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Solvent-Polymer Interaction. II. Measurements of Liquid Solvent Molecules Associating with Polymer Sites and of Their Transport Behavior in Polymer Membrane by Thermogravimetry, GLC, and Mass Spectrometry

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**Solvent-Polymer Interaction. II.
Measurements of Liquid Solvent Molecules
Associating with Polymer Sites and of Their
Transport Behavior in Polymer Membrane by
Thermogravimetry, GLC, and Mass Spectrometry**

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ABSTRACT

The measurements of sorption and diffusion behavior of liquid ethanol and water solvent mixtures in polyurethane membrane were made simultaneously by thermogravimetry. The individual amounts of sorbed water and ethanol in the polymer membrane were estimated by thermogravimetry and differentiated by mass spectrometry. In addition, from a single dynamic thermogravimetric experiment the activation energy for solvent molecules desorbing from the polymer membrane was also determined. The thermodynamic activity of ethanol vapor in equilibrium with the ethanol-water-polyurethane system was determined by gas-liquid chromatography. The clustering functions, the mean numbers of solvent molecules in the clusters, and those associating with polymer sites were evaluated by applying simplified mathematical derivatives using the experimentally determined values of activity and volume fraction of solvent molecules. It was found that at

lower ethanol concentration the tendency for ethanol molecules to cluster together is high. At higher ethanol activity, ethanol-polymer site interactions predominantly occurred.

Similar results were observed for ethanol-water molecules. However, water molecules in this particular system did not exhibit a self-associating tendency nor interact with the polymer sites. It was concluded that the Zimm-Lundberg clustering theory can be adequately applied to the interpretation of sorption and diffusion behavior of liquid ethanol-water mixtures in the polymer membrane.

INTRODUCTION

Previous studies on solvent-polymer interactions revealed that it was adequate and satisfactory to use the Zimm-Lundberg clustering theory for the treatment of sorption data of both solvent vapor-polymer [1-3] and liquid solvent-polymer systems [4]. In the latter case the Zimm-Lundberg clustering theory was applied to the interpretation of sorption behavior of a two-component solvent mixture, ethanol-water, in the polyurethane membrane. It was found that at lower ethanol concentration (or higher water activity) the tendency for ethanol molecules to cluster in the polyurethane membrane is greater than that for water molecules. At ethanol activity of 0.51 (51.1% by volume in aqueous phase), ethanol demonstrates an ideal sorption behavior in the membrane phase and then exhibits a localized sorption phenomenon at higher ethanol concentrations. A similar clustering tendency and behavior was also reported for ethanol-water molecules.

The Zimm-Lundberg clustering theory was originally developed on the basis of statistical mechanical considerations employing molecular distribution functions [1, 5]. One of the advantages of this theory over others lies in that it gives a direct measurement of non-random mixing of penetrant (solvent) molecules in the polymer matrix without the use of any preconceived model. It thus demonstrates how the sorption process alters with changing solvent content from one of sorption on a few highly specific sites to a diffuse swelling phenomena.

Phenomenologically, a complete understanding of the transport process of solvent molecules in the polymer membrane requires the measurements of both sorption and diffusion behavior over an extended solvent concentration. In addition, other parameters such as solvent-polymer site and solvent-solvent cluster interactions, which might affect the overall transport process, should be taken into account.

The present paper reports a study on the interactions of the ethanol-water mixture with specific polymer sites and the diffusion behavior of ethanol and water molecules in a relatively unswollen

polyurethane membrane at 25 ± 0.1 C. The solvent concentration used was varied systematically from 0 to 100% by volume of ethanol composition. The equilibrium solubility coefficient (S) and the diffusion coefficient of these solvent molecules in the polyurethane membrane were determined simultaneously by thermogravimetry (TG). Mass spectrometry (MS) was employed to estimate or differentiate ethanol and water compositions in the sorbed polymer membrane. The thermodynamic activity of ethanol in the vapor phase in equilibrium with the ethanol-water-polyurethane system in the aqueous phase was determined by gas-liquid chromatography (GLC). Finally, the effects of solvent concentration, solvent-polymer site, and solvent-solvent cluster interactions on the mechanism of the overall transport process are discussed with the aid of the Zimm-Lundberg clustering theory.

EXPERIMENTAL

Materials and Reagents

The polyurethane was obtained as a thin film from Molded Products Co., Easthampton, Massachusetts. It is a thermoset solid polyurethane prepared by reacting a polyurethane prepolymer with 4,4'-methylene-bis(2-chloroaniline). Its general properties are those of an elastomer. Its density is 1.1292 g/ml. The thermal stability of the materials is from TG: initial temperature of thermal degradation, 204.6°C; temperature range of total degradation of 10.0 mg sample, 204.6 to 545.0°C; activation energy for degradation, 17.8 kcal/mole; from differential thermal analysis (DTA): maximum endothermic peak temperature at 290.3°C (corresponding to the maximum temperature of thermal decomposition or depolymerization reaction).

The solvent was reagent grade absolute ethanol, obtained commercially, and it was used without further purification. Doubly distilled water was used in all equilibrium sorption experiments.

Preparation of Samples for Sorption-Desorption Study

The general procedures used for the preparation of polyurethane membrane samples (test samples) for sorption studies and analysis of sorption data by TG technique have been described in detail in previous papers [6, 7]. Briefly, test samples were punched from the polyurethane film with a paper punch (No. 1) in a definite size and shape (diam, 0.62 cm; thickness, 0.0770 to 0.0778 cm; weight, 25.5 to 27.2 mg). Prior to use in sorption studies the test samples were soaked in 95% ethanol for 48 hr and rinsed repeatedly with distilled water. An additional

soaking in 50% ethanol for 24 hr with subsequent rinsing with distilled water was performed. Finally, the test samples were rinsed with acetone, dried to constant weight, and stored in an evacuated desiccator until ready for use.

Sixteen different aqueous ethanol solutions were prepared volumetrically. The concentrations of these solutions varied from 0 to 100% of ethanol by volume. Eight pieces of approximately the same initial dry weight of test samples were placed in each of the glass sorption tubes containing 20.0 ml of ethanol solutions. The tubes with samples were then immersed in a thermally controlled water bath adjusted to $25 \pm 0.1^\circ\text{C}$ for exactly 30 days. After this time the sorbed test sample was removed from the ethanol solution and excess liquid on the membrane surface was blotted with tissue paper. Immediately (within 70 sec) the sorbed test sample was introduced into the TG instrument, the weight of the sorbed test sample was recorded, and a TG-desorption run under preset dynamic conditions [7] was carried out. The programming temperature was set between ambient temperature and 170°C . The dynamic TG-desorption curve thus obtained was used for the determination of the S value of solvent molecules in and the activation energy for desorption (E_{desp}) of solvent molecules from the polymer membrane.

