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SORPTION, DIFFUSION AND ENERGETICS PROPERTIES OF POLYPROPYLENE SAMPLES IN AROMATIC SOLVENT

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ABSTRACT:

Data on swelling quotient have been used to investigate the sorption and diffusion properties of three aromatic solvents into pol propylene (PP) in the temperature range 28°C-60°C. The initial kinetic data, used to study the transport modes and the degree of PP-solvent interactions showed non-Fickian diffusion mechanism and low interactions respectively. The diffusion properties: diffusivity, solubility and permeability were found to be inversely dependent on the molar volume and enthalpic interaction constant χ_H but increased with increase in sorption temperature. The energetics of the systems studied exhibited negative values for entropy and enthalpy of sorption for all three solvents, but only in the case of PP-benzene system was the free energy very small and negative too.

Keywords: Sorption, permeability, selectivity, interaction, energetics.

INTRODUCTION

The examination of sorption and diffusion properties of small organic molecules in polymeric membranes has been the object of numerous works (Liao et all 1997, Michaels et al 1969, Unnikrishman 1997). It is week-known that the permeation process consists of three consecutive stages: sorption of the penetrant molecule on one surface of the membrane, activated transport of penetrant through the membrane, and desorption from the surface of the membrane. The diffusion properties of liquids have been related to the extent of polymer-penetrant interactions. Such interactions as hydrogen bonding, polarity, solubility parameter δ_s solubility parameter difference (Michaels et al 1969) have been employed to explain the differences in the rates of diffusion. It was found out that preferential permeation was achieved when the polarities of solvent and polymer match, such that polar solvents have the tendency to permeate polar membrane more readily than non-polar solvents and vice versa. In addition, Huang and Lin reported in Michaels et al (1969) that when the solubility parameters of the polymer membrane and solvent are close together, greater sorption and faster permeation of solvent are expected than with solvents whose solubility parameters are quite different from that of the polymer. Michaels et al (1969). reported that liquid flux rates through polypropylene films are enhanced when the absolute difference between the solubility parameters of the polymer and solvent is reduced.

Haung et al reported in Michaels et al (1969) found that molecular size and shape affected the permeation through polyethylene film, and through cellophane and polyvinyl alcohol membranes, as the permeation rate for molecules of similar shape and chemical nature exhibited faster permeation rates with decreasing length of penetrant molecule. On the other hand, Michaels et al (1969), found that for liquids of similar solubility parameters, the permeation rate increased with decrease in the apparent cross-sectional area. Unnikrishnan and Thomas (1997). found that the diffusion coefficient, enthalpy and entropy of sorption and activation energy of sorption increased with increase in the molar volume/molar mass and interaction parameter χ_H, for cross-linked rubber, whereas Liao et al (1997), found that the diffusivity solubility and permeability in urethane-modified Bismaleimides elastomer increased with decrease in the molar volume, molar mass, but increased with decrease in interaction parameter.

Attention has also been focused on -pre-treatment of membranes before sorption experiments. Paul and Ebra-Lima reported in Michaels et al (1969), showed that flux rate was not a perfectly linear function of the driving pressure for a pressure induced diffusion of organic liquids into highly swollen rubbery-membrane. Michaels et al (1969), reported that solvent annealing enhanced permeation rate as in the case of toluene through PP film annealed in p-xylene at 100°C which was increased by 4x compared to untreated film while iso-octane flux was enhanced by 15x. A similar finding was reported for diffusion, but the selectivity of a pair of liquids was found to be reduced. The significance of such studies is in the separation of organic molecule mixtures, concentration of proteins, treatment of effluent waters and demineralization of sea water.

In the present study, we report the results of sorption/diffusion studies of three aromatic solvents of approximately zero polarity into PP films. Other properties selected for study are the molar volume and, enthalpic interaction constant χ_H, so as to gain more insight into how these properties affect the diffusion properties. The enthalpic interaction constant χ_H, was calculated from the Flory-Huggins theory by equation(1)

$$\chi_H = V_s(\delta_s - \delta_B)^2/RT \qquad (1)$$

where δ is solubility parameter, V is molar volume, R and T are gas constant and absolute temperature respectively. S and B are for solvent and polymer respectively.

