Sorption Kinetics and Thermodynamic Equilibrium of Some Solvents in Polymer Films Using the Pressure Decay Method at Low Pressures

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This paper presents the study of sorption kinetics and thermodynamic equilibrium of chloroform and methanol sorption in thin polyvinyl acetate (PVAc) films. Experiments were conducted on a laboratory set-up using a pressure-decay technique. The obtained data were compared with other literature data obtained using other experimental method and are in good agreement. Comparison between the actual experimental and other literature data obtained using different investigation techniques are in good agreement.

Keywords: polymer films, solvent sorption, pressure-decay technique

The structure of polymeric films and membranes and their separation properties are influenced by many factors such as the type of used polymer, the nature and the size of the solvent molecule and also, the synthesis conditions.

Kinetics and thermodynamic equilibrium in polymer-solvent systems are very important in a number of processes including the production and the drying of polymeric films and membranes, the trace removal of solvents and monomers in polymers, the controlled release of active principles of drugs, the mass transfer modeling in polymer membranes, etc.

Accelerated development and diversification of industries which make use of polymeric materials has led to an increased research in this field worldwide.

The polymer complex structure causes a very different thermodynamic behavior in comparison to the standard solutions and the phase equilibrium description requires considerable experimental data and also, the use of complex models.

In literature, the diffusion and the thermodynamic equilibrium in binary polymer-solvent systems are investigated by several methods, mainly gravimetric (Magnetic Suspension Balance, Quartz Spring Balance, Quartz Crystal Balance), NMR, FTIR-ATR [1-8].

The pressure decay method of solvent sorption used in this paper is based on the principle of a direct dependence of the pressure variation at a constant volume and the mass absorbed by the polymer film in a given time. Although this method is not new, it has been used particularly in high pressure studies (>> 1 bar) of diffusion and solubility of gases in liquids and polymeric membranes [9-13].

This paper presents a study on diffusion and phase equilibria in binary systems such as methanol-PVAc and chloroform-PVAc at low pressure (<1 bar), at different solvent activities. To validate the applicability of this method in the working conditions, the diffusion coefficients and the thermodynamic equilibrium values were compared with literature data. An important feature of our set-up is that depending on the pressure transducer used and the solvent molecular weight, measurement accuracies comparable to semi-micro balances can be achieved (eg: 0.05 mg for water).

Experimental part

Materials and methods

Experiments were performed on the polymer polyvinyl acetate (PVAc) (Sigma-Aldrich) with two solvents, methanol and chloroform (Merck).

PVAc films were obtained by solvent evaporation from a dichloromethane-PVAc solution, 4%*wt*, dried in a laboratory oven, then under vacuum at 65°C for 24 h.

Scheme of the experimental set-up is shown in figure 1.

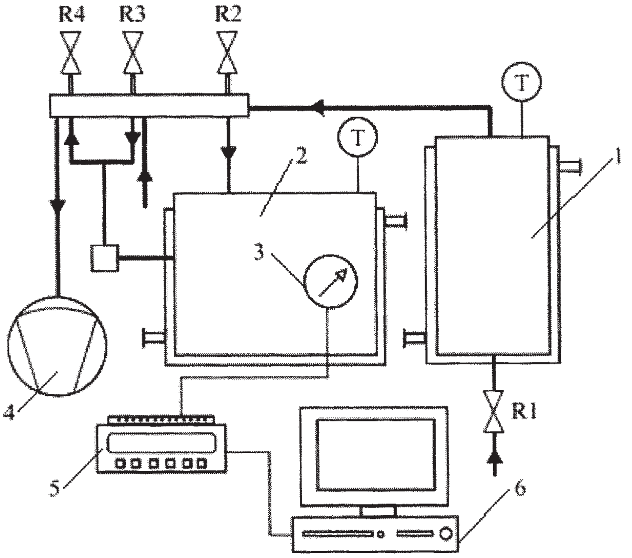

Fig. 1. Diagram of the experimental set-up
1- solvent tank, 2- sorption cell, 3- pressure transducer, 4- vacuum pump, 5- data logger, 6- computer, T- temperature sensors, R1, R2, R3, R4- valves