Differentiation of Ethanol-Water Composition of Sorbed Test Samples

The composition of ethanol and water in the sorbed polyurethane membrane was differentiated with a Du Pont 21-491B double-focusing mass spectrometer (MS). A schematic diagram for preparation of desorbed solvents from test samples for MS analysis is shown in Fig. 1. Briefly, one disk of test samples was blotted with a tissue paper to remove any excess liquid on the membrane surface. It was then cut into two or three pieces and placed in the tube B. The very end of the tube B was dipped into liquid nitrogen (N_2). First the system A and C was heated and evacuated for about 1 hr or more. Then B was evacuated for 5 min. The system was then flushed with helium (He) for 2 min. Liquid N_2 was removed from B and placed under A. B was heated in an oil bath for about 40 min to raise the temperature from room temperature to 170°C and maintained at 170°C for 30 min. Finally, the stopcock of A was closed. The content of A was analyzed by MS. The peak heights thus obtained for ethanol and water were compared with those of known values of standard ethanol-water mixtures prepared previously. Three different groups of test samples, 2, 40, and 80% by volume of ethanol solutions were analyzed.

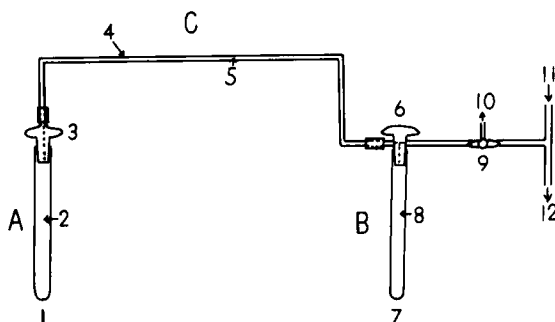


FIG. 1. A schematic diagram for the preparation of desorbed solvents from test polyurethane samples for MS analysis. (1) Glass tube receiver; (2) ~8 mm. i.d. glass tube receiver; (3) vacuum stopcock; (4) ~60 cm length of glass tubing; (5) ~2 mm. i.d. glass tubing; (6) 3-way stopcock; (7) sorbed test samples container; (8) ~8 mm. i.d. container; (9) 3-way stopcock; (10) to vacuum system; (11) He in; (12) to Hg U tube.

Determination of Ethanol Activity in the Vapor Phase by GLC

The thermodynamic activity of ethanol, a_E , in the vapor phase in equilibrium with the ethanol-water-polyurethane system in aqueous phase at constant temperature and pressure was determined by GLC. The determination was made with a Varian Gas Chromatograph 2100 Series using the following experimental set up:

Sample size: 20 μ l

Flow rate of carrier gas: He, 20 ml/min

Column and packing materials: 12 ft long and $\frac{1}{4}$ in. of stainless steel column packed with 5% triton X-305 on Teflon 6

Detector: air-hydrogen flame ionization detector

Attenuation and range: 1 and 2, 10^{-11}

Temperature settings: column, 120°C; injector, 200°C; detector, 200°C

Recorder chart speed: 0.5 in./min

Two or three injections were made for each group of sample solutions. The value of a_E was then evaluated from the ratio of the peak area (measured with a planimeter) of ethanol vapor above the ethanol solution to that of pure ethanol vapor.

Determination of Volume Fraction of Solvent Molecules in Polymer Membrane

The volume fraction, ϕ_1 , for type 1 molecules (that is, penetrant molecules or solvent molecules, ethanol and water molecules) in the polymer membrane and that of the polymer membrane, ϕ_p , were measured by the water or solvent displacement method with a pycnometer. The additive property of volume fraction was assumed in the computation of these values.

Evaluation of Diffusion Coefficient by Desorption Method with TG

An isothermal TG-desorption technique was used in the determination of diffusion coefficient or diffusivity (D) [6, 7]. Under isothermal conditions the chamber containing a quartz hangdown tube, a quartz concentric tube, a sample pan, and a platinum thermocouple (for measuring sample temperature) were pre-immersed into a thermostat adjusted to the same temperature of the initial 30-day sorption experiments (i.e., $25 \pm 0.1^\circ\text{C}$). When the equilibrium temperature was achieved in the chamber (5 to 10 min), the sampling process was followed. After the temperature in the chamber (containing test sample) was re-equilibrated (2 min), the TG instrument was turned on and the weight vs time recorded on chart paper until constant weight was obtained. It took 10 to 16 hr to complete a desorption experiment, depending upon the solvent concentration in the polymer membrane. At least two TG runs were made for each group of test samples. The isothermal TG-desorption curve thus obtained was used for the evaluation of the D value of solvent molecules in the polymer membrane.

RESULTS AND DISCUSSION

Solubility Coefficient of Solvents in the Polyurethane Membrane

The S value of ethanol and water in the polyurethane membrane was computed from the difference between the initial reading (equilibrium saturation value) of the sorbed samples and the constant weight reading after the completion of the TG-desorption run (equivalent to the dry film weight). Similarly, the S values of pure water and of pure ethanol were determined using the sorbed samples obtained from the pure water and pure ethanol testing solutions. The individual amount of water in

the ethanol-water sorbed samples was evaluated from the total solubility data by assuming the same constant amount of water being sorbed as was the case of pure water. MS was also used to differentiate the ethanol-water composition of the sorbed materials. Mass spectra for such differentiation of the three typically selected test samples (i.e., 2.00, 40.0, and 80.0%, v/v) are shown in Fig. 2. Figure 3 compares the results obtained from the TG (black circles) and MS (open circles) approaches. The numerical S values of ethanol and total solubility data for all groups of test samples are tabulated in Tables 1, 3, and 4.

As expected, the ethanol content in the membrane stimulated by the two approaches is almost identical although a little lower S values were obtained with MS (Fig. 3). In other words, a slightly higher amount of water was sorbed by the polyurethane membrane than was predicted by TG. This suggests that with increasing ethanol activity, ethanol molecules possibly enhance the sorption of water by breaking the hydrogen bonds among water molecules in the liquid water clusters [8] and carrying more free water molecules into the polyurethane membrane. Furthermore, a linear dependence of S on the concentration of aqueous ethanol solutions ($[C]_{aq}$) is seen in Fig. 3.

