) loss of the UV-OH from polymer, these plots seem to follow the relationship given in equation 5.2. i.e, the amount extracted is proportional to the square root of time. This shows that the migration is Fickian upto this level of extraction. The extraction rate subsequently decreases to lower value, but this is not surprising considering the fact that equation 5.2 is valid only when the concentration in the middle plane of the test film does not vary with time. After this level, the concentration in the middle plane changes and the migration occurs at a slower rate.

For this stabiliser, there seems to be no equilibrium partitioning between additive in the polymer and in the solvent. This is as expected, since UV-OH is fairly or sparingly soluble in all these simulants and solubility of UV-OH in the polymer is very low at these temperatures (See inset to Table 5.1). Furthermore, except at 70°C, UV-OH is present as supersaturated solution in the polymer and in this situation, the initial loss is created by the dissolution of the additive from the polymer surface. This surface loss results in a concentration gradient across the polymer film, which is the driving force for the diffusion of the additive within the bulk polymer. Therefore, the initial loss is governed by the loss of the surface additive of the polymer and this is the fastest step of the loss mechanism. Consequently, the loss rate is determined by the diffusion of UV-OH in the bulk of the polymer which resulted in Fickian behaviour.

Equation 5.2 can also be used to estimate the characteristic diffusion coefficients(D_p) of additive UV-OH into these solvents. Therefore, for initial period of (up to ≈50%) migration, a least square regression was fitted to these migration plots and from the gradient of this plots, D_p was obtained. These values together with their intrinsic diffusion coefficients (Chapter 3) and equilibrium solubilities (Chapter 4) in the polymer are given in Table 5.1. From this Table 5.1, it can be seen that the solvent causes a significant increase in the D_p values compared to that of intrinsic diffusion coefficients. This shows that the intrinsic diffusion coefficient values have been modified to take the effect of swelling due to the penetration of the solvent into the polymer matrix. To investigate the solvent penetration of the polymer further, the solvent uptake of all the solvents by the

SOLVENT/SIMULANT	CHARACTERISTIC DIFFUSION COEFFICIENT (cm^2/sec.)			
	5°C	23°C	40°C	70°C
water	8.65×10^{-11}	4.04×10^{-10}	5.62×10^{-9}	5.15×10^{-8}
3% acetic acid	1.07×10^{-10}	4.70×10^{-10}	6.43×10^{-9}	5.58×10^{-8}
ethanol	2.99×10^{-10}	9.07×10^{-10}	1.10×10^{-8}	8.17×10^{-8}
50% ethanol	1.38×10^{-10}	6.04×10^{-10}	8.01×10^{-9}	6.76×10^{-8}
olive oil	2.31×10^{-10}	1.38×10^{-9}	1.53×10^{-8}	9.92×10^{-8}
glycerol-trioleate	3.89×10^{-10}	1.09×10^{-9}	1.26×10^{-8}	8.60×10^{-8}
heptane	1.61×10^{-8}	2.78×10^{-8}	1.68×10^{-7}	4.30×10^{-7}
INTRINSIC DIFFUSION COE.	2.44×10^{-11}	2.70×10^{-11}	1.45×10^{-9}	1.72×10^{-8}
SATURATED SOLUBILITY ($\times 10^4$% w/w)	7.9	32	181	1590

Table 5.1 Characteristics diffusion coefficients obtained for stabiliser UV-OH in various solvents and simulants at temperatures 5°C, 23°C, 40°C and 70°C.

polymer films were measured by immersing a pre-weighed polymer films in a solvent at the required temperature, then the films were weighed periodically until it reached equilibrium. Since the test films used in the migration tests were too small to give a measurable result in some cases, films of 2.5 mm thickness were used. The net weight increase of film was calculated as a percentage gain from the original value and these values can be seen in Table 5.2. This reveals that at all temperatures, uptake of heptane is the highest and the water is the lowest. The magnitude of the characteristic diffusion coefficient values follow the same order as solvent uptake values.

D_p in heptane is very high at all temperatures compared to all other solvents. This is mainly due to high heptane uptake by the polymer film (21%) which results in swelling of the polymer matrix. As a consequence of this, the D_p increases 25 and 134 times when compared with the intrinsic diffusion coefficients(I.D.C) values at 70°C, 23°C respectively. Furthermore, at 5°C the increase of D_p is about 660 times over the I.D.C. value. This shows that the effect of swelling on diffusion coefficients is more pronounced for low diffusion coefficient values. On the other hand, water, 3% acetic acid are poor swelling agents and do not modify the polymer matrix to a great extent with the result that the characteristic diffusion coefficients are of the same order as the intrinsic

SOLVENT	% OF SOLVENT UPTAKE BY LDPE FILMS(w|w%)			
	5°C	23°C	40°C	70°C
water	0.07	0.20	0.32	0.43
3% acetic ac.	0.10	0.28	0.35	0.36
ethanol	0.25	0.44	0.67	0.77
50% ethanol	0.16	0.25	0.41	0.53
olive oil	0.39	0.84	1.21	1.27
gly. triolea.	0.34	0.69	1.09	1.09
heptane	4.01	8.60	13.50	21.09

Table 5.2. % solvent uptake of LDPE films in various solvents and simulants.

diffusion coefficients. Ethanol, 50% ethanol, olive oil, trioleate can be considered as intermediate cases, which penetrate the polymer matrix to a certain degree. As a result of this the characteristic diffusion coefficients values for these solvents lies in between the above two extremes. Nevertheless even in the case of olive oil it can be an order of magnitude greater in swollen than in unswollen polymer film.

The difference between the diffusion coefficients of the stabiliser in the presence and absence of water were also observed by Westlake and Johnson[23] for UV-OH in their extraction studies. They have evaluated the diffusion coefficients of UV-OH in LDPE film immersed in water at 44°C and found an increase of 1.5 times over the intrinsic values. This also supports our observation that even a poor swelling agent such as water can have a significant influence on diffusion rates.

2. UV-nC8 (2-hydroxy-4-octoxy-benzophenone)

The results of the migration tests carried out for UV-nC8 is shown graphically in Figures 5.2A-D for temperatures 5°, 23°, 40° and 70°C, where the rate of migration per unit area is plotted against the square root of time. The relevant characteristic diffusion coefficients, together with intrinsic diffusion coefficient and

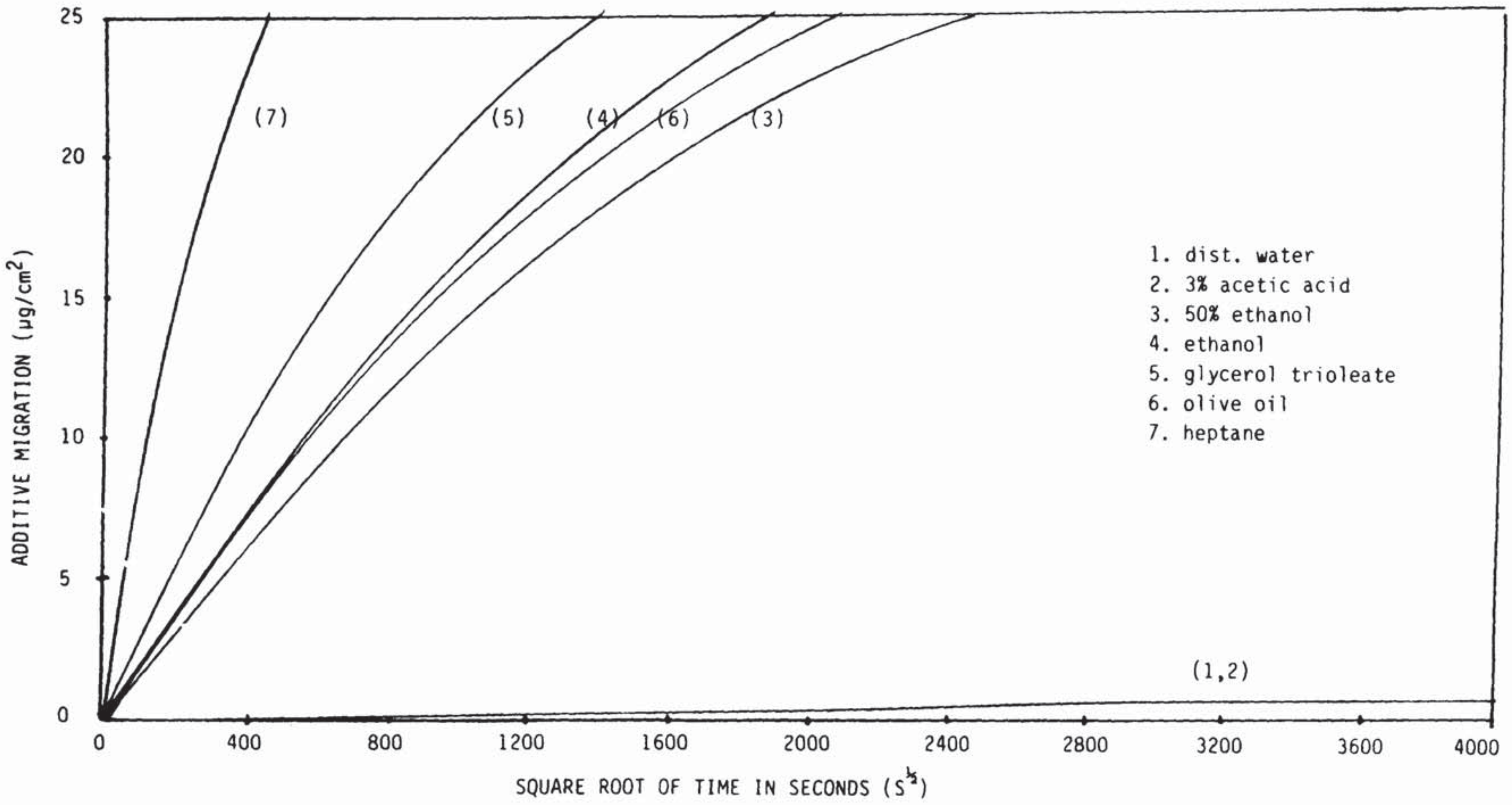


Figure 5.2A Migration of UV-nC8 from LDPE films into various solvents at 5°C.

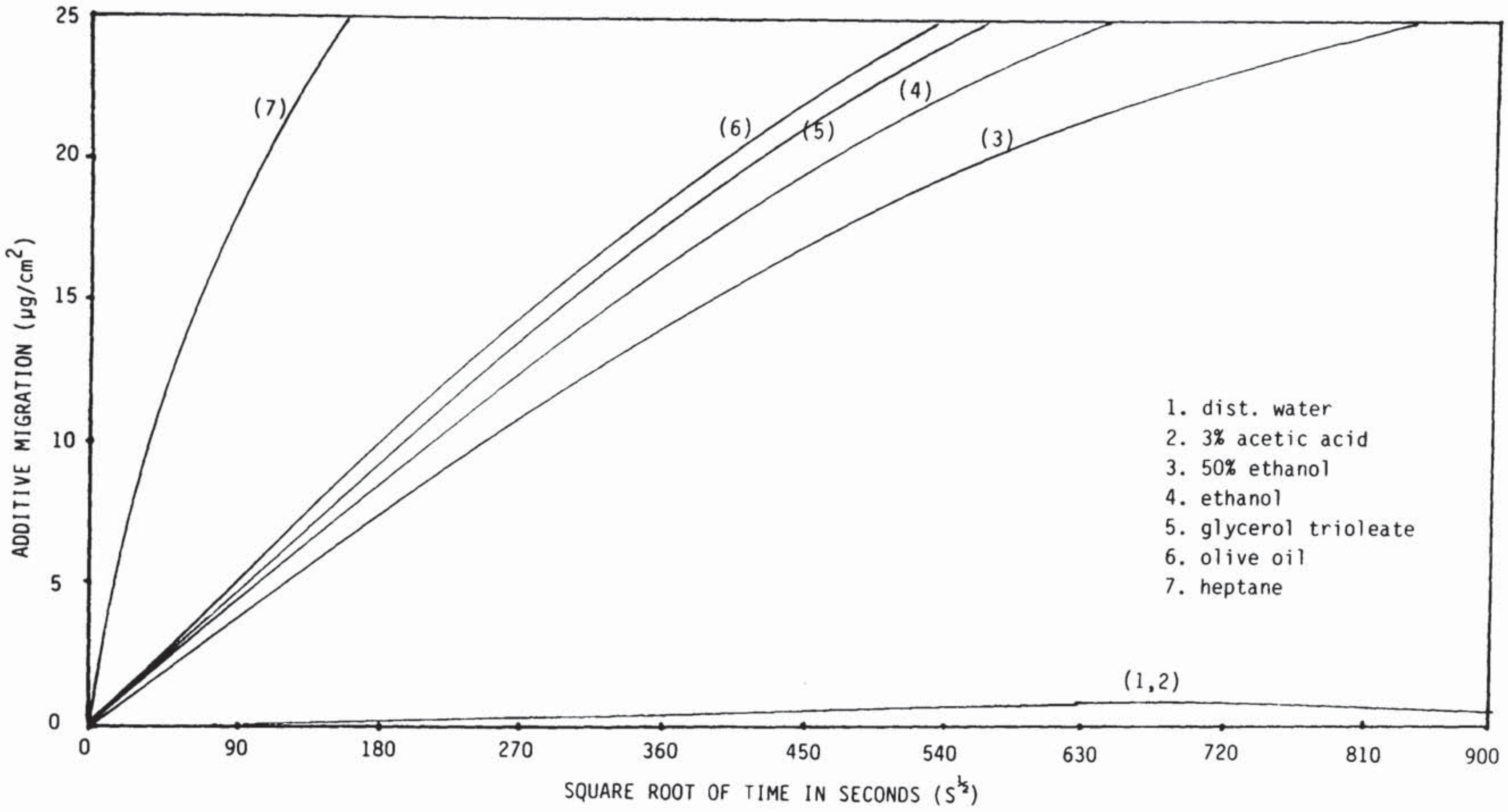


Figure 5.2B Migration of UV-nC8 from LDPE films into various solvents at 23°C.

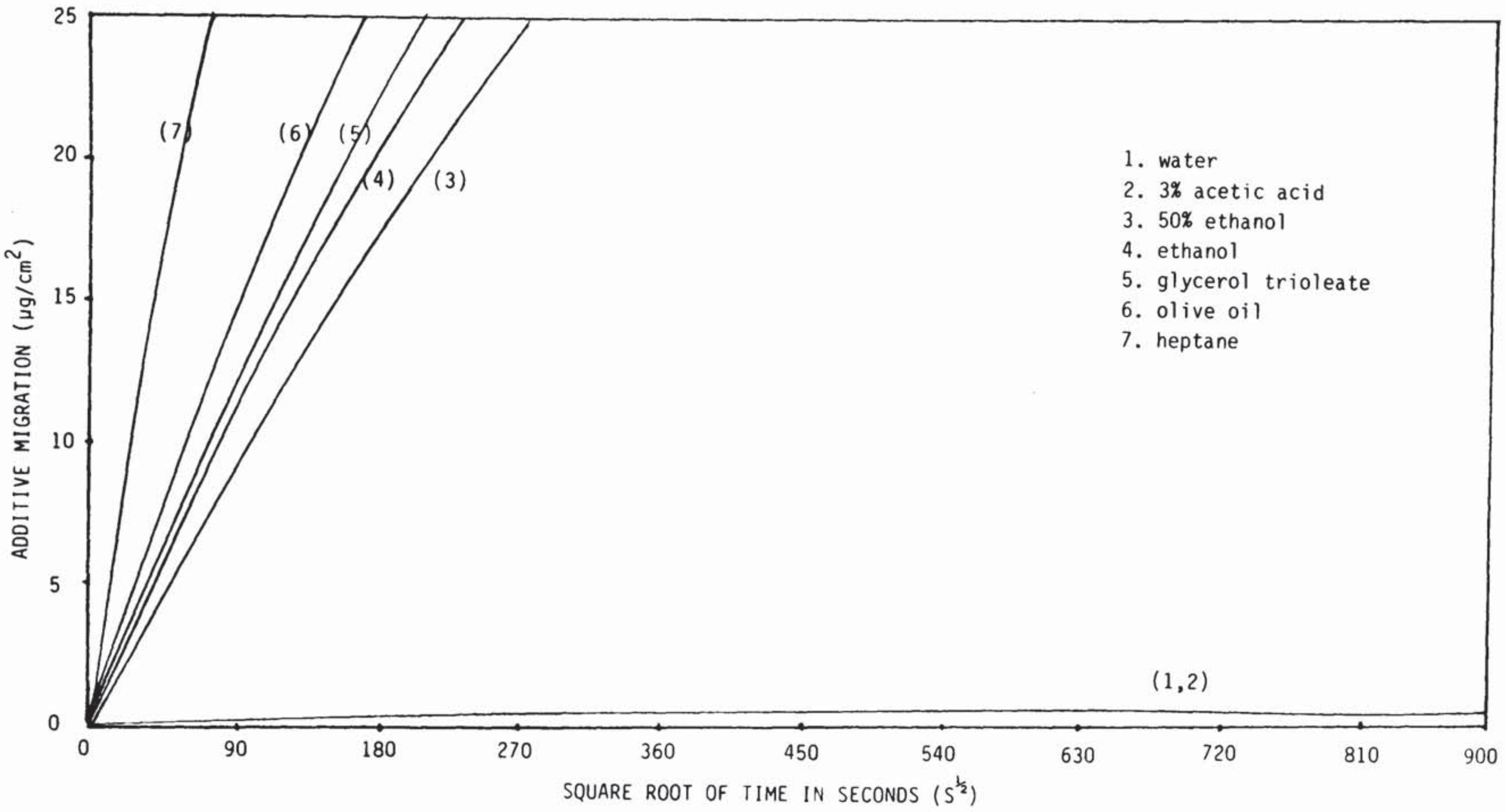


Figure 5.2C Migration of UV-nC8 from LDPE films into various solvents at 40°C.

