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Solution and Diffusion of Vapor Mixtures in Polybutadiene

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Solution and diffusion behavior of binary vapor mixtures, comprised of acetone, benzene, and cyclo- and normal-hexane, was studied by the weighing method at 25°C. Each sorption isotherm of these organic vapors was of the type III isotherm of the Brunauer classification, which is convex to the pressure axis. The total concentration of the binary mixtures at absorption equilibrium was higher than the sum of the equilibrium concentration of the component penetrants. Also, the total concentration depended upon the order of serial absorption of the component vapors. In the absorption of cyclo- and normal-hexane, for instance, the total concentration was higher for the case in which cyclo-hexane, more soluble penetrant, was absorbed first and normal-hexane, less soluble penetrant, successively than for the case in which the order of absorption was reversed, and the equilibrium concentration of simultaneous absorption of the vapor mixture was in-between. The results indicate that the thermodynamic interaction between the more soluble penetrant and the polymer is strong enough to modify the initial state of the system prior to the successive absorption of the less soluble penetrant, or the simultaneous absorption. For each absorption kinetics, a break was observed in absorption curve of vapor mixtures. In all systems, the break became noticeable at higher concentrations. By assuming no interference between diffusing penetrant molecules of different species, absorption curves were calculated based upon the free-volume concept. For all systems studied, data points above the break deviated upward a little from the calculated curve.

KEY WORDS: Solution/Diffusion/Vapor   Mixture/Polybutadiene/Acetone/
                     Benzene/cyclo-Hexane/normal-Hexane/Free-volume   Con-
                     cept/

INTRODUCTION

The interest in solution, diffusion, and permeation behavior of gases and gas mixtures in nonporous polymer membranes has been growing year by year with accelerating development of many important practical applications. These applications, which include selectively permeable membranes and various protective coatings, depend wholly or largely on the behavior. In the last four decades, many studies have been made on the behavior of pure gases and vapors in polymers.[1-5] In comparison with the case of pure gases and vapors, however, still a little information is available on characteristics of the solution and the transport behavior of mixtures of gases and vapors in nonporous polymer membranes.[1,3,4,6-8]

In the permeation of mixtures of gases, or vapors, through a nonporous polymer membrane, each gas molecule can independently dissolve and diffuse in the membrane if component gases exhibit very low solubilities in the polymer. The solution and transport characteristics of the gas mixture are then predicted from data of the behavior with pure gases.[1,3,6] When a gas mixture includes more soluble component(s), however, the solution and transport behavior of a component is affected by the

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presence of more soluble component(s). Thus it is anticipated that the behavior of the gas mixture is not simply correlated with that of pure component gases.

If a penetrant-polymer system concerned is in the glassy state, transport behavior of a gas mixture is usually analyzed by the dual-mode transport, or mobility, model. On the other hand, the transport behavior of a system of gas mixture and rubbery polymer is interpreted in terms of the free-volume model. These models respectively explain well the permeation behavior of gas mixtures through nonporous polymer membrane in the glassy and the rubbery regions at relatively low penetrant concentrations.[3,4,8] However, the permeation behavior in the region of higher penetrant concentrations has not been studied, both experimentally and theoretically, yet.

In this paper we will describe the solution and diffusion behavior of vapor mixtures in polybutadiene sheet. The vapor mixtures comprise soluble penetrants in the polymer. The objective of the present study is to clarify characteristic features of solution and diffusion behavior of binary mixtures of soluble vapors in rubbery polymer membrane. The observed absorption curves of vapor mixtures will be compared with calculated curves based upon the free-volume concept.

EXPERIMENTAL

Materials

Sheets of polybutadiene (PB), BR02LL Japan Synthetic Rubber Company, were used in the present study. Contents of cis-1, 4, trans-1, 4, and 1, 2-vinyl isomers of the PB sample, which were determined by the infrared absorption method, are 93, 3, and 4%, respectively. To facilitate absorption measurements by the weighing method, few crosslikages were introduced in the PB sample. A crosslinking agent dicumyl peroxide was added to the PB sample by 0.4 wt%, and mixing was made in a roller mill at 50°C. The PB sheet was then compressed at 160°C for 20 minutes. The PB sheets of 1.0-1.1 mm thick were used in measurements.