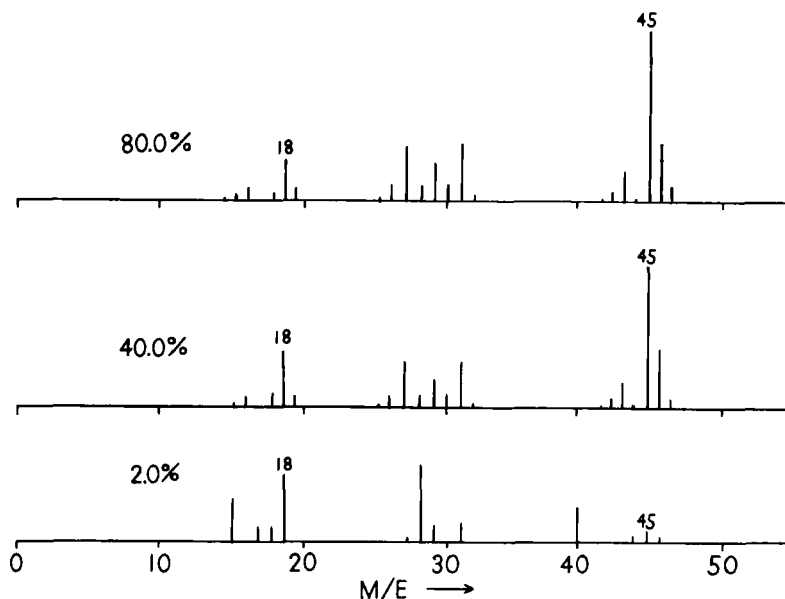


FIG. 2. Mass spectra of ethanol and water desorbed and differentiated from the sorbed polyurethane membrane. Shown are test samples obtained from 2.0, 40.0, and 80.0% by volume of the test solutions.

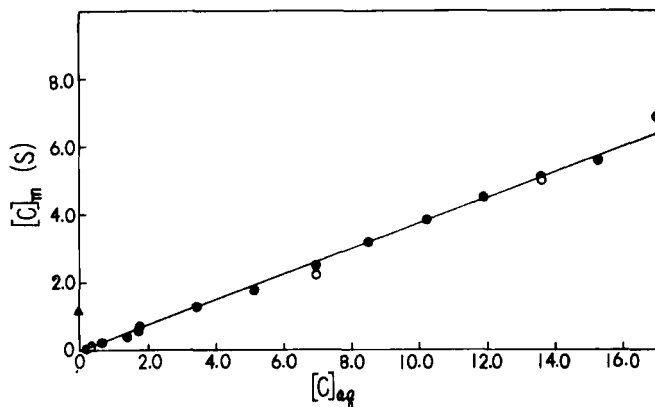


FIG. 3. Dependence of the concentration of ethanol in the polyurethane membrane, $[C]_m$ (or the equilibrium solubility, S), on the aqueous ethanol concentration, $[C]_{aq}$. $[C]_m$ is in $\mu\text{moles ethanol}/\mu\text{l membrane}$; $[C]_{aq}$ is in $\mu\text{moles ethanol}/\mu\text{l solution}$. (•) Concentration of ethanol in the sorbed ethanol-water mixture in the polyurethane membrane determined by TG (after correction for the constant concentration of water). (○) Concentration of ethanol in the sorbed ethanol-water mixture in the polyurethane membrane differentiated by MS. (△) Concentration of pure water in the polyurethane membrane. (⊙) Concentration of pure ethanol in the polyurethane membrane.

The solubility data in Table 4 also indicate that ethanol has much stronger affinity for polyurethane elastomer than water. (The S ratio for ethanol/water is $6.87/1.19 \cong 6.0/1.0$). It is not surprising, however, that the rather low water solubility found in this particular polymer is similar to the reported sorption behavior in a number of other polymers such as rubber hydrochloride [9], silicone rubber [10], poly(methyl methacrylate) [10], poly(ethyl methacrylate) [11], and ethyl cellulose [12]. Two factors, the hydrophobic properties of polymer chain structure and ethanol molecules and the formation of liquid water clusters in the liquid state (or aqueous phase) may influence this sorption behavior. This will become clearer when the site and cluster interactions in the membrane phase are taken into consideration.

Thermodynamic Activity of Ethanol and Water in Vapor Phase

At constant pressure and temperature the thermodynamic activity, a_E , in the vapor phase in equilibrium with the ethanol-water-polyurethane system is expressed by the relationships:

$$a_E = \frac{P_E}{P_E^0} = \frac{\text{mole}_E}{\text{mole}_E^0} = \frac{(\text{mass/mol wt})_E}{(\text{mass/mol wt})_E^0} = \frac{\text{mass}_E}{\text{mass}_E^0} \quad (1)$$

where P_E and P_E^0 are the equilibrium vapor pressure of ethanol above various concentrations of ethanol solutions and of the pure ethanol component, respectively.

However, the peak area of ethanol vapor in the chromatogram determined with GLC using a flame-ionization detector (FID) is related by

$$\text{area}_E = K_{\text{FID}} \text{mass}_E \quad (2)$$

Similarly, for a pure component of ethanol vapor,

$$\text{area}_E^0 = K_{\text{FID}} \text{mass}_E^0 \quad (3)$$

where K_{FID} is a proportional constant characteristic for ethanol molecules responding to FID.

Equations (2) and (3) imply that for a detector responding to the mass flow rate, the peak area is directly proportional to the total mass of the eluted component [13].

Dividing Eq. (2) by Eq. (3),

$$\frac{\text{area}_E}{\text{area}_E^0} = \frac{K_{\text{FID}} \text{mass}_E}{K_{\text{FID}} \text{mass}_E^0} = \frac{\text{mass}_E}{\text{mass}_E^0} \quad (4)$$

Comparison of Eqs. (1) and (4) leads to

$$a_E = \frac{P_E}{P_E^0} = \frac{\text{area}_E}{\text{area}_E^0} \quad (5)$$

Thus by simply measuring the GLC peak area of ethanol vapor and then dividing by the peak area of pure ethanol vapor, the activity of ethanol, a_E , was obtained. Some numerical values of a_E are listed in Table 1. The reproducibility of these measurements is $\pm 3.0\%$.

