

## Sorption and Diffusion of Water in a Rubbery Polyurethane

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### Synopsis

Unsteady-state water sorption measurements have been carried out over the temperature range 27–40°C. on a polyurethane elastomer composed of MDI, 1,4-butanediol, and polybutylene adipate (MW 2000) in the mole ratios 3.2:2:1. The sorption isotherm is concave upward above an activity of 0.6, reaching a saturation water concentration of 1.6 g./100 cc., the heat of mixing is zero, and the diffusion constant decreases slowly and linearly with increasing water concentration. The overall behavior is attributed to the immobilization of sorbed water in clusters. Analysis of the sorption process in terms of the cluster integral reveals that the interaction of water with specific polymer sites occurs at the lowest concentrations but that clustering dominates for water activities greater than 0.45. Since the activation energy for diffusion decreases with increasing water concentration, from 11,000 cal./mole at zero concentration to about half that value at saturation, plasticization of the polymer also affects the transport process.

The results presented here, taken from research in progress, serve to clarify the nature of the water transport process in a polyester polyurethane and lend additional support and definition to several features of the emerging picture of water sorption and diffusion in relatively unswollen polymers. Moreover, results on polyurethanes have some added practical interest, in that such polymers belong to the small group of relatively unswollen polymers with the highest water vapor permeability, generally with values exceeding 500 g.-mil/m.<sup>2</sup>-24 hr. [ $1 \times 10^{-6}$  cm.<sup>3</sup>(STP)-cm./cm.<sup>2</sup>-sec.-cm. Hg] at a relative humidity difference of 90%.

The unsteady-state sorption measurements were made with a Cahn electrobalance, part of a standard vacuum system for such measurements, with all components housed in a thermostated cabinet. The polyester-based polyurethane used was a laboratory-grade extrusion-molded sample provided by the Mobay Chemical Company. It was composed of MDI, 1,4-butanediol, and poly(butylene adipate) (mol. wt. 2,000) in the mole

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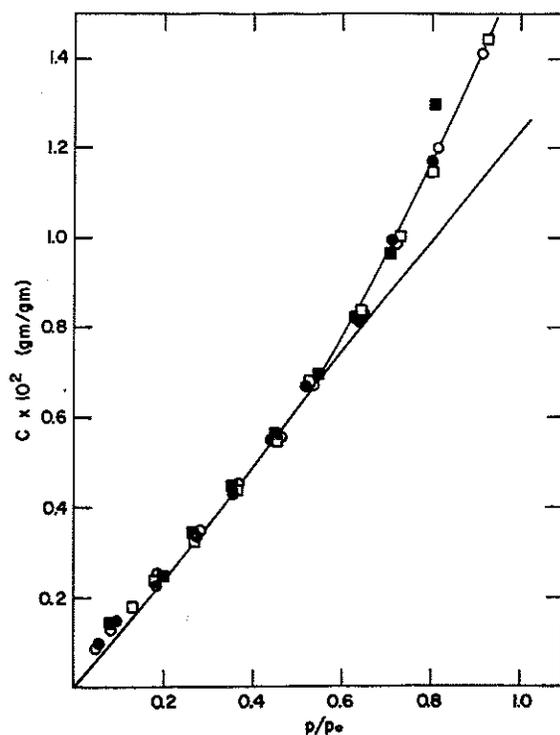


Fig. 1. Sorption isotherm for water vapor; concentration  $c$  against partial pressure  $p/p_0$ : (○) sorption; (●) desorption.

ratios 3.2:2.0:1.0. All the data reported here were obtained on a sample of 12.4 mil thickness.

The sorption isotherm obtained at 40°C. is represented in Figure 1 as a plot of concentration against partial pressure ( $p/p_0$ ). There is no evident hysteresis between the concentrations determined on the sorption cycle (open points) and desorption cycle (filled points) and the data from the two runs are coincident. The isotherm follows (approximately) Henry's law,  $c = kp$ , to a partial pressure of 0.4–0.5 and then curves upward in a manner that is common to systems with strong sorbent-sorbate interactions. Of equal importance is the observation that the sorption isotherms obtained over the temperature range 27–40°C., although not illustrated here, are essentially superimposable, indicating that the heat of mixing is virtually zero for water in this polyurethane.

The diffusion constant  $D$  was determined from the initial slope of  $m_t/m_\infty$  versus  $t^{1/2}$ , where  $m_t$  and  $m_\infty$  are the weight increases at time  $t$  and at equilibrium.<sup>1</sup> Values for  $D$  are shown in Figure 2, plotted against the initial water concentration  $c$  in the film corresponding to each pressure increment. There is apparently a marked inverse dependence of  $D$  on  $c$  and, in fact,  $D$  decreases by a factor of one and a half or more over the total concentration range. The precision of the data do not allow accurate

curve fitting but it appears that  $D$  versus  $c$  curves determined at several temperatures ranging from 30 to 40°C. tend to converge at higher water concentrations. Correspondingly, the apparent activation energies,  $E_D = -(R d \ln D)/d(1/T)$ , estimated from a straight line fit to the  $D$  versus  $c$  curves, decrease from about 11,000 cal./mole at zero water concentration to about 7,000 cal./mole at 1.2% water.