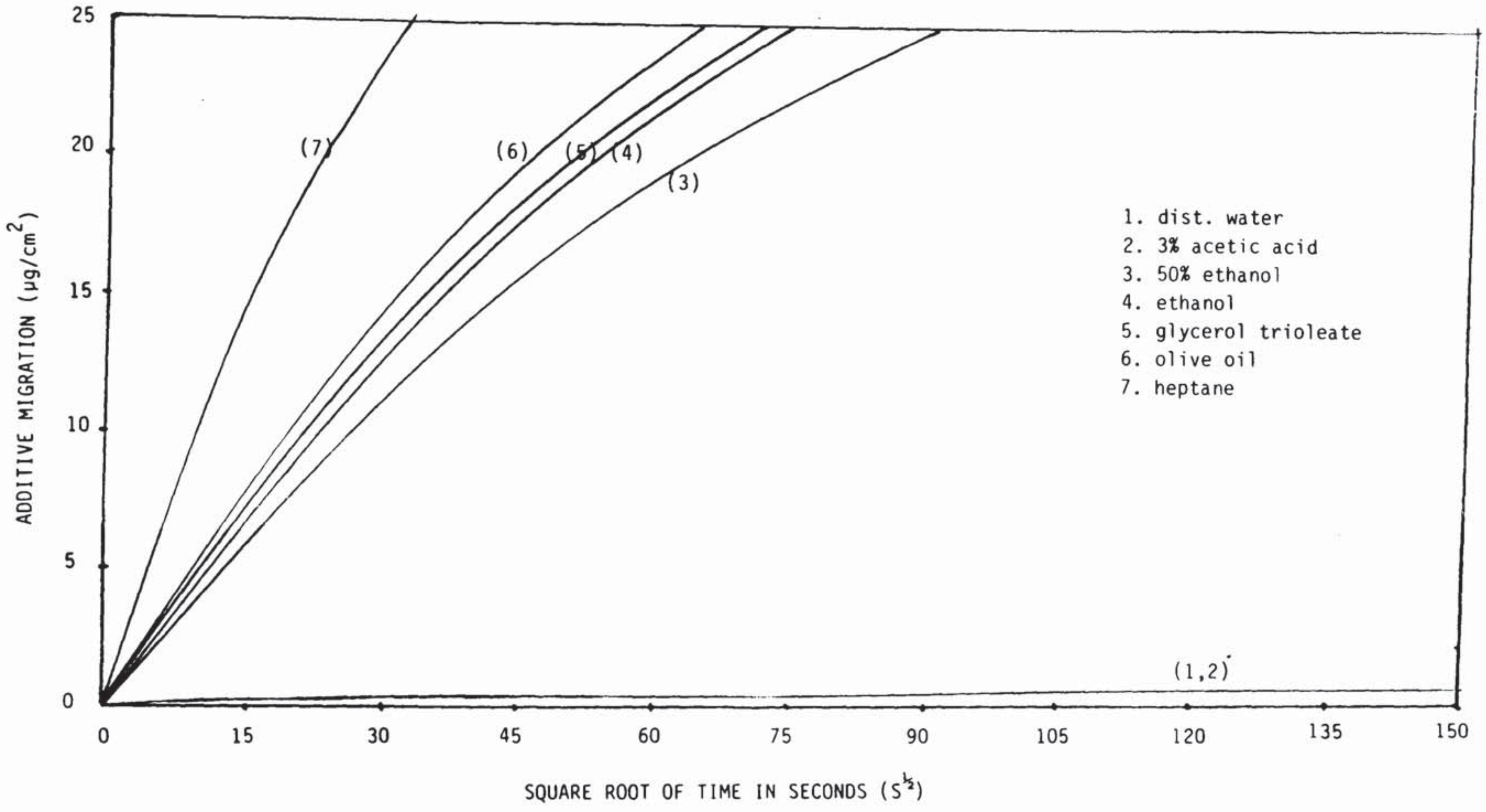


Figure 5.2D Migration of UV-nC8 from LDPE films into various solvents at 70°C.

saturated solubility data are given in Table 5.3. The behaviour of UV-nC8 towards ethanol, 50% ethanol, olive oil and glycerol trioleate is similar to the case of UV-OH, where the migration pattern is Fickian. Moreover, the typical increase of the D_p values from those of I.D.C values due to varying solvent penetration power is dominant.

The migration studies carried out with water and 3% acetic yields were quite interesting. The amount of UV-nC8 extracted out from the polymer film is very low at all temperatures or in other words, the concentration of the UV-nC8 in the polymer remains almost constant over the whole experimental period. Therefore, this migration belongs to the 4th category described in the section 5.2.3. The saturated solubility values given in Table 5.3 shows that this compound is fairly soluble in the polymer, but since it is less soluble in water, the rate of removal of the additive from the surface is very low and this seems to be the rate determining factor of the migration. This observation shows that the overall rate of loss of an additive from polymers into a surrounding medium will be dependent not only on the diffusion rate in the polymer but also on the rate of romoval of the additive from the surfaces by dissolution. Furthermore, the rate of dissolution from the surface, which creates a concentration gradient, will depend on the solubility of the additive in the liquid and in the polymer. A much

SOLVENT/SIMULANT	CHARACTERISTIC DIFFUSION COEFFICIENT (cm^2/sec.)			
	5°C	23°C	40°C	70°C
water				
3% acetic acid				
ethanol	5.56×10^{-10}	1.76×10^{-9}	2.04×10^{-8}	1.42×10^{-7}
50% ethanol	2.81×10^{-10}	1.16×10^{-9}	1.47×10^{-8}	1.16×10^{-7}
olive oil	4.70×10^{-10}	2.50×10^{-9}	2.67×10^{-8}	1.62×10^{-7}
glycerol-trioleate	7.40×10^{-10}	1.96×10^{-9}	2.14×10^{-8}	1.38×10^{-7}
heptane	3.60×10^{-8}	5.88×10^{-8}	3.39×10^{-7}	8.13×10^{-7}
INTRINSIC DIFFUSION COE.	6.03×10^{-11}	5.08×10^{-10}	5.26×10^{-9}	2.96×10^{-8}
SATURATED SOLUBILITY ($\times 10^4$ % w/w)	700	2970	10300	30500

Table 5.3 Characteristics diffusion coefficients obtained for stabiliser UV-nC8 in various solvents and simulants at temperatures 5°C, 23°C, 40°C and 70°C.

higher solubility in the polymer than in the solvent, which is the case for UV-nC8/water system, will result in a very low dissolution rate. Therefore, it seems that in this case, loss of the additive from polymers is also determined by the rate of dissolution at the polymer surface and, once a concentration gradient is created, the diffusion in the bulk polymer becomes the rate determining factor.

Again the swelling action of heptane on the rate of migration is significant, at 5°C the increase of D_p over Intrinsic Diffusion Coefficient (I.D.C.) is 600 times while at 70°C it is only 28 times. Therefore, as for UV-OH, again the swelling action is more pronounced on lower diffusion coefficients at low temperatures. However, this does not apply to other solvents.

3. UVS-H (4-benzoyl-3-hydroxyphenyl ethoxythioglycollate)

Migration plots of UVS-H stabiliser can be seen in Figures 5.3A-D at 5°, 23°, 40°, 70°C. Though the initial trend shows the Fickian behaviour (except for heptane), all other plots show an unusual plateau indicating equilibrium after about 80% loss of the additive. Up to this level the rate of migration is similar to the case of UV-OH and the relative characteristic diffusion data are given in Table 5.4. As with UV-OH, diffusion of the

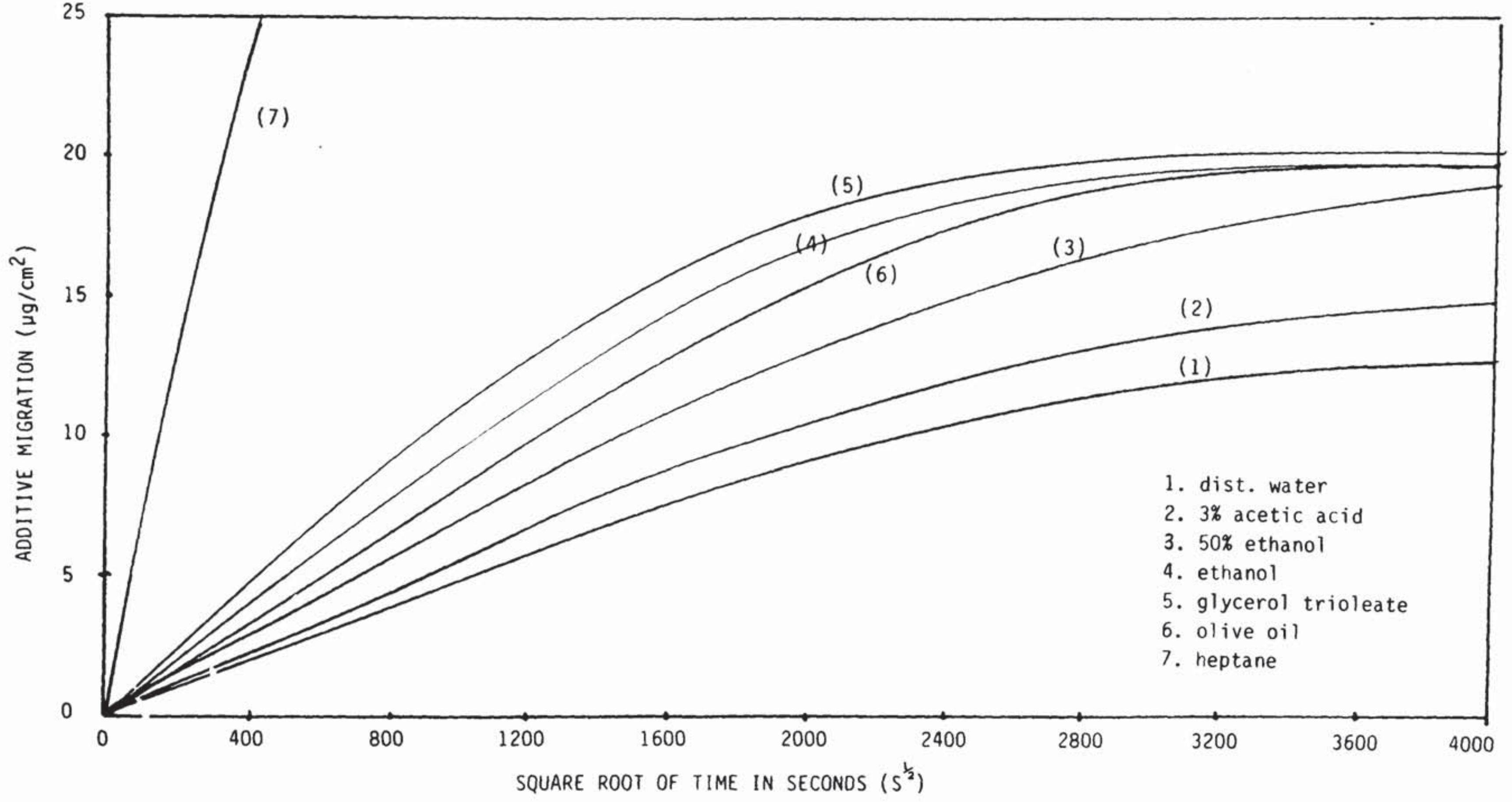


Figure 5.3A Migration of UVS-H from LDPE films into various solvents at 5°C.

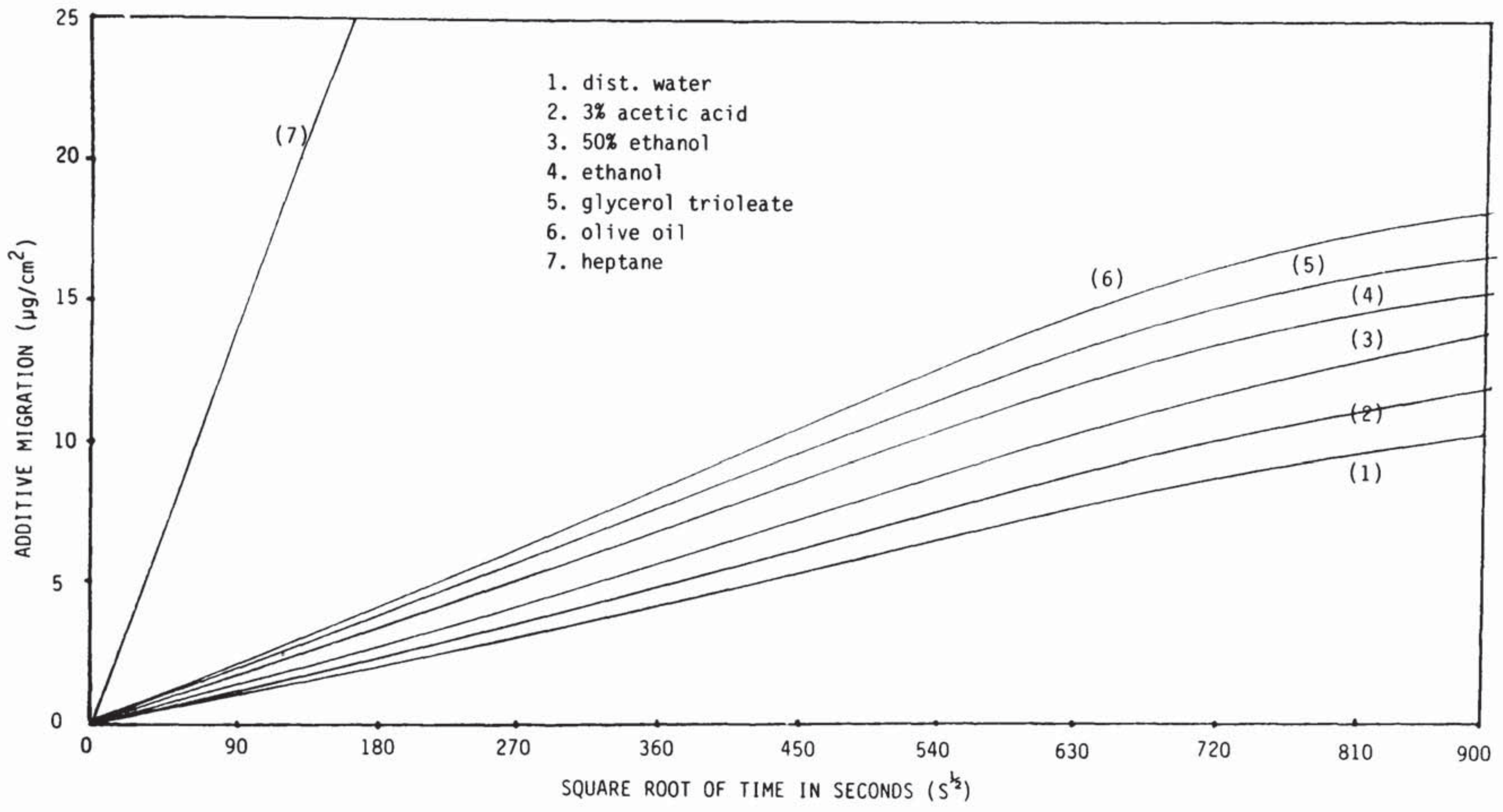


Figure 5.3B Migration of UVS-H from LDPE films into various solvents at 23°C.

