

SHORT COMMUNICATIONS

## Sorption of Alcohol Vapors in a Disubstituted Polyacetylene

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Nonporous and glassy polymer membranes usually show low permeability in gas transport. Poly[1-(trimethylsilyl)-1-propyne] (P(TMSP)), one of the disubstituted polyacetylenes previously synthesized by us,<sup>1</sup> is in the glassy state at room temperature. Preliminary studies have revealed that the P(TMSP) membrane shows exceptionally high permeability for gases<sup>2</sup> and that the permeability decreases with time being kept under vacuum.<sup>3</sup> It is also reported that the membrane show excellent permselectivity for ethanol in the pervaporation of ethanol-water liquid mixtures.<sup>4</sup> In this study the sorption behavior of alcohol vapors in the P(TMSP) membrane is investigated.

The sample membrane about  $1.8 \times 10^{-2}$  cm thick was prepared at 25°C by slow evaporation of benzene from a 1% solution cast on a mercury surface. The differential sorption and desorption experiments were carried out using a sorption apparatus equipped with an electromagnetic microbalance (Model GAB-1, Chyo Balance Corp.) at 25°C. Vapors of methanol, ethanol, and 2-propanol were used as penetrants. The experiments were made for 8 to 10 successive pressure intervals in the range from zero to about 80% of respective saturated vapor pressures.

Figure 1 shows the sorption isotherms of the alcohol vapors. Also the preliminary data for acetone vapor are included in the figure. The characteristic feature of the isotherms for the

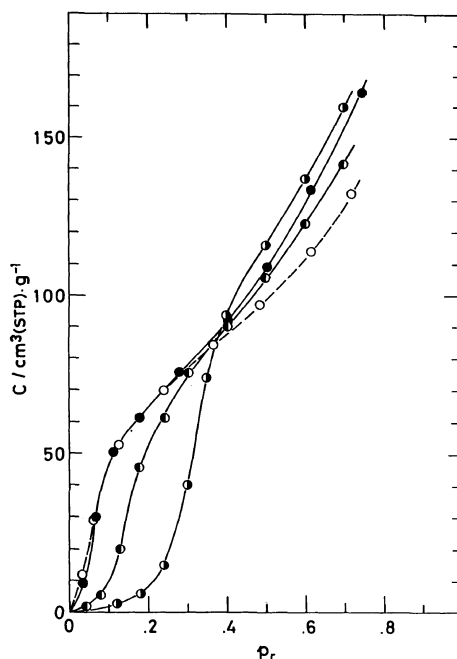


Figure 1. Sorption isotherms of penetrant vapors in P(TMSP) at 25°C. (○), methanol; (●), ethanol; (●), 2-propanol; (○), acetone.

alcohols is that each of them has two inflection points. In the case of methanol, for example, the isotherm is convex to the pressure axis in the pressure range  $0 < p_r < 0.3$  and  $0.5 < p_r$ , and is concave in the range  $0.3 < p_r < 0.5$ . Here  $p_r$  is defined by the ratio of vapor pressure to its saturated value. For acetone, however, the existence of the first inflexion point is less evident.

In many cases, the sorption behavior of gases in glassy polymers has been explained in terms of the dual-mode sorption model.<sup>5</sup> In the present systems, however, this model seems not to be applied successfully. The isotherms in very low pressure range, *e.g.*, for methanol  $p_r < 0.3$ , are convex to the pressure axis, while the dual-mode model predicts the opposite curvature in the pressure range. The similar type of isotherms to those in Figure 1 has been reported for the adsorption of methanol on graphitized carbon black,<sup>6</sup> but no explanation has been given as yet.

To explain the complex shape of the isotherms obtained another treatment should be needed. We here assume that the sorption occurs in two different ways, *i.e.*, adsorption on the external and internal polymer surfaces and dissolution into the polymer network. Then the equilibrium concentration  $C$  can be expressed as

$$C = C_A + C_S \quad (1)$$

where  $C_A$  and  $C_S$  denote the concentration sorbed by adsorption and dissolution mechanisms, respectively.

