

Sorption Equilibrium and Kinetics of Benzene-Poly(n-Hexyl-L-Glutamate) System

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The sorption of benzene on mainly poly(n-hexyl L-glutamate) is examined by the temperature dependence of sorption isotherm and by differential sorption method.

The sorption isotherms at various temperatures are reduced to single isotherm which relates the volume fraction of benzene in the system to relative vapor pressure. This shows the enthalpy for mixing is almost zero. The isotherm is explained by random mixing model of side chain of polypeptide and solvent modified by elastic free energy contribution. Thus, the interaction parameter χ_1 may be almost temperature independent, and be composed mainly of local conformational entropy contribution.

The intrinsic diffusion coefficient obtained by differential sorption method increases slightly up to relative vapor pressure 0.8, which shows the free space of side chain region is relatively large. At higher relative vapor pressure than 0.8, the intrinsic diffusion coefficient decreases with vapor pressure, which reflects the clustering tendency of benzene molecules as is clear in cluster size calculated from sorption isotherm.

1. Introduction

In the previous papers¹⁻³⁾, the authors have elucidated that the sorption and diffusion of small molecular substances in the synthetic polypeptides would take place at the aperture between the helices. Especially, the sorption of benzene by poly(n-alkyl L-glutamates) whose side chain length is larger than butyl ester, is explained by the random mixing model of side chain and solvent modified with elastic free energy contribution.⁴⁾

In the present paper, for the purpose of clarifying the above relation in more detail, the sorption of benzene by poly(n-hexyl L-glutamate) at various temperatures is studied. Furthermore, using the differential sorption method, the concentration dependence of diffusion behavior of benzene is examined.

2. Experimental

Materials

Poly(n-hexyl L-glutamate) (PHeLG) is prepared

by ester exchange reaction of poly(methyl L-glutamate) supplied by Kyowa Hakko K.K. (Japan) whose viscosity-average degree of polymerization is 1100-1200. The method of ester exchange reaction is described elsewhere in detail.²⁾ The membrane of PHeLG is prepared by dissolving the 5% polymer in dichloroethane and by air drying of the thin layer of the above solution on a mercury surface, and finally vacuum drying at 70°C for a day. The thickness is 1.6×10^{-2} cm on an average. The density of the membrane is 1.113 g/cm^3 which is determined by the floatation method using calcium chloride aqueous solution. The membrane has an α -helical structure as is confirmed by infrared absorption spectrum observation. Benzene used as penetrant is of extra pure grade.

Sorption Experiment

The sorption experiment of benzene is performed by the usual gravimetric method using a quartz spiral balance. As for the differential sorption, in order to

cause almost the same successive increase of benzene sorption, vapor pressure of benzene in sorption chamber is increased stepwise, according to the pre-determined sorption isotherm. The temperature dependence of sorption behavior is observed at the range of 10°C to 40°C. The temperature control of the sorption chamber is made by water circulation in a jacket of the chamber within $\pm 0.1^\circ\text{C}$.

3. Results and Discussion

The sorption isotherms of benzene on PHeLG at various temperatures are shown in Fig. 1. Naturally,

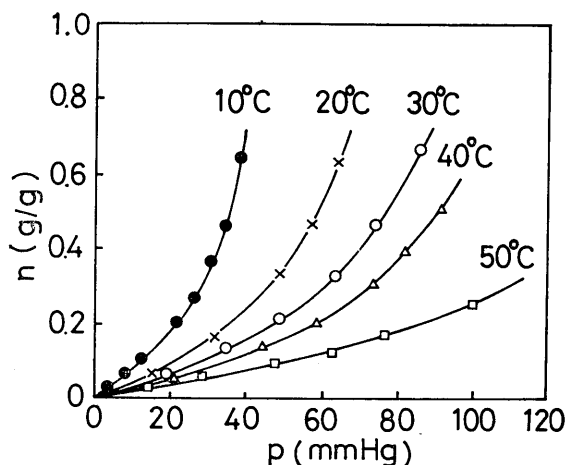


Fig. 1. Sorption isotherms (sorption amount n g/g polymer vs. vapor pressure pmmHg) of benzene on PHeLG at various temperatures

the sorption amount at the same pressure is larger in the case of low temperature than that of higher temperature. All curves are simply concave upwards, which is a characteristic for dissolution (random mixing of solvent and solute) type. The isotherms can be reduced to single curve, when the volume fraction of solvent of the system v_1 is plotted against relative vapor pressure p/p_0 of benzene (Fig. 2). By the way, the same behavior is observed for POcLG as is shown in Fig. 3.

The above result, in which the single reduced sorption isotherm is obtained, clearly shows that the enthalpy of mixing of pure benzene and these polymers is almost zero.

