

Use of Thermal Gravimetric Analysis, GLC, and Mass Spectrometry in Sorption Studies III: Evaluation of Clustering Functions of Ethanol-Water-Polyurethane System

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Abstract □ An equilibrium sorption study on the ethanol-water-polyurethane system over an extended ethanol concentration range was conducted by means of thermal gravimetric analysis, GLC, and mass spectrometry. From a single dynamic experiment, the equilibrium solubility in and the activation energy of desorption from the polymer matrix were evaluated simultaneously. The equilibrium sorption behavior of ethanol and water in the polymer matrix was interpreted in terms of the modified Zimm-Lundberg clustering theory applied to the liquid phase. The results indicate that the activation energy for desorption of ethanol decreases to a minimum and then increases with an increasing amount of sorption. The clustering function suggests that there is a greater tendency for ethanol molecules to cluster in the polymer matrix at lower ethanol activity but that there is no tendency for water molecules to cluster together. Water molecules show ideal sorption behavior at high water content and localized sorption on specific polymer sites at lower water content. Below 43% by weight or 0.51 activity, ethanol demonstrates ideal behavior; but at higher ethanol compositions, localized sorption takes place. There is also a great tendency for ethanol and water molecules to cluster together in the polymer matrix. The mean cluster size for ethanol is 1.4-2.5 molecules, while that for ethanol-water is 2.5-3.9 molecules.

Keyphrases □ Ethanol-water-polyurethane system—clustering functions evaluated using thermal gravimetric analysis, GLC, and mass spectrometry □ Polyurethane-water-ethanol system—clustering functions evaluated using thermal gravimetric analysis, GLC, and mass spectrometry □ Polymer-solute (solvent) interactions—clustering functions of ethanol-water-polyurethane system □ Clustering of penetrant molecules in polymer matrix—studied using thermal gravimetric analysis, GLC, and mass spectrometry, Zimm-Lundberg theory □ Sorption of solvent molecules in polymer matrix—clustering functions of ethanol-water-polyurethane system □ Thermal gravimetric analysis—determination of clustering functions for ethanol-water-polyurethane system □ GLC—determination of clustering functions for ethanol-water-polyurethane system □ Mass spectrometry—determination of clustering functions for ethanol-water-polyurethane system

Previous studies in these laboratories demonstrated the usefulness of thermal gravimetric analyses in sorption studies of selected liquid compounds with nylon (1) and with the diffusion and solubility of a series of aliphatic alcohols in polyurethane (2). This report continues these studies, exploring the clustering effects of sorbed molecules in a specific polyurethane using thermogravimetry, GLC, and mass spectrometry. Since polyurethanes have a wide range of applications in medicine, pharmacy, and dentistry, the information presented here should be of fundamental value in understanding aspects of solute (or solvent)-polymer interactions.

The tendency for penetrant molecules or solvent molecules to cluster in the polymer matrix can be interpreted by the Zimm-Lundberg clustering theory. Zimm (3) and Zimm and Lundberg (4) modified the formulas for the theory of solutions proposed by

Kirkwood and Buff (5) and applied them to solvent vapor-high polymer systems.

The Zimm-Lundberg clustering theory was developed on the basis of statistical mechanical considerations employing molecular distribution functions. This theory has one advantage over others in that it gives a direct measurement of nonrandom mixing of penetrant molecules in the polymer phase without the use of any preconceived model. It thus shows how the sorption process changes with increasing solvent content from one of sorption on a few highly specific sites to a diffuse swelling phenomenon. It has been found useful and applicable to the treatment of vapor phase sorption data of solvent-high polymer systems (4, 6-9) in molecular terms at isothermal conditions. However, the present report is concerned with equilibrium sorption measurements of the ethanol-water-polyurethane system in the liquid phase as a function of widely varying concentrations or activities of ethanol at $25 \pm 0.1^\circ$. The possible mechanism of sorption behavior of penetrant molecules in the polymer matrix is also discussed.