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TABLE 1,

The density ρ_s boiling point B.P., molar volume V_s the solubility parameter δ_s, and enthalpic interaction parameter at 25°C.

Solvent	δ_s (g cm^{-3})	B.P (°C)	V_s (cm^{3}mol^{-1})	δ_s MPa$^{1/2}$	χ_H
Benzene	0.874	80.1	89.4	18.60	0.0014
Toluene	0.867	110.6	106.9	18.20	0.0154
Xylene[a]	0.860	144.4	123.6	18.00	0.0322

PP δ_B = 18.80MPa$^{1/2}$, V_B = 46.7 cm^{3}mol^{-1} [a] Data for xylene are the mean of the three components.

TABLE 2:

Comparison of Diffusivity D, Solubility S, Permeability P., n and K of Equation (5) at Different Sorption Temperatures (°C).

Solvent	Dx10^{-8} (cm s^{-1})	S (cm^{3}g^{-1})	Px10^{-6} cm^{4}g^{-1}s^{-1}	n	K
	28°C 12.2	35.3	4.31	0.75	0.050
Benzene	40°C 13.7	40.2	5.51	0.72	0.055
	60°C 17.8	46.2	8.22	0.62	0.072
	28°C 6.1	33.1	2.02	1.10	0.013
Toluene	40°C 9.2	35.1	3.23	0.76	0.050
	60°C 24.5	37.2	9.11	0.70	0.068
	28°C 7.8	36.0	2.81	1.14	0.006
Xylene	40°C 8.5	42.1	3.58	0.92	0.025
	60°C 9.1	46.1	4.20	0.83	0.035

TABLE 3

: Selectivity Pi/Pj of PP film at different temperatures.

Permeants	Temperature °C 28	40	60
Benz/Tol.	2.1	1.7	0.9
Tol./Xyl.	0.7	0.9	2.2
Benz./Xyl.	1.5	1.5	2.0

Benz = benzene, Tol, = toluene, Xyl. = Xylene.

TABLE 4:

Comparison of the Activation Energies of Diffusion E_D: of Solubility E_s, or Permeability E_p, Entropy ΔS, Enthalpy ΔH, and free Energy ΔG of sorption into Polypropylene films

Solvent	E_D(kJmol^{-1})	Es(kJmol^{-1})	E_p(kJmol^{-1})	ΔS(Jmol^{-1}K^{-1}	ΔH(kJmol^{-1})	ΔG(kJmol^{-1}
Benzene	+4.16	+ 2.97	+ 7.17	- 23.9	+7.66	+14.86
Toluene	+15.31	+ 5.46	+17.20	-36.4	+2.99	+13.95
Xylene	+ 1.94	+ 2.49	+4.30	-27.8	+ 6.38	+14.75

2.0 EXPERIMENTAL

2.1 MATERIALS

The polypropylene (PP) films used for the investigation was a homopolymer sample M_w 3.2 x 10^5, density 0.90gcm^{-3} percent crystallinity 45%, supplied by Bag Manufacturing Company Limited, BAGCO, Lagos, Nigeria. The solvents used were BDH reagent grade and were used without further purification. The physical properties of these solvents are listed in Table 1.

2.2 METHOD

2.2.1 Sorption/Weight Gain

Samples of PP film (0.1g) were weighed out via digital Mettler balance AT 400 with precision =± 0.1mg. The weighed sample was put into a sample bottle and enough solvent (about 20cm^3) was added into the bottle just to cover the film, and then the bottle stoppered. The stoppered bottle was then immersed into a thermostated water bath at 28°C for different time intervals ranging from 2 to 240 mins or until maximum absorption of solvent had occurred. Fresh samples of PP sample were used for each sorption experiment.

After the swelling time, the films were brought out from the sample bottle and wiped between filter papers and weighed again to obtain the weight of the swollen sample. The sorption was carried out in different solvents and at other temperatures: 40°C and 60°C. The sorption/swelling data were obtained from the expression (Liao et al 1997)

$$Q_t = \frac{M_t - M_o}{M_o} \times \frac{1}{\rho_s} \times 100 \qquad (2)$$

where Q_t is swelling quotient at time t, M_o and M_t are initial and swollen mass of film, and ρ_s is the density of the swelling solvent.