To fill the tank with solvent, the sorption cell (2) is sealed, (R1) valve is closed, (R2) and (R4) valves are opened and the vacuum pump (4) is operated until vacuum is achieved. Then, (R2) and (R4) valves are closed, (R1) valve is opened and its nozzle is immersed in a container with solvent. Due to the difference between the system and the laboratory pressures, the solvent enters the tank and the valve (R1) is closed. To remove the tank air traces, it is connected to the sorption cell by opening the valve (R2) and the vacuum is restored several times. The sorption cell is then brought

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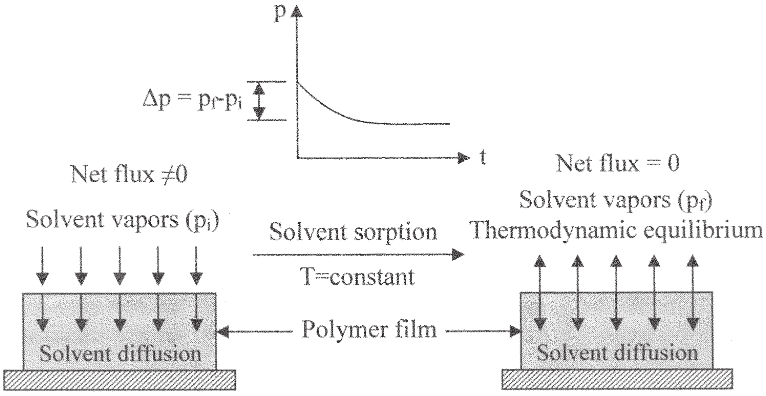

Fig. 2. The working principle of the pressure decay method

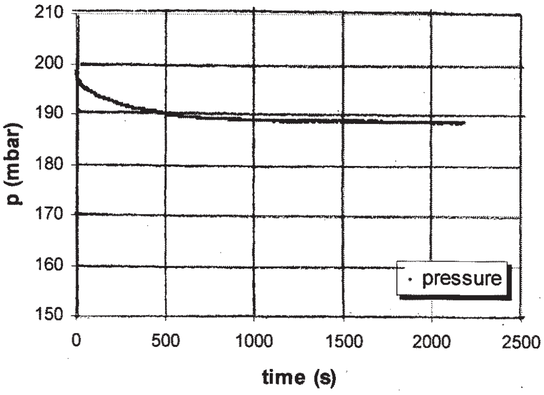

Fig. 3. Example of the pressure variation during solvent absorption in polymer films

to the atmospheric pressure and the sample material (PVAc film) is placed inside the cell, on an aluminum disc and afterwards, the cell is sealed.

The sorption cell (3) and the solvent tank (1) are brought to the desired temperature by using two thermostats (not shown here), and the temperature is kept constant throughout the experiment with an accuracy of ±0.1K using type K thermocouples. Next the sorption cell is vacuumed and filled with a known amount of methanol or chloroform from the tank in order to establish the desired activity of the solvent.

During the experiment, the pressure transducer (3) measures the pressure time variation which is recorded by the data logger (5) and the data are processed by computer (6).

The working principle of pressure decay method is described in figure 2.

At initial time (t_i) the solvent vapors begin to diffuse into the dried polymer film which lowers the pressure in the sorption cell. The absorption takes place a certain amount of time, after which the thermodynamic equilibrium is reached and the pressure transducer does not show any change. The pressure drop is converted into mass variation of the absorbed solvent using Antoine equation and the ideal gas equation of state.

Antoine equation is used to calculate the solvent activity (a) in the sorption cell as the ratio of the vapor pressure in the cell (p_c) and the solvent pressure at the operating temperature (p_{sat}) as $a = p_c / p_{sat}$.

$$\log_{10} p = A - \frac{B}{C+T} \tag{1}$$

where p – the saturation vapor pressure of the solvent, A, B, C – Antoine constants, T- operating temperature.

The ideal gas equation of state is used to calculate the mass of solvent vapors:

$$pV = \frac{m}{M} RT \tag{2}$$

where p – pressure, V – volume, m – mass, M- molecular weight, R – gas constant, T – temperature.