The amount of equilibrium sorption of penetrant molecules (included are ethanol and water molecules) in the polyurethane film was measured by thermal gravimetric analysis. From a single dynamic (nonisothermal) thermal gravimetric analysis experiment, the solubility (equilibrium sorption value) of penetrant molecules in and the activation energy for desorption of penetrant molecules from the polyurethane film were determined simultaneously at a specific ethanol activity. The amount of sorption of individual water molecules was obtained from thermal gravimetric analysis sorption data by assuming a constant amount of water sorbed in the polyurethane film independent of the amount of ethanol sorbed in the film. Mass spectrometry was also used to estimate the ethanol-water composition of the sorbed material. The activity of ethanol in the vapor phase at equilibrium with the ethanol-water-polyurethane system was measured by GLC. Then the clustering functions for penetrant molecules in the polyurethane film at each different ethanol activity were evaluated from the activity *versus* volume fraction sorption isotherms of the ethanol-water-polyurethane system.

THEORETICAL

Mathematical Derivatives of Clustering Functions—The original equation of Kirkwood and Buff (Eq. 19 of Reference 5) for a two-component system is:

$$G_{11}C_1 = kT \left(\frac{\partial C_1}{\partial P} \right)_{T, \mu_2} - 1 \quad (\text{Eq. 1})$$

Table I—Physical Properties of Ethanol and Water at 25°

Compound	Formula Weight	Density ^a , g./ml.	Mola ^b Volume, ml./mole	Boiling ^a Point	Dipole ^c Moment, debyes	Heat ^d of Vaporization, kcal./mole	Energy ^e of Hydrogen Bonding, kcal./mole	Activation Energy ^f of Desorption, kcal./mole
Ethanol	46.07	0.78505	58.37	78.40°	1.73	9.40	5.64	8.50
Water	18.00	0.99704	18.05	100.00°	1.82	9.71	9.00	9.83

^a Values obtained from "Handbook of Chemistry and Physics," 44th ed., The Chemical Rubber Publishing Co., Cleveland, Ohio, 1963. ^b Values calculated from the relationships $d = M/V$ and $V = M/d$. ^c Values obtained from "Tables of Experimental Dipole Moments," A. L. McClellan, Ed., W. H. Freeman, San Francisco, Calif., 1963. ^d Values from "Lange's Handbook of Chemistry," 8th ed., McGraw-Hill, New York, N. Y., 1956. ^e Values from L. Pauling, "The Nature of the Chemical Bond," 2nd and 3rd eds., Cornell, Ithaca, N. Y., 1940 and 1960. ^f Activation energy of desorption of solvent or solute from the polyurethane film determined by thermogravimetry.

Table II—Physical Properties of Dry Polyurethane

Sample Size and Shape		Initial Dry Film Weight Range, mg.	Average Weight, mg.	Density, g./ml.	Temperature of Initial Thermal Degradation	Activation Energy of Thermal Degradation, kcal./mole
Diameter, cm.	Thickness, cm.					
0.640	0.0770-0.0778	25.5-25.7	25.5	1.1274	204.56°	17.8
		25.8-26.0	25.9	1.1329		
		26.7-26.9	26.9	1.1319		
		27.0-27.2	27.1	1.1246		
				1.1292 (av.)		

where G_{11} and C_1 are the cluster integral and molecular concentration for type 1 molecules, respectively, k is the Boltzmann constant, T is the absolute temperature, P is the vapor pressure, and μ_2 is the chemical potential for component 2.

On the basis of some thermodynamic properties and relationships and by further mathematical modifications, Zimm (3) transformed Eq. 1 into:

$$\frac{G_{11}}{V_1} = -\phi_2 \left[\frac{\partial(a_1/\phi_1)}{\partial a_1} \right]_{P,T} - 1 \quad (\text{Eq. 2})$$

or:

$$\frac{G_{11}}{V_1} = -(1 - \phi_1) \left[\frac{\partial(a_1/\phi_1)}{\partial a_1} \right]_{P,T} - 1 \quad (\text{Eq. 3})$$

where a_1 , ϕ_1 , and V_1 are the activity, volume fraction, and partial molecular volume of type 1 molecules, respectively, and ϕ_2 is the volume fraction of component 2 (polymer material); G_{11}/V_1 is called the clustering function. It denotes a tendency for type 1 molecules to cluster in the polymer matrix. Three physical meanings may be considered:

Case I—If values of $G_{11}/V_1 > -1$, there will be a tendency for type 1 molecules to cluster together. In other words, the concentration of type 1 molecules is higher than average in the neighborhood of a given type 1 molecule. This is due to the fact that the first type 1 molecule enters the polymer structure, loosens the structure, and makes it easier for subsequent molecules to enter in the neighborhood of the first one than to go elsewhere.