Further analysis of the sorption behavior can be made in terms of the clustering integral  $G_{11}$  of Zimm and Lundberg:<sup>2</sup>

$$G_{11}/v_1 = -\phi_2 [\partial(a_1/\phi_1)/\partial a_1]_{P,T} - 1$$

where  $a_1$ ,  $\phi_1$ ,  $v_1$  are respectively the activity, volume fraction, and molar volume of type I (solvent) molecules. The quantity  $\phi_1 G_{11}/v_1$  expresses the clustering tendency as the mean number of solvent molecules in the neighborhood of a given solvent molecule in excess of that corresponding to the average solvent concentration.

The quantity  $a_1/\phi_1$  which appears in the cluster function has been calculated from the smoothed sorption isotherm and is plotted as the dashed curve in Figure 3. It goes through a maximum at a  $\phi_1$  value of about 0.005. It is worth noting that the inverse of this quantity, namely  $\phi_1/a_1$ , is essentially the Henry's law solubility constant. The contrast between the behavior shown in Figure 3 and the apparent invariance of  $k$  over the initial range of activities in Figure 1 is merely an illustration of the fact that any variation in  $k$  at low concentrations is suppressed when the data is plotted on a concentration ordinate.

The clustering function,  $G_{11}/v_1$ , shown by the solid curve, increases from strongly negative values at very low  $\phi_1$  to rather large positive values near the saturation water concentration. A partial interpretation of this behavior can be made in terms of models examined by Zimm and Lundberg. For Langmuir type absorption  $G_{11}/v_1$  is negative, and this suggests that the negative values of  $G_{11}/v_1$  at low concentrations arise from the interaction of water with specific polymer sites. Ideal solution behavior corresponds to  $G_{11}/v_1 = -1$ ; therefore, the increasingly positive values above  $\phi_1 = 0.0055$ , corresponding to  $a_1 = 0.3$ , represent an increasing degree of clustering, leading to a mean concentration in the clusters which is more than 35-fold higher than the average water concentration.

The near zero heat of mixing implies that the interactions of water in the polymer are dominated by penetrant-penetrant contacts. Although this appears consistent with the rather high values of  $G_{11}/v_1$ , the mean cluster size,  $\phi_1 G_{11}/v_1 + 1$ , is only 1.5 molecules of water. However, since the cluster size represents an average over all penetrant species this small value is not incompatible with a process in which entering water molecules above  $\phi_1 = 0.0055$ , the concentration at which  $G_{11}/v_1 = -1$ , are involved almost exclusively in clusters as required by the near zero heat of mixing. It might be noted that the treatment of water clustering in terms of a polymerization model leads to a decreasing fraction of free water with increasing water concentration, leaving only 20% monomeric water at saturation.<sup>3</sup>

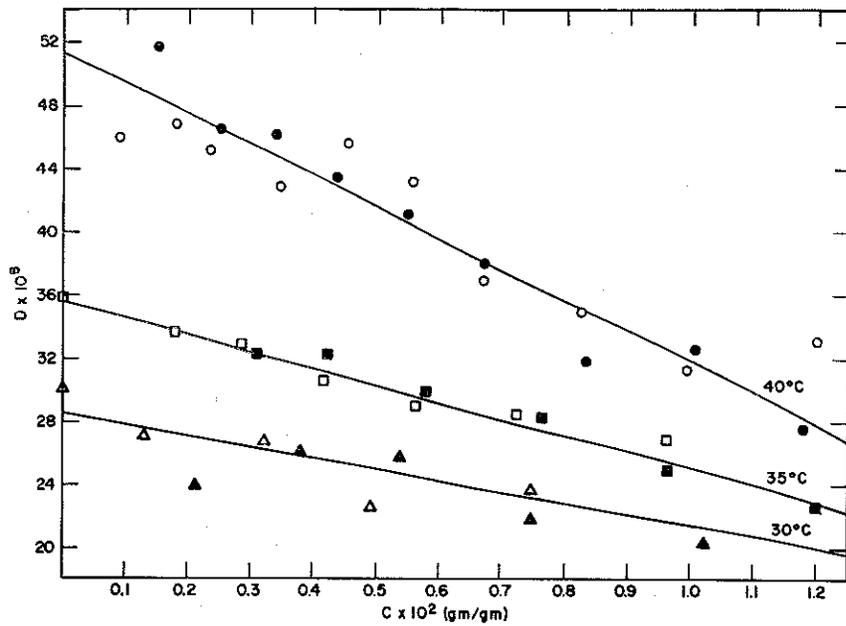


Fig. 2. Dependence of the diffusion constant  $D$  for water vapor on concentration  $c$  in film: (O) sorption; (●) desorption.