The data for the slopes of plots of percent swelling quotient Q_t against square root of time of swelling for polypropylene in solvents at different temperatures (Figure 1) the polymer-solvent interaction term K and the mode of solvent transport into the PP, n, (figure 3) were determined by least squares regression analysis.

3.0 RESULTS AND DISCUSSION

3.1 SOLVENT SORPTION

The percent swelling quotient at time, t:

Q_t and at infinity Q_{00} of solvents in polypropylene films provided the data for the solvent sorption. The data are plotted in figures 1 and 2. In figure 1, plots of benzene at different temperatures, which is representative of plots of % Q_t against square root of time increase with increase in sorption time. In Figure 2, at 28°C, it is evident that the slopes of the kinetic region is in the order benzene> toluene> xylene, in the order benzene toluene xylene, in qualitative agreement with the fact that permeation of polymer membrane by solvent is inversely proportional to molar volume and enthalpic interaction constant χ_H (Liao et al 1997).

3.2 TRANSPORT COEFFICIENTS

The transport coefficients usually studied are diffusivity, D; permeability P, and solubility S.

3.2.1 THE DIFFUSIVITY

The integral diffusivity D of molecules through polymer films in related to amount of the penetrant sorbed at time t, Q_t and at equilibrium Q_∞ by the differential form of Fick's second law equation for the initial diffusion into films (eq (3), where h is film thickness,

$$Q_t / Q_\infty = 4(Dt/h^2\pi)^{1/2} \quad (3)$$

The integral diffusivity D is obtained from the relation (Crank 1975)

$$D = \frac{(h\theta)^2}{(4Q_\infty)} \quad (4)$$

where θ is the slope of the straight line plot of Q_t/Q_∞ against square root of time ($t^{1/2}$), h is the film thickness. The data on diffusivity of solvent molecules at different temperatures, are reported in Table 2. For a particular solvent, the diffusivity increases with increase in temperature, the increase being gentle for the benzene-sorbed, and xylene-sorbed PP, but rapid for the xylene-sorbed PP. A decrease in diffusivity from benzene through xylene agrees with an increase in the enthalpic interaction parameter χ_H and increase in molar volume of these solvents. These results support the theory of enhanced diffusivity with solvents whose solubility parameter match that of polymer (Michaels et al 1969) and the inverse dependence of diffusivity on molar volume of (Unnikrishnan et al 1997, Liao et al 1997) solvent respectively.

3.2.2. SOLUBILITY

The solubility S of solvent in the film was determined from the constant swelling quotient as the amount of solvent sorbed per gram of polymer. The solubility data are also listed in Table 2. In Table 2, it is clear that the decrease in solubility of solvent molecules in the case of benzene and toluene agree with an increase interaction parameter χ_H, and molar volume at any particular temperature as reported earlier (Unnikrishnan 1997), Liao et al 1997). For all the three solvents studied, the solubilities increase with increase in the temperature of sorption in qualitative agreement with the fact that higher temperatures will tend to loosen and make more flexible the polymer chains allowing more sorption to take place. But unexpectedly, the solubility of xylene at all the three temperatures matches that of benzene, and is therefore