Case II—If values of $G_{11}/V_1 = -1$, this shows ideal solution 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 sites.

Equation 3 is very useful, since the right-hand side of the equation is in terms of experimentally measurable quantities, activity (a_1), and volume fraction (ϕ_1) of type 1 molecules.

The quantity $\phi_1 G_{11}/V_1$ is a measure of 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. The mean size of a cluster is given by $(\phi_1 G_{11}/V_1 + 1)$. This cluster size represents an overall average of the penetrant species (type 1 molecules).

Thermodynamic Activity of Type 1 Molecules—Thermodynamically, it is always true that at equilibrium at constant temperature and pressure the chemical potential of component 1 in the liquid phase, $\mu_1(L)$, is equal to the chemical potential of the same

component in the vapor phase, $\mu_1(V)$. That is:

$$\mu_1(L) = \mu_1(V) \quad (\text{Eq. 4})$$

However, at pressures of a few atmospheres or less, the vapor phase obeys the ideal gas law, so that the chemical potential of component 1 in the vapor phase can be represented by Eq. 5:

$$\mu_1(V) = \mu_1^\circ + RT \ln P_1 \quad (\text{Eq. 5})$$

where μ_1° is the chemical potential of pure component 1 at the standard state of pure gas at $P = 1$ atm. and temperature T ; R is the universal gas constant.

If component 1 in the liquid phase obeys Raoult's law, it is true that:

$$P_1 = P_1^\circ N_1 \quad (\text{Eq. 6})$$

and Eq. 5 can be rewritten as:

$$\mu_1(V) = \mu_1^\circ + RT \ln N_1 \quad (\text{Eq. 7})$$

where N_1 is the mole fraction of component 1 in the liquid phase, and μ_1° is the chemical potential of pure component 1 at the standard state of pure liquid at $N_1 = 1$ and temperature T .

If component 1 in the liquid phase deviates from Raoult's law, then:

$$P_1 \neq P_1^\circ N_1 \quad (\text{Eq. 8a})$$

but:

$$P_1 = P_1^\circ a_1 \quad (\text{Eq. 8b})$$

Therefore, Eq. 5 may be rewritten as:

$$\mu_1(V) = \mu_1^\circ + RT \ln a_1 \quad (\text{Eq. 9})$$

where a_1 is the activity of component 1 (that is, type 1 molecules) in the vapor phase in terms of the relative pressure, and μ_1° now represents the chemical potential at the standard state of pure liquid at $a_1 = 1$ or $N_1 = 1$ and temperature T . In this study, pure liquid ethanol at the mole fraction $N_E = 1$ or $a_E = 1$ and pure liquid water at the mole fraction $N_W = 1$ or $a_W = 1$ were taken as the standard states for type 1 molecules at a temperature of 25.0°.

Therefore, the activity of type 1 molecules in the liquid phase may be evaluated from measurements of the relative pressure, P_1/P_1° ; these data, in turn, can be used in Eq. 3 to calculate the clustering functions.

Table III—Sorption Data and Activation Energy of Desorption for Ethanol–Water–Polyurethane System at $25 \pm 0.1^\circ$

Initial Concentration of Aqueous —Ethanol Solutions— wt. %	moles/l.	Total Amount of Sorption, g. Solute/g. Film	Activation Energy of Desorption, kcal./mole
0.	0.	0.0190	9.83 (pure water)
0.78	0.170	0.0219	9.13
1.57	0.341	0.0232	8.69
3.16	0.682	0.0262	8.64
4.76	1.02	0.0296	8.49
6.36	1.36	0.0318	7.87
7.98	1.70	0.0377	7.12
12.9	2.73	0.0471	7.32
16.2	3.41	0.0551	7.57
33.2	6.92	0.1170	7.27
52.1	10.2	0.1757	8.41
73.4	13.6	0.2574	8.43
100.0	17.0	0.2702	8.50 (pure ethanol)

EXPERIMENTAL

Materials—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 measurements. Table I summarizes some physical properties of ethanol and water.

The polyurethane was obtained¹ as a thin film. It is a thermoset solid polyurethane prepared by reacting a polyurethane prepolymer with 4,4'-methylenebis(2-chloroaniline). Its general properties are those of an elastomer (Table II).