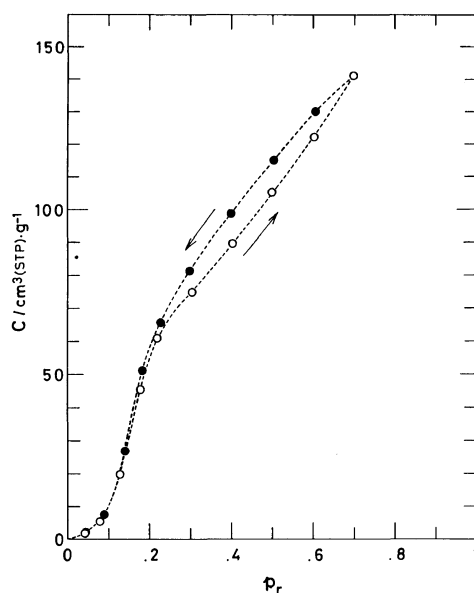
The scanning electron micrographs (SEM) of the surface and freeze fracture of the sample have indicated the rough membrane surface and a lot of voids of cylindrical shape inside the sample. Also, an adsorption experiment of nitrogen at liquid nitrogen temperature has revealed that the membrane has a large specific surface area, about  $550 \text{ m}^2 \text{ g}^{-1}$ . These are consistent with the relatively low bulk density, less than  $0.75 \text{ g cm}^{-3}$ . The details of the SEM observation and the adsorption experiment

will be presented in a forthcoming article. From these observations, the assumption may be justified that a considerable portion of the sorbed molecules are actually adsorbed on the internal and external polymer surfaces.

In addition, for penetrants such as alcohols, lateral interaction (penetrant-penetrant interaction) must be taken into account. Several theories show that the isotherms for monolayer adsorption incorporated with lateral interaction should have one inflection point. According to the equation derived theoretically by Fowler,<sup>7</sup> the adsorbed concentration  $C_A$  may be written as

$$C_A = C'_A \theta, \quad p_r = \frac{\theta}{(1-\theta)K} \exp(-k\theta) \quad (2)$$

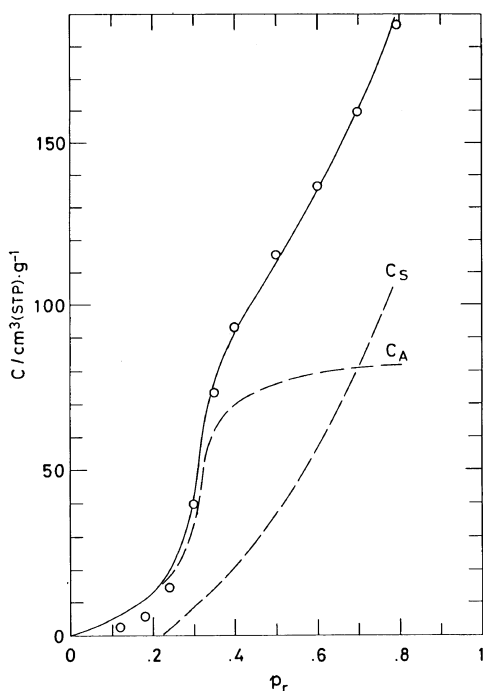
Here  $\theta$  denotes the degree of coverage in monolayer adsorption sites, and  $C'_A$ ,  $K$ , and  $k$  are parameters. Analogous to the Langmuir-type adsorption isotherms,  $C'_A$  is related to the saturated population of monolayer adsorption sites, and  $K$  to affinity of adsorptive molecules to adsorbent. The  $k$  is a measure of lateral



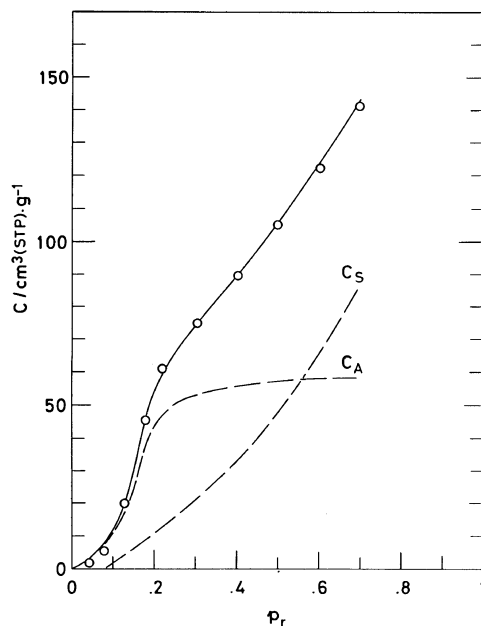
**Figure 2.** Sorption and desorption isotherms of ethanol in P(TMSP) at 25°C. (○), sorption; (●), desorption. The dotted lines are experimental.

interaction energy.