The activity of water, a_W (Table 2), was evaluated from the partial vapor pressure of water in the binary ethanol-water system at 25.0°C

TABLE 1. Mean Numbers of Ethanol Molecules in Clusters and Associating at Polymer Sites in Ethanol-Water-Polyurethane System at $25 \pm 0.1^\circ\text{C}$

Concentration of aqueous ethanol solution (vol %)	Solubility coefficient of ethanol in membrane, S $\left(\frac{\mu\text{mole solvent}}{\mu\text{l membrane}}\right)$	Activity of ethanol vapor (a_E)	Volume fraction of ethanol in membrane (ϕ_E)	Clustering of function of ethanol in membrane $\left(\frac{G_{E-E}}{V_E}\right)$	Mean numbers of ethanol molecules in cluster $\left(\frac{\phi_E^G E-E}{V_E}\right)$	Mean numbers of ethanol molecules associating at polymer sites $\left(\frac{\phi_E^G E-E-P}{V_E}\right)$
4.00	0.206	0.13	0.007	+57.3	+0.38	-
20.0	1.22	0.31	0.047	+13.5	+0.66	-0.09
40.0	2.48	0.48	0.12	+12.3	+1.48	-0.34
51.1	3.22	0.51	0.16	- 1.0	-0.16	-0.73
60.0	3.89	0.53	0.19	-23.0	-	-0.34
80.0	5.27	0.68	0.24	-23.0	-	-0.14
100.0	6.31	1.00	0.28	-60.0	-	-

TABLE 2. Mean Numbers of Water Molecules in Clusters and Associating at Polymer Sites in Ethanol-Water-Polyurethane System at $25 \pm 0.1^\circ \text{C}$

Concentration of aqueous ethanol solution (vol %)	Activity of water vapor (a_W)	Volume fraction of water in membrane (ϕ_W)	Clustering of function of water in membrane ($\frac{G_W - W}{V_W}$)	Mean numbers of water molecules in cluster ($\frac{\phi_W G_{W-W}}{V_W}$)	Mean numbers of water molecules associating at polymer sites ($\frac{\phi_W G_{W-P}}{V_W}$)
4.00	0.96	0.022	-1.0	-0.02	-0.015
20.0	0.89	0.021	-1.0	-0.02	-0.015
40.0	0.79	0.019	-1.0	-0.02	-0.013
51.1	0.78	0.019	-1.0	-0.02	-0.013
60.0	0.75	0.018	-1.0	-0.02	-0.012
80.0	0.62	0.016	-1.0	-0.02	-0.011
95.6	0.30	0.010	-30.0	-	-0.007
97.6	0.18	0.007	-132.6	-	-0.005

TABLE 3. Mean Numbers of Ethanol-Water Molecules in Clusters and Associating at Polymer Sites in Ethanol-Water-Polyurethane System at $25 \pm 0.1^\circ\text{C}$

Concentration of aqueous ethanol solution (vol %)	Solubility coefficient of ethanol-water in membrane, S ($\frac{\mu\text{mole solvent}}{\mu\text{l membrane}}$)	Activity of ethanol-water vapor (a_{E-W})	Volume fraction of ethanol-water in membrane (ϕ_{E-W})	Clustering function of ethanol-water in membrane ($\frac{G_{E-W}}{V_{E-W}}$)	Mean numbers of ethanol-water molecules in membrane ($\frac{\phi_{E-W} G_{E-W}}{V_{E-W}}$)	Mean numbers of ethanol-water molecules associating at polymer sites ($\frac{\phi_{E-W} G_{E-W} - P}{V_{E-W}}$)
4.00	1.40	0.35	0.029	+51.9	+1.47	-0.09
20.0	2.41	0.53	0.068	+30.0	+1.98	-0.21
40.0	3.67	0.62	0.14	+20.5	+2.87	-1.11
51.1	4.41	0.63	0.18	- 1.0	-0.18	-1.92
60.0	5.08	0.63	0.21	- 1.0	-0.18	-2.21
70.0	5.71	0.65	0.24	-46.7	-	+2.28
90.0	6.76	0.57	0.27	-132.4	-	+1.39
92.6	6.95	0.51	0.27	-509.9	-	-

obtained from the literature [14]. This evaluation was based on the assumption that polymer can be treated as an inert matrix [10]. That is, only a_E and a_W are the significant variables in the ethanol-water-polyurethane equilibrium system.

The activity of ethanol-water, a_{E-W} , is presented in Table 3.

These values were taken from the square root of the product of the activities of ethanol and of water. These values are essential for evaluating cluster functions of ethanol-water molecules in test samples.

Generally speaking, the activity of ethanol increases with increasing aqueous ethanol concentration. However, an inverse trend is found for a_W . The activity of ethanol-water molecules varies only slightly with the concentration of ethanol in the aqueous phase (Table 3).

Volume Fraction of Solvent Molecules in Polymer Membrane

The volume fraction, ϕ_1 , for type 1 molecules in the polymer membrane is expressed as

$$\phi_1 = \frac{V_1}{V_1 + V_p} = \frac{V_1}{V_{\text{total}}} \quad (6)$$

and the volume fraction of the polymer membrane is related by

$$\phi_1 + \phi_p = 1 \quad (7)$$

where V_1 and V_p are the volume of type 1 molecules in the polymer membrane and that of polymer membrane itself; ϕ_p is the volume fraction of the polymer membrane.

The usual definitions of V_1 and V_p are

$$V_1 = \frac{\text{wt}_1}{d_1} \quad (8a)$$

and

$$V_p = \frac{\text{wt}_p}{d_p} \quad (8b)$$

where w_{t_1} and d_1 are the weight and density of type 1 molecules in the polymer membrane; w_p and d_p are the weight and density of the polymer membrane. w_{t_1} and w_p were measured by TG. The values of d_1 and d_p were determined by the water or solvent displacement method with a pycnometer. The values of d_1 for pure solvents were taken from the literature. Finally, V_1 and V_p were calculated by using Eqs. (8a) and (8b).

Knowing V_1 and V_p , ϕ_1 was calculated by applying Eq. (6), and ϕ_p in turn from Eq. (7). The numerical values of ϕ_E , ϕ_W , and ϕ_{E-W} are listed in Tables 1, 2, and 3. Although, as is expected, the values of ϕ_E and ϕ_{E-W} increase with increasing S values, the ϕ_W values are about constant through the concentration range of ethanol studied (up to 80.0%, v/v). (However, ϕ_W declines sharply from 95.0% up to 100.0%.)