Preparation of Samples—Test samples were punched from the polyurethane film with a paper punch, No. 1, 0.63-cm. diameter. Cylindrical-shaped samples were cut of 0.62-cm. diameter, 0.0770–0.0778-cm. thickness, and 25.5–27.2-mg. weight. All test samples for each different ethanol concentration or activity were as uniform as possible, and variation never exceeded 0.5% (thickness or weight) from sample to sample. The test samples were soaked in 95% ethanol for 48 hr. and then 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 a desiccator until ready for use.

Thirteen different aqueous ethanol solutions were prepared volumetrically. The concentrations of these solutions varied from 0 to 100% ethanol by volume. Eight pieces of approximately the same initial dry weight of polyurethane film were placed in an all-glass sorption tube containing 20.0 ml. of ethanol solution. The tubes were then stoppered (screw cap with Teflon-faced rubber liner) and immersed in a thermally controlled water bath adjusted to $25.0 \pm 0.1^\circ$.

Preliminary measurements indicated that the equilibrium sorption occurred within several weeks. For uniformity, the sorption tubes with samples were kept in the water bath for exactly 30 days. After this time, the plastic sample was removed from the test ethanol solution and excess liquid was blotted with tissue paper. Immediately (within 70 sec.) the plastic sample was introduced into the thermal gravimetric analysis instrument, the sample weight was recorded, and a thermogram was run.

Thermal Gravimetric Analysis for Desorption Studies—Descriptions of the thermal gravimetric analysis instrument and the method of running a desorption experiment were presented previously (2); in the present study the desorption runs were made in a dynamic manner by increasing the temperature at a constant rate.

A stream of nitrogen was passed through concentrated sulfuric acid and then into the chamber containing the test sample, at a constant flow rate of 200 ml./min., to flush and remove any adhering gases or decomposed gaseous products evolved during the desorption experiment. The nitrogen gas, in turn, was led out of the chamber into a series of gas-washing bottles. After the sorbed plastic sample was placed in the thermal gravimetric analysis system, the instrument run was initiated and the weight loss *versus* tempera-

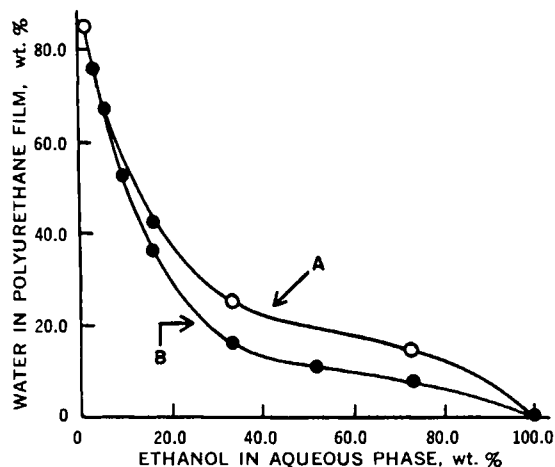


Figure 1—Weight percent water in polyurethane film versus weight percent ethanol in aqueous phase at 25° . Key: A, mass spectrometry; and B, thermal gravimetric analysis.

ture (and time) was recorded on chart paper until a constant weight was obtained. This thermogram was used for evaluation of the solubility of solvent molecules in and the activation energy for desorption of solvent molecules from the polymer film. The solubility was determined from the difference between the initial reading (equilibrium sorption value) and the constant weight reading on the thermogram after complete desorption. The activation energy for desorption was evaluated from the corresponding thermogram by employing Brodov's method (1, 10). To ensure reproducibility, at least two test samples for each different group of ethanol solutions were run. The relative precision of the calculated solubility for each group of test samples was 2.5% or less. The reproducibility for activation energy of desorption was about 1.0–3.0%.