Acetone, benzene, and cyclo- and normal-hexane were used as the organic penetrants. These penetrants of G. R. grade were used without further purification.

Method

Solution and diffusion behavior of pure vapors and vapor mixtures was studied by the weighing method at 25°C. The apparatus used for absorption measurements is shown in Fig. 1. A sheet of slightly crosslinked PB is suspended from a calibrated quartz spring, QS, in an evacuated sample chamber, SC. Each organic liquid in a vapor-source tube, VS1 or VS2, is outgassed by successive freezings, pumpings, and thawings. Vapor of the organic penetrant in question is then admitted into the chamber at a pressure p. The pressure is read with a Baratron® pressure transducer (Type 221A, MKS), PT, or with a mercury manometer, MM. A large vapor reservoir, R, is attached to the system so that the absorption of the vapor by the polymer sheet do not cause a measurable change in the pressure. The increase in mass of the sheet due to absorption of the vapor is then measured as a function of time by observing the extension of the spring through a cathetometer, CM. The sample chamber and the vapor reservoir are
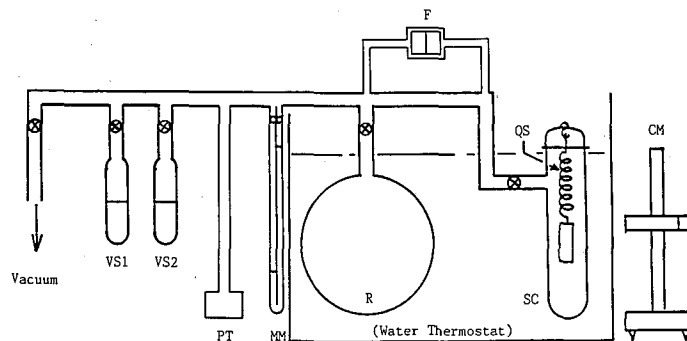
Fig. 1. The apparatus for measuring absorption of binary vapor mixtures.

immersed in a water bath which is controlled to $\pm0.1°C$. The unfavorable condensation of vapors on the inner wall of the glass tubing line is avoided by the function of ribbon heater wound on the glass tubing. Mixing of the binary mixture of vapors is effected by the rotation of a four-bladed glass fan, F, situated in the limb of the glass tubing line. The fan is well operated by a magnetic stirrer.

　　Absorption measurements with a binary vapor mixture A/B were performed in three different ways. First, vapor A at a certain pressure was introduced in the system and the absorption kinetics of the vapor was measured. After having been attained absorption equilibrium of vapor A in the polymer, vapor B of a given pressure was introduced in the penetrant-polymer system and absorption measurements were made successively. In the second manner, the order of the successive absorption of the component vapor was reversed: that is, vapor B was absorbed first by the polymer and the absorption of vapor A followed. The third procedure was the simultaneous absorption of the vapor mixture A/B. Vapors A and B at respectively given pressures, which had been mixed well by the glass fan, were introduced into the sample chamber simultaneously and the increase of the weight of the polymer sheet was observed. All measurements were performed at 25°C.

RESULTS AND DISCUSSION

Sorption Isotherms

　　Figure 2 shows the sorption isotherms of pure organic vapors in the slightly crosslinked PB sheet at 25°C. C is the concentration of organic penetrant absorbed by the polymer at equilibrium and p, p_0 are the pressure and the saturated pressure of each penetrant, respectively. Benzene is the most soluble and acetone is the least soluble penetrannt in PB. Among two hexanes cyclo-compound is more soluble. All sorption isotherms are convex to the pressure axis and are classified into the type III isotherm according to the Brunauer classification.[9]