Mean Numbers of Type 1 Molecules in Clusters and Associating at the Polymer Sites

The Zimm-Lundberg clustering functions, which have been described previously [4], are represented by

$$\frac{G_{11}}{V_1} = -\phi_2 \left[\frac{\partial (a_1/\phi_1)}{\partial a_1} \right]_{P,T} - 1 \quad (9)$$

or

$$\frac{G_{11}}{V_1} = -(1 - \phi_1) \left[\frac{\partial (a_1/\phi_1)}{\partial a_1} \right]_{P,T} - 1 \quad (10)$$

where G_{11}/V_1 is called the clustering function. It denotes a tendency for type 1 molecules to cluster in the polymer phase.

Equation (10) is very useful since the clustering function, G_{11}/V_1 , is in terms of only two experimentally measurable quantities, a_1 and ϕ_1 , of type 1 molecules. Three physical meanings are implied:

Case I. If values of $G_{11}/V_1 > -1$, there is a tendency for type 1 molecules to cluster together. That is, the concentration of type 1 molecules is higher than average in the neighborhood of a given type 1 molecule.

Case II. If values of $G_{11}/V_1 = -1$, this shows an ideal solution (sorption) behavior. A particular type 1 molecule in such a system excludes its own volume to the other molecules but otherwise does not affect the distribution.

Case III. If values of $G_{11}/V_1 < -1$, this is interpreted in terms of localized sorption of type 1 molecules on specific polymer sites.

Practically, the clustering function for type 1 molecules was evaluated from the a_1 vs ϕ_1 sorption isotherm [4]. Then the mean number, $\phi_1 G_{11}/V_1$ (which measures the mean number of type 1 molecules in the neighborhood of a given type 1 molecule in excess of the mean concentration of type 1 molecules), was computed accordingly (Tables 1, 2, and 3).

Specifically, for Langmuir-type sorption, G_{11}/V_1 is negative as reflected by Case III. The negative values of G_{11}/V_1 suggest that solvent-polymer site interactions occur. This is of particular interest in the present study. The mathematical model for this type of interaction can be further modified (Eq. 21 of Ref. 5) as

$$\frac{\phi_1 G_{12}}{V_1} = \left[\frac{\partial \phi_2}{\ln a_1} \right]_{P,T} = -\phi_1 \left[\frac{\partial \ln \phi_1}{\partial \ln a_1} \right]_{P,T} \quad (11)$$

where $\phi_1 G_{12}/V_1$ defines the mean number of type 1 molecules in the neighborhood of a point (polymer site) occupied by type 2 molecule (polymer segment) in excess of the mean concentration of type 1 molecules. It was calculated from the slope of the plot of $\ln \phi_1$ vs $\ln a_1$ and multiplied by the corresponding ϕ_1 . Figure 4 shows such plots. The calculated values of $\phi_E G_{E-P}/V_E$, $\phi_W G_{W-P}/V_W$, and $\phi_{E-W} G_{(E-W)-P}/V_{E-W}$ are given in Tables 1, 2, and 3, respectively.

The plot of $\ln \phi_E$ vs $\ln a_E$ is linear only up to 0.48 of a_E (or 0.12 of ϕ_E) as is seen from Fig. 4. In the linear portion the values of $\phi_E G_{E-P}/V_E$ are smaller as compared to the corresponding values of $\phi_E G_{E-E}/V_E$ (Table 1). This suggests that some clustering of ethanol molecules is expected to occur in the polymer membrane at the lower a_E and the smaller ϕ_E because the polymer segments must occupy adjacent sites. However, ethanol molecules exhibit an ideal sorption behavior at 0.51 of a_E and 0.16 of ϕ_E . Thus one ethanol molecule excludes its own volume to the other molecules with a distribution of about 0.16 molecules in an ethanol cluster and 0.73 molecules associating at a polymer site. Finally, at higher a_E (nonlinear portion

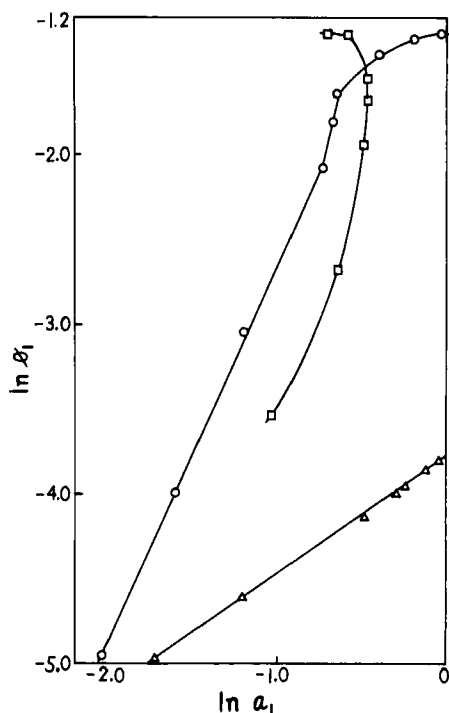


FIG. 4. Plot of $\ln \phi_1$ as a function of $\ln a_1$ for the determination of the mean number of solvent molecules associating at the polyurethane sites. (\circ) Ethanol, (\triangle) water, and (\square) ethanol-water.

of the curve), although the clustering function G_{E-E}/V_E is strongly negative, indicating that the localized sorption behavior takes place, the $\phi_E G_{E-P}/V_E$ is only from 0.34 to 0.14 molecules. This is in contradiction to the disciplines of the clustering theory since ethanol molecules neither cluster together nor associate at the polymer sites at the higher a_E and larger ϕ_E . The possible explanation for this peculiar behavior is given below. At the lower a_E , the first ethanol molecule enters the polyurethane chain structure, loosens the structure, and makes it easier for subsequent ethanol molecules to enter in the neighborhood of the first one than to go elsewhere; therefore they cluster together. As a_E increases, ϕ_E increases (i.e., the amount of

sorption increases). However, because the polyurethane membrane cannot swell large enough for accommodation of excess solvent molecules, ethanol molecules diffuse out from the initial position and distribute homogeneously in the amorphous zone of the polyurethane chains under the driving forces of volume fraction or chemical potential gradient. Besides, if the binding forces for the ethanol-ethanol cluster are through hydrogen bond formation between ethanol molecules ($-\text{OH}$ groups), the computed $\phi_E G_{E-E}/V_E$ values would not exceed one molecule because only one $-\text{OH}$ group in each ethanol molecule is available for hydrogen bonding. In other words, the cluster size of ethanol should not go over a stage of dimer. The slightly larger value of $\phi_E G_{E-E}/V_E$ (1.48 molecules) found at 0.48 of a_E must imply that the hydrophobic property of ethanol molecules (CH_3CH_2- group) also play an important role in the solvent-polymer interactions. This not only interprets the stronger affinity of ethanol molecules toward the polyurethane chain structure but also demonstrates the greater tendency for ethanol-ethanol contact in the cluster. Similarly, if the ethanol-polymer site interaction is also through hydrogen bonding between the $-\text{OH}$ group of ethanol molecules and the carbonyl group or the urethane group