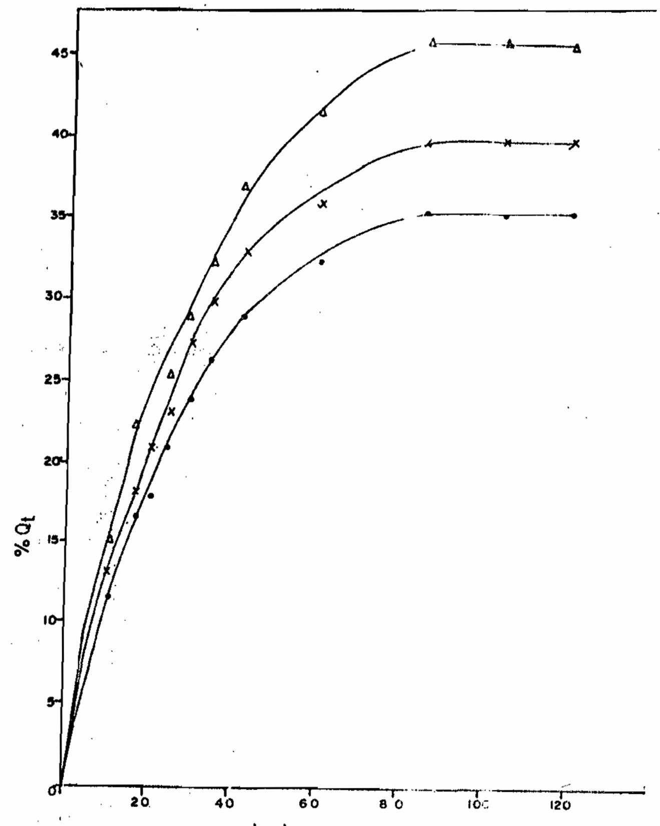

Figure 1: Percent Swelling Quotient Q_t against Square Root of Time $t^{1/2}$ for PP in Benzene at 28°C (•), 40°C (x), 60°C (Δ)

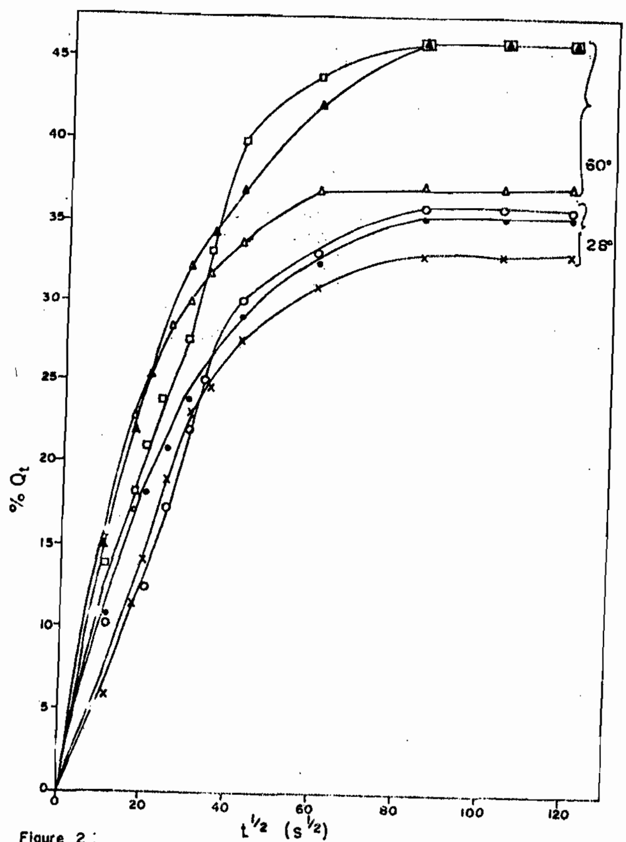

Figure 2: Percent Swelling Quotient Q_t against Square Root of Time $t^{1/2}$ for PP in Solvents at 28°C Benzene (•), Toluene (x), Xylene (o), 60°C Benzene (▲), Toluene (Δ), Xylene (□)

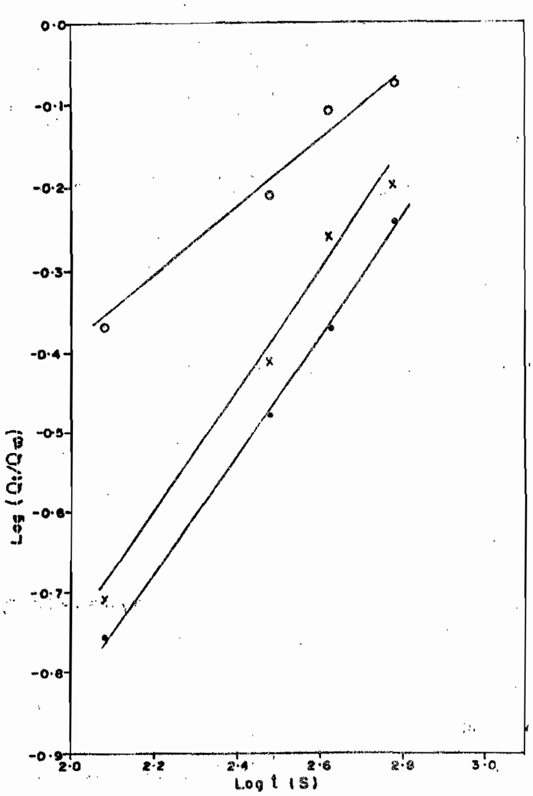

Figure 3: Log (Q_t/Q_∞) against Log t for PP in Toluene at 28°C (•), 40°C (x), 60°C (o)