Successive and Simultaneous Absorption Behavior

　　Sorption isotherms of benzene/n-hexane mixtures in the PB sample at 25°C are shown in Fig. 3. This mixture is a combination of the most soluble and the second least
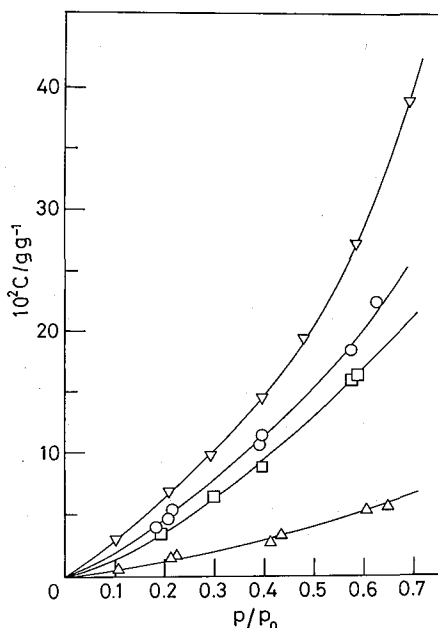
Fig. 2. Sorption isotherms of the systems of benzene (∇), cyclo-hexane ($\bigcirc$), normal-hexane ($\square$), and acetone ($\triangle$) and the slightly crosslinked PB sheet at 25°C.
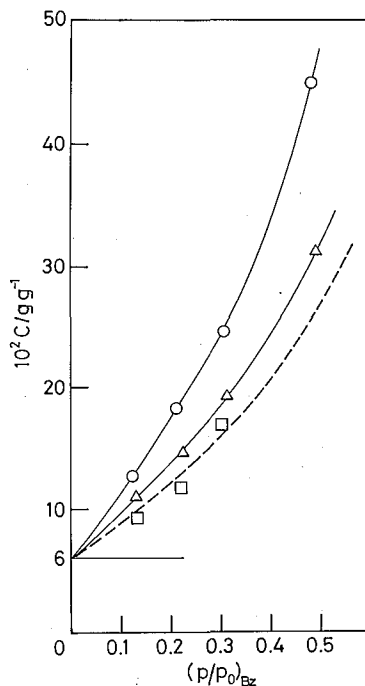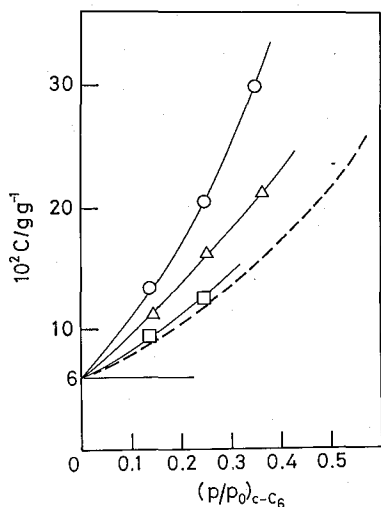
Fig. 3. Sorption isotherms of the system of benzene/normal-hexane mixtures and the slightly crosslinked PB at 25°C and at $p=4.85$ cmHg of n-hexane.
Absorption runs were made in three ways: benzene first ($\bigcirc$), n-hexane first ($\square$), and simultaneously ($\triangle$). A dashed line was calculated by assuming simple additivity in equilibrium concentration of the penetrants.

soluble penetrants. This isotherms represent the total amount of the penetrants absorbed in the polymer as a funnction of the relative pressure of benzene with keeping the pressure of n-hexane constant. A horizontal line drawn at a value of C about 6×10^{-2} g/g represents the amount of n-hexane absorbed in the measurement with pure vapor at a constant pressure p of 4.85 cmHg ($p/p_o=0.31$). A dashed line was calculated by assuming simple additivity for the amount of the two penetrants in the polymer at absorption equilibrium.

The plots for the serial absorption in which more soluble penetrant benzene was absorbed first and less soluble penetrant n-hexane successively, represented by circles, locate far above the calculated dashed line. The results of the measurements in which the order of absorption of the two penetrants was reversed, represented by squares, are almost on the dashed line. The data points of the simultaneous absorption, represented by triangles, are intermediate between the plots for the two serial absorption experiments. The increase of the equilibrium concentration of the vapor mixture may suggest that the nature of the polymer sheet would be modified by the prior absorption

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n-hexane is more soluble than acetone in PB, and the data points obtained from measurements in which the absorption of n-hexane was made first are above the dashed line which was calculated by assuming simple additivity in penetrant concetrations at absorption equilibrium. The plots for measurements in which the order of absorption was reversed and those for the simultaneous absorption are slightly below the calculated curve.