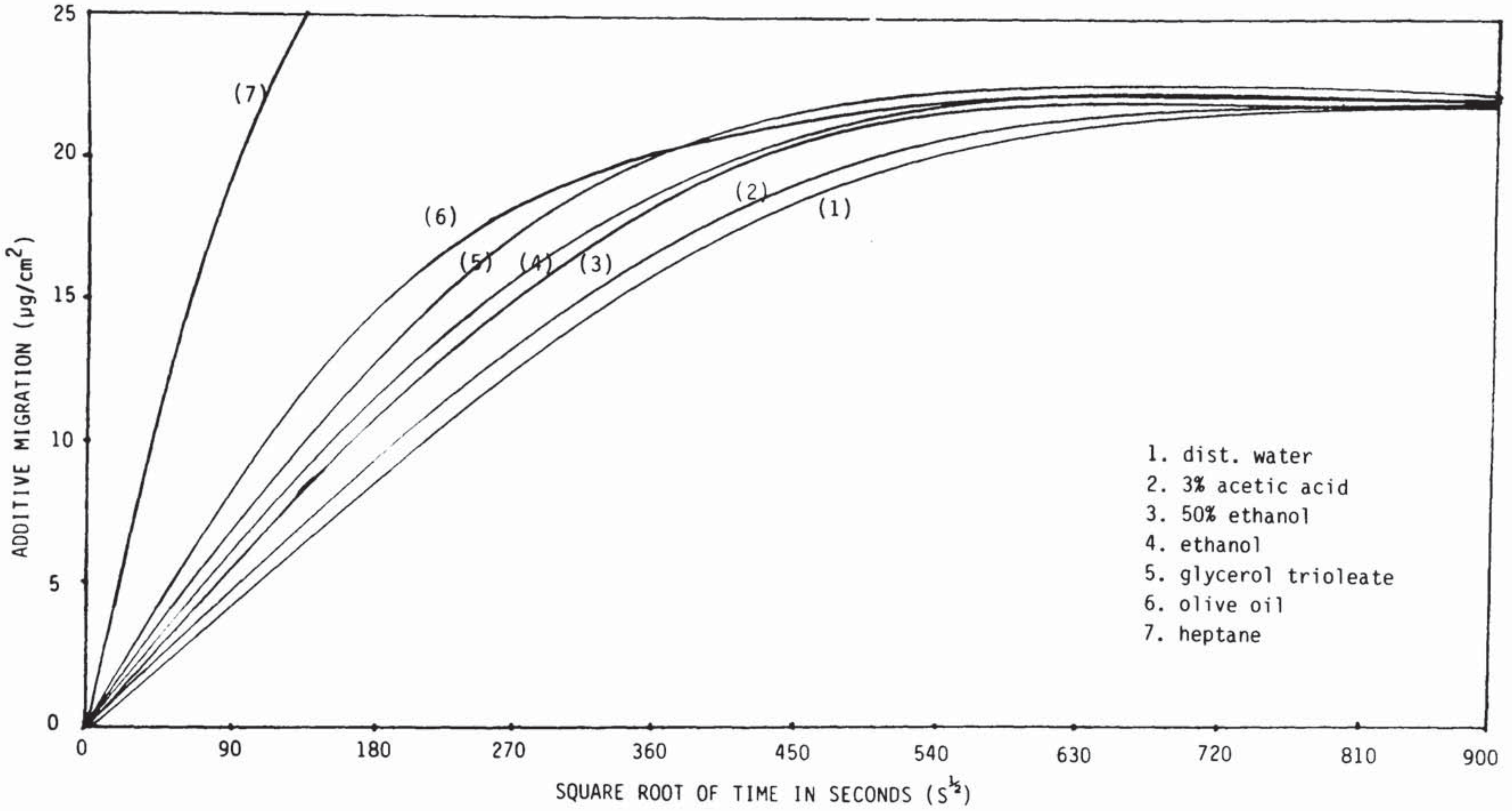


Figure 5.3C Migration of UVS-H from LDPE films into various solvents at 40°C.

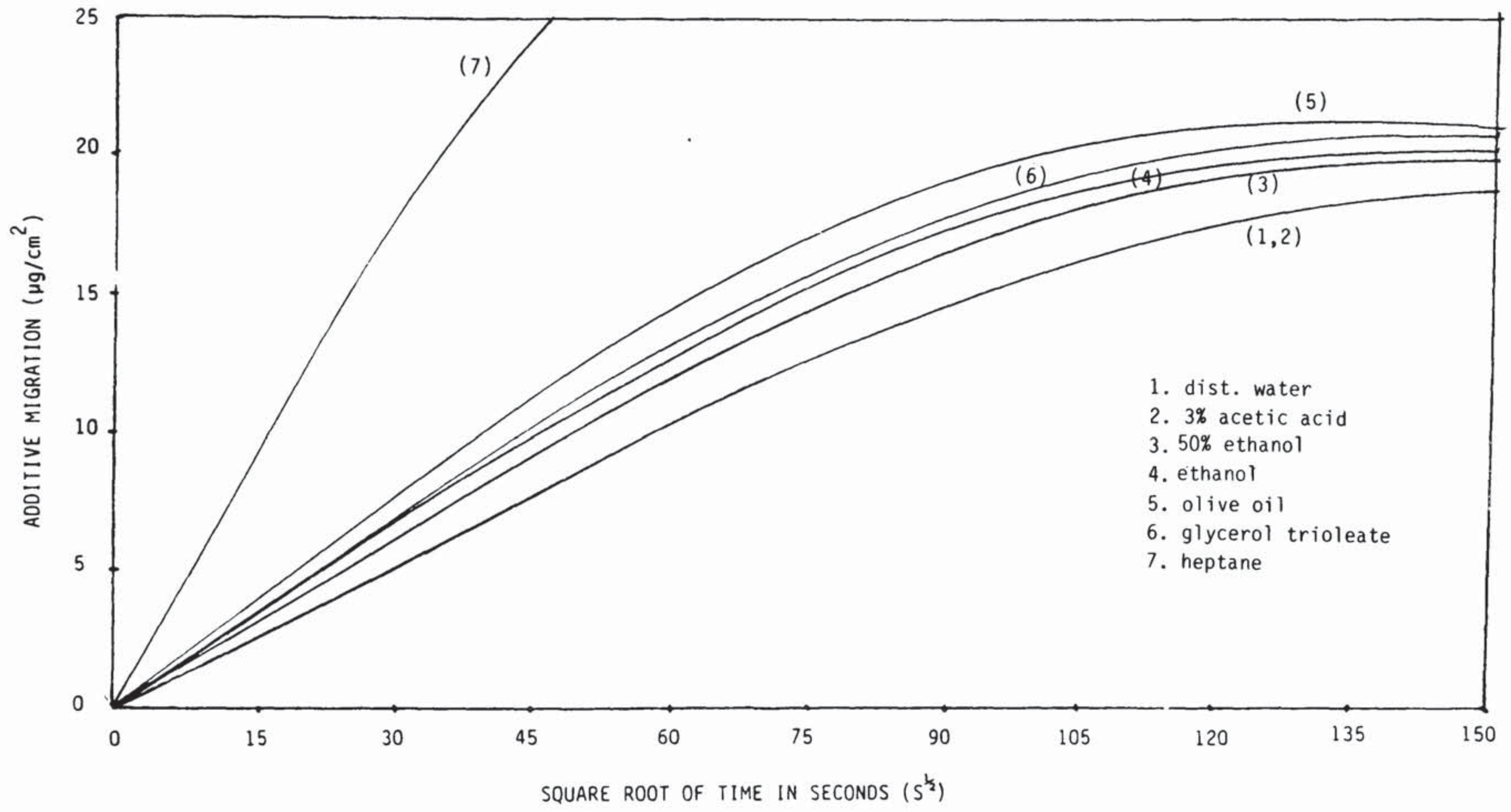
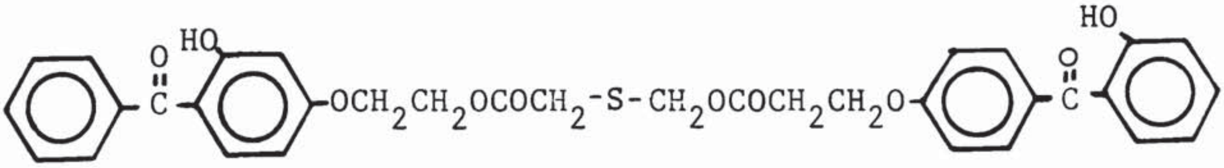


Figure 5.3D Migration of UVS-H from LDPE films into various solvents at 70°C.

SOLVENT/SIMULANT	CHARACTERISTIC DIFFUSION COEFFICIENT (cm^2/sec.)			
	5°C	23°C	40°C	70°C
water	2.22×10^{-11}	1.20×10^{-10}	1.95×10^{-9}	2.25×10^{-8}
3% acetic acid	2.62×10^{-11}	1.40×10^{-10}	2.17×10^{-9}	2.35×10^{-8}
ethanol	7.63×10^{-11}	2.71×10^{-10}	3.76×10^{-9}	3.43×10^{-8}
50% ethanol	4.12×10^{-11}	2.07×10^{-10}	3.03×10^{-9}	3.02×10^{-8}
olive oil	5.86×10^{-11}	4.22×10^{-10}	5.07×10^{-9}	4.01×10^{-8}
glycerol-trioleate	9.62×10^{-11}	3.30×10^{-10}	3.48×10^{-9}	3.63×10^{-8}
heptane	6.15×10^{-9}	1.48×10^{-9}	7.02×10^{-8}	1.90×10^{-7}
INTRINSIC DIFFUSION COE.	6.34×10^{-12}	7.08×10^{-11}	5.67×10^{-10}	7.35×10^{-9}
SATURATED SOLUBILITY ($\times 10^4$ % w/w)	85	390	1200	8850

Table 5.4 Characteristics diffusion coefficients obtained for stabiliser UVS-H in various solvents and simulants at temperatures 5°C, 23°C, 40°C and 70°C.

stabiliser within the bulk polymer is the rate determining factor of the rate of migration. Since UVS-H is fairly soluble in these solvents, the achievement of equilibrium cannot be due the equilibrium partitioning nor can this be due to the binding of UVS-H to the polymer matrix, because heptane removes all the stabiliser present in the polymer matrix. The probable explanation is the formation of a transformation product of UVS-H. Though the films were processed under closed mixing conditions, it is possible that during the processing minute amount UVS-H may have dimerized in the presence of minute amount of oxygen to give disulphide(I). Since the disulphide is a fairly large molecule the diffusion in the polymer matrix has been lowered to a great extent. This also shows that not only the chemical nature of the migrant is important, but also its possible that transformation product has an influence on the rate of migration.



(I)

Again the swelling action of heptane upon lower diffusion coefficients is significant. At 5°C the increase of the magnitude of D_p over I.D.C is 970 times while at 70°C the increase is only 25 times.

4. UVS-nC(X), X=1,4,8,12,18, 4-benzoyl-3-hydroxyl phenyl ethoxy alkylglycollate

The typical plots obtain for this series are shown in Figures 5.4A-B for UVS-nC8 and Figures 5.5A-B for UVS-nC18 at temperatures 40°C and 70°C respectively. Similar plots were obtained for other stabilisers. Again the magnitude of characteristic diffusion coefficients obtained are dependent upon the amount of solvent uptake of the polymer sample, except for water, for all members of the series. Migration into 3% acetic acid can be measured to a significant level at 40° and 70°C only. Since the solubility of this series in water is very poor, the behaviour towards 3% acetic acid is rather unexpected. It might be expected that the behaviour of the stabiliser towards 3% acetic acid is similar to that of water. Since the migration into water could not be measured at any of these temperatures, extractability into 3% acetic suggest two factors. 1. the additive is soluble in 3% acetic acid or, 2. the additive on the surface of the polymer may react with 3% acetic acid to give a soluble product in the water. A possible

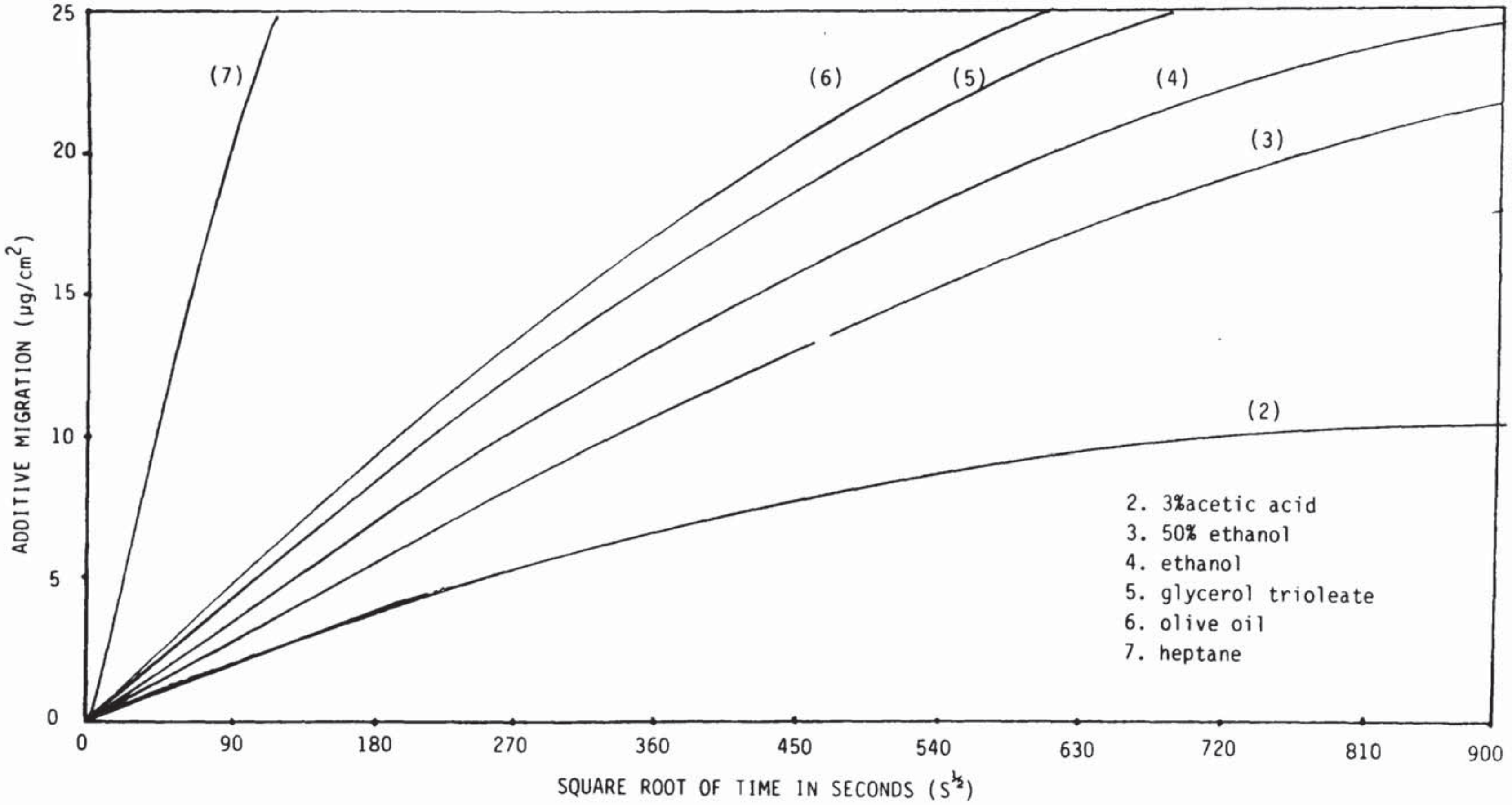


Figure 5.4A Migration of UVS-nC8 from LDPE films into various solvents at 40°C.