($-\text{N}-\overset{\text{H}}{\underset{\text{O}}{\parallel}}\text{C}-\text{O}-$, see Fig. 5) in the polyurethane chains, the values of $\phi_E G_{E-P}/V_E$ will be limited to one molecule only (the maximum value

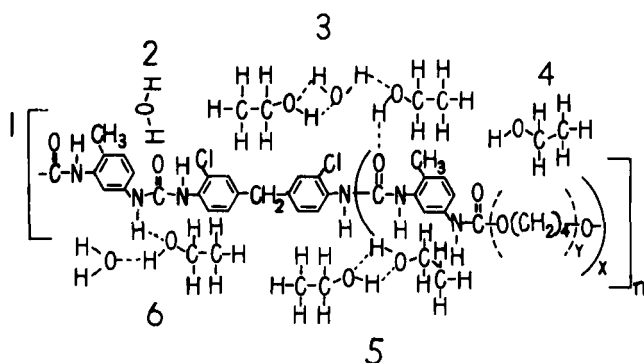


FIG. 5. The repeating unit of the polyurethane segment and the possible mechanism of the solvent-solvent (clustering) and the solvent-polymer site (associating) interactions in the polyurethane membrane. (1) The repeating unit of polyurethane segment; (2) water monomer; (3) ethanol-water-ethanol-polyurethane cluster; (4) ethanol monomer; (5) ethanol dimer; and (6) water-ethanol-polyurethane cluster.

is 0.73 molecules). All these together are consistent with the experimental findings reported here.

In the case of water sorption, an excellent linear relation was found between $\ln \phi_W$ and $\ln a_W$ through the whole ranges of ϕ_W and a_W studied (Fig. 4). The clustering function reveals that water molecules exhibit an ideal sorption behavior at higher water content down to 0.62 of a_W (or 80.0% by volume of ethanol concentration). Then, water molecules show a localized sorption at lower a_W as was indicated by the values of G_{W-W}/V_W (Table 2). However, the values of $\phi_W G_{W-P}/V_W$ and of $\phi_W G_{W-W}/V_W$ are only around 0.01 to 0.02 molecules. Evidently water molecules do not cluster together in the polyurethane membrane nor associate at the specific polymer sites of polyurethane. This is logical since only a very small amount of water was sorbed. Thus the location of water molecules in the polyurethane membrane is 1) homogeneously distributing in the amorphous region of the polymer matrix, and 2) associating with ethanol molecules to form ethanol-water clusters and then interacting with the polyurethane sites. The latter case is discussed in the following section.

The third clustering function is concerned with the ethanol-water molecules. The nonlinear curve of the plot of $\ln \phi_{E-W}$ vs $\ln a_{E-W}$ is shown in Fig. 4, and the numerical values of $\phi_{E-W} G_{E-W}/V_{E-W}$ and of $\phi_{E-W} G_{(E-W)-P}/V_{E-W}$ are presented in Table 3. The values of $\phi_{E-W} G_{E-W}/V_{E-W}$ range from 1.5 to 2.9 molecules, indicating that on the average at least 1 to 2 ethanol molecules and 1 water molecule are involved in an ethanol-water cluster. At higher a_{E-W} (i.e., from 0.14 to 0.27 of ϕ_{E-W} or from 40.0 to 90.0% by volume of ethanol solution), the values of $\phi_{E-W} G_{(E-W)-P}/V_{E-W}$ are between 1 to 2 molecules. This suggests that 1 molecule of ethanol and some fractions to 1 molecule of water are associating at the polymer site with the ethanol molecule serving as a bridge among the water-ethanol-polyurethane cluster complex. This result also provides a logical and consistent interpretation for the previous findings that water molecules do not form a cluster nor associate at the polyurethane sites.

Activation Energy of Desorption

The nonisothermal (or dynamic) TG-desorption curves can be used for evaluation of activation energy for desorption of solvent from the polymer matrix by applying Broido's approximation method [15] as

has been described previously [7]. Broido's approach applies only to first-order reactions including the majority of simple pyrolyses (i.e., for situations where the simple Arrhenius equation is applicable). It can be used equally well for the treatment of the kinetics of desorption of solvent from the solid polymer membrane if the polymer matrix can be treated as an inert matrix [10] and first-order desorption kinetics is presumed.

The simplified equation of Broido's approximation method is

$$\log \log (1/Y) = - (E_{\text{desp}}/2.303R)(1/T) + \text{constant} \quad (12)$$

where E_{desp} denotes the activation energy of desorption, R is the universal gas constant, and T the absolute temperature. The term Y is defined as

$$Y = (W_t - W_\infty)/(W_0 - W_\infty)$$

where W_t is the weight of sample at time t , W_0 is the initial sample weight, and W_∞ is the weight at infinite time of reaction or the residue weight at the end of the process under study.

In practice, a plot of $\log \log (1/Y)$ (the y-axis) vs $1/T$ should yield a straight line if the data are accurate and the reaction is first order. Then E_{desp} is calculated from the slope. Figure 6 shows the excellent plots of linear relationship for four typically selected test samples employing Eq. (12). All E_{desp} values were calculated by the method of least-squares and tabulated in the last column of Table 4. They are the average of two or three determinations. The relative precision is about 2.5%.