Determination of Ethanol Activity in Vapor Phase—The activity of ethanol, a_1 , in the vapor phase above various concentrations of ethanol solutions can be determined in terms of relative pressure, P_1/P_1° , by GLC. Furthermore, at equilibrium at constant temperature and pressure, the following relations are true:

$$a_1 = \frac{P_1}{P_1^\circ} = \frac{\text{mole}_1}{\text{mole}_1^\circ} = \frac{(\text{mass/mol. wt.})_1}{(\text{mass/mol. wt.})_1^\circ} = \frac{\text{mass}_1}{\text{mass}_1^\circ} \quad (\text{Eq. 10})$$

However, the area of the peak in GLC with a flame-ionization detector (FID) is:

$$\text{area}_1 = K_{\text{FID}} \text{mass}_1 \quad (\text{Eq. 11})$$

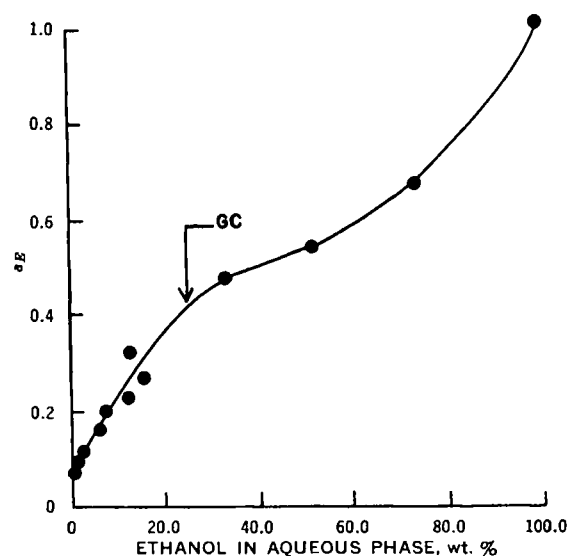


Figure 2—Ethanol activity in vapor phase as a function of aqueous phase ethanol composition at 25° .

¹ Code No. MP950, Molded Products Co., Easthampton, Mass.

Table IV—Volume Fraction Data for Ethanol–Water–Polyurethane System at $25 \pm 0.1^\circ$

Initial Concentration of Aqueous Ethanol Solutions		ϕ_E	ϕ_W	ϕ_P
wt. %	moles/l.			
3.16	0.682	0.0066	0.0224	0.971
16.2	3.41	0.0468	0.0212	0.932
33.2	6.92	0.123	0.0190	0.858
52.1	10.2	0.192	0.0180	0.790
73.4	13.6	0.241	0.0160	0.743
100.0	17.0	0.271	0.0000	0.729

where K_{FID} is a proportionality constant for type 1 molecules.

Equation 11 shows that for a detector responding to the mass flow rate, the peak area is proportional to the total mass of the eluted component (11).

Similarly, for a pure component of type 1 molecules:

$$\text{area}_1^\circ = K_{FID} \text{mass}_1^\circ \quad (\text{Eq. 12})$$

Dividing Eq. 11 by Eq. 12, one gets:

$$\frac{\text{area}_1}{\text{area}_1^\circ} = \frac{K_{FID} \text{mass}_1}{K_{FID} \text{mass}_1^\circ} = \frac{\text{mass}_1}{\text{mass}_1^\circ} \quad (\text{Eq. 13})$$

Comparison of Eqs. 10 and 13 gives:

$$a_1 = \frac{P_1}{P_1^\circ} = \frac{\text{area}_1}{\text{area}_1^\circ} \quad (\text{Eq. 14})$$

Therefore, by simply measuring GLC peak areas for type 1 molecules in the vapor phase and then dividing by the peak area of pure type 1 molecules in the vapor phase, the activities of type 1 molecules were determined.

Determination of Volume Fraction of Type 1 Molecules in Polymer Film—Experimentally, the volume fraction, ϕ_1 , for type 1 molecules can be evaluated from the following:

$$\phi_1 = \frac{V_1}{V_1 + V_p} = \frac{V_1}{V_{\text{total}}} \quad (\text{Eq. 15})$$

But:

$$V_1 = \frac{\text{wt}_1}{D_1} \quad (\text{Eq. 16a})$$

$$V_p = \frac{\text{wt}_p}{D_p} \quad (\text{Eq. 16b})$$

$$\phi_1 + \phi_p = 1 \quad (\text{Eq. 16c})$$

where V_1 , wt_1 , and D_1 are equilibrium sorption volume, equilibrium sorption weight, and density, respectively, of type 1 molecules at the same temperature; V_p , wt_p , and D_p are volume, weight, and

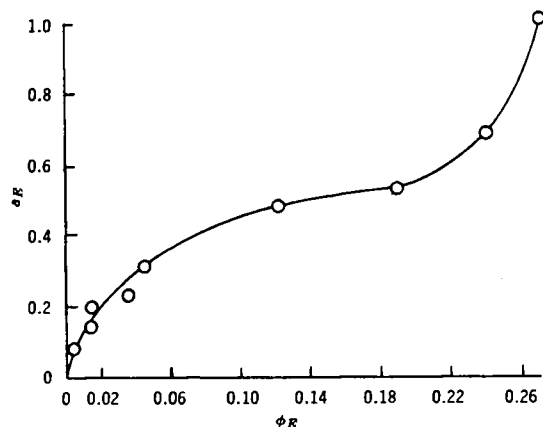


Figure 3—Ethanol activity as a function of volume fraction of sorbed ethanol in polyurethane film at 25° .