From the results shown in Figs. 3, 4, and 5, the following conclusion may be drawn. The equilibrium concentrations of the vapor mixture in the PB sheet, which are obtained from absorption of less soluble penetrant followed by that of more soluble one, are higher than the concentrations calculated by assuming simple additivity in the amount of the penetrants at absorption equilibrium. While, values of the eqilibrium concentration obtained from measurements in which the order of absorption of the penetrants is reversed are almost the same as the calculated values.

In order to obtain knowledge about a mechanism underlying the behavior observed, the sorption isotherms were analyzed in terms of the polymer solution theory developed by Flory and Huggins,[10] and the thermodynamic interaction parameter χ of various penetrant-polymer combinations were evaluated. However, the values of χ and their dependence on concentration did not give any suggestion for the interpretation of the observed behavior for vapor mixtures. The sorption isotherms were also analyzed by employing the method of clustering function.[11] The concentration dependence of the clustering function for the respective systems did not differ much from one another, and an information which improves our understandings of the experimental results could not also be obtained. The interpretation of the results obtained from the successive and the simultaneous absorption measurements of mixtures of organic vapors is still an open question.
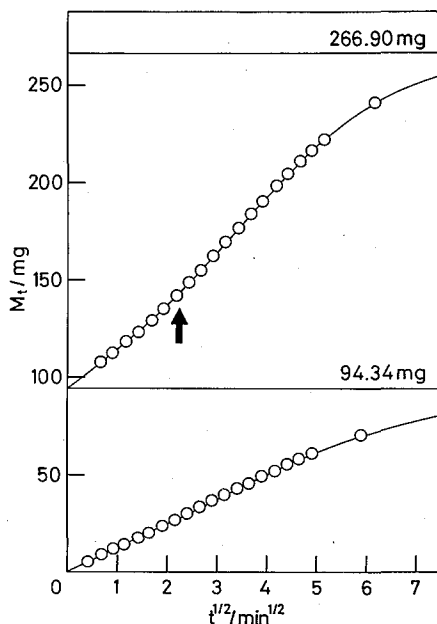

Fig. 6. The successive absorption curves for the system of the cyclo-hexane/normal-hexane mixture and the slightly crosslinked PB at 25°C. Absorption of n-hexane at $p = 4.75$ cmHg followed that of c-hexane at $p = 3.46$ cmHg.

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Absorption Kinetics

Figure 6 shows the results of the successive absorption measurements for the c-hexane/n-hexane mixture in the PB sheet at 25°C. M_t is the mass of vapor absorbed by the polymer sheet at time t. First, c-hexane vapor was absorbed by PB at $p=3.46$ cmHg, and then n-hexane vapor at $p=4.75$ cmHg was absorbed. The lower half of the figure shows the absorption curve for pure c-hexane. As expected the diffusion kinetics is of the Fickian type.

The successive absorption of n-hexane is shown in the upper half of the figure. The initial stage of the absorption is well represented by a straight line. However, after about four minutes the plots start deviating upward. The break at which the deviation starts is indicated by an arrow sign in the figure. After the break the plots is not linear but is concave toward the time axis, and approaches the final equilibrium value. The PB sheet which involves a certain amount of c-hexane at absorption equilibrium is considered to be in the rubbery state. Nevertheless, the diffusion kinetics of n-hexane in the matrix is not of Fickian type. This unexpectable result suggests that the thermodynamic interaction between the more soluble penetrant and the polymer is strong enough to affect the successive absorption kinetics of the less soluble penetrant.

Figure 7 shows the observed and the calculated kinetics of the simultaneous absorption of the c-hexane/n-hexane mixture in the PB sheet at 25°C. Here, M_∞ is the mass of vapor(s) at absorption equilibrium. Circles and a (full) line represent the data points and the calculated curve, respectively.