As is described above, the sorption isotherm shows a characteristic for the random mixing of the polymer and solvent. In this case, the portion of the polymer which contributes to the random mixing is

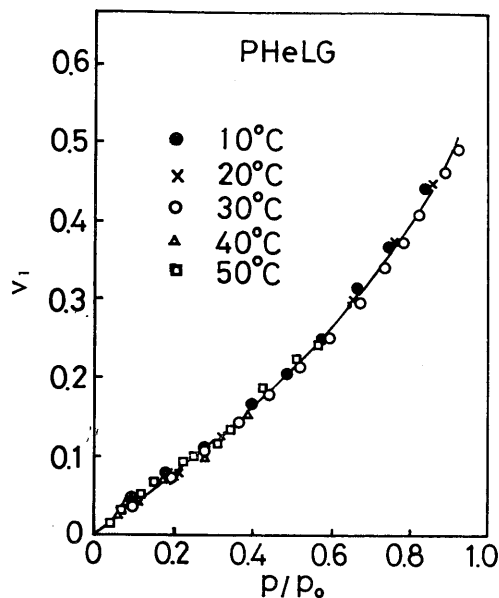


Fig. 2. Reduced sorption isotherm (volume fraction of solvent v_1 vs. relative vapor pressure p/p_0) of benzene on PHeLG

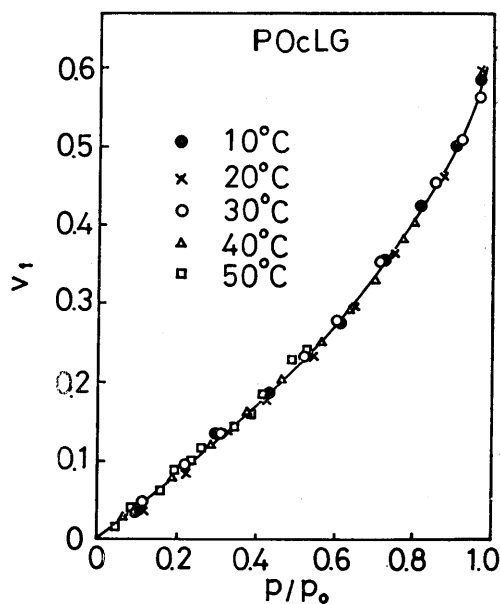


Fig. 3. Reduced sorption isotherm (volume fraction of solvent v_1 vs. relative vapor pressure p/p_0) of benzene on POcLG

the side chain region. As the second order transition temperature of the side chain region for PHeLG is -10°C ,⁵⁾ the flexibility of the side chain at room temperature is sufficient, and the application of the random mixing theory of side chain and solvent of Flory-

Leonard⁶⁾ may be considered to be adequate. However, increase of the experimental sorption amount with increase of relative vapor pressure is smaller than the predicted value of Flory-Leonard model as is shown in the following (Fig. 4). Thus, in this case, also, the elastic free energy change accompany-

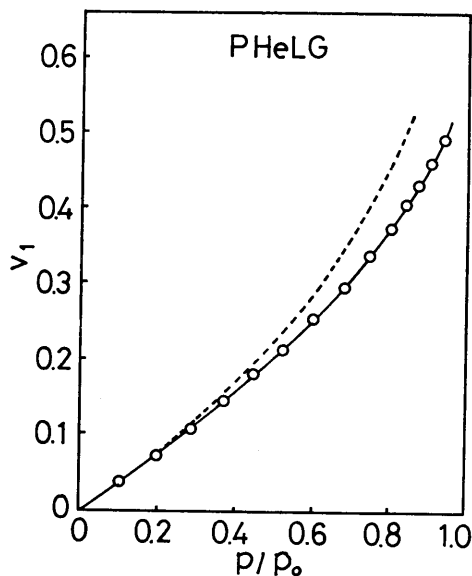


Fig. 4. Observed and calculated sorption isotherms of benzene on PHeLG at 25°C: \circ , observed value; \cdots , calculated curve with Flory-Leonard model with $\chi_1 = -0.24$; $-$, calculated curve by Eq. (1) with $\chi_1 = -0.24$ and $x = 2.7$

ing the extension of side chain occurred by the mixing with solvent should be taken into account. The conclusion is as follows:⁴⁾

$$\ln a_1 = \ln v_1' + v_2' + \chi_1 v_2'^2 + (v_2'^{1/3} - v_2')/x \quad (1)$$

where, v_1' and v_2' are volume fractions of solvent and side chain, respectively, in the solvent-side chain mixed system, $a_1 = p/p_0$ is the activity of benzene, χ_1 is the interaction parameter between polymer (side chain) and solvent, and x is the segment number of the side chain. The forth term of the right hand side of Eq. (1) is the corrected term of elastic free energy. Applying the first to the third term of the right hand side of Eq. (1) (Flory-Leonard model) to the experimental isotherm at 25°C results in the coincidence only at the low pressure range, and the broken line of Fig. 4. The value of χ_1 is obtained to be -0.24 . The difference between broken line and the experimental result in the higher pressure range corresponds

to the elastic term, and the value of x is obtained as 2.7 on average. This value of x is adequate considering the molecular ratio 2.0 and the molecular length ratio 4.1 of side chain to benzene. The solid line of Fig. 4 is the calculated curve based on Eq. (1). By the way, corresponding to Fig. 3, the application of the above treatment to POcLG-benzene system is shown in Fig. 5. In this case, $\chi_1 = -0.36$, and average $x = 3$.

