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SWELLING EQUILIBRIUM AND SORPTION KINETICS OF POLYVINYL ACETATE FILM

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Abstract

The absorption and diffusion kinetics of solvent molecules into polyvinyl acetate film has been studied at different temperatures (13, 25 and 37°C). The maximum swelling quotient was found to be dependent on the solvent and the temperature of absorption. The initial slope method was utilized to determine the diffusion mode, which was found to deviate from Fick's law and hence described as anomalous. The gravimetric absorption, data were analysed based on Crank's model.

The early time sorption kinetic data were obtained to investigate the diffusion mechanism of the solvent in the PVA molecule. It was observed that the maximum swelling quotients for the solvents increase in the order, n-hexane < Carbontetrachloride <Water .The absorption and the diffusion characteristics of the solvents in the PVA film were evaluated and the variation properties discussed in terms of the nature of the solvent, temperature, interaction constants between the polymer chains and the molecular mass of the polymer. Our report shows that absorption of these solvents could not cause the dissolution of the PVA film at these temperatures.

Keywords: Solubility, permeability, swelling-equilibrium, absorption, polymer.

Introduction

Considerable interest has been focused on the absorption and diffusion of organic solvent because their ability to permeate at different rates enhances the separation of components of their liquid mixtures through polymeric membrane [1-5]. Polymers swell if they interact with the solvents at all, and the degree of this interaction is determined by the degree of crosslinking. The degree of the swelling can be measured and related to the thermodynamic properties of the system [6]. Many crystalline polymers, particularly the non-polar ones do not dissolve except at temperatures near their crystalline melting points because crystallinity decreases as the melting point is approached. The melting point itself is depressed by the presence of the solvent, hence solubility can often been achieved at temperatures significantly below the melting point and if the difference in the solubility parameter of the solvent and the polymer is less than 2.0. [6]. Consequently, this approach to polymer solubility pioneered by Burrel has been extensively employed particularly in the paint industry [8] and in the present study.

The purpose of this work is to study the swelling and sorption properties of polyvinyl acetate film. It is assumed that the change in total free energy is the direct sum of the elastic free energy and the free energy of mixing [8, 9 and 10].

The interaction parameter x of the polymer-solvent systems was determined by the solubility parameter theory [12] and the solubility of the polymers was obtained by Gee's theory [13] as well as group oontribution theory [14].

Furthermore, the diffusion kinetics were also studied at three different temperatures. Previous studies revealed that the transport of solvents through polymers is affected by polymer structure, cross linking density, mode of crosslinking, presence of fillers, penetrant size and temperature [2, 15, 16, 17].

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In the present study, we have tried to investigate the different transport behaviour of organic solvent molecules in polyvinylacetate film. The picture of the diffusion profile, the transport coefficients, which include solubility (S), diffusion coefficient (D), permeability (P) and the diffusion mechanism are investigated and discussed.

The motivation for this work is due to the important roles that PVA plays as films in good-surface coatings and adhesives.

Materials and Methods

The polyvinylacetate (PVA) from which the film was prepared was homopolymer sample obtained from Nycil Limited, Ota. Ogun-State, Nigeria. The PVA films 0.32 thickness used for this project was prepared in the chemistry laboratory, University of Agriculture, Abeokuta, Nigeria.The polyvinyl acetate film was prepared according to the method of Frye and Horst [25]. About 1.5g of the polymer was added to 50ml of warm (80°C) 1.2-dichloroethane. After complete dissolution, the solution was allowed to cool. A chemically cleaned glass tube of 5-6cm diameter was immersed directly into the warm polymer solution contained in the beaker and the solvent was allowed to evaporate for 48hours. After evaporation of the solvent the polymer film was separated from the end of the glass tube. The polymer film was dried in a desiccator.

The solubility parameter for PVA is (17-21.07), (MPa)½ and its melting point =35-50°C [18].

The solvents used in this swelling experiment were all BDH reagent grade and were used without further purification. The physical properties of PVA and the solvents used in this work are given in Table 1.

Table 1:The physical properties of polyvinyl acetate (PVA), n-hexane, carbon tetrachloride (CCl_4) and Water (H_2O) [18, 19]

Polymer/Solvent	Dipole Moment	Molar Volume ($cm^3 mol^{-1}$) at 25°C	Solubility Parameter	M.pt (°C)
PVA	$1.77\text{-}2.3X10^{-18}$	74.52	17.9-21.07	35-50°C
n-Hexane	0	131.6	14.8	
CCl_4	0	97.1	17.8	
H_2O	1.85	18.0	24.2	

The choice of solvents was limited due to the solubility of PVA and its reaction with mineral acids and alkali as well as with primary and secondary alcohols. There was no reaction with the solvents chosen.