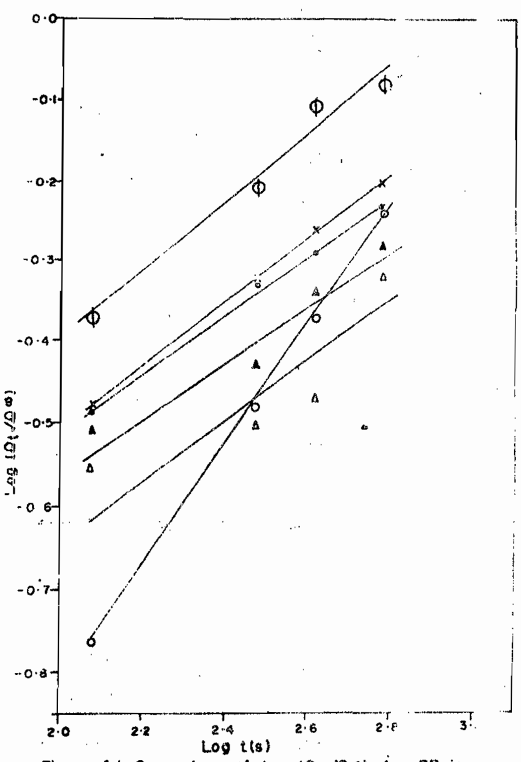

Figure 4: Comparison of Log (Q_t/Q_∞) for PP in Solvents at Different Temperatures
28°C Benzene (•), Toluene (o), Xylene (▲)
60°C Benzene (x), Toluene (Φ), Xylene (△)

unexpectedly larger than that of toluene. This may be associated with the composite nature of the xylene solvent, in which case some components are sorbed more than others. The inability of enthalpic interaction constant χ_H, to explain the solubility may be associated with suggestion of Huyskens and Siegel (1988) that other factors of solvents, eg the exchange entropy correction term B, also play some significant role.

3.2.3. PERMEABILITY

The permeability P of organic molecules in polymer membranes was calculated from the product of diffusivity and solubility (Unnikrishnan 1997, Liao et al 1997). The data on permeability of the three aromatic solvents reported in Table 2 suggest that permeability decreases with increase in the enthalpic interaction parameter χ_H and molar volume of solvent molecules, in the same way as the earlier diffusion characteristics discussed (Unnikrishnan et al 1997, Liao et al 1997). In addition, for a particular solvent, permeability is seen to increase with increase in the sorption temperature. One may also point out that the influence of the mixture in xylene solvent played up in raising the permeability to levels comparable (except at 60°C) to that of toluene. Judging from the values of molar volume and χ_H, these properties should even be smaller than that of toluene.

3.2.4 SELECTIVITY

The significance of selectivity in sorption studies is in the potential use of membrane in separation processes for solvent/vapour mixtures. The selectivity of a membrane to solvent molecules is defined by the permeability ratio p_i/p_j (Michaels et al 1969) where p_i and p_j are the permeabilities of solvents i and j respectively. The data on selectivity at the different temperatures are listed in Table 3. It is evident in this table, that the variation of permselectivity with temperature depends on the solvent pair, and the sorption temperature. The selectivity of benzene to toluene decreases with increase in temperature, the value at 27°C (2.1) being about double the value at 60°C(0.9). On the other hand, the selectivity of toluene relative to xylene, and benzene relative to xylene increase with increase in temperature of sorption, and are shown to be same at 60°C. The low selectivity of PP to solvent molecules may be attributed to the stiffness of the polymer chains due to the pendant methyl groups, and such stiffness is expected to decrease with increase temperature as shown by toluene/xylene and benzene/xylene pairs.

It is to be noted that the selectivity data in Table 3 have been obtained from independent diffusivities of solvent molecules which give approximate separation capacity of the film which may differ from the actual selectivity of the components from their mixture (Michaels et al (1969).