Because pressure is relatively small, the interactions between solvent molecules are negligible and the ideal gas equation of state can be used for calculations with good accuracy. The validity of this correlation was verified with the Z parameter found in the polynomial form (3) of Peng-Robinson equation of state for real gases (4) [14] and the error introduced is less than 2.5%.

$$Z^3 + (B-1)Z^2 + (A-2B-3B^2)Z + (B^3 + B^2 - AB) = 0 \tag{3}$$

where Z- the compressibility factor, A, B- terms that depend on the factors a and b

$$P = \frac{RT}{V-b} - \frac{a(T)}{V^2 + 2bV - b^2} \tag{4}$$

Results and discussions

Thermodynamic equilibrium

To model the thermodynamic equilibrium, the literature presents several models including Flory-Huggins, UNIQUAC, UNIFAC, UNIFAC-FV.

Since their introduction, these models have been continuously reviewed and improved, so currently there are several versions found in literature [15-21].

The Flory-Huggins is a lattice model which describes the correlation between solvent activity and the polymer volume fraction as:

$$\ln a = \ln(1-\phi_2) + \phi_2 + \chi_{12}\phi_2^{\,2} \tag{5}$$

where a - solvent activity, Φ_2 - volume fraction of the polymer, χ_{12}- the Flory-Huggins interaction parameter.

UNIQUAC and UNIFAC models can successfully describe the phase equilibria only in low molecular weight compounds.

For theoretical modeling of the dependence of solvent concentration in the polymer film and the solvent activity UNIFAC-FV model was used [22]. It was developed based on the UNIFAC model from the need for a theoretical description of phase equilibria in polymer solutions:

$$\ln a_i = \ln a_i^C + \ln a_i^R + \ln a_i^{FV} \tag{6}$$

where a_i – solvent activity, $\ln a_i^C$ -combinatorial component which takes into account the differences in molecular size, $\ln a_i^R$ - residual component which takes into account the molecular interactions.

The third term $\ln a_i^{FV}$ represents the contribution of the free volume of the polymer molecules:

$$\ln a_i^{FV} = 3c_i \ln\left(\frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}_M^{1/3} - 1}\right) - c_i\left(\frac{\tilde{v}_i}{\tilde{v}_M} - 1\right)\left(1 - \frac{1}{\tilde{v}_i^{1/3}}\right)^{-1} \tag{7}$$

where c_i – adjustable parameter for the solvent, $\tilde{v}_i$ - reduced volume of the solvent, $\tilde{v}_M$ - reduced volume of the mixture.

Methanol-PVAc system

To determine the thermodynamic equilibrium values, experiments were conducted at a temperature of 313.15 K for different solvent activities.

Figure 4 shows the experimental values of solvent activity as a function of solvent concentration and are

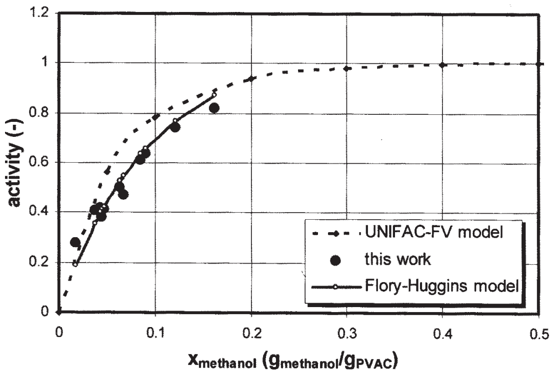

Fig. 4. Activity of methanol in methanol-PVAc system

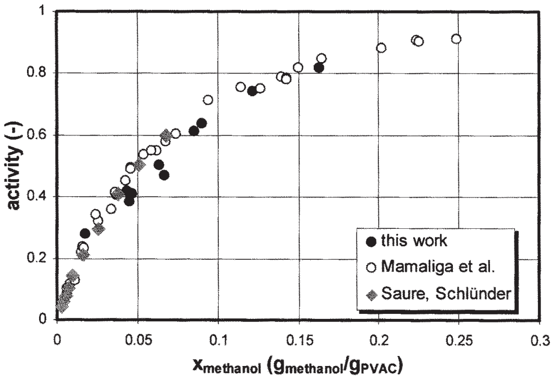

Fig. 5. Activity of methanol in methanol-PVAc system. Comparison with experimental data from literature

consistent with estimates based on UNIFAC-FV model at a constant value of χ = 1.048 in the Flory-Huggins model. The positive value for χ indicates a repulsive interaction between solvent and polymer molecules. This aspect can mean that methanol is not a very good solvent for PVAc.