The curve for the simultaneous absorption was calculated according to the following manner. First, values of the diffusion coefficient D for the system of pure c-hexane and PB and that of pure n-hexane and PB were determined respectively from series of absorption and desorption measurements. The absorption and desorption curves for the system of n-hexane and PB were also of the Fickian type. D was determined from the slope of the initial linear part of the absorption and the desorption curves.[2] For both systems the values of D thus determined were almost independent of concentration. The values of D for the systems of c-hexane - PB and n-hexane - PB at almost
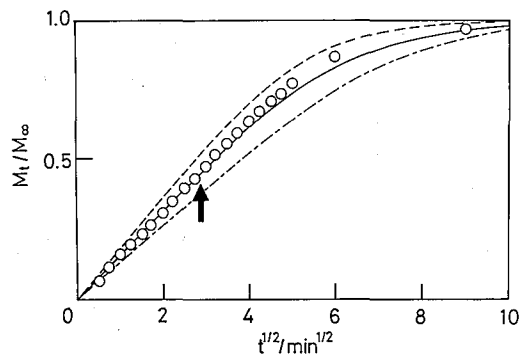

Fig. 7. Simultaneous absorption kinetics of the mixture of cyclo-hexane ($p=2.45$ cmHg) and normal-hexane ($p=4.93$ cmHg) at 25°C. Data points (○) and calculated curves for c-hexane (—·—·—), n-hexane (— — —), and c-hexane/n-hexane mixture (————).
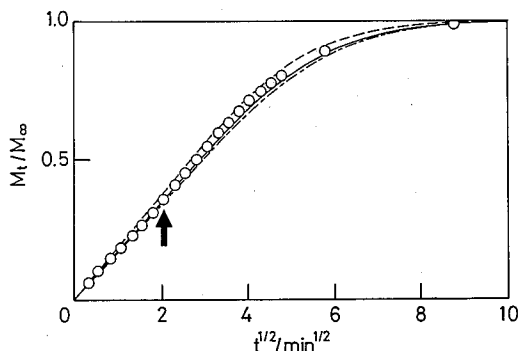
Fig. 8. Simultaneous absorption kinetics of the mixture of benzene ($p = 4.67$ cmHg) and normal-hexane ($p = 4.78$ cmHg) at 25°C. Data points (○) and calculated curves for benzene (—·—), n-hexane (———), and benzene/n-hexane mixture (————).

the same final concentrations as those in the simultaneous absorption were 5.7×10^{-7} and 1.1×10^{-6} cm²s⁻¹, respectively.

Second, curves for absorption of the pure penetrants in PB sheet were calculated using these D values. If D is constant, the relation between M_t and t is given by solving the Fick diffusion equation with proper initial and boundary conditions.[2] That is,

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[- \frac{D(2n+1)^2 \pi^2 t}{X^2} \right] \qquad (1)$$

where X is the thickness of the sheet and n is the integer. In Fig. 7, the calculated curves for absorption of pure c-hexane and n-hexane vapors in PB are represented by a chain and a dashed lines, respectively.

Finally, the curve of the simultaneous absorption of the vapor mixture was calculated by assuming simple additivity in diffusion of the component vapors. That is, based upon the free-volume concept[8] the independence of the diffusion processes of the respective penetrants was assumed in the calculation.

The linear relationship for the data points hold in the region of about 50% of M_∞. In this region the observed results agree well with those of the calculation. For longer times the data points deviate upward a little from the calculated curve. The break at which the deviation starts is indicated by an arrow. It was found that the break became more apparent at higher concentrations.

The simultaneous absorption of the benzene/n-hexane mixture in the PB sheet is shown in Fig. 8. The calculated curve was obtained by using D of 9.0×10^{-7} and 1.1×10^{-6} cm²s⁻¹ for the systems benzene-PB and n-hexane - PB, respectively. Again a break of the plots of data is seen in the region of about 40% of M_∞, and above the break data points deviate upward from the calculated curve. Though it may be envisaged that rather strong thermodynamic interaction among the respective penetrants and the polymer segments is responsible for the appearance of the break in the absorption curve, the real implication of the appearance of the break and the upward deviation from the calculated curve above the break has not been known to us yet. It is considered that further accumulation of data from direct measurements of diffusion of mixtures of organic vapors in the rubbery polymers is needed to get an insight into this

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problem.

ACKNOWLEDGEMENTS

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