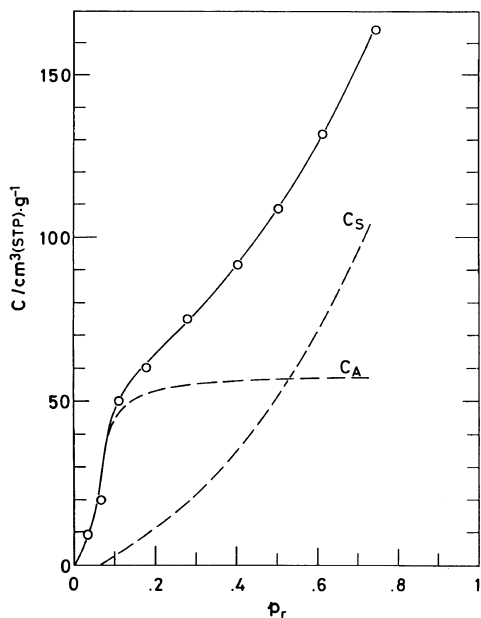
When the P(TMSP) membrane is leached in the alcohols, it swells or at least softens. Thus the alcohols are thought to be highly soluble to the P(TMSP) membrane. The dissolution mechanism of the alcohol vapors in P(TMSP) matrix may be considered to be the same as that in ordinary amorphous polymers. Figure 2 shows the sorption and desorption isotherms of ethanol in P(TMSP). There exists a certain kind of sorption-desorption hysteresis in the pressure range  $p_r > 0.1$ . On the other hand, two isotherms coincide with each other in the limited pressure range near the origin. This indicates that no effective loosening of the polymer network occurs when  $p_r < 0.1$  for ethanol. Based on these facts, we express the dissolved concentration  $C_S$  using the solubility coefficient which has exponential dependence on the excess pressure over a threshold  $p_D$ . The  $p_D$  represents a relative



**Figure 3.** Calculated isotherm curve for methanol. The parameters used are:  $C'_A = 88.9 \text{ cm}^3 \text{ (STP) g}^{-1}$ ;  $K = 0.50$ ;  $k = 3.70$ ;  $S_0 = 94.5 \text{ cm}^3 \text{ (STP) g}^{-1}$ ;  $\gamma = 1.20$ ;  $p_D = 0.22$ .



**Figure 4.** Calculated isotherm curve for ethanol. The parameters used are:  $C'_A = 61.8 \text{ cm}^3 \text{ (STP) g}^{-1}$ ;  $K = 1.15$ ;  $k = 3.35$ ;  $S_0 = 75.5 \text{ cm}^3 \text{ (STP) g}^{-1}$ ;  $\gamma = 0.98$ ;  $p_D = 0.08$ .



**Figure 5.** Calculated isotherm curve for 2-propanol. The parameters used are:  $C'_A = 58.6 \text{ cm}^3 \text{ (STP) g}^{-1}$ ;  $K = 3.2$ ;  $k = 3.0$ ;  $S_0 = 67.2 \text{ cm}^3 \text{ (STP) g}^{-1}$ ;  $\gamma = 1.25$ ;  $p_D = 0.06$ .

pressure at which the effective dissolution starts. Thus we have

$$C_S = S_0 \exp[\gamma(p_r - p_D)] \cdot (p_r - p_D) \quad (3)$$

$(p_r \geq p_D)$

where  $S_0$ ,  $\gamma$ , and  $p_D$  are parameters. In the region where  $p_r < p_D$ , we simply assume that  $C_S = 0$ . By introducing  $p_D$  the physical meanings of  $S_0$  and  $\gamma$  become more or less different from those in ordinary dissolution process.

Figure 3, 4, and 5 respectively show the calculated isotherm curves for methanol, ethanol, and 2-propanol, which are calculated with the aid of eq 1, 2, and 3. The parameters used are given in the figure captions. The data points are well reproduced in each system. The discrepancy, which can be seen in low pressure range for methanol may be due to an oversimplification of the lateral interaction between penetrant molecules. Among the parameters obtained,  $p_D$  is found to approach zero as the size of alkyl group of alcohols increases. And the values of  $k$  obtained for

the alcohols have reasonable correlation with their cohesive energy densities. More detailed analysis including sorption kinetics study is underway in our laboratory.

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