Solvent Uptake Experiment

About 0.10g PVA film was weighed on a digital metler balance AT 400 with precision ± 0.0001g Micrometer (with up to 0.01 mm accuracy) was used to measure the thickness of the film. The weighed sample was put in a sample bottle and enough solvent was added into the bottle to cover the film and the bottle was stoppered. The stoppered bottle was immediately immersed in a water bath at 13°C for varying time interval, 5, 15, 30, 50 75, 105, 120, 140, 160, 180 minutes until maximum solvent uptake had been attained.

The swollen films were brought out from the sample bottle after the immersion period, the adhering solvent droplets wiped out within 30 seconds, with filter paper and then weighed again to obtain the weight of the swollen film. This experiment was carried out with fresh PVA samples at 13, 25 and 37°C in triplicates, to investigate the effect of temperature on swelling. The whole procedure was repeated with fresh PVA samples until the films had attained maximum swelling when weight gain become constant using carbon tetrachloride (CCl_4) and water. After equilibration, the swelling ratio (S.R.) of the polymer was calculated by assuming additivity of volume according to the method of Liao *et al* 1997 [3]:

$$S.R. = \frac{\dfrac{Wd}{\rho_{polymer}} + \dfrac{Ws - Wd}{\rho_{solvent}}}{\dfrac{Wd}{\rho_{polymer}}} \qquad (1)$$

where Wd and Ws are the weight of dry and swollen polymers respectively and ρ is density. Further treatment of equation (1) becomes

$$S.R.\left[1+\left(\frac{\Delta W}{Wd}\right)\left(\frac{\rho_B}{\rho_S}\right)\right] \qquad (2)$$

Where ΔW is the difference between dry mass Wd and masses of swollen polymer Ws. Equation (2) reduces to equation (3) for the percentage swelling quotient Qt [20]. Assuming ρ_B is constant: equation (2) becomes

$$Q\% = (\Delta W/Wd)(100/\rho_s) \qquad (3)$$

It is this swelling quotient that is used in this work. The solvent used for these sorption experiments were carefully chosen to cover a range of polarity; (0.0-1.85) for the Dipole Moment and solubility parameter in the range 14.8-24.2 (MPa)½.

Results and Discussion

The absorption and diffusion kinetics of solvent molecules (n-hexane, carbon tetrachloride (CCl_4) and water (1120) into PVA film has been studied at different temperatures. The solvent used in this study represents three solvent types, aliphatic hydrocarbon (n-hexane) Non-Polar Aprotic (CCl_4) and polar protic (1120). The solvents were chosen carefully, to cover a range of polarity 0.0 for n-Hexane to 0.0 for Cd_4 and 1.85 for H_2O (Dipole moments) and solubility parameter in the range 14.8 for n-hexane, 17.8 for Cd_4, and 24.2 for H_2O.

The result of the absorption experiments are expressed in percentage swelling quotient (Qt) according to equation (3). The values were plotted against the square root of the time of immersion of PVA in each solvent at different temperatures. Fig. 1, shows the plot of % Qt against $t^{½}$ in n-hexane at 13, 25 and 37°C. The same profile was obtained for water and CCl_4 at these temperatures. Equilibrium of absorption was attained faster at higher temperatures than at lower temperature.

The plots of percentage swelling quotient (% Qt) against the square root of time ($t^{½}$) in n-hexane, carbon tetrachloride and water at 25°C are in Fig. 2. This trend is observed at 13 and 37°C.

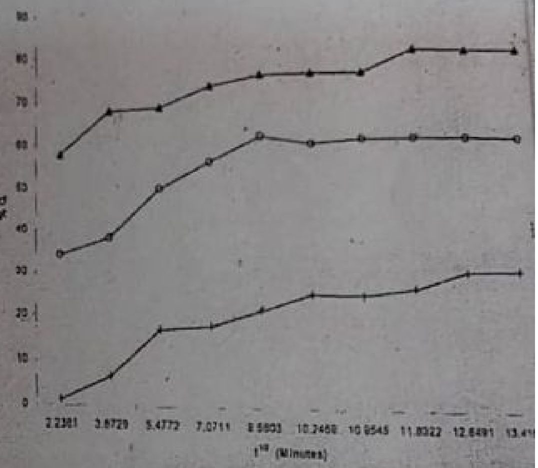

Fig. 1: Variation of Percentage Swellin Quotients (%Qt) of Polyvinylacetat (PVA) film in n-hexane with time 13°C (+), 25°C (0), and 37°C (

Table 2: **Temperature dependence of the interaction parameter (χ) and the maximu swelling quotient (Qm) in n- hexane, Carbon tetrachloride and water, at 13° 25°C and 37°C.**