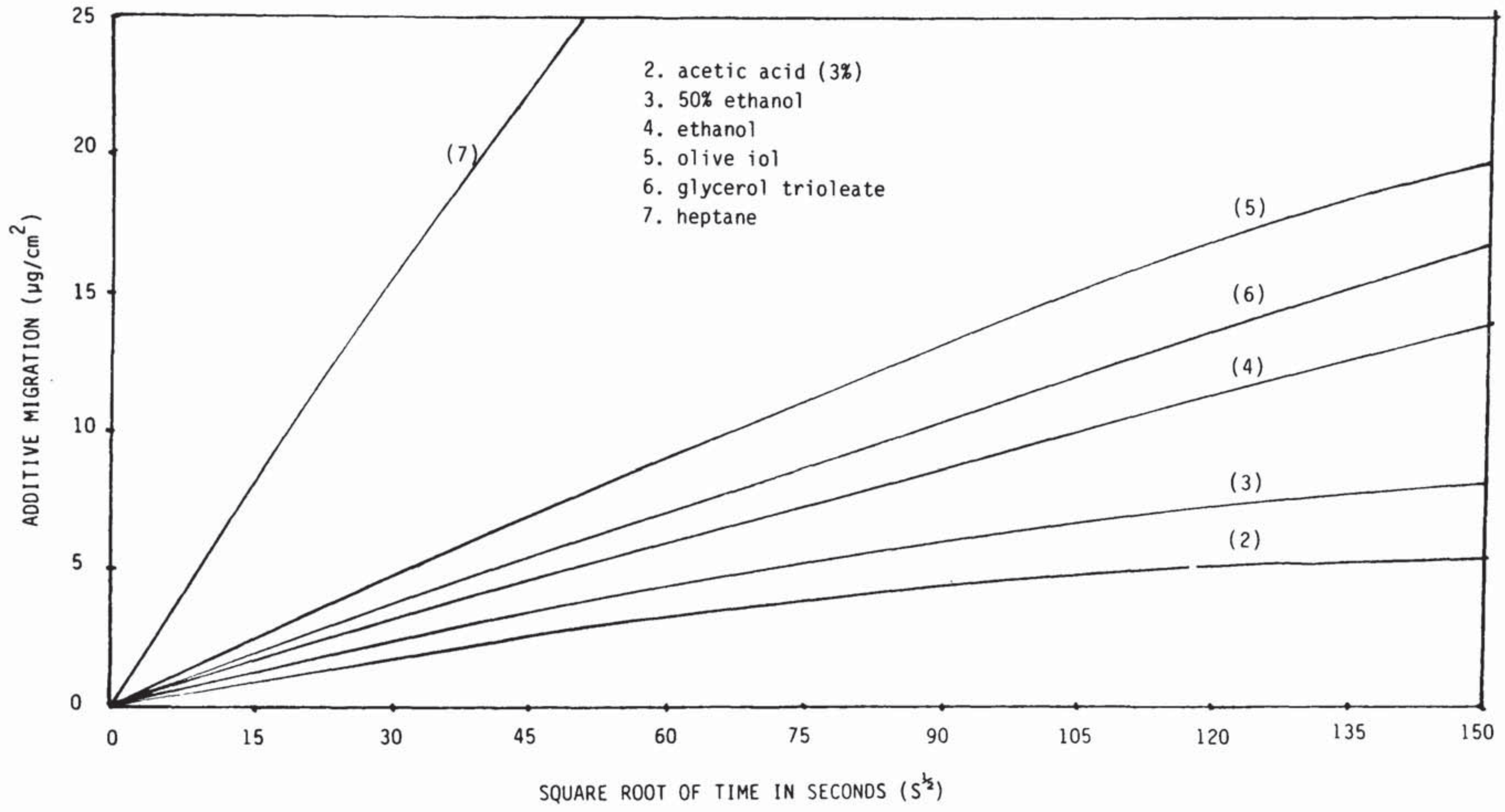


Figure 5.4B Migration of UVS-nC8 from LDPE films into various solvents at 70°C.

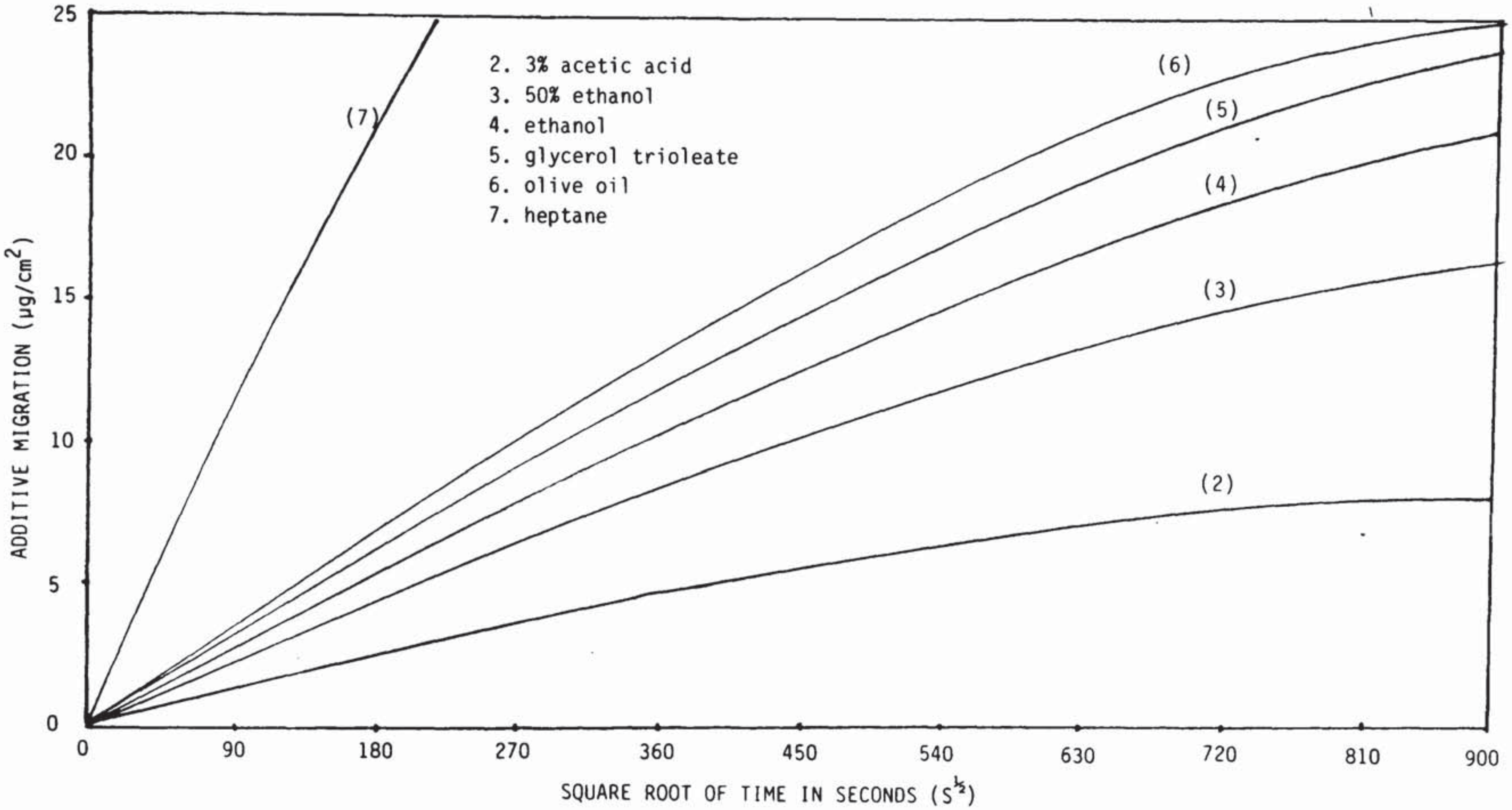


Figure 5.5A Migration of UVS-nC18 from LDPE films into various solvents at 40°C.

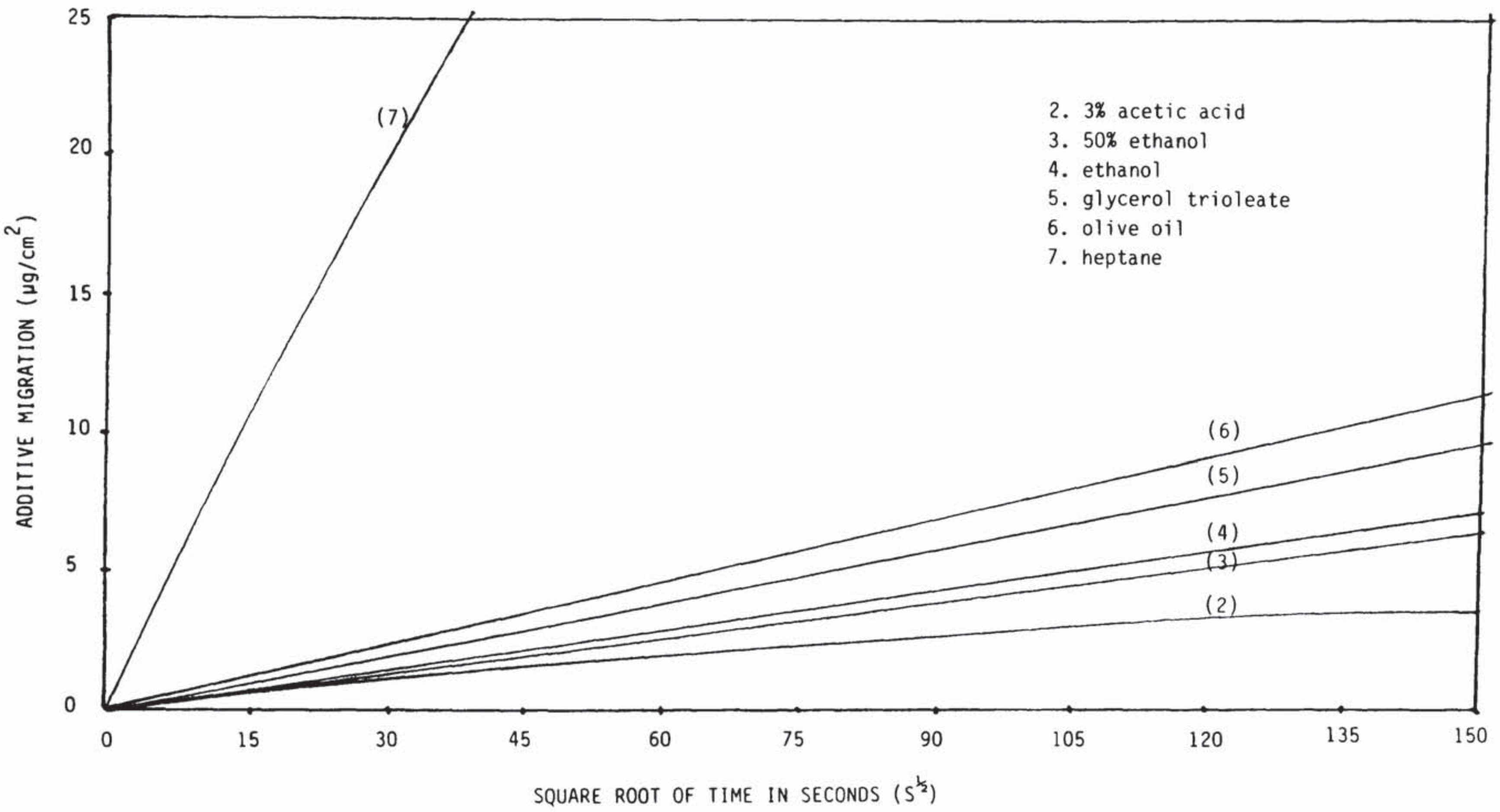
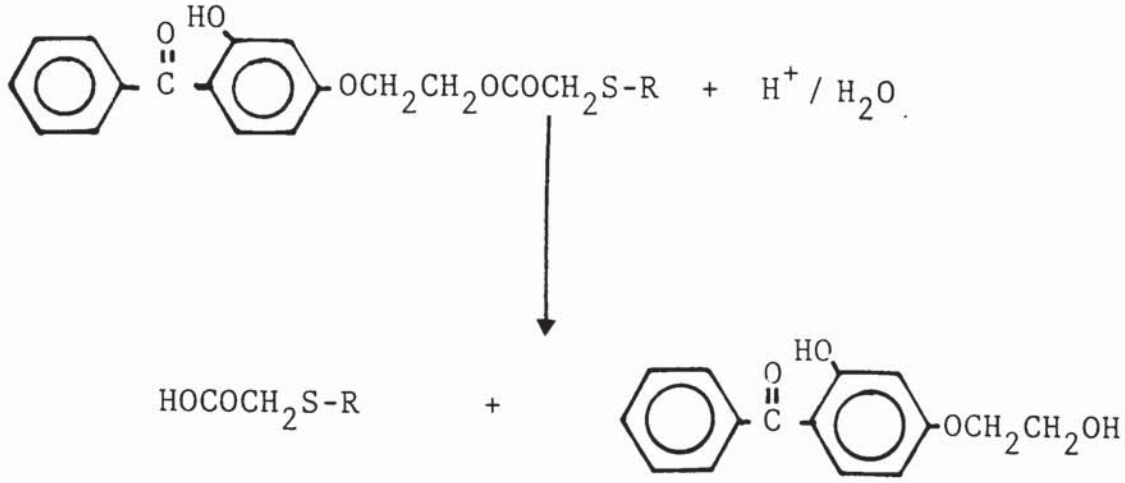


Figure 5.5B Migration of UVS-nC18 from LDPE films into various solvents at 70°C.

mechanism for this type of reaction may be the catalysed hydrolysis of UVS-:



According to this reaction the dissolution of breakdown products from the surface of the polymer to the solution is possible because of the solubility of these compounds in water medium. This could be the more probable reason for this type of behaviour. This observation suggests that not only may the additive be transformed in the polymer but the additive migrated out can also be transformed. The relevant data of D_p values together with I.D.C. and saturated solubility data are given in Table 5.5-5.9 for the stabiliser UVS-nC1, UVS-nC4, UVS-nC8, UVS-nC12 and UVS-nC18 respectively.

Extraction into the water could not be measured at all temperatures. Therefore, for this case as in the case of UV-nC8, the rate of the migration is controlled by the rate of dissolution of the additive at the surface of the polymer. This is possible due to the high additive

SOLVENT/SIMULANT	CHARACTERISTIC DIFFUSION COEFFICIENT (cm^2/sec.)			
	5°C	23°C	40°C	70°C
water				
3% acetic acid	2.08×10^{-11}	9.80×10^{-11}	1.38×10^{-9}	1.28×10^{-8}
ethanol	1.15×10^{-10}	3.58×10^{-10}	4.51×10^{-9}	3.56×10^{-8}
50% ethanol	4.98×10^{-11}	2.30×10^{-10}	3.16×10^{-9}	2.86×10^{-8}
olive oil	8.65×10^{-11}	5.37×10^{-10}	6.21×10^{-9}	4.26×10^{-8}
glycerol-trioleate	1.43×10^{-10}	4.50×10^{-10}	5.40×10^{-9}	3.91×10^{-8}
heptane	9.67×10^{-9}	1.66×10^{-8}	9.93×10^{-8}	2.57×10^{-7}
INTRINSIC DIFFUSION COE.	1.02×10^{-11}	8.74×10^{-11}	6.10×10^{-10}	7.93×10^{-9}
SATURATED SOLUBILITY ($\times 10^4$%w/w)	1200	2820	4040	8850

Table 5.5 Characteristics diffusion coefficients obtained for stabiliser UVS-Cl in various solvents and simulants at temperatures 5°C, 23°C, 40°C and 70°C.

SOLVENT/SIMULANT	CHARACTERISTIC DIFFUSION COEFFICIENT (cm^2/sec.)			
	5°C	23°C	40°C	70°C
water				
3% acetic acid	5.11×10^{-12}	2.85×10^{-11}	4.62×10^{-10}	5.32×10^{-9}
ethanol	2.42×10^{-11}	8.9×10^{-11}	1.29×10^{-9}	1.24×10^{-8}
50% ethanol	1.02×10^{-11}	5.46×10^{-11}	8.50×10^{-10}	9.22×10^{-9}
olive oil	1.77×10^{-11}	1.35×10^{-10}	1.77×10^{-10}	1.46×10^{-8}
glycerol-trioleate	3.13×10^{-11}	1.11×10^{-10}	1.52×10^{-9}	1.36×10^{-8}
heptane	1.81×10^{-9}	3.50×10^{-9}	2.32×10^{-8}	6.91×10^{-8}
INTRINSIC DIFFUSION COE.	2.16×10^{-12}	2.06×10^{-11}	1.78×10^{-10}	2.84×10^{-9}
SATURATED SOLUBILITY ($\times 10^4$ %w/w)	740	1520	2450	5350

Table 5.6 Characteristics diffusion coefficients obtained for stabiliser UVS-nC4 in various solvents and simulants at temperatures 5°C, 23°C, 40°C and 70°C.

SOLVENT/SIMULANT	CHARACTERISTIC DIFFUSION COEFFICIENT (cm^2/sec.)			
	5°C	23°C	40°C	70°C
water				
3% acetic acid	11.24×10^{-12}	4.59×10^{-11}	3.83×10^{-10}	4.37×10^{-9}
ethanol	4.83×10^{-11}	1.12×10^{-10}	1.27×10^{-9}	8.57×10^{-9}
50% ethanol	1.46×10^{-11}	5.90×10^{-11}	7.30×10^{-10}	5.57×10^{-9}
olive oil	3.07×10^{-11}	2.32×10^{-10}	2.41×10^{-9}	1.80×10^{-8}
glycerol-trioleate	7.01×10^{-11}	1.67×10^{-10}	1.80×10^{-9}	1.12×10^{-9}
heptane	5.16×10^{-9}	8.10×10^{-8}	3.73×10^{-8}	1.07×10^{-8}
INTRINSIC DIFFUSION COE.	5.63×10^{-12}	5.26×10^{-11}	3.36×10^{-10}	2.86×10^{-9}
SATURATED SOLUBILITY ($\times 10^4$ % w/w)	2700	4350	7250	13750

Table 5.7 Characteristics diffusion coefficients obtained for stabiliser UVS-nC8 in various solvents and simulants at temperatures 5°C, 23°C, 40°C and 70°C.