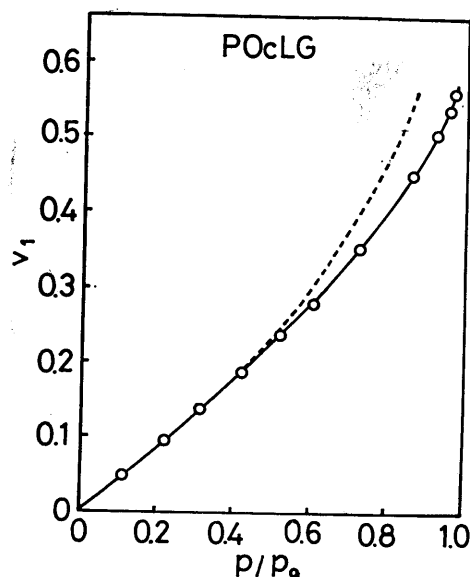


Fig. 5. Observed and calculated sorption isotherms of benzene on POcLG at 25°C: \circ , observed value; \cdots , calculated curve with Flory-Leonard model with $\chi_1 = -0.36$; $-$, calculated curve by Eq. (1) with $\chi_1 = -0.36$ and $x = 3$

The elastic contribution of Eq. (1) is considered to be independent on temperature, because the chemical potential of vapor phase (left hand side) and the elastic chemical potential are both proportional to RT .

The facts that the sorption isotherms at various temperatures are reduced to single curve and that the elastic term should be independent on temperature, would derive the conclusion that the χ_1 value may be almost independent on temperature. As is well known⁷⁾, χ_1 should be considered to be a free energy contribution except the conformational entropy in liquid lattice. Namely, χ_1 is composed of enthalpy change of mixing and the rather local conformational entropy change accompanying with the mixing. The contribution of the latter to χ_1 should be independent

on temperature, because the χ_1 is the ratio of the free energy to temperature. The molecular order of benzene in pure liquid should be relatively high considering the geometry of the molecule. Therefore, it is adequate to consider that the local conformational entropy would increase by mixing.

The differential sorption rate curves (sorption amount n , g/g polymer vs. square root of time $t^{1/2}$, min.^{1/2}) at 25°C for PHeLG-benzene system are shown in Fig. 6, in which the numbers show the vapor pressure of benzene which is increased successively. By the way, as the soluble tendency is significant at high vapor pressure of benzene for POcLG, the film deforms, and quantitative analysis is difficult.

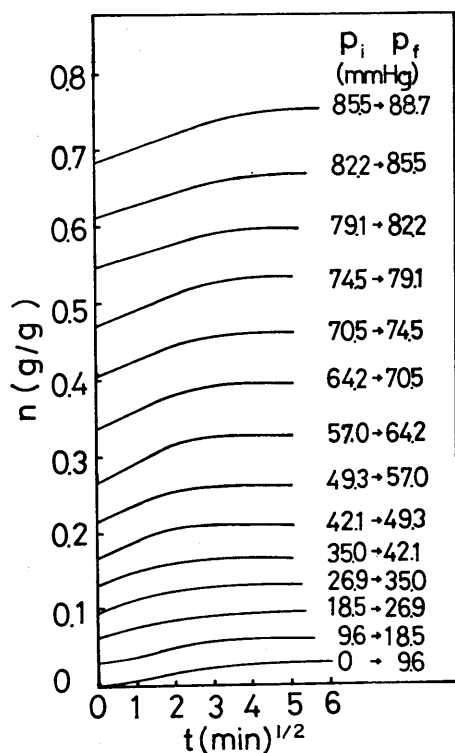


Fig. 6. Differential sorption rate curves (sorption amount n g/g polymer vs. square root of time $t^{1/2}$, min.^{1/2}) of PHeLG-benzene system at 25°C. The number shows the vapor pressure of benzene at the initial and final stages of each successive sorption process.