3.3 MODE OF TRANSPORT

The percent swelling quotient data obtained in section 3.1 have been fitted in the expression (Unnikrishnan et al 1997, Liao et al 1997)

$$\text{Log}\,(Q_t/Q_\infty) = \text{Log}\,K + n\log t \qquad (5)$$

where Q_t and Q_∞ are the percent swelling quotient at time t and at infinity (equilibrium sorption), k and n are

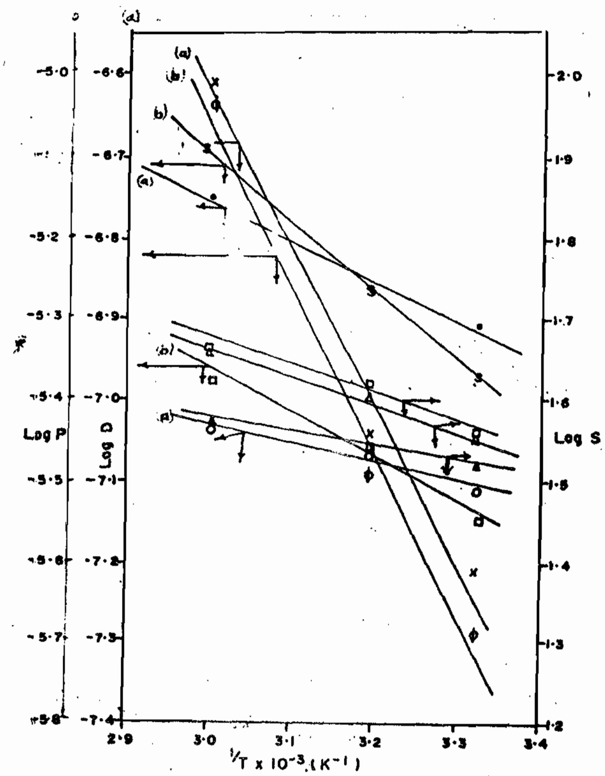

Figure 5: Arrhenius Plots of Log D against 1/T for PP in Solvents; Benzene (•), Toluene (X) Xylene (o); Log S, Toluene (▲), Benzene (Δ), Xylene (□), Log P Benzene (s) To..ne (ϕ) Xylene (▫)

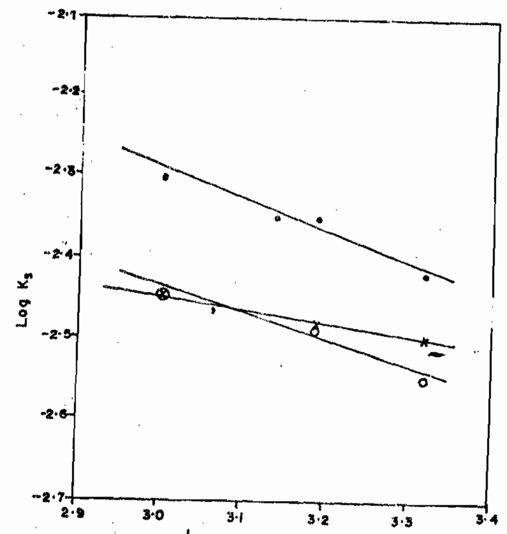

Figure 6: Van't Hoff Plots of Log K_s against 1/T for PP in Solvents; Benzene (•) Toluene (x), Xylene (o)

constants that determine the structural characteristics of film and polymer-solvent interaction, and the mechanism of solvent molecule transport into membranes respectively. The plot of log (Q_t/Q_∞) against log t for toluene given in Figure 3 is representative of such plots. Again Figure 4 compares log (Q_t/Q_∞) against log t at 28°C for the three solvents used for the study. The values of K and n obtained by least square regression analysis are listed in Table 2. The values of K at any particular temperature generally decrease with increase in the enthalpic enteraction parameter, boiling point and molar volume of solvents from benzene through toluene to xylene. The magnitude of n, it has been stated denotes the mechanism of transport. For Fickian diffusion mode n=o.5, but has value n=0.5 to 1.0 for the relaxation-controlled mode, and described as anomalous; while when n>1.0, it is described as the super relaxation controlled type. In Table 2, it is evident that magnitude of n varied from 0.62 in benzene at 60°C to as high as 1.14 in xylene at 28°C, suggesting that the diffusion process is non-Fickian and therefore, anomalous. One notes in addition that n values decrease with increase in temperature for a particular solvent and that only in benzene is there a tendency towards Fickian diffusion at 60°C.