SOLVENT/SIMULANT	CHARACTERISTIC DIFFUSION COEFFICIENT (cm^2/sec.)			
	5°C	23°C	40°C	70°C
water	-		-	
3% acetic acid	6.76×10^{-12}	2.8×10^{-11}	2.38×10^{-10}	2.88×10^{-9}
ethanol	3.65×10^{-11}	7.13×10^{-11}	8.04×10^{-10}	5.83×10^{-9}
50% ethanol	10.85×10^{-12}	4.22×10^{-11}	5.13×10^{-10}	3.78×10^{-9}
olive oil	1.96×10^{-11}	1.50×10^{-10}	15.61×10^{-10}	9.11×10^{-9}
glycerol-trioleate	4.58×10^{-11}	1.24×10^{-10}	13.38×10^{-10}	8.26×10^{-9}
heptane	2.23×10^{-9}	3.56×10^{-9}	2.00×10^{-8}	4.65×10^{-8}
INTRINSIC DIFFUSION COE.	3.47×10^{-12}	3.31×10^{-11}	1.80×10^{-9}	1.78×10^{-9}
SATURATED SOLUBILITY ($\times 10^4$ %w/w)	2350	4050	7250	13750

Table 5.8 Characteristics diffusion coefficients obtained for stabiliser UVS-nC12 in various solvents and simulants at temperatures 5°C 23°C, 40°C and 70°C.

SOLVENT/SIMULANT	CHARACTERISTIC DIFFUSION COEFFICIENT (cm^2/sec.)			
	5°C	23°C	40°C	70°C
water				
3% acetic acid	3.96×10^{-12}	1.72×10^{-11}	1.51×10^{-10}	1.91×10^{-9}
ethanol	2.07×10^{-11}	5.48×10^{-11}	6.40×10^{-10}	4.48×10^{-9}
50% ethanol	7.92×10^{-12}	3.30×10^{-11}	4.21×10^{-10}	3.35×10^{-9}
olive oil	1.45×10^{-11}	9.70×10^{-11}	1.04×10^{-9}	6.4×10^{-9}
glycerol-trioleate	2.07×10^{-11}	7.50×10^{-11}	8.53×10^{-10}	5.66×10^{-9}
heptane	1.97×10^{-9}	3.15×10^{-9}	1.42×10^{-8}	3.30×10^{-8}
INTRINSIC DIFFUSION COE.	2.21×10^{-12}	2.01×10^{-11}	1.21×10^{-10}	1.28×10^{-9}
SATURATED SOLUBILITY ($\times 10^4$ % w/w)	2250	4100	6600	13570

Table 5.9 Characteristics diffusion coefficients obtained for stabiliser UVS-nC18 in various solvents and simulants at temperatures 5°C, 23°C, 40°C and 70°C.

solubility in the polymer to that in the water. Again the action of heptane upon lower diffusion coefficients is significant.

The above discussion can be summarised as follows:

1. The migration media plays vital role in determining the amount of additive migration.
2. Highly swelling solvents increase the rate of migration drastically, and this effect is more pronounced at lower temperatures than at higher temperatures.
3. If the additive is soluble in the media, the rate of migration can be described as Fickian, where the rate of migration is proportional to the square root of time.
4. All the solvents penetrate into the polymer to a certain extent, this increases the resulting mobility of the additive in the polymer and the magnitude depends on the swelling power of the solvent.
5. If the additive is more soluble in the polymer than the migration media, the rate of migration is determined by the rate of dissolution of the additive on the polymer surface.
6. The additive can be transformed to some other form when it is incorporated into the polymer matrix. In this case the rate of migration may be completely

different from that of an original additive.

7. Additives also can be transformed when they come into contact with a solvent and this may result in indifferent migration rates than predicted from that of a pure additive.
8. The intrinsic diffusion coefficient of the additive is modified to an extent depending upon the amount of solvent absorption.

5.2.4 Effect of Stabiliser Structure on Rate of Migration

Figures 5.6 and 5.7 represents the migration of UVS-H, UV-nC(X),(X=1,4,8,12,18) into olive oil and ethanol at 70°C. Addition of a methyl group instead of H results in an increase in the rate of migration in UVS-C1 compared to that of UVS-H. This may be due to the effect of reducing hydrogen bonding of the UVS-H. Further increase in the alkyl chain results in decrease in the rate of migrations of UVS-nC4, UVS-nC8, UVS-vC12 and UVS-nC18 in ethanol. The rate of migration of UVS-nC4 and UVS-nC8 into olive oil is in some what in the reverse order than from that in ethanol, perhaps this may be due to the increase of the solubility of UVS-nC8 in olive oil compared to ethanol. The increase of the alkyl chain of the stabiliser results in a decrease in intrinsic diffusion coefficients (as shown in Chapter 3) but similar saturated solubility values in the polymer. Therefore, the different rates observed may be attributed to lowering

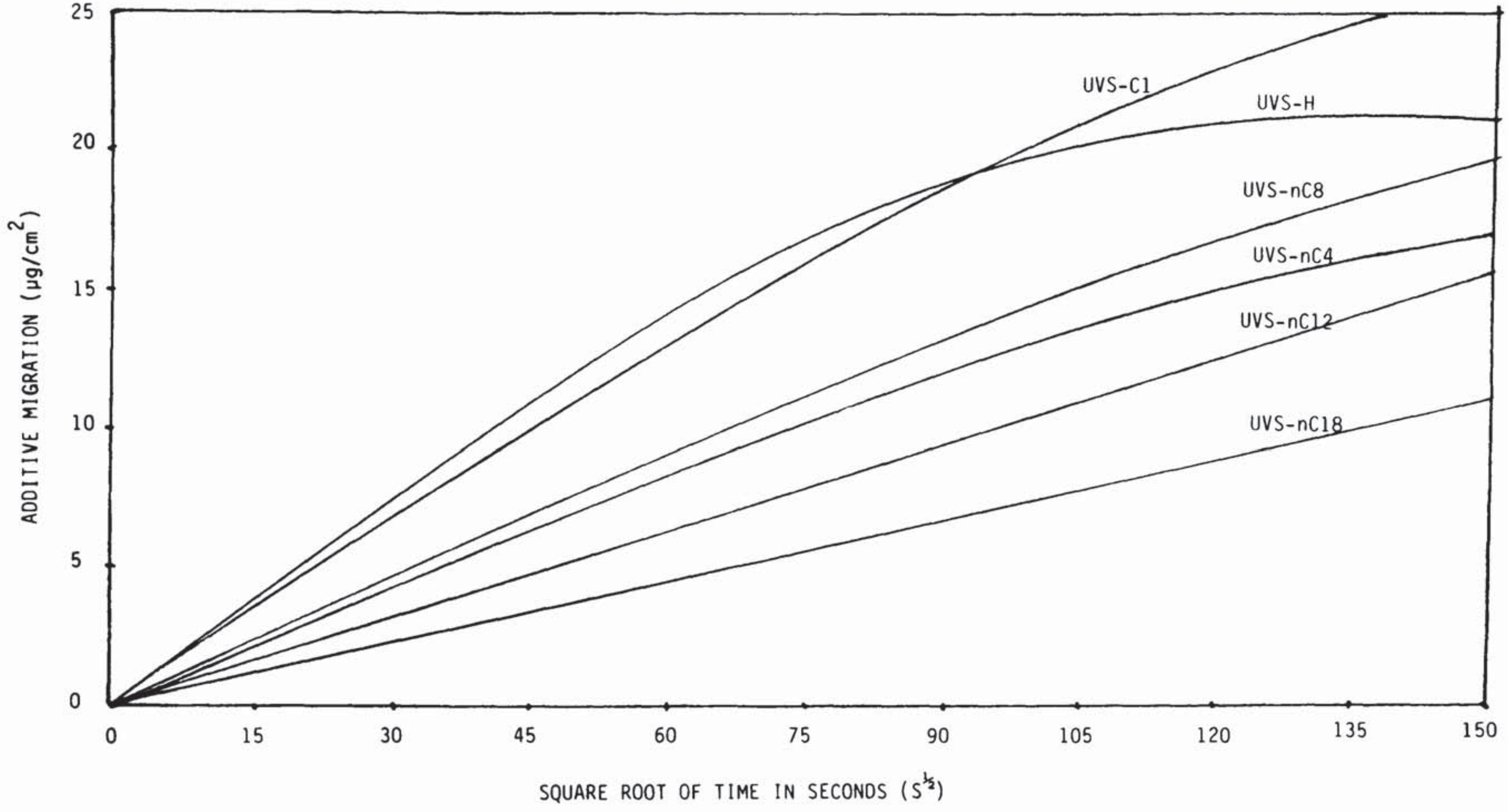


Figure 5.6 Migration of UVS-nC(X) stabilisers from LDPE films into olive oil at 70°C.

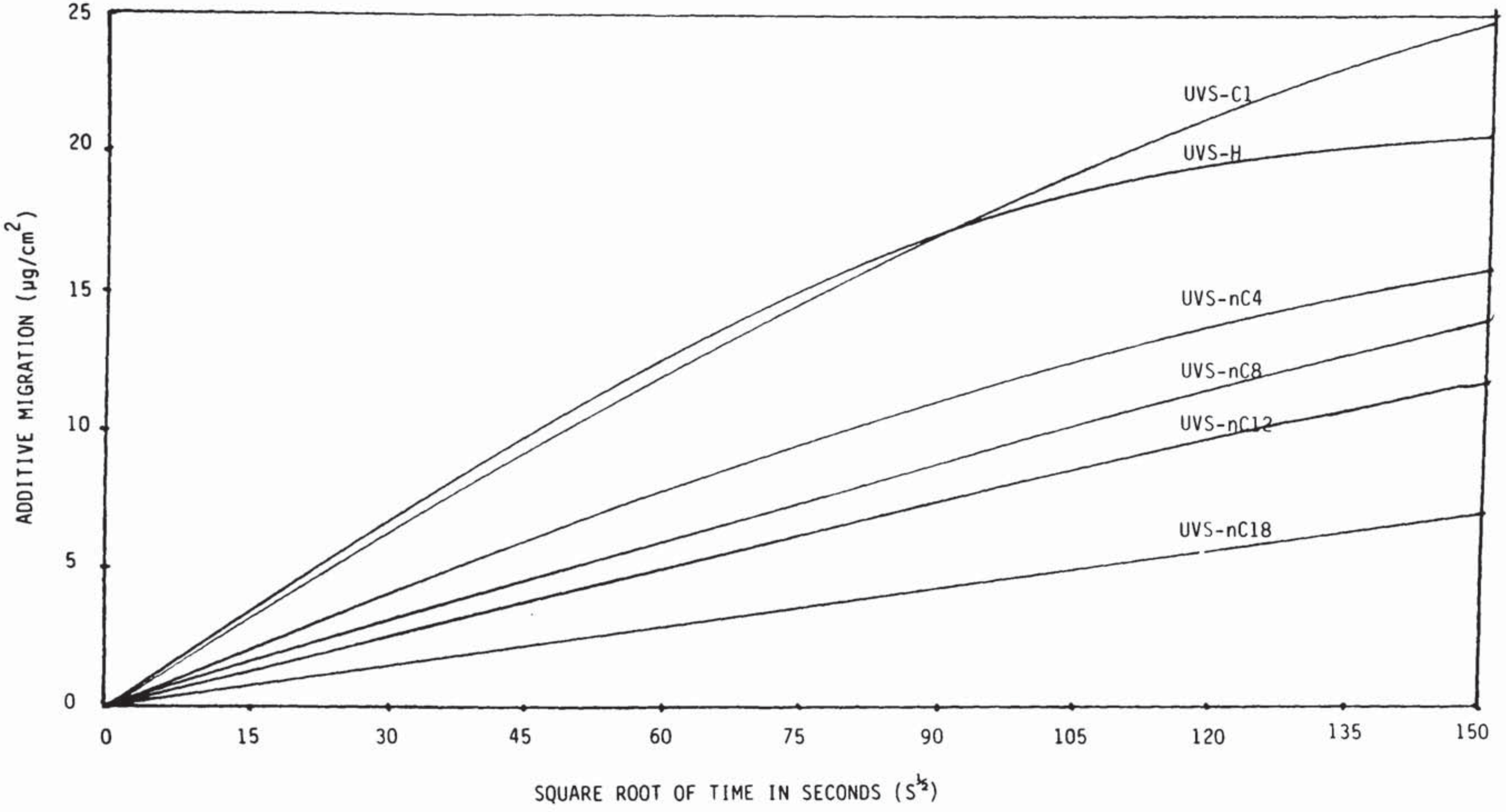


Figure 5.7 Migration of UVS-nC(X) stabilisers from LDPE films into ethanol at 70°C.

diffusion rates of the additive in the pure polymer.

5.2.5 Effect of Temperature on Characteristic diffusion Coefficients.

Temperature has a pronounced effect on migration rates not only through the changes in solubility, partition coefficients and swelling powers, but also through possible change in the state of the polymer migrant as well as the solvents. However, it is observed from the intrinsic diffusion data(Table 3.1) that in the temperature range of migration data, the change in the diffusion rate is generally less than a factor of 1000.

Since the diffusion of an additive in the polyer matrix is an activated process, it can described in terms of a Arrhenius type equation.

$$D = D_0 \exp(-E_d/RT) \qquad 5.3$$

Where D_o is the free exponential factor and E_d is the activation energy. Plots of Log D versus 1/T obtained for additive UV-nC8 for the migration into water, ethanol, olive oil, glycerol trioleate and heptane are given Figure 5.8. Similar plots were also obtained for other stabilisers.

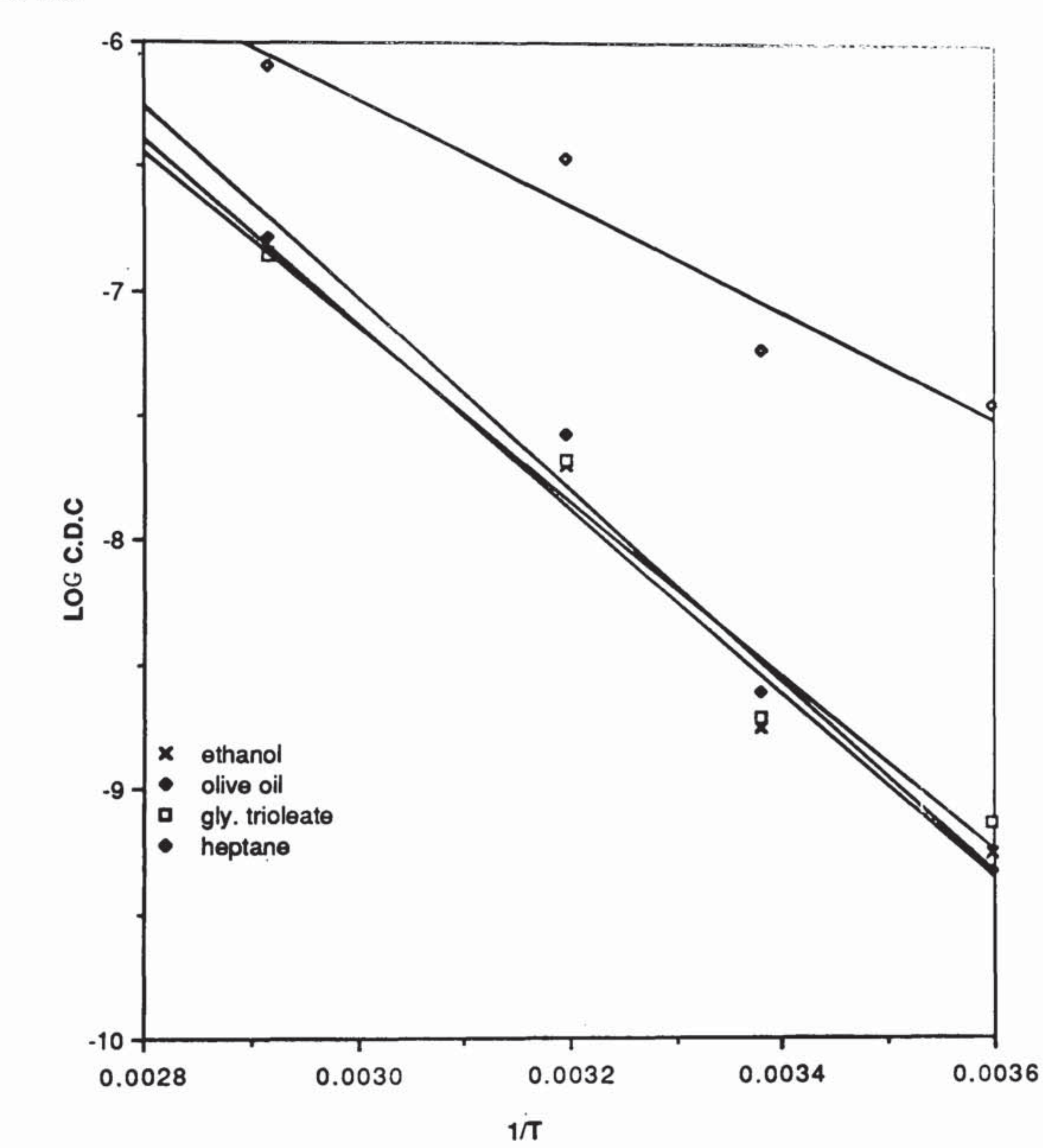


Figure 5.8 Arrhenius type plots of log C.D.C verses (1/T) for stabiliser UV-nC8.