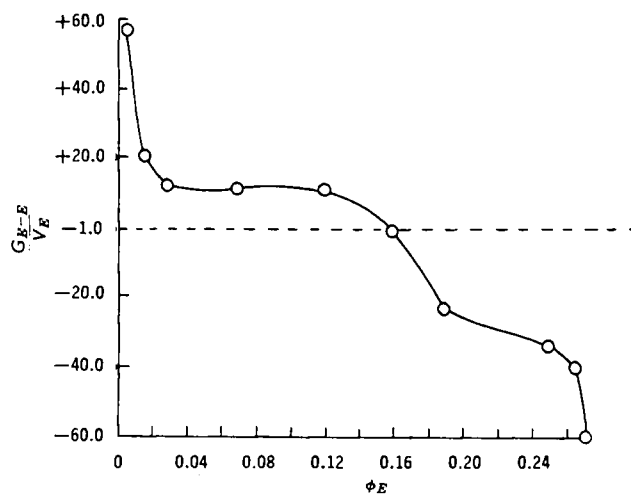


Figure 4—Clustering function for ethanol in ethanol–water–polyurethane system at 25° .

density of the polymer film in that order; and ϕ_1 and ϕ_p are volume fractions of type 1 molecules and the polymer film, respectively.

The equilibrium sorption weight of type 1 molecules was determined by thermal gravimetric analysis, and the density of type 1 molecules in the liquid state at the same temperature was obtained from the literature. The density of the polymer film was measured by the water or solvent displacement method with a pycnometer. Finally, ϕ_1 was calculated from the measured V_1 and V_p . By knowing ϕ_1 , ϕ_p can be computed from Eq. 16c.

RESULTS AND DISCUSSION

Table III summarizes the sorption data and activation energy of desorption for the ethanol–water–polyurethane system at 25° . The total amount of sorption increases with increasing concentration of ethanol. The amount of sorption of pure water is about 7.0% of the amount of sorption of pure ethanol. The activation energy of desorption of solvent molecules from the polymer film decreases with an increasing amount of total sorption to a minimum and then increases again. This suggests a possible change in the sorption mechanism. The activation energy of desorption of pure water from the polymer film is a little higher than that of pure ethanol.

Figure 1 shows the plot of weight percent of water in the polyurethane film versus weight percent of ethanol in the liquid phase. The weight percent of water in the polyurethane film was differentiated from the total amount of sorbed solvent molecules in the film by mass spectrometry (open circles in Fig. 1). The other curve of Fig. 1 (black circles) was obtained from thermal gravimetric analysis sorption data by assuming a constant amount of water

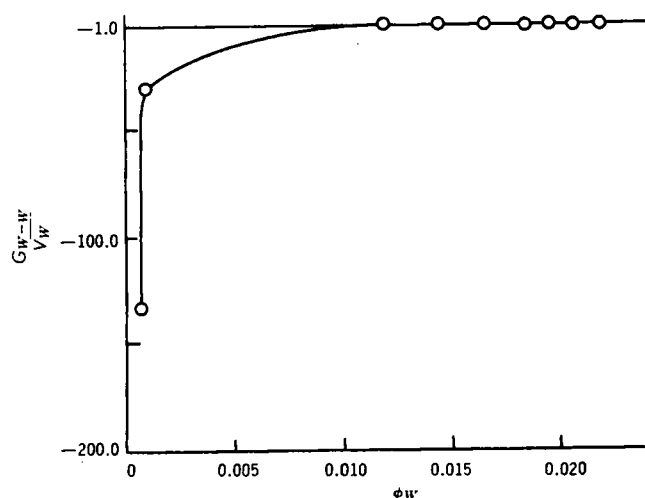


Figure 5—Clustering function for water in ethanol–water–polyurethane system at 25° .