Solvent	χ			% Qm ($cm^{-3}g^{-1}$)			Slope ($cm^{-3}g^{-1}sec$ ½		
	13°C	25°C	37°C	13°C	25°C	37°C	13°C	25°C	37
n-hexane	0.3773	0.3897	0.3899	30.20	66.50	85.10	3.4765	3.6127	3.7
Carbon tetrachloride	0.0518	0.0689	0.0691	36.90	71.30	90.40	3.5014	5.2561	5.4
Water	0.0229	0.0230	0.0236	45.60	75.40	96.51	3.6047	7.4219	7.9

The results of the percentage maximum swelling quotient (% Qm) and the slopes of the plots such as logQt/Qm against log t for these solvents at the three temperatures are presented in Table 2. The %Qm values increase from n-hexane to CCl_4 to H_2O. This result is consistent with Gee's theory [13] in that the solubility parameter of water (24.2 MPa½) is the closest to that of PVA (21.07).

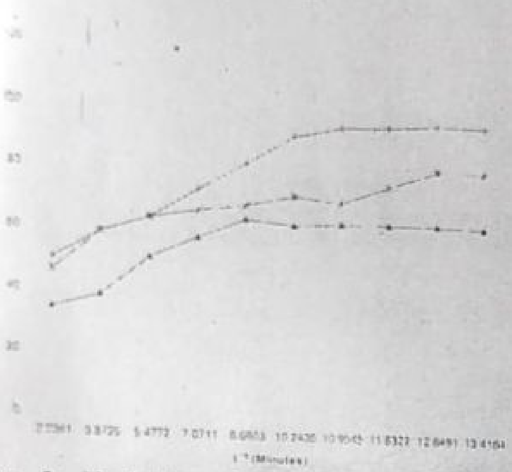

Fig. 2: Variation of Percentage Swelling Quotients (%Qt) of Polyvinylacetate (PVA) film with time in different solvents at 25°C, (+) H_2O, (*) CCl_4 and (▲) n-hexane.

The Flory Huggins interaction parameter. (χ) for the polymer/solvent system was calculated according to the solubility parameter Theory (SPT) [12,22].

In Table 2, the values of interaction parameter (χ) are also presented. The interaction and swelling ratio will be a maximum when the solubility parameter of the polymer matches that of the solvent [13]. This trend was indeed observed [Table 1 and 2].

Sorption Data

In order to investigate the type of diffusion mechanism, the sorption data of the solvent-polymer systems have been fitted to the following equation [23].

$$\log\left(\frac{Qt}{Qm}\right) = \log k + n \log t \qquad (3)$$

and the values of k and n obtained presented in Table 3. Where Qt and Qm are the swelling quotients at time t and at equilibrium respectively. k is a constant that depends on the polymer morphology and the polymer interaction. The values of n determining the mode of transport of solvent through the polymer film. For Fick's transport n = 0.5, when n = 1.0, the diffusion is relaxation controlled; but when n lies between 0.5 and 1.0, the mode is describes as anomalous [6 and 28]. The variations of these values are shown in table 3 for n-hexane, water, and CCl_4. The least square plots of log Q/Q_m versus log t is in Fig. 3.

In this report, the values of n and k suggest that the diffusion of these solvents into PVA at 13, 25 and 37°C are non-Fickian but better described as anomalous.

Table 3: Solvent effect of Absorption properties, Diffusivity D; Solubility S; meability P; n, and k of equation (3) at different temperatures.

Solvent	D x 10^7 (cm^{2}S ½)			S (cm^3 g^{-1})			P x 10^7 (cm^{2}S½g^{-1})			n			k		
	13°C	25°C	37°C	13°C	25°C	37°C	13°C	25°C	37°C	13°C	25°C	37°C	13°C	25°C	37°C
n-hexane	0.69	1.90	2.60	0.1196	0.4388	0.5619	2.519	3.255	5.214	0.51	0.53	0.56	0.12	0.29	0.295
Carbon-tetrachloride	0.45	1.03	1.09	0.2392	0.5792	0.6635	3.561	5.430	6.665	0.49	0.59	0.58	0.114	0.20	0.31
Water	0.36	0.58	1.23	0.4564	0.7541	0.9636	3.642	5.471	7.536	0.54	0.62	0.51	0.16	0.21	0.22

The values of n increases with increase in temperature in case of n-hexane, highest for water at 25°C. It also varies with solvent types. The k values increase with increase in temperature but decrease as the interaction parameter ,of the PVA-solvent system decreases. The variation of the k values with temperature suggests that the PVA interacted strongly with these solvents as the temperature increases.