Evidently E_{desp} is constant through the whole ranges of ethanol concentrations investigated. The E_{desp} for pure water is 9.10 kcal/mole and for pure ethanol is 8.49 kcal/mole. Excluding these two values, the average value of E_{desp} for 14 groups of test samples is 8.50 kcal/mole, which is essentially equal to the E_{desp} of pure ethanol. The constancy of E_{desp} indicates the involvement of the same desorption mechanism and breaking of the same type of intermolecular forces such as hydrogen bondings during the desorption process. In addition, the values of E_{desp} for pure ethanol and for pure water are comparable to those values of heat of vaporization, ΔH_v , for ethanol and water. (For examples, for pure ethanol, $E_{\text{desp}} = 8.49$ kcal/mole,

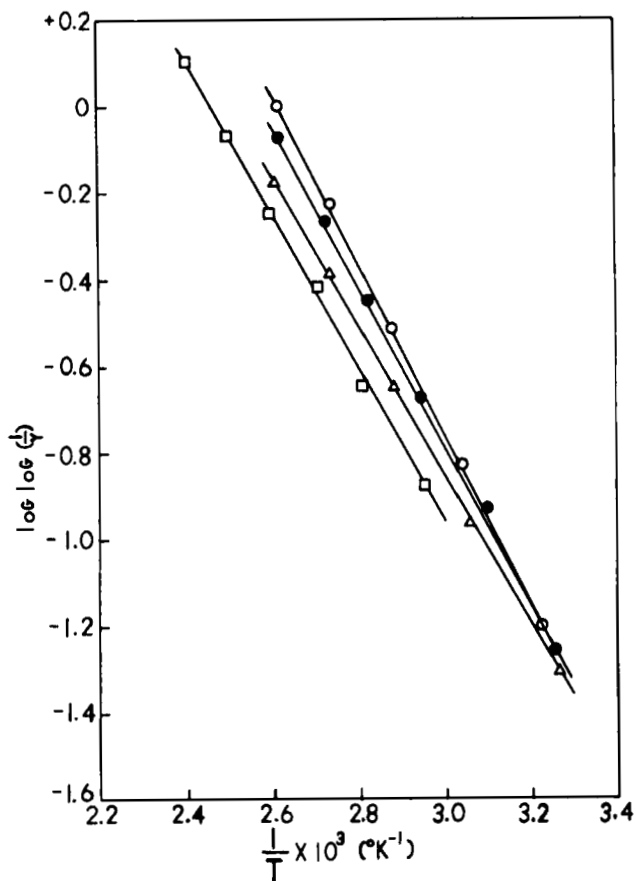


FIG. 6. Plot of $\log \log (1/Y)$ vs $1000/T$ for calculating the activation energy of desorption of solvents from the polyurethane membrane. (\circ) 0% (pure water). (Δ) 10.0%, (\square) 30.0%, and (\bullet) 100.0% (pure ethanol) by volume of test solutions.

$\Delta H_V = 9.40$ kcal/mole; for pure water, $E_{\text{desp}} = 9.10$ kcal/mole, $\Delta H_V = 9.71$ kcal/mole.) This suggests (but does not prove) that the mechanism of the desorption of solvent molecules from the polymer matrix is similar to the dynamic process of evaporating the corresponding liquid solvent molecules from the liquid phase. An analogous comparison has been made between the process of evaporation of volatile liquids and the chemical reactions in the literature. It was reported that the

TABLE 4. Solubility Coefficient, Diffusion Coefficient of Solvents in, and the Activation Energy of Desorption of Solvents from the Polyurethane Membrane at $25 \pm 0.1^\circ\text{C}$

Concentration of aqueous ethanol solution (vol %)	Solubility Coefficient of solvents in membrane, S ($\frac{\mu\text{mole solvent}}{\mu\text{l membrane}}$) $\frac{\text{Total}}{\text{Ethanol}}$	Diffusion coefficient of solvents, in membrane, $D \times 10^8$ ($\frac{\text{cm}^2}{\text{sec}}$)	Activation energy of desorption of solvents from membrane, E_{desp} ($\frac{\text{kcal}}{\text{mole}}$)
0	1.19	3.52	9.10
1.00	1.26	3.37	8.67
2.00	1.32	3.25	8.21
4.00	1.40	3.23	8.64
8.00	1.59	3.03	8.25
10.0	1.73	2.75	8.10
16.0	1.98	2.58	8.19
20.0	2.42	2.33	8.44
30.0	2.99	2.09	8.45
40.0	3.67	2.04	8.49
50.0	4.38	2.05	8.56
60.0	5.08	2.16	8.66
70.0	5.71	2.26	8.69
80.0	6.46	2.69	8.68
90.0	6.76	3.05	8.82
100.0	6.87	3.32	8.49

activation energies calculated from the Arrhenius plots correspond numerically to the latent heats of vaporization [16].

Diffusion Coefficient of Solvents in Polymer Membrane

The diffusivity or diffusion coefficient (D) of solvent molecules in polymer matrix was evaluated from the isothermal TG-desorption curve by employing a simplified equation in the form [6]

$$\log [Q(t)/Q(\infty)] = \log(8/\pi^2) - [(\pi^2 D / (2.303 L^2)) (t)] \quad (13)$$

where $Q(t)$ is the weight of liquid solvents per unit area of the plane sheet remaining in the solid polymer at time t , $Q(\infty)$ is the total weight of liquid solvents diffusing out of the plane sheet at infinite time [for a system which undergoes a complete desorption, $Q(\infty)$ should equal to the equilibrium solubility, S], and L is the thickness of membrane.

In analysis, desorption data were taken directly from the TG-desorption curves and converted to $\log [Q(t)/Q(\infty)]$ and plotted versus time t . Then D was calculated from the slope of the linear plot. Some typical plots (0, 20.0, 50.0, 70.0, and 100.0%, v/v) are presented in Fig. 7 (other groups of test samples give the same diffusional pattern of plottings and are therefore neglected). Linear

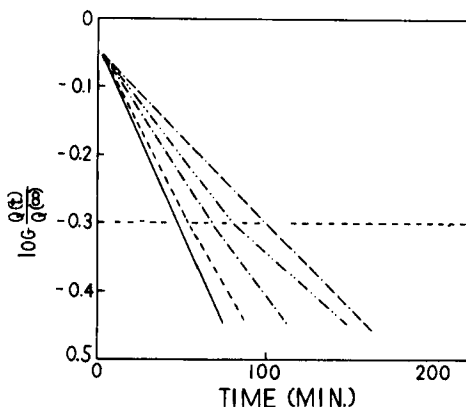


FIG. 7. Plot of $\log Q(t)/Q(\infty)$ vs time for calculating the diffusion coefficient of solvents in the polyurethane membrane. (—) 0%, (- · - ·) 20.0%, (- · · -) 50.0%, (- - -) 70.0%, and (- -) 100.0% by volume of test solutions.

relations obeying Eq. (13) were found to exist in the range of 0% up to approximately 50% desorption (i.e., $\log[Q(t)/Q(\infty)] = -0.30$) and thus only these portions were used for calculating the slopes. The slopes were computed by the method of least-squares. Furthermore, these linear plots also demonstrate that the diffusion of ethanol and water molecules in the polyurethane membrane is characteristically Fickian and D is constant for each specific group of test samples in the early stage of desorption.