3.4 ENERGETICS

To investigate the energetics of the sorption and diffusion, the solvent-uptake was performed at 28°C, 40°C and 60 c. It had been shown earlier in Figure 1 and 2, that temperature affects the rate of diffusion. The terms of energetics studied are activation energy, entropy, enthalpy and free energy of sorption and diffusion.

To obtain the activation energy for sorption, the values of diffusivity D at different temperatures were fitted into the Arrhenius type expression of the form.

$$\text{Log } D = \log D_o - E_D/RT \qquad (6)$$

where E_D represents the activation energy of diffusion, R the gas constant and T is the absolute temperature. Similarly, the activation energies of solubility E_s and permeability E_p can be obtained.Arrhenius plots of logD against 1/T(K), log S against 1/T(K) and log P versus 1/T(K) for solvent sorption are given in Figure 5. The estimated values of E_D, E_S and E_p are presented in Table 4. In Table 4 it is evident that the activation energies of diffusion, solubility and permeability for PP-toluene system are highest of the three solvents, which indicates the higher temperature sensitivity of PP-toluene system as was exhibited by the diffusivity, solubility and permeability at 60 C (Table 2).

The equilibrium sorption constant K_s was defined by the member of moles of penetrant sorbed per unit mass of polymer (Unnikrishnan et al 1997).

$$K_S = \frac{\text{Number of moles of penetrant sorbed}}{\text{Unit mass of the polymer}} \qquad (7)$$

On application of Vant Hoff's expression to the system, the equilibrium sorption constant K_s is related to the entropy ΔS and enthalpy ΔH as in equation (8)

$$\text{Log } K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad (8)$$

R and T are gas constant and absolute temperature respectively. By plotting logK_s against 1/T(K), ΔS and ΔH can be obtained from the y-intercept and slope respectively (figure 6). The values of ΔS and ΔH are listed in Table 4. The values of ΔS and ΔH have been used in the calculation of free energy ΔG of sorption and the values of ΔG for the three solvents are also reported in Table 4. First, one notices that the ΔS values are negative in all cases, suggesting that the solvents are in the liquid state in the sorbed state. The ΔS values for benzene and xylene are comparable, but the decrease in ΔS values from benzene to toluene is in agreement with increases in enthalpic interaction constant χ_H, and molar volume of penetrant. The enthalpy of sorption, ΔH, is endothermic as expected, with the ΔH values increase in X_H and molar volume of solvent. Tht the free energy of sorption is positive suggests that PP may not dissolve in these solvents at 28°C.

In addition, a constant value of positive ΔGs independent of PP-solvent was recorded. On the contrary, the ΔG for toluene sorption is positive, suggesting the insolubility of PP in the solvent. The higher values, comparable to those in benzene with regard to ΔS, ΔH and ΔG may be closely related to composite nature of xylene solvent sample used for the study.

CONCLUSION

We have in the present investigation presented the results of sorption, diffusion and energetics properties of three aromatic solvents into PP. It has been shown that penetrant transport through PP films is dependent on the molar volume, enthalpic interaction parameter of the solvent, and the temperature of sorption. The diffusion characteristics; diffusivity, solubility and permeability, have been shown to exhibit inverse dependence on the molar volume and enthalpic interaction constant, but increase with increase in the sorption temperature. The selectivity of toluene/xylene and benzene/xylene pairs seemed to increase slightly with increase in temperature, whereas a decrease was found in the case of benzene/toluene pair. The low values of K constant correspond with low interaction between PP and the solvents used and the diffusion mechanism has been shown to be non-Fickian, ie anomalous. The energetics of the systems showed that the entropy and enthalpy of sorption were negative and positve respectively and the free energy of solution was generally positive and nearly constant for all polymer-solvent systems. The data for PP-xylene system seemed to be irregular and this has been explained by the composite nature of the liquid xylene used for the study.

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