Due to the limited temperature data obtained it is not clear whether the characteristic diffusion coefficients behave in a true Arrhenius way. These plots suggest, that the increase in temperature results in increase in the rate of migration, but the extrapolation of high temperature data (above 40°C) to lower temperatures could lead to uncertainty. The activation energies from these plots were obtained by fitting a least square regression line to the evaluated characteristic diffusion coefficients points and these are given in Table 5.10. It is not advisable to draw any firm conclusions since these activations energy calculations are very sensitive to experimental errors and even a small experimental error can strongly influence activation energy values. Table 5.10 shows that generally activation energy values lie between 35 kJ/mol and 90 kJ/mol, and heptane has the lowest value while water has the highest value. This shows that the swelling action of a solvent can decrease the activation energy by a considerable amount than a non swelling solvent. The activation energy obtained for ethanol is slightly lower than that of olive oil suggests that this could be due the change of the state of the olive oil from liquid to solid at 5°C and this may be reflected in the value of the activation energy.

	ACTIVATION ENERGY (kj|mol)				
stabiliser	water	ethanol	olive oil	gly. triole.	heptane
UV-OH	80.41	71.07	75.74	68.90	42.69
UV-nC8	-	70.35	73.19	66.69	40.17
UVS-H	86.93	77.34	80.23	75.21	52.52
UVS-nC8	-	68.59	75.86	70.98	36.57
UVS-nC18	-	66.33	72.00	64.92	39.13

Table 5.10 . Activation energies of stabilisers in various solvents and simulants.

5.3 Conclusions

1. The migration of an additive from a polymer to the surrounding media is primarily determined by the partition coefficient of the additive.

2. If the partition coefficient favours the solvent, i.e. if the additive is more soluble in the liquid than the polymer, the migration of additive into the solvent can be described as Fickian and the rate of migration entirely depends on the mobility of the migrant in the bulk polymer.

3. If the additive is not soluble in the liquid, then the rate of migration is determined by the rate of dissolution of the surface additive in the solvent.

4. Most solvents do penetrate into the polymer to varying degrees. This leads to modification of the mobility of the migrant in the polymer and the magnitude of its mobility depends on the swelling power of the contacting solvent.

5. For highly swollen solvent, the effect of migration at low temperatures is more pronounced than at higher temperatures.

6. The Arrhenius relationship for characteristic

diffusion coefficients may not be valid over wider temperature range.

7. The Activation energy of migration depends upon the swelling power of the solvent.

8. In some cases additives may be transformed to other product, if this happens the resulting mobility of the additive is completely different from that of the original compound.

9. Additives may be transformed as a result of the action of solvent, if this happens the rate of migration can exceed solubility limits.

CHAPTER SIX

VOLATILISATION LOSS OF ADDITIVES FROM LOW DENSITY POLYETHYLENE

CHAPTER SIX

VOLATILISATION LOSS OF ADDITIVES FROM LOW DENSITY POLYETHYLENE

The determination of the volatility of pure stabilisers and that from low density polyethylene films were attempted in the temperature region 50-100°C. In this chapter, the experimental procedures for the above evaluations will be discussed. The volatility rates will be discussed in terms of kinetic equations and the total loss mechanism will be treated using Billingham and co-workers[6] additive loss model.

6.1 Volatilisation Process

The volatility of additive is a manifestation of thermal motion of molecules on the surface of the sample. Therefore, it is related to the heat of evaporation or sublimation (ΔH) of stabilisers in terms of the Clausius-Clapeyron equation[26]:

$$d\ln p/dT = \Delta H/RT^2 \qquad 6.1$$

where p is the additive vapour pressure, T absolute temperature, and R is the gas constant. Since the vapour pressure of an additive is proportional to its rate of evaporation, the most experimental techniques for the determination of volatility of pure additive were based on the weight loss techniques[20,102-105]. The vapour pressure exerted by the additive in subsaturated solution in the polymer is proportional to its concentration, therefore the methods based on the volatility loss of additives from polymer samples were based on the measurement of concentration variations in polymer samples[19]. In the present study, similar approach to the above has been made. Volatilities of pure stabilisers were determined by the weight loss technique and the volatility of stabilisers from LDPE films were followed by the concentration variation of stabiliser in polymer film.

6.1.1 Experimental Procedures

6.1.2 Volatility of Pure Stabilisers

The determination of pure stabiliser volatility was carried out in a similar way that used by Scott and Plant [20]. The volatility cell is shown in Figure 6.1. 5g of recrystallised stabiliser was placed in a 20 ml low-form beaker of internal diameter 3.5 cm . The open surface area of antioxidant was therefore 9.6 cm^2. The total volume of the volatility cell was 678 cm^3.

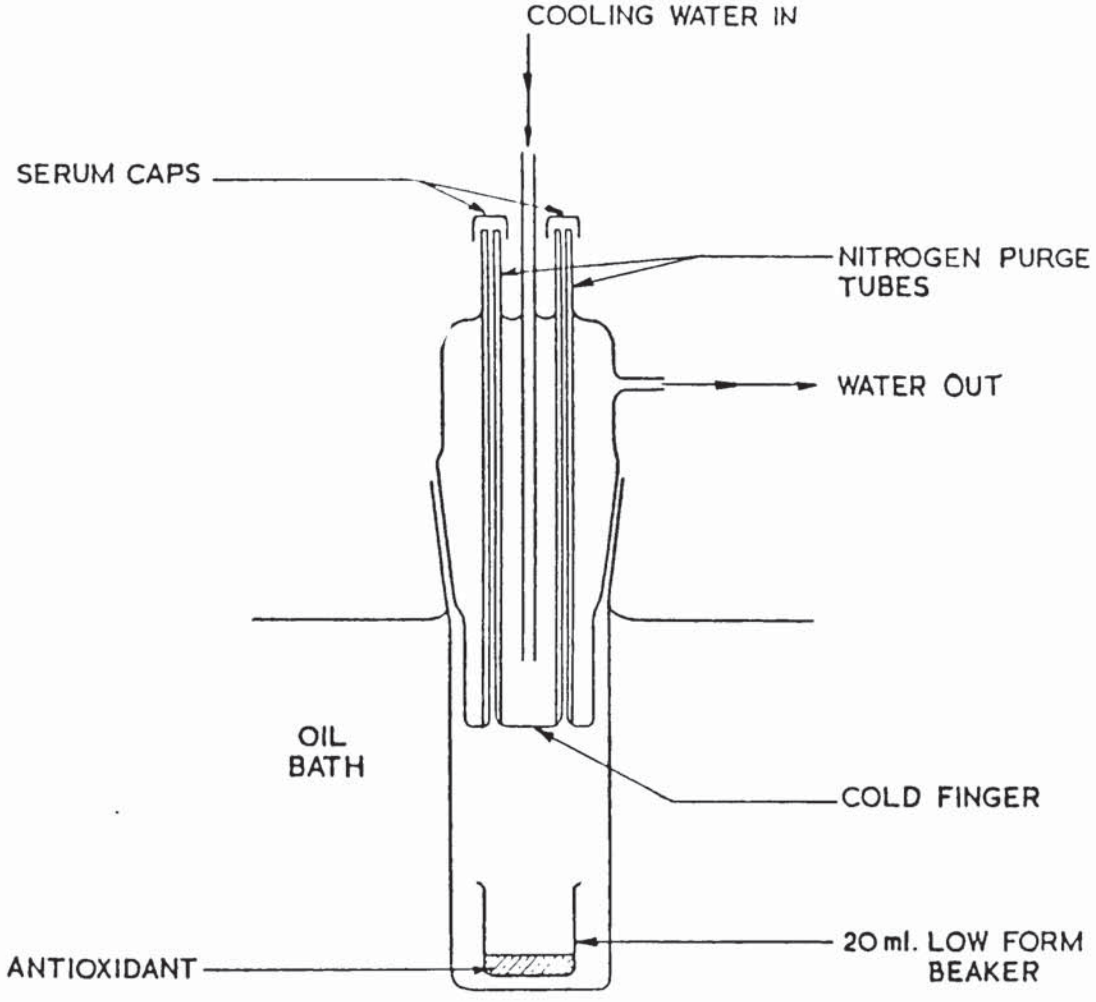


Figure 6.1. Apparatus for measurement of stabiliser volatility.

The beaker was placed in the chamber of the volatility cell, which was immersed in an oil bath at the required temperature. The top of the cell was closed by a cold finger through which cooling water (15°C-18°C) was passed. The cell was quickly purged with nitrogen through the capilary tubes in the cold finger and, after two minutes had elapsed for gas expansion, the purging tubes were sealed with serum caps.

The beaker was periodically weighed to determine the amount of antioxidant which had volatilised and condensed on the cold finger. The gas purging procedure was repeated and the cold finger was cleaned each time the beaker was replaced in the cell. The data obtained are the weight loss of the stabiliser with respect to time.

6.1.3 Determination of Volatility of Stabilisers from LDPE Films.

In order to use the same experimental condition as in the case of pure stabilisers, similar volatility cell was used for the determination of volatility of stabilisers from LDPE films. Films having stabiliser concentration 1000μg/cm^3(0.1%w/w) and having thickness of 0.025 cm were prepared according to the method given Chapter 2, and the test coupons of 3cm x 3cm were cut from these films. These films were equilibriated at 100°C under dry nitrogen for 15 minutes in order to have the same morphology. The surfaces of these test coupons were cleaned with cold ethanol in order to remove any contaminated traces of additives. Initial concentration of these coupons were evaluated by uv/vis spectroscopy by extracting a control test coupon into spectroscopic grade ethanol. For all other films net absorbances of the films were measured in the same region and recorded through uv spectroscopy. These test coupons were hung in the volatility cell as shown in Figure 6.2. A similar procedure to that for pure stabilisers were followed except, that the net absorbance of the uv/vis spectra of the film in the 250-350nm were recorded frequently. Subsequently, the net absorbances were used to evaluate the concentration of the films as shown in Section 2.5.1. The initial data obtained are the concentration changes of the stabiliser in the film with respect to volatilisation time.

Three experiments were performed for each stabiliser for the same temperature to assess the reproducibility of results. The temperature of study in the range between 50-100°C. Due to lack of time only four stabilisers were used to evaluate their volatilisation losses.

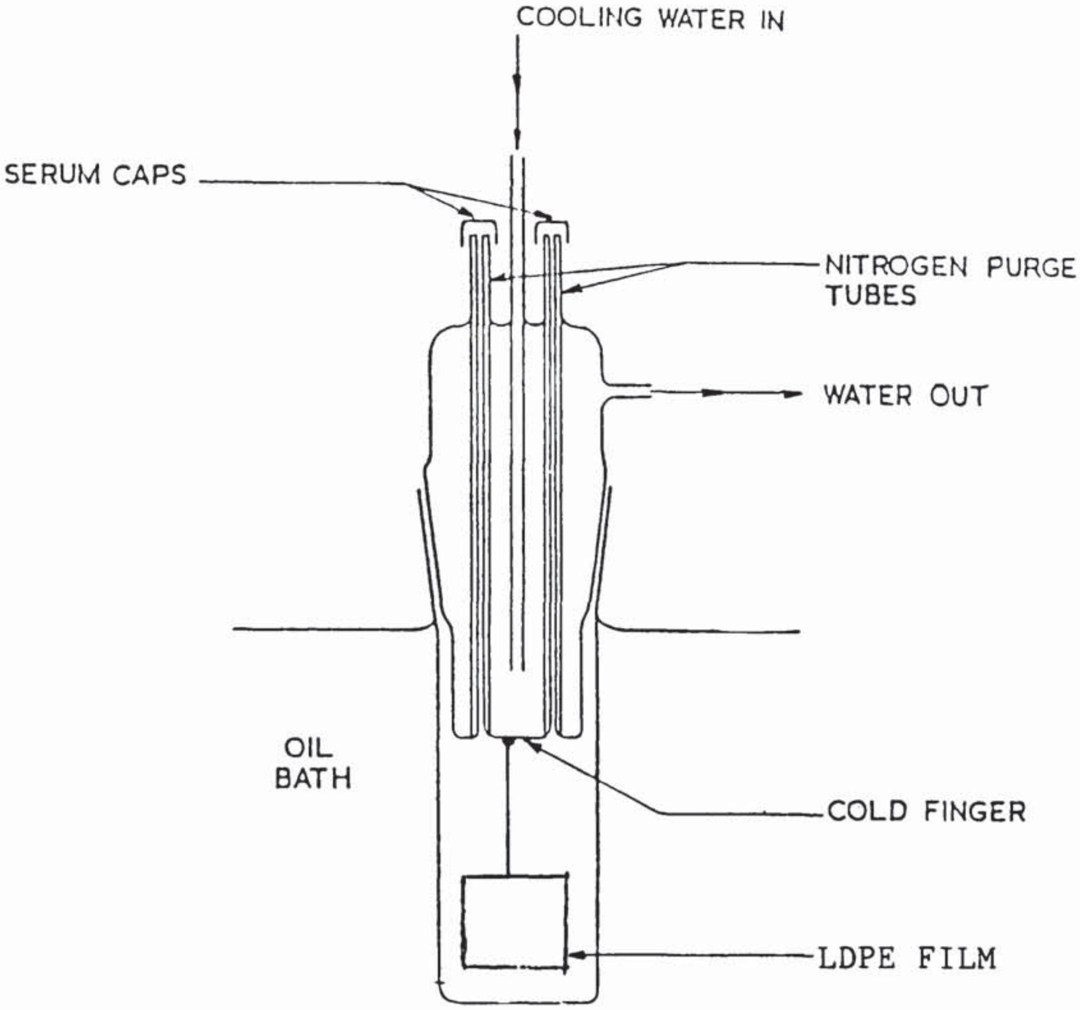


Figure 6.2. Apparatus for measurement of stabiliser loss from low density polyethylene films.

6.2 Results and Discussion

6.2.1 Volatility of Pure Stabilisers

The volatility of pure additives (Table 6.1) were evaluated in the temperature range 50° - 100°C. The results obtained for weight lost against time were not reproducible and it has been observed that the experimental error was more than 200% in some cases. This is in contrary to the observation made by Scott and Plant[20], who showed that their results obtained were highly reproducible. Perhaps this may be due to the high temperatures used in their study (>100°C) and the additives they used were at these temperatures mainly liquids. Except for UV-nc8, all the stabilisers showed an initial increase of the weight rather than decrease. It was thought that this may be due to the water absorption from air to the stabilisers. Therefore, further investigation was carried out using anhydrous calcium chloride as a water absorbing agent at the bottom of the volatility cell. These results did not show any weight increases, this shows that the reason for the weight increase was the water absorption not the oxidation of the sample. Although, this problem was overcome, the results were still not reproducible, especially for the solid additives. All these additives were well dried in an vacuum oven at 40°C over calcium chloride prior to the experimental procedure and these

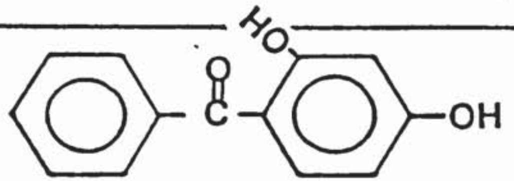
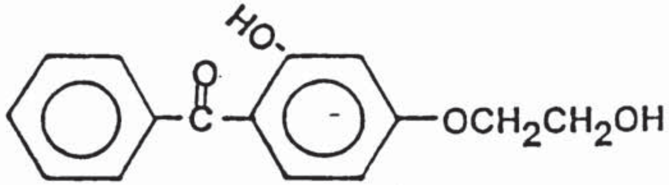
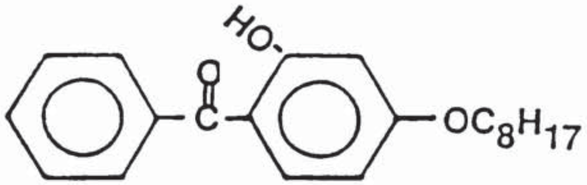
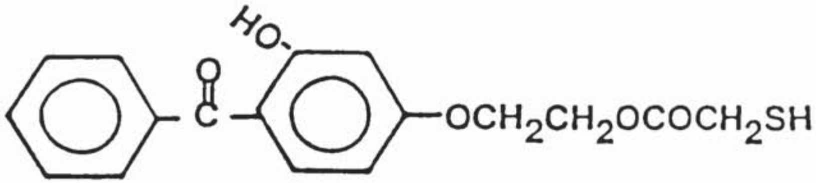
stabiliser	code name	mol.wt
	UV-OH	214.22
	UV-C2OH	258.27
	UV-nC8	326.25
	UVS-H	332.37

Table 6.1 List of stabilisers together with their code names.

errors cannot be due to the evaporation of the water from the additive.