The determined total D values (contributed by both ethanol and water molecules) in the polymer membrane are listed in Table 4. The concentration dependence of D on the solvent content in the membrane phase is shown in Fig. 8. Two interesting features can be seen in the figure. First, both D vs $[C_m]_{\text{total}}$ and D vs $[C_m]_{\text{EtOH}}$ plots exhibit symmetrically similar concave curves. Second, D decreases with increasing solvent content (either with $[C_m]_{\text{total}}$ or $[C_m]_{\text{EtOH}}$) to a minimum (at 40.0%, v/v, of aqueous ethanol solution) and then increases slightly but symmetrically with increasing $[C_m]$

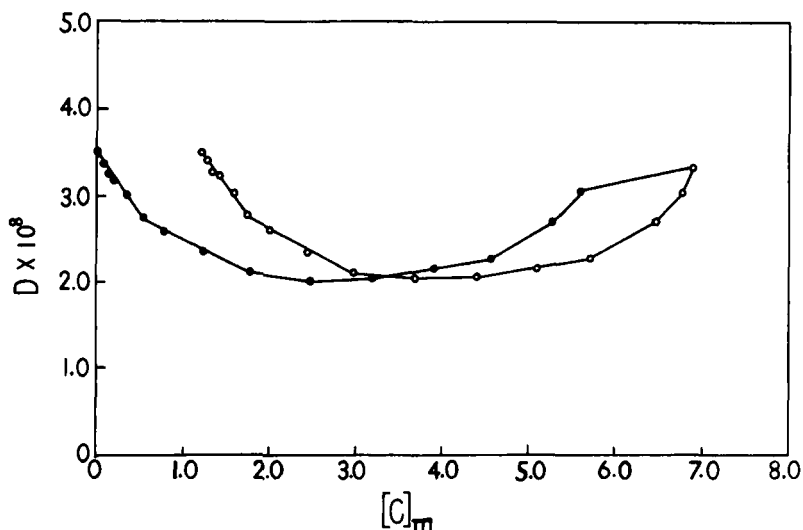


FIG. 8. The dependence of diffusion coefficient, D , on the initial solvent concentration (or equilibrium solubility) in the polyurethane membrane. (\circ) $D \times 10^8$ (cm^2/sec) vs $[C_m]_{\text{total}}$ ($\mu\text{moles solvent}/\mu\text{l}$ membrane). (\bullet) $D \times 10^8$ (cm^2/sec) vs $[C_m]_{\text{EtOH}}$ ($\mu\text{moles ethanol}/\mu\text{l}$ membrane).

again. This variation of D with $[C_m]$, however, is limited to a factor of about 2 (1.7).

The symmetrical shape of the curves is attributed to the similar properties and factors such as the size of diffusional entity, intermolecular forces, and molecular mobilities (for example, $D_{H_2O} = 3.52 \times 10^{-8}$, $D_{EtOH} = 3.32 \times 10^{-8}$ cm²/sec), of solvent molecules that may produce equivalent diffusion rates in the polymer matrix. In other words, at lower ethanol content the diffusional behavior of solvents in the membrane phase is predominantly contributed by water molecules, while at higher ethanol concentration the diffusion transport is mainly performed by ethanol molecules.

The decrease in D with increasing $[C_m]_{total}$ or $[C_m]_{EtOH}$ to a minimum at 40.0% (where $D = 2.04 \times 10^{-8}$ cm²/sec) by volume of ethanol concentration is ascribed to the nonideal effect such as solvent-solvent interaction (self-association, i.e., clustering). This effect is quantitatively obvious from Tables 1 and 3 where the mean numbers for ethanol-ethanol clusters are from 0.38 to 1.48 and those for ethanol-water clusters from 1.47 to 2.87 molecules, respectively, from the aqueous ethanol concentration range of 4.0 to 40.0% by volume. The polymerization of solvent molecules to form clusters of increasing molecular size (of diffusional entity) from one (free solvent molecule) to about four molecules ($1 + 2.87 \cong 4$) would certainly result in reducing the molecular mobility. Thus a consistent decrease in D with increasing $[C_m]_{total}$ or $[C_m]_{EtOH}$ was observed.

The increase in D with increasing $[C_m]_{total}$ or $[C_m]_{EtOH}$ beyond the inversion point (40.0% by volume) agrees well with the usual dependence of the diffusivity on the concentration of plasticizing organic vapors [17]. However, the mean numbers of ϕ_{E-P}^G/V_E (Table 1) and of $\phi_{E-W}^G(V_{E-W})-P/V_{E-W}$ (Table 3) suggest that the nonideal solvent-polymer site interaction occurred. This provides the additional information that the site interactions enhance the solvent diffusion rate. That is, the site interactions probably operate cooperatively with the diffusion behavior. Regarding mechanism, the site interactions reduce the size of the diffusional entity from ethanol-water and ethanol-ethanol clusters and then replaces them with weaker intermolecular forces, such as hydrogen and/or hydrophobic bondings, resulting in an increase in molecular mobilities and hence diffusivity. Finally, the highest D value for pure ethanol probably results from the highest mobility of the unbound free ethanol molecules as predicted by the clustering functions since pure ethanol molecules neither cluster together nor associate at the polymer sites (Tables 1 and 3).

Although other possible factors such as mechanical properties of polymer chains (i.e., internal stress effects) and surface concentration interference [18] may also influence the diffusion behavior of solvents in the polymer membrane, the use of integral desorption experiments by the TG technique to measure the diffusion behavior eliminates these possibilities. The clustering functions provide an adequate approach for interpreting the sorption and diffusion behavior of an ethanol and water mixture in the polyurethane membrane. It is anticipated that the theory can be applied equally well to the other liquid solvent-polymer systems if suitable modification is made.

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