In Fig. 6, the time required for attaining the sorption equilibrium is relatively short and about 10 minutes. In the low vapor pressure range, the sorption curves are sigmoid shape, and then shows the pseudo-Fickian type⁹⁾ whose characteristic is the ten-

dency of approaching to the equilibrium quite slowly. Above the relative vapor pressure 0.45 (absolute pressure 42 mmHg), the initial straight line portion characteristic to the Fickian sorption appears. Letting $\Delta n(t)$ to be the increase of sorption amount in time t , $\Delta n(\infty)$ to be its equilibrium value, and L to be thickness of membrane, the straight line is represented by the next familiar equation⁹⁾.

$$\frac{\Delta n(t)}{\Delta n(\infty)} = 4 \left(\frac{Dt}{L^2} \right)^{\frac{1}{2}} \left[\pi^{\frac{1}{2}} + \sum_{m=1}^{\infty} (-1)^m \operatorname{ierfc} \left\{ \frac{mL}{(Dt)^{\frac{1}{2}}} \right\} \right] \quad (2)$$

The diffusion coefficient D of the Eq.(2) corresponds to the polymer fixed diffusion coefficient D^p and is obtained directly from the experimental reduced sorption curve, $\Delta n(t)/\Delta n(\infty)$ vs. \sqrt{t}/L relation. The mutual diffusion coefficient D^v and intrinsic diffusion coefficient D are expressed using volume fraction of polymer v_2 as follows:¹⁰⁾

$$D^v = D^p / v_2^2, \quad D = D^p / v_2^3 \quad (3)$$

The D is the coefficient which relates to the molecular motion directly, excluding the bulk flow of the whole system.

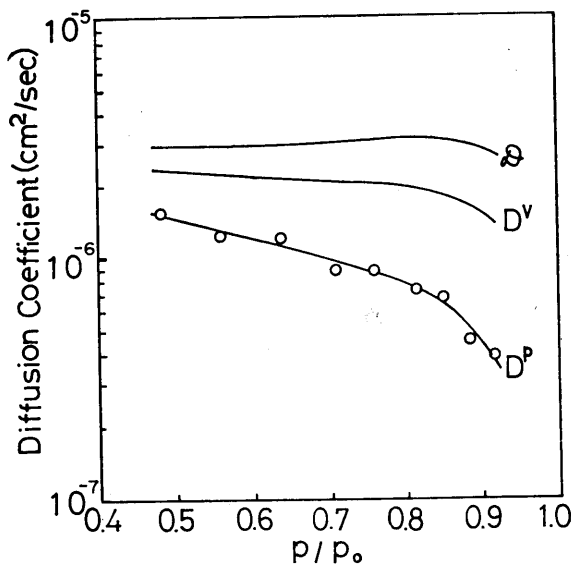


Fig. 7. Polymer-fixed diffusion D^p , mutual diffusion coefficient D^v and intrinsic diffusion coefficient D vs. relative vapor pressure of benzene

D^p , D^v and D are shown in Fig. 7 against relative vapor pressure of the benzene. The D increases slightly up to relative vapor pressure 0.8, and then decreases with increase of vapor pressure. Though

the free volume of the system should increase with solvent sorption generally, the fact that the increase of D with vapor pressure is small, shows that the free space of polymer itself would be relatively large comparing with the usual amorphous polymer.¹¹⁾ Furthermore, the decrease of D in high pressure region may be considered as the result of clustering of benzene molecules. This would be reasonable referring the Cohen-Turnbull's theoretical treatment¹²⁾ about the mobility of molecule, and is adequate considering the geometry of benzene molecule and independence of χ_1 on temperature.

In fact, the cluster size of the benzene in the system clearly shows the above tendency as is shown in Fig. 8. The cluster size is calculated by the following Zimm and Lundberg's equation.¹³⁾

$$\text{Cluster function } G_{11}/\bar{V}_1 = -v_2[\partial(a_1/v_1)/\partial a_1]$$

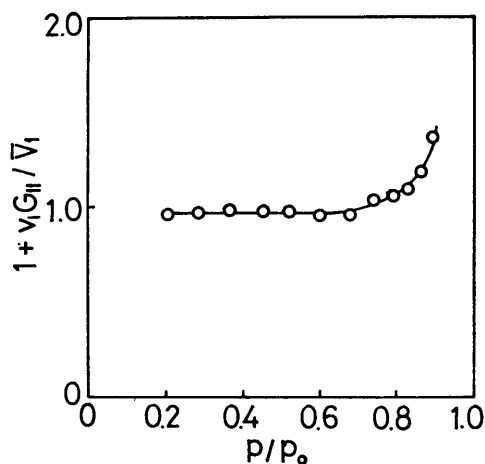


Fig. 8. Cluster size $1 + v_1 G_{11} / \bar{V}_1$ of benzene vs. relative vapor pressure

$$\text{Cluster size} = 1 + v_1 G_{11} / \bar{V}_1 \quad (4)$$

where, \bar{V}_1 is the molar volume of solvent. The clustering tendency is apparent over the relative vapor pressure 0.8, and the cluster size is about 1.5 at relative vapor pressure 0.9.

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