Our data set was compared with two sets of experimental data obtained by different techniques, I. Mamaliga et al [1] used MSB gravimetric technique (magnetic suspension balance), R. Saure and E. Schlünder isopiestic method [24]. Figure 5 shows that the three methods give similar results with a very small error.

Chloroform-PVAc system

For this system experiments were conducted at two temperatures of 298.15 K and 313.15 K for different solvent activities. As the literature shows no studies on this system, the experimental data could not be compared. The activity variation as a function of solvent concentration is shown in figure 6. As expected, the temperature does not influence the phase equilibrium.

Sorption data are best fitted at a constant value of χ = -1.51 (fig.7). The negative value for χ indicates an attractive interaction between solvent and polymer molecules making chloroform a better solvent than methanol.

Sorption kinetics

The equation describing diffusion is Fick's second law:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (8)$$

where *C*- concentration, *D*- diffusion coefficient, *t*- time, *x*- diffusion length

The solution to equation (8) found by Crank [25] can be used to calculate the diffusion coefficients in binary solvent-polimer systems:

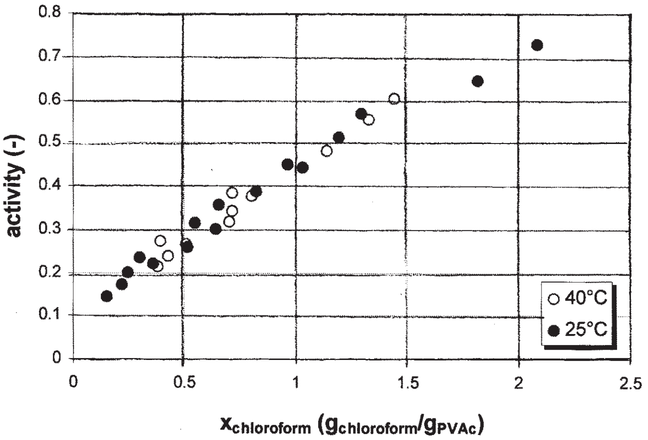

Fig. 6. Activity of chloroform in chloroform-PVAc system

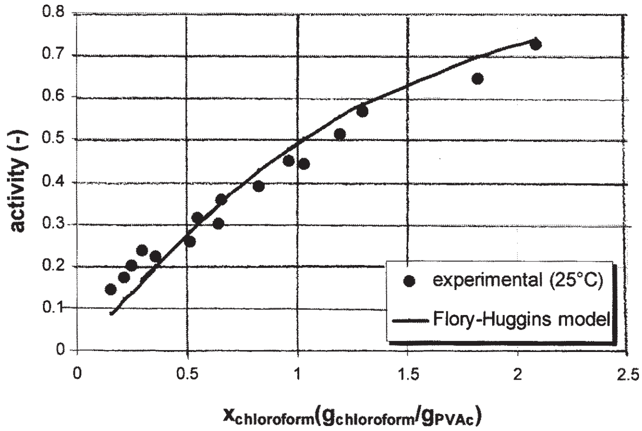

Fig. 7. Fitting of experimental data with Flory-Huggins model

$$\frac{M_t}{M_{eq}} = 1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[\frac{-D(2n+1)^2\pi^2 t}{l^2}\right]$$ with the approximation for small times: $\frac{M_t}{M_{eq}} = \frac{2}{\sqrt{\pi}}\frac{\sqrt{D}}{l}\sqrt{t}$ where M_t - mass of the absorbed solvent at time *t*, M_{eq} - mass of absorbed solvent at equilibrium, D- diffusion coefficient of the solvent in polymeric film, *l* -film thickness. From the slope of the plotted variation of M_t/M_{eq} as a function of $\sqrt{t}$ the diffusion coefficient is calculated $D = \frac{\pi}{4}S^2 l^2$.