In their study, Scott and Plant[20], used temperatures above 100°C and the additives used were liquids, so that the water absorption and producing a uniform surface of the additive did not present with a problem. Since the volatility of an additive depends on the surface area of the sample, this variability of the results may be due to the variation of the sample surface. Therefore in order to obtain a uniform sample surface, these additives were melted under a dry nitrogen atmosphere and left to cool to room temperature. It was observed that the sample after solidification was a hard amorphous solid and the surface was not uniform. The results obtained in this way were not reproducible as the earlier results. Because of these difficulties, these experiments have to be terminated and due to lack of time any other experimental procedures could not be pursued.

6.2.2. Volatilisation Loss of Additives from Polymer Films

The evaluation of volatilisation loss of stabilisers from polymer films did not present the above problem. The stabilisers listed in Table 6.1 were used to investigate the volatility of additives from LDPE at temperature range 50-100°C. During the test period, oxidation of the films was not observed up to 500 hours at 100°C and this been confirmed by infra-red spectroscopy, where no oxidation species in the films were found. After 500 hrs at 100°C oxidation species began to appear in test coupons and these species interfered with the stabiliser absorbance in the uv/vis spectra. Therefore, after this period additives were extracted from the polymer film into spectroscopic grade ethanol and the extractants were subject to uv-spectroscopy analysis.

The initial data obtained was the concentration changes of the polymer test coupon with respect to the volatilisation time. Three simultanious experiments were carried out for the same stabiliser and for the same temperature showed an experimental error of 20%. This could be due to the possible variation of the thickness and the initial concentration of the stabiliser in the sample. Since initial concentrations varied ±100μg/cm^3, data obtained were normalised to 1000μg/cm^3 by assuming that the volatilisation loss time is proportional to initial concentration.

Although, no definite theories have been proposed for volatilisation loss of additives from polymers, the kinetic curves expressing the volatilisation loss of additives has been shown to follow first-order kinetics[8,12,18, 102-104] according to equation 6.2.

$$C(t)/C_o = 1 - \exp(-kt) \qquad 6.2$$

or in logarithm form

$$-\ln (C_o - C(t))/C_o = kt \qquad 6.3$$

where C_o is the initial concentration of the additive in the polymer film, C(t) is the amount of additive left the polymer film at time t, and k is the rate constant. The plots obtained according to equation 6.3 can be seen in figures 6.3-6.6 for stabilisers UV-OH, UV-C2OH, UV-nC8 and UVS-H respectively. Except at the latter stage loss of UVS-H at 100°C, all others follow first-order kinetics. This behaviour also observed by other workers[8,12,18] but at rather high temperatures, and this observation shows that the first-order rate equation is also applicable to the temperature range of this study, despite the low vapour pressures of stabilisers like UV-nC8 and UVS-H.

Billingham and Calvert[6] pointed out that whatever the loss mechanism of additive from the polymer, the kinetic curves expressing the loss always follow the first-order rate equation. Our results show that this suggestion is valid for the stabilisers used in this study. This is an important observation, since the kinetic curves expressing the volatility of pure additives always follow zero order[20,26,109]. But this is not true even

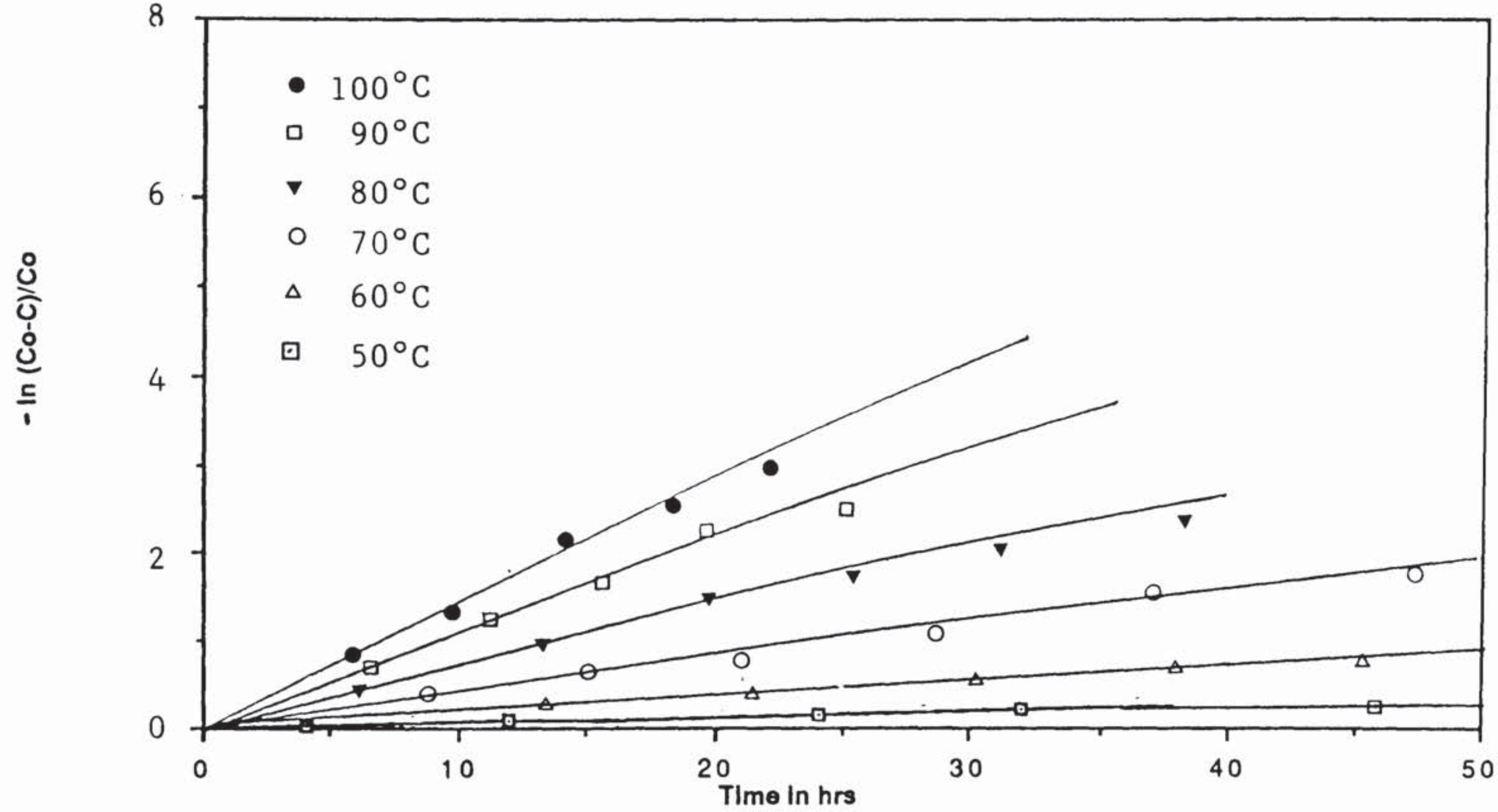


Figure 6.3 First order kinetic curves of volatilisation of UV-OH from LDPE films.

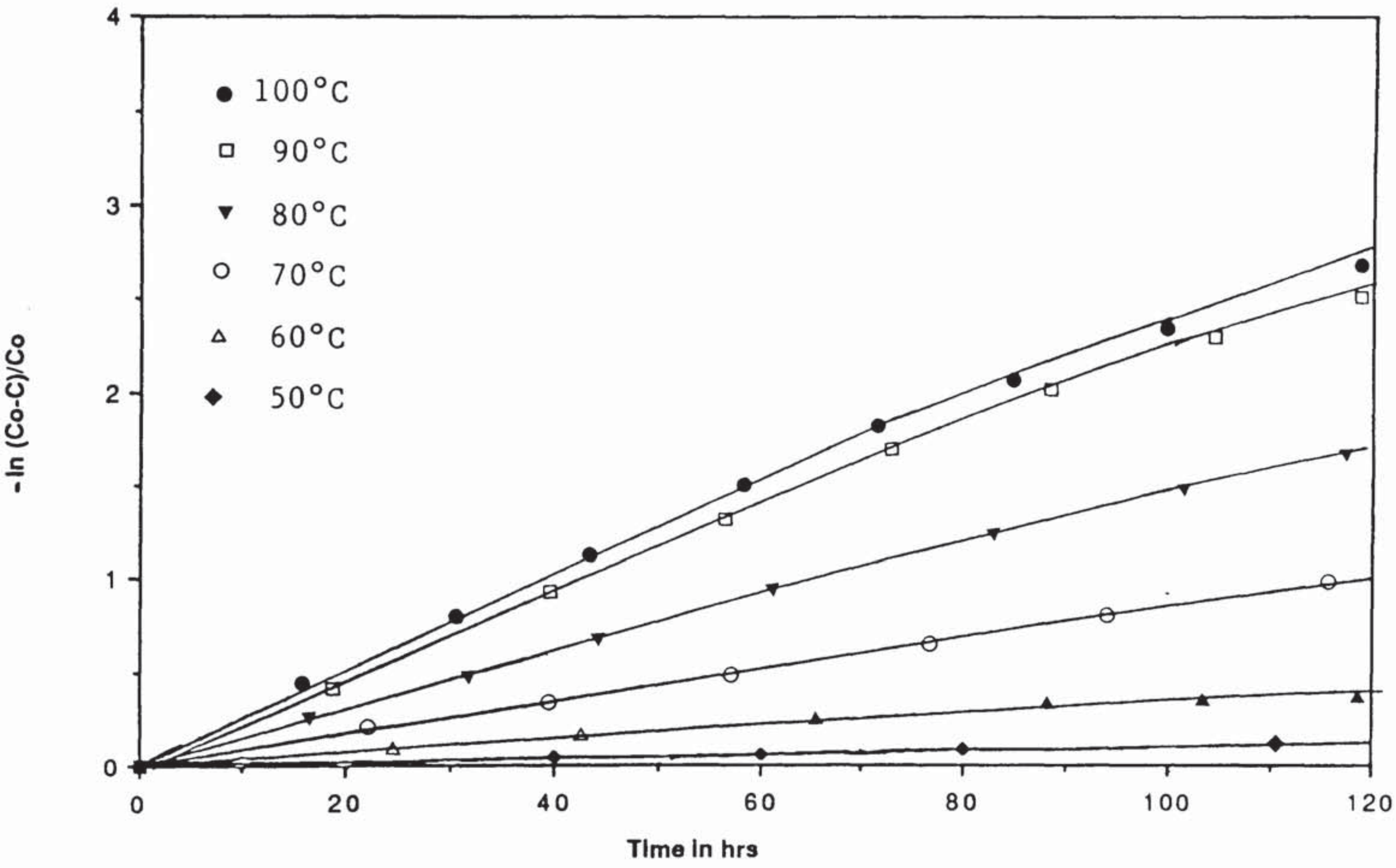
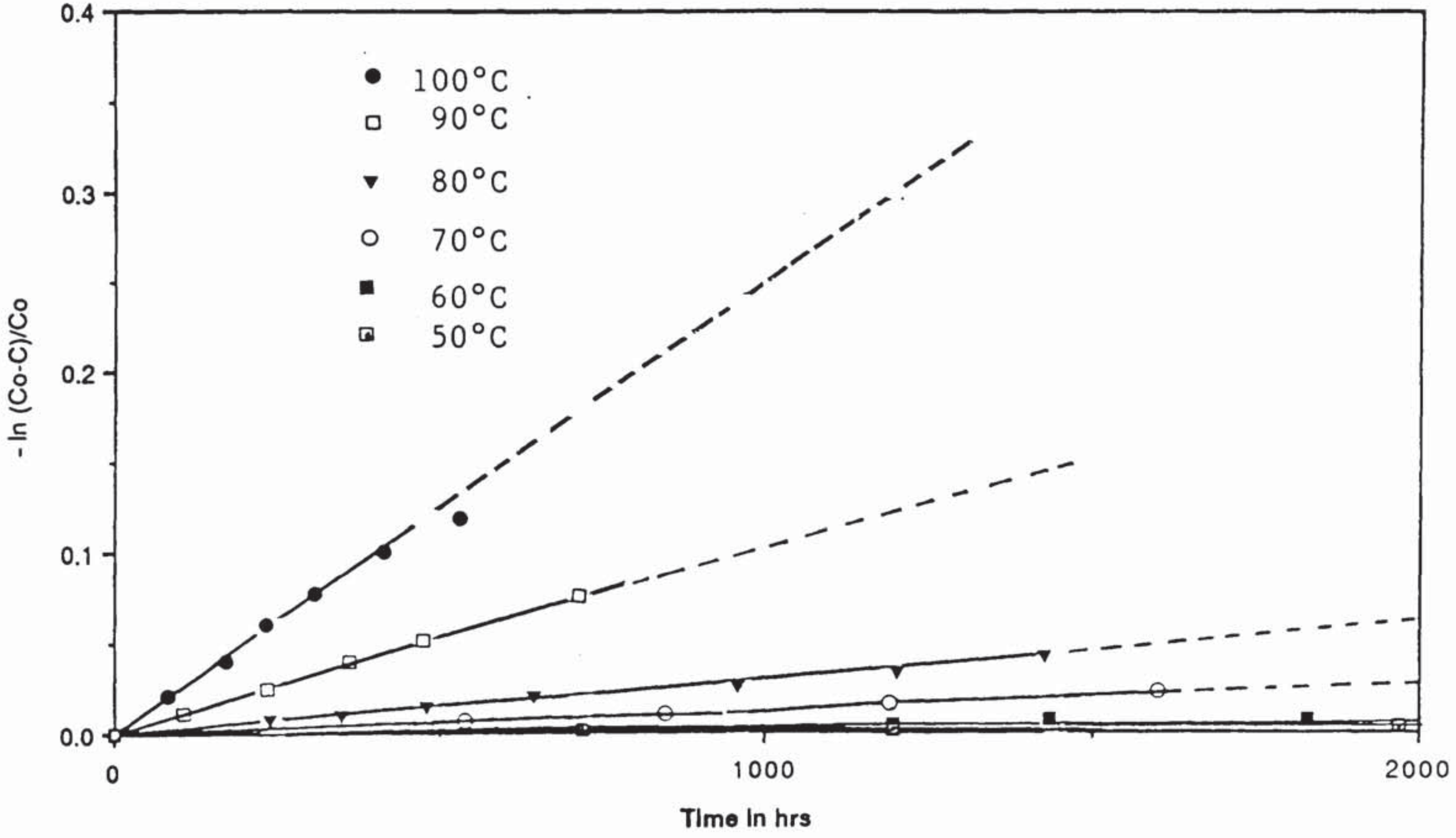


Figure 6.4 First-order kinetics curves of volatilisation of UV-C20H from LDPE films.



'Figure 6.5 . First-order kinetic curves of volatilisation of UV-nC8 from LDPE films.

---- extrapolated line

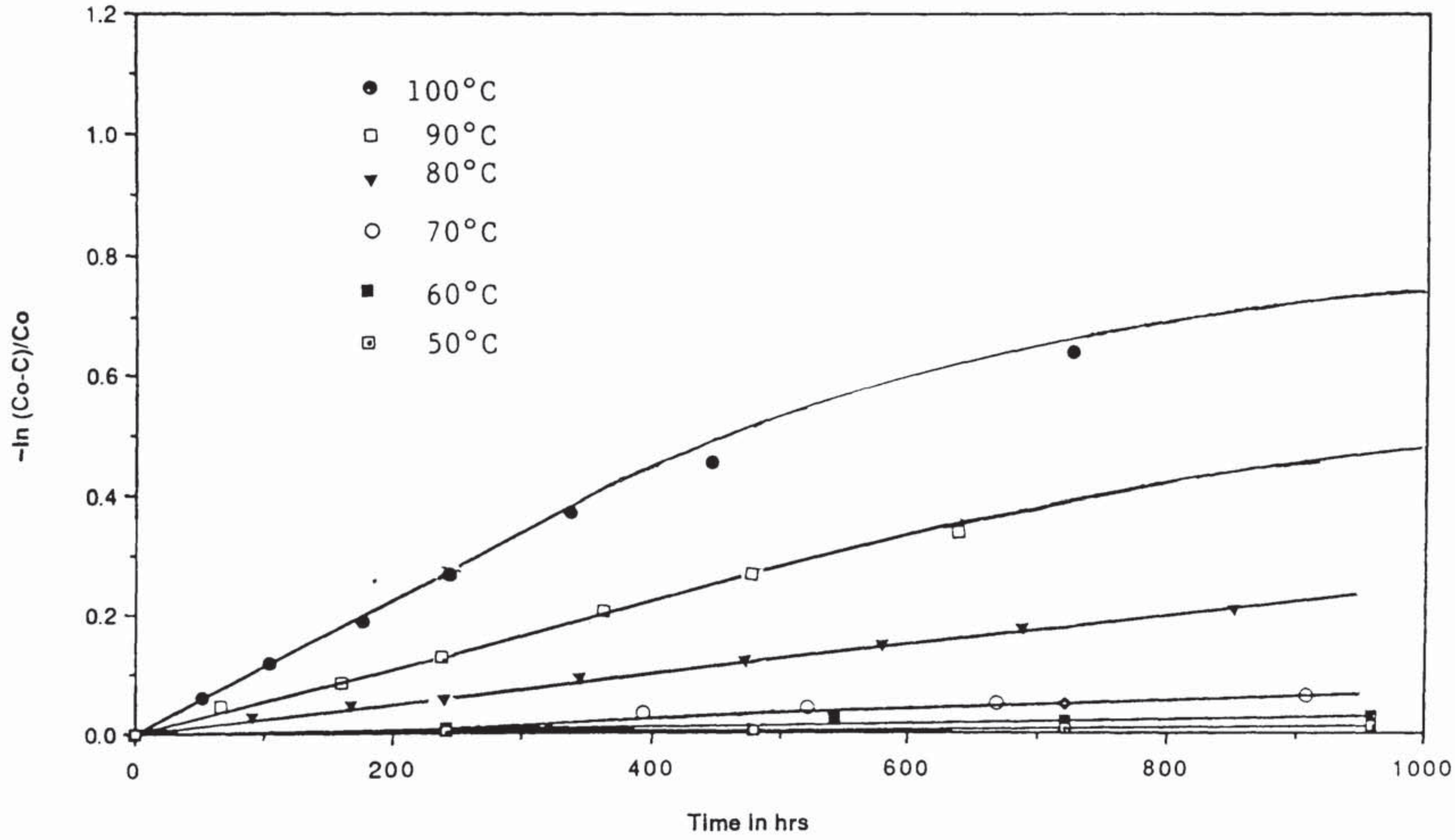


Figure 6.6.First-order kinetic curves of volatilisation of UVS-H from LDPE films.

when the additive is present in the polymer as a supersaturated solution, as for the case of UV-OH.