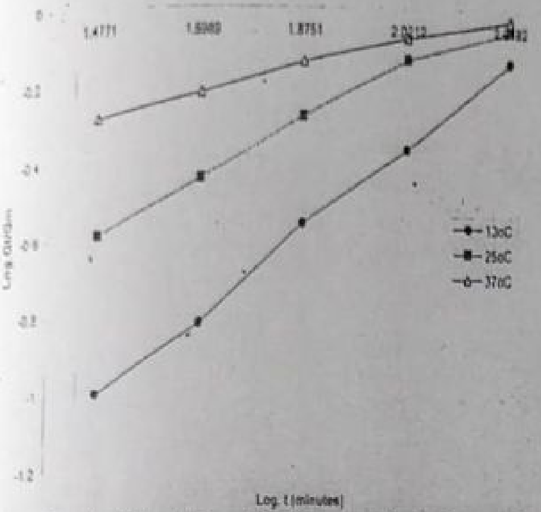

Fig. 3: A plot of log Qt/Qm against log t for PVA in n-haxane at 13^{0}C(•), 25^{0}C (■) and 37^{0}C (▲)

Transport Coefficient

The diffusion coefficient (D) of a solvent in a polymer membrane is described by Fick's second law of diffusion. [24 and 28] according to equation 4.

$$D = \left(\frac{\pi}{16}\right)\left[\frac{h\theta}{Qm}\right]^2 \qquad (4)$$

where h is the membrane thickness hθ is the slope of the linear plot of the sorption Qt against square root of time (t½) and Qm is the equilibrium absorption. The D values show an increase with increase in molecular mass of the solvent, and temperature as the interaction parameter decreases as presented in Tables 2 and 3.

The solubility (S) of permeant in PVA also increase with increase in temperature and in all cases with decrease in interaction parameter (Tables 2 and 3). Solvent molecules slowly diffuse to the polymer to produce a swollen gel leading to high polymer-polymer intermolecular forces as a result of crystallinity or strong Hydrogen bonding [6].

Hydrogen - bonding effects are of considerable importance in the separation of organic solvent mixtures through polymer films and permeation is enhanced when the polarity of polymer and solvent match closely. Solvents whose solubility parameters are close to that of the polymer are absorbed more and diffuse faster into the film than solvents with widely differing solubility parameter values [4].

The permeability also increases with increase in temperature as high temperature increases the fluidity of the polymer chains and make them more flexible thereby enhancing solvent permeability.

The permeability values vary irregularly both with molecular mass and the molar volume. This result is consistent with the view that molecular mass of a polymer has been found to have little effect on permeability of polymers except in the very low range of molecular masses [6 and 18].

The activation energy of absorption was obtained from the Arrhenius plots of diffusion coefficient (D) [24,28] according to the relation:

$$D = D_o e - {}^{E_a}\!/_{RT} \qquad (5)$$

where D is the diffusion coefficient, D_0 is the frequency factor, E_a is the activation energy of diffusion, R is the Gas constant and T the absolute temperature.

The estimated values of the activation energy (E_a) are presented in Table 4.

Table 4: Activation energies of absorption (Ea), enthalpies of absorption (ΔH) and entropy (ΔS) of absorption

Solvent	Ea (kJmol^{-1})	ΔH (kJ)	ΔS (kJ mol^{-1})	(ΔG kJ mol^{-1})
n-hexane	12.76	-19.64	-1.72x10^{-3}	-19.13
Carbon-tetrachloride	18.52	-1375	-1.20 x 10^{-3}	-14.11
Water	31.20	-9.93	-0.766 x 10^{-3}	-9.70

The calculated Ea obtained from the slopes of the curves shows a decrease with increase in the molecular mass of the solvent but increase with decrease in molar volume of solvent.

The degree of swelling of a polymer can be measured and related to the thermodynamic properties of the system [6]. In this work, the equilibrium absorption constants (ks) of solvents into PVA satisfy the Van't Hoff equation [26] plots, from which the entropy, enthalpy and hence free energy of absorption for each polymer solvent system were estimated. The equilibrium absorption constant (ks) was estimated from the amount of solvent absorbed per unit mass of polymer. The values of these thermodynamic parameters are presented in Table 4.

The enthalpies of absorption decrease with decrease in molecular mass of solvent. The negative A S values are in agreement with the theory that sorbed solvent molecules remain in the liquid state [7]. The energies of absorption showed that absorption of solvent could not lead to the dissolution of polyvinylacetate at these temperatures.

Conclusion

The swelling equilibrium and diffusion kinetics of the polyvinylacetate film in various solvents were studied at different temperatures. It was observed that the maximum swelling quotients determined for each solvent was dependent on both the solvents and the temperature of absorption. The initial slope method was employed to investigate the diffusion mechanism. Our results suggest that the diffusion process slightly deviates from the normal Fickian behaviour; it may therefore be described as anomalous [6, 27, 28].

The transport coefficients of the PVA, such as solubility, diffusivity, permeability, and sorption kinetic parameters were found to be dependent on temperature and solvent types.

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