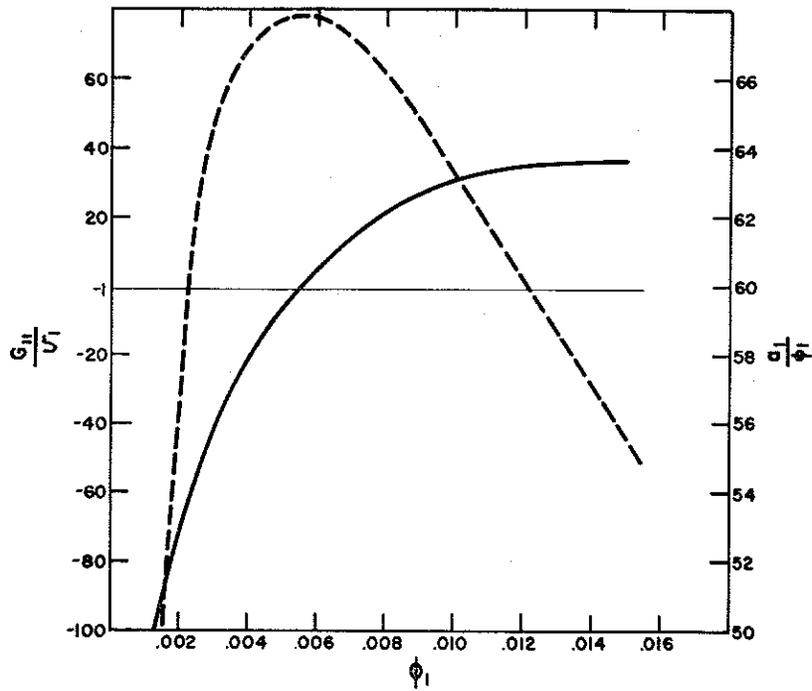


Fig. 3. Plots of (---) ratio of the activity to the volume fraction of water vapor  $a_1/\phi_1$  and (—) the cluster function  $G_{11}/v_1$  as a function of the sorbate volume fraction  $\phi_1$  and activity  $a_1$ .

The decrease in the diffusion constant with increasing water concentration is now commonly attributed to the polymerization of an increasing fraction of water to form clusters of decreased mobility.<sup>3,4</sup> Barrie<sup>3</sup> has treated a simple model for this process based on the assumption that the polymer can be treated as an inert matrix. This provides reasonable agreement with observed behavior of the diffusion coefficient of water in silicone rubber. However, in the polyurethanes there is the additional complication of specific site interactions which play an important role in the overall sorption process and which can also be expected to influence the diffusion behavior. In the present case, an analysis is needed for resolving the competitive processes of site and cluster interactions in terms of appropriately chosen models similar to the dual mode sorption treatment developed by Vieth et al.<sup>5,6</sup>

The several features of the sorption and diffusion behavior in this polyurethane elastomer are similar to the behavior reported for water in a number of other polymers with rather low water solubilities, particularly ethyl cellulose,<sup>7</sup> rubber hydrochloride,<sup>4</sup> silicone rubber,<sup>3</sup> poly(methyl methacrylate),<sup>3</sup> and poly(ethyl methacrylate).<sup>8</sup> Positive deviations from Henry's law behavior occur in all these polymers at higher activities. Although zero heat of mixing is also observed in ethyl cellulose and in poly(ethyl methacrylate) separately above and below its glass transition, silicone rubber has an endothermic heat of mixing.

The decrease in the diffusion constant with increasing water concentration found in the polyurethane elastomer stands in sharp contrast to the usual dependence of the diffusion constant on the concentration of plasticizing organic vapors but is found in every one of the above polymers where such behavior has been studied. In silicone rubber, where the saturation concentration is only 0.1%, an order of magnitude decrease in  $D$  occurs with increasing  $c$ . However, in several polymers with higher water concentration, including ethyl cellulose, poly(methyl methacrylate), as well as the polyurethane studied here, the decrease in  $D$  with  $c$  is limited to a factor of about two. This does not necessarily indicate that clustering is more limited in the fraction of otherwise unbound water. It could also be the result of plasticization by water vapor as, for example, suggested by the observed decrease in activation energy for the diffusion constant of water in the polyurethane sample.

Evidently a complete understanding of the process of water transport requires the measurement of both sorption and diffusion behavior carried out both over a range of concentration and temperature with, perhaps, additional supporting data on plasticization from mechanical measurements.

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