Table V—Clustering Functions for Ethanol in Ethanol–Water–Polyurethane System at $25 \pm 0.1^\circ$

Initial Concentration of Aqueous Ethanol Solutions		a_E	ϕ_E	$\frac{G_{E-E}}{V_E}$	$\frac{\phi_E G_{E-E}}{V_E}$	$1 + \frac{\phi_E G_{E-E}}{V_E}$
wt. %	moles/l.					
3.16	0.682	0.13	0.0066	+57.3	0.4	1.4
16.2	3.41	0.31	0.0468	+13.5	0.7	1.7
33.2	6.92	0.48	0.123	+12.3	1.7	2.5
43.4	8.71	0.51	0.163	-1.0	0.2	0.8
52.1	10.2	0.53	0.192	-23.0	—	—
73.4	13.6	0.68	0.241	-23.0	—	—
100.0	17.0	1.00	0.271	-60.0	—	—

Table VI—Clustering Functions for Water in Ethanol–Water–Polyurethane System at $25 \pm 0.1^\circ$

Concentration of Aqueous Ethanol Solutions		a_W	ϕ_W	$\frac{G_{W-W}}{V_W}$	$\frac{\phi_W G_{W-W}}{V_W}$	$1 + \frac{\phi_W G_{W-W}}{V_W}$
wt. %	moles/l.					
3.16	0.682	0.96	0.0224	-1.0	0.0	1.0
16.2	3.41	0.89	0.0212	-1.0	0.0	1.0
33.2	6.92	0.79	0.0190	-1.0	0.0	1.0
43.4	8.71	0.78	0.0189	-1.0	0.0	1.0
52.1	10.2	0.75	0.0180	-1.0	0.0	1.0
73.4	13.6	0.62	0.0160	-1.0	0.0	1.0
93.4	16.3	0.30	0.0099	-30.1	—	—
96.4	16.6	0.18	0.0074	-133.0	—	—

sorbed in the polyurethane film independent of the amount of ethanol sorbed in the film. It is obvious that the two curves are very close. At higher concentrations of ethanol, the amount of sorption of water estimated by mass spectrometry is higher than that determined by thermal gravimetric analysis. Possibly, ethanol molecules may enhance the sorption of water molecules in the polymer film by breaking the hydrogen bonds in liquid water clusters and carrying more free water molecules into the polymer matrix.

Figure 2 shows the plot of ethanol activity as a function of percent of ethanol in the aqueous phase for the ethanol–water–polyurethane system. The activity of ethanol is directly proportional to the concentration of ethanol in the liquid phase. However, the activity of water, although not shown here, was computed from the partial vapor pressure of water in the ethanol–water binary system at 25.0° obtained from the literature (12).

Table IV lists some volume fraction data for the ethanol–water–polyurethane system at 25.0° . In general, the volume fraction of ethanol in the polyurethane film, ϕ_E , increases with an increasing concentration of ethanol in solution. The volume fraction of the polymer film, ϕ_p , shows opposite behavior, while ϕ_W for water does not vary significantly.

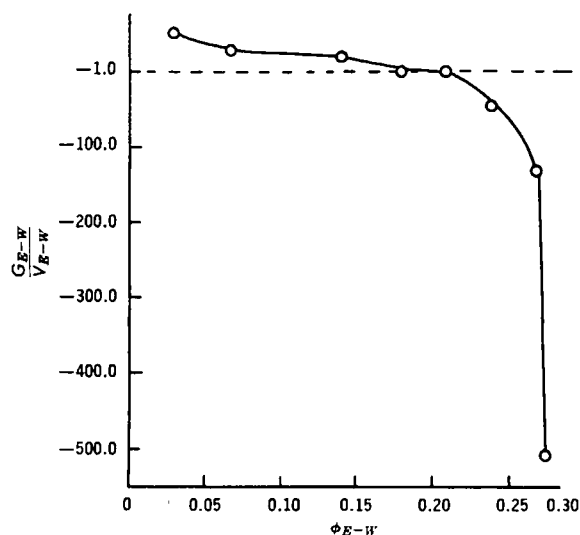


Figure 6—Clustering function for ethanol and water mixtures in ethanol–water–polyurethane system at 25° .