The rate constants obtain from these plots are given in Table 6.2. The rate constant obtained for UV-OH has the highest value and UV-nC8 has the lowest. It seems that the rate constant is dependent on not only on the volatility of pure additive but also in several other factors. This was thoroughly discussed by Billingham and Calvert[6] and shown that the volatility rate depends upon two factors. Initially it is determined by the rate of evaporation of the additive from the polymer surface which will create a concentration gradient near the surface. Subsequently additive lost from the surface must be replaced from the bulk so that both overall rate of volatility and the form of the concentration profile near the surface both depend upon the rate of mass transfer across the sample surface and the bulk diffusion rate. Therefore, the rate constant will be a function of the bulk diffusion coefficients and the mass transfer parameter across the surface of the film. They correlated the latter with pure additive volatility(V_o) and solubility(S) in the polymer in the form of a following equation:

$$V_p = V_o C_s / S = HC_s \qquad 6.4$$

Temp. °K	Rate constants (sec^{-1})			
	UV-OH	UV-C2OH	UV-nC8	UVS-H
323	1.95×10^{-6}	2.75×10^{-7}	3.81×10^{-10}	3.42×10^{-9}
333	5.25×10^{-6}	8.23×10^{-7}	9.86×10^{-10}	8.47×10^{-9}
343	1.25×10^{-5}	1.99×10^{-6}	3.74×10^{-9}	6.98×10^{-8}
353	2.21×10^{-5}	4.21×10^{-6}	8.41×10^{-9}	6.98×10^{-8}
363	3.24×10^{-5}	6.90×10^{-6}	2.95×10^{-8}	1.57×10^{-7}
373	4.21×10^{-5}	7.06×10^{-6}	7.06×10^{-8}	3.20×10^{-7}

Table 6.2 Rate constants of stabilisers

where C_s is the concentration of the additive in the polymer surface, V_p is the amount of additive evaporated from the polymer surface.

Although, most workers did not recognise the fact that equilibrium solubility plays an important role in volatilisation process, there are instances where the compatibility of an additive had been estimated from their volatility measurements[8,139]. Temchin et al.[8,102-104] correlated the compatibility(C) of an additive in the form of the following equation: ($C= V_o/V_p$). Furthermore, it is well established that the vapour pressure exerted by the additive above a saturated solution in the polymer is identical to that of pure additive. In contrast, additive present in a polymer as a subsaturated solution presents a different situation as discussed in Chapter 1 (section 1.4.2). The solubility and volatility of an additive seems to play an important role for the volatilisation loss of UV-OH, UV-C2OH and UV-nC8. These three have relatively similar intrinsic diffusion coefficients in the polymer but have different volatilities and solubilities in the pure polymer. The addition of octoxy or ethanol group to UV-OH reduces the volatility of the pure additive and importantly increases the solubility of the additive in the polymer. For example, ratio of solubility of UV-nC8 to UV-OH at 100°C is 6.6 (Table 4.1). Therefore, the net result of both these factors is to decrease the value of H in equation 6.4, (which is the ratio of volatility/ equilibrium solubility) which in turn reduces the rate of volatilisation loss.

Since the volatility of pure additives were not available from this study it is not clear which mechanism dominates the loss procedure. The smaller molecules such as UV-OH and UV-C2OH are relatively more volatile than high molecular weight UV-nC8 and UVS-SH, their high rate constants suggest that volatilisation is diffusion dominant. On the other hand, stabilisers like UV-nC8 and UVS-H have very low rate constants, and therefore it is expected that these losses may be dependent on the evaporation rate of the additive from the polymer surface.

The increase in molecular weight of the stabiliser seems to decrease the rate constants for compounds UV-OH, UV-C2OH and UV-nC8. However, different rate constants obtained for similar molecular weights compounds such as UV-nC8 and UVS-H suggests that rate constants also depends on the above mention parameters. The decrease in the rate constants for the volatility of 2-hydroxy-4-n-alkoxybenzophenones from polypropylene was demonstrated by Holcick at el.[19]. They observed that rate constants of the above series decreases with increasing molecular weight of the additive in a homologous in the form of a following equation[19]:

$$\text{Log } k = 0.59 - 0.021 \text{ M.} \qquad 6.5$$

Similarly, Durmis et al.[18] found that the decrease of the evaporation of 2-hydroxy-4-n-alkoxybenzophenones as the length of alkyl chain increases during storage of polypropylene sheets at 22-25°C. However, both workers did not discussed this decrease in terms of volatility, solubility or diffusivity. Therefore, it is not clear what mechanism dominates the loss procedure of either of these studies.

The rate of volatility of UVS-H changes after 80% of loss of additive from the polymer. As suggested in Chapter 5 (Section 5.2.3) it seems that the formation of disulphide during the processing may have caused this behaviour. Since the diffusion and volatility of this disulphide is low, the rate of volatilisation decreases to a very low value.

6.2.3 Temperature Dependence of Rate Constants

Since, rate of volatilisation loss of an additive from a polymer is a kinetic quantity, depends on the condition of the experiment, it is expected that temperature dependence of volatility to follow an Arrhenius type equation:

$$k = k_o \text{EXP}(-E_d/RT) \qquad 6.6$$

where E_d is the activation energy, T is the absolute temperature, R is the gas constant, k is the rate constant. This shows that the temperature dependence of the logarithm of the rate constant is proportional to the inverse of the absolute temperature. Such plots can be seen in Figure. 6.7, where log k is plotted against the inverse of absolute temperature. Though, UV-nC8 and UVS-H gave a linear relationship, the UV-OH and UV-C2OH show a decrease in activation energy as the temperature increases. Since similar behaviour was observed for the temperature dependence of intrinsic diffusion coefficient values in this temperature range, this is further evident that the volatility rate for these two stabilisers may be diffusion dominated while for other two, evaporation rate from the polymer surface may be the rate determining factor. The importance of this gradient is rarely discussed in literature. Schmitt and Hirt[26] showed that the temperature dependence of vapour pressure of pure stabilisers follows the Clausius-Clapeyron equation, with a break at the melting point of the additive. They calculated the latent heat of evaporation of the additive from the gradient above the melting point of the additive and latent heat of sublimation from the gradient below the melting point of the additive. It is not clear from our data or from literature data, that the rate constant would follow the same pattern as pure additive. This is because that most of the literature studies were carried out above the melting point of the polymer. The relevant

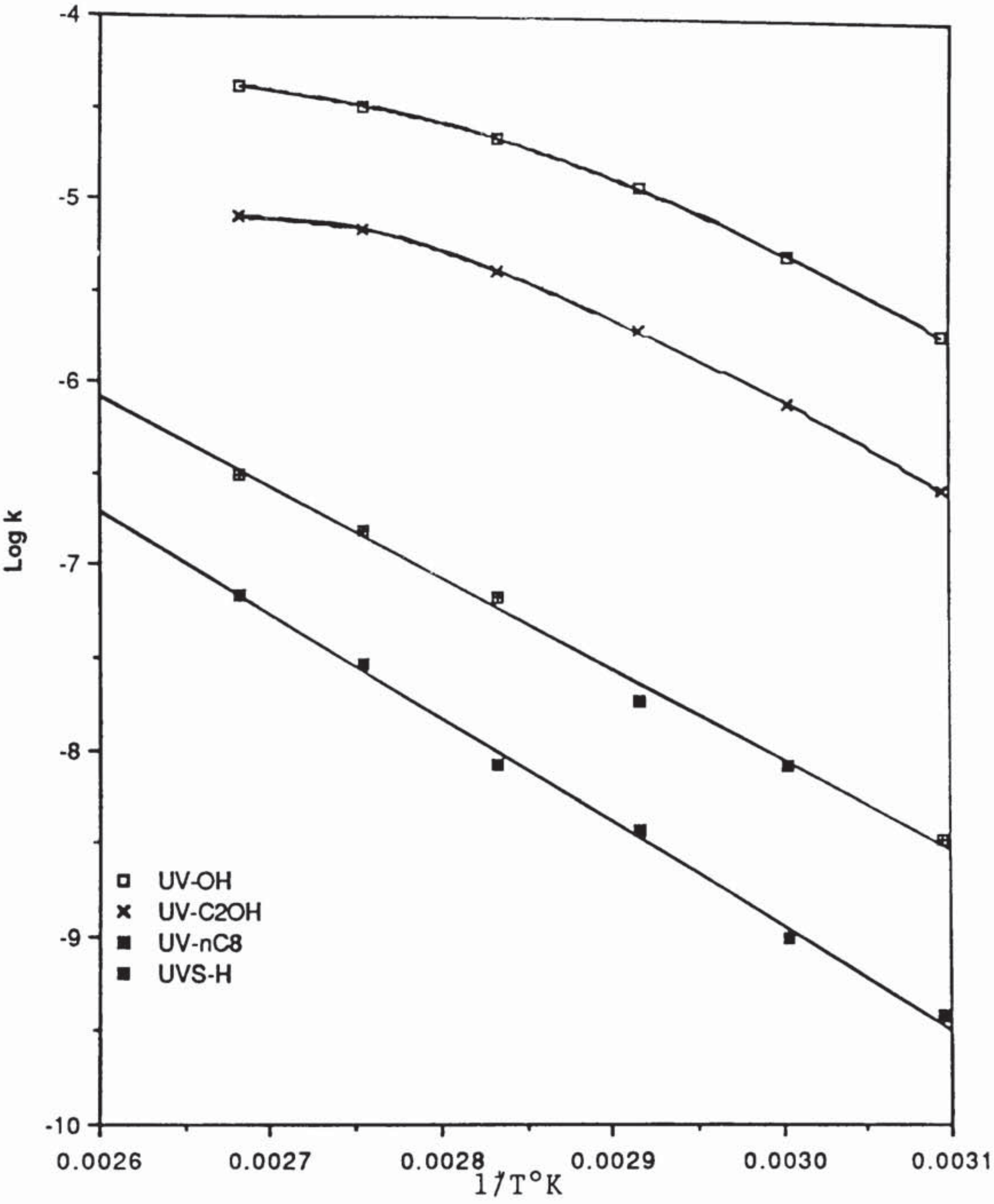


Figure 6.7 Arrhenius plots of Log rate constants verses (1/T) for stabilisers UV-OH, UV-C2OH, UV-nC8 and UVS-H.

activation energy data given in Table 6.3 were obtained by fitting a least square regression to the set of data points. It is apparent from this data that the evaporation controlled loss mechanism has a much higher activation energies than diffusion controlled volatility, and since these stabilisers have similar activation energy of diffusion, this suggests that the activation energy by the evaporation controlled volatility may also depends on the latent heat of sublimation or evaporation. The relevant data for the activation energy of diffusion and literature data available for latent heat of sublimation and evaporation data are given in Table 6.3. Unfortunately, the latent heat of sublimation and evaporation data for UV-nC8 and UVS-H were not available in the literature. Therefore, it is unclear which factors may influence the activation energies of these two substances.

	Activation energy (Kj/mol)			
	UV-OH	UV-C2OH	UV-nC8	UVS-H
activation en. of volatilisat.	61.88	69.56	106.22	93.36
literature data	*133.66^{a} *91.52^{b}	-	93.01^{c}	-
activation en. of diffusion	60.96	58.89	57.34	63.02
heat of subli.	133.76^{d}	-	-	-
heat of evapor.	86.94 ^{d}	-	-	-

Table 6.3. Activation energy together with literature data of heat of sublimation, and evaporation .

a. ref.102 , b. ref.18 , c. ref.103 , d. ref.26 . * = for pure compounds

6.3 Conclusions

1. The Weight loss technique may not be a reliable method of estimating the volatility of solid additives at low temperatures(below 100°C).

2. Loss of additives from a polymer film follows first order kinetics irrespective of the loss mechanism.

2. The rate constant seems to depend on three parameters, i.e, additive equilibrium solubility, additive volatility and diffusion coefficient.

3. The volatility of an additive from polymers may be completely different from that of pure additives, even if the additive presents as a super saturated solution.

4. If the volatility controlled by evaporation of the additive from the polymer sample, then the temperature dependence rate constant follow a Arrhenius relationship. On the otherhand if it is controlled by diffusion, the activation energies take lower values as the temperature increases. Therefore, the extrapolation of high temperature data to low temperatures may not be reliable.

CHAPTER SEVEN

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

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7.1 General Conclusions

The studies on a series of benzophenone type stabilisers on their migration rates from polymer have shown the complex nature of the loss of an additive from a polymer. However, a more systematic study of the factors that could be responsible for loss of an additive have revealed few important factors. The loss of an additive from a polymer to its contacting media is primarily depends on factors such as its intrinsic diffusion coefficient, additive volatility and partition coefficients. Furthermore, the swelling capabilities of the contacting media of the polymer will have a drastic effect on the rate of loss of an additive. The increase swelling action of solvents increases the rate of diffusion coefficients and it seems that this increase is a function of solvent absorb into the polymer. In some extreme cases(such as contact with heptane), the structure of an additive is insignificant when compared to swelling action of a solvent on its loss from a polymer. Moreover, evidence indicate that a design of an additive to minimise additive loss is a complicated process and it seems that this could be achieved only for a given set of conditions. Therefore, the bound additives into a polymer matrix may still remain as a possible approach to obtain non-migrating polymer additve system.

7.2 Suggestions for Future work

A retrospective view of present work reveals gaps which appear to justify further work. these include:

1. More structural variation on the hydroxybenzophenone, substitued polar, branched and aromatic rings could give some further insight of the loss mechanism.

2. It has been seen that temperature dependence of diffusion does not follow an Arrhenius type relationship over a wider temperature range. This is been thought to the variation of morphological properties of the polymer films used in this study. Therefore, further studies on this area will be beneficial.

3. In this study, it has been suggested that regular solution theory could be used to predict the additive solubility in polymers through their melting points and heats of fusions. Unfortunately, most of the additives used in this study were liquids and therefore, study of some additives in which melting points lie in this temperature region could give further details of the above observations.

4. Evidence were seen about the importance of the partition coefficients on migration of additives from polymers into solvents and food simulants. However, due to lack of time, the partition coefficients of these stabilisers in relevant solvents were could not be measured. Therefore, a detailed study of partition coefficients of these additives in solvents and simulants will be needed.

5. The migration studies were limited only to solvents and simulants. Therefore, it will be interesting to observe that how these stabilisers respond to actual food-stuffs. Though the analytical analysis would be difficult, it is important that possibilities of obtaining some data of this area will be examined.

6. It has been observed that the transformation products formed during processing and subsequently in contact with solvents may have been responsible for indifferent migration pattern observed in some stabilisers. Therefore, further studies on the chemical analysis of such compound will be essential.

7. The volatility of pure compounds were could not be evaluated in this study due the complications observed in the experimental procedure used. A proper experimental procedure for the investigation of the pure additive volatility is needed.

8. In this study, volatility studies were limited to few stabilisers. A complete study of the rest of the series could be carried out.

9. A mathematical model has been suggested[6] for the loss of an additive from polymers. In this study, data for the additive solubility, diffusion coefficients and loss into solvents and into air have been obtained. Therefore, further data on pure additive volatility and solubility on pure solvents will give results to testify the validity of such models.

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