Methanol-PVAc system

As in the determination of thermodynamic equilibrium case, the diffusion of methanol in PVAc films was investigated at a temperature of 313.15 K. The solvent concentration strongly influences the sorption kinetics and the diffusion coefficients must be determined on small

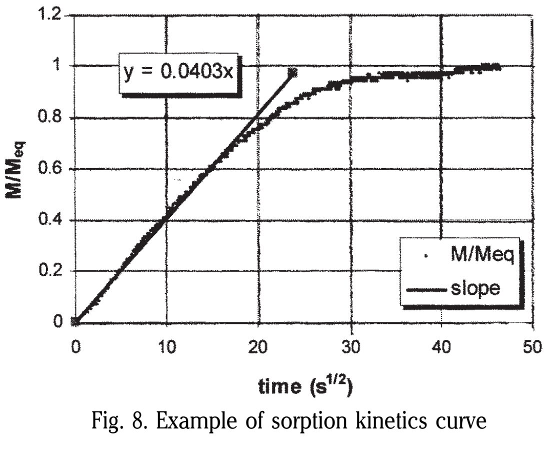

Fig. 8. Example of sorption kinetics curve

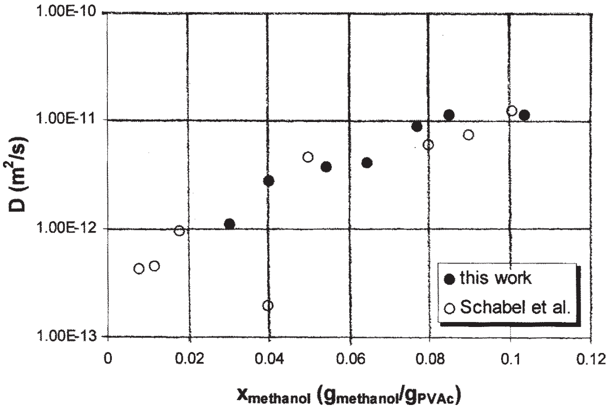

Fig. 9. Diffusion coefficients of methanol in PVAc

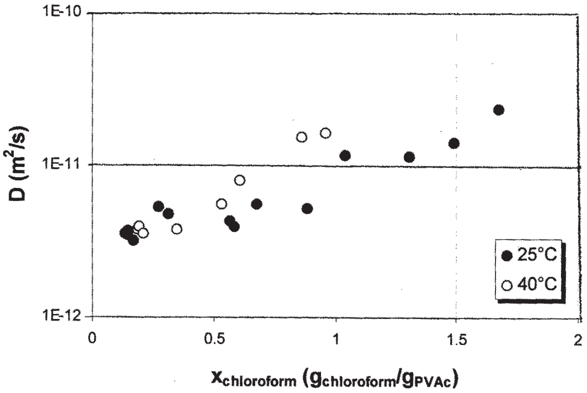

Fig. 10. The diffusion coefficient valuess of chloroform in PVAc

intervals of $g_{solvent}/g_{polymer}$ fraction. Thus, the diffusion coefficient takes an average value over the averaged concentration interval.

The results obtained were compared with those found in literature [23] and are shown in figure 9. One can observe the methanol concentration influence on the diffusion coefficients and also, the consistency between this study and other literature data.

Chloroform-PVAc system

Sorption isotherms experiments were carried out at temperatures of 298.15 K and 313.15 K, respectively. The diffusion coefficient values are shown in figure 10 and one can notice an influence of both temperature and solvent content $g_{chloroform}/g_{PVAc}$. A validation of these values was not possible as this binary system has not been investigated so far.

Conclusions

The objective of this study was to investigate the kinetics and thermodynamics of solvent sorption in polymer films using a pressure-decay set-up.

The diffusion coefficient values are influenced by the operating temperature and the solvent content of the polymeric film, an increase of these factors leading to an increase in its values.

The comparison of experimental data and values found in literature shows that the pressure decay method described in this paper can be used successfully to determine diffusion coefficients and phase equilibrium values in solvent-polymer systems.

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