A typical plot of ethanol activity, a_E , versus volume fraction of ethanol, ϕ_E , is shown in Fig. 3. From this sorption isotherm, the clustering functions for ethanol molecules in the polyurethane film were evaluated. Similar treatments were performed for the evaluation of clustering functions of water molecules and of ethanol–water molecules in the polymer matrix.

The clustering function for ethanol molecules in the polyurethane film is plotted in Fig. 4 (numerical values are listed in Table V). It is obvious that there is a greater tendency for ethanol molecules (compared to water molecules) to cluster together at the smaller volume fractions of sorption (or at the lower concentrations or activities of ethanol, as can be seen from Table V), then pass through ideal behavior at a volume fraction of 0.16 (or activity of 0.51), and finally demonstrate localized sorption on specific polyurethane segment sites. The mean number of clustering is from 0.4 to 1.5, whereas the mean cluster size is about 1.4–2.5 molecules.

Figure 5 shows the clustering function for water molecules. Water molecules would not cluster together in this particular system. As can also be seen from Table VI, water molecules show a wide range of ideal sorption behavior from a low to a high ethanol concentration of 73.4% by weight and then show a localized sorption phenomenon.

By assuming that ethanol and water molecules may also cluster together in this particular system, the clustering functions for ethanol–water molecules were evaluated (Fig. 6 and Table VII). However, the activity of ethanol–water molecules, a_{E-W} , was taken from the square root of the product of the activities of ethanol and water molecules, and additive properties of the volume fractions were assumed. In general, the clustering phenomena for ethanol–water molecules are very similar to those of ethanol molecules themselves, except that the ideal behavior of ethanol–water molecules shifts from 43.4 to 52.1% by weight. The mean cluster number ranges from 1.5 to 2.9, and the mean cluster size ranges from 2.5 to 3.9 molecules.

In summary, the Zimm–Lundberg clustering theory was applied to the treatment of sorption data of the ethanol–water–polyurethane system in the liquid phase at $25 \pm 0.1^\circ$. The results indicate that there is a greater tendency for ethanol molecules to cluster together than for water molecules. Water molecules in this particular system do not appear to cluster together, even though the evaluation of clustering functions for water molecules is only an approximation approach. The tendency for ethanol–water molecules to cluster together is high.

The mechanism or sorption behavior of ethanol and water molecules in the polyurethane film may be interpreted as follows. At the lower ethanol concentration or activity, the first ethanol or water

Table VII—Clustering Functions for Ethanol–Water in Ethanol–Water–Polyurethane System at $25 \pm 0.1^\circ$

Concentration of Aqueous Ethanol Solutions		a_{E-W}	ϕ_{E-W}	$\frac{G_{E-W}}{V_{E-W}}$	$\frac{\phi_{E-W}G_{E-W}}{V_{E-W}}$	$1 + \frac{\phi_{E-W}G_{E-W}}{V_{E-W}}$
wt. %	moles/l.					
3.16	0.682	0.354	0.0287	+51.9	1.5	2.5
16.2	3.41	0.525	0.0676	+30.0	2.0	3.0
33.2	6.92	0.616	0.142	+20.5	2.9	3.9
43.4	8.71	0.631	0.182	-1.0	-0.2	0.8
52.1	10.2	0.631	0.210	-1.0	-0.2	0.8
62.7	12.1	0.647	0.238	-46.7	—	—
85.2	15.2	0.566	0.270	-132.4	—	—
89.3	15.7	0.505	0.273	-509.9	—	—

molecule enters the polyurethane chain structure, loosens the structure, and makes it easier for subsequent ethanol or water molecules to enter in the neighborhood of the first one than to go elsewhere; therefore, they cluster together. As the concentration or activity of ethanol increases, the amount of sorption increases. However, because the polyurethane film cannot swell enough for accommodation of excess penetrant molecules, ethanol and water molecules diffuse out from the initial position and become a homogeneously localized sorption phenomenon under the driving forces of concentration or chemical potential gradient. The binding forces for the ethanol–water–polyurethane system are through hydrogen-bond formation between ethanol and/or water molecules and the polar groups (such as urethane groups) of polyurethane segments. However, the hydrophobic properties of ethanol molecules play an important role in the interpretation of stronger affinity for ethanol molecules toward the polyurethane chain structure. The formation of water clusters (13) between liquid water molecules in the liquid phase gives a consistent explanation for the lower content of water sorbed in the polyurethane film.

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