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다분산성 Poly(α-methylstyrene)-Cyclohexane계의 상평형에 관한 연구

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Phase Equilibrium in Multicomponent Poly(α-methylstyrene)-Cyclohexane System

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요 약 : 다분산성 poly(α-methylstyrene)과 cyclohexane으로 되는 quasibinary system에 대하여 중합체의 분자량분포에 따른 critical point의 변화를 조사하므로서 온도와 농도에 따른 interaction parameter χ 및 mutual interaction parameter g를 산출할 수 있는 실험식을 확립하였으며 Flory의 θ-온도도 결정하였다. 음이온 중합으로 얻어진 poly(α-methylstyrene)을 재침전법으로 분별하였다. 분별시료들의 중량평균분자량은 1.13×10^5에서 6.04×10^5 g/mol의 범위였으며 $\overline{M}_w/\overline{M}_n$ 값의 범위는 1.14에서 1.73이었다. 이들 분별시료들의 cloud point는 turbidimeter로 측정하였고 coexistence curve는 분리된 상의 농도를 측정하여 구하였다. 이때 측정된 온도와 농도의 범위는 각각 8.2～27.4 ℃와 0.5～21 wt%이었다. 분리된 두상의 체적비와 cloud point를 결정하고 이들 critical point data를 이용하여 다음과 같은 $g(T,\phi)$ 및 $\chi(T,\phi)$에 관한 실험식을 산출하였다. $g(T,\phi)=0.508+66.00/T+0.223\phi+0.072\phi^2$, $\chi(T,\phi)=0.290+64.56/T+0.302\phi+0.216\phi^2$. 계수 χ_1 및 χ_2(식 6)도 온도 의존성이라고 가정하면 $\chi(T,\phi)$는 다음과 같이 변형되었다. $\chi(T,\phi)=0.377+37.79/T+(-0.567+270.13/T)\phi$. 이들 실험식들로부터 산출된 θ-온도범위는 34.00～34.31℃이었고, 이값은 이미 발표된 값과 잘 일치하였다.

Abstract : The expressions of polymer-solvent interaction parameter χ and the mutual interaction parameter g for the quasibinary system consisting with multicomponent poly(α-methylstyrene) and cyclohexane were formulated as a function of concentration and temperature employing critical point data obtained from the measurements of phase volume ratio. The Flory's theta solution temperature was also evaluated. An effort has been made to observe how the average molar mass and molar mass distribution of the original polymer sample effect to the variation of critical point of the solution system studied. The polymer, synthesized by anionic bulk polymerization, was fractionated by fractional precipitation method to give a series of fractions having values of $\overline{M}_w/\overline{M}_n$ from 1.14 to 1.73 and

mass-average molar mass range of 1.13×10^5 to 6.04×10^5 g/mol. Cloud points are determined by turbidity titrations. Concentration determinations for the phases separated lead to the construction of coexistence curves. Temperature range observed was 8.2~27.4℃ and polymer concentration detected was in the range of 0.5~21% by weight. The critical point data obtained both from the volume ratio of two phases separated and cloud point curve yielded $g(T,\phi)$ and $\chi(T,\phi)$ function as, $g(T,\phi)=0.508+66.00/T+0.223\,\phi+0.072\,\phi^2$, $\chi(T,\phi)=0.290+64.56/T+0.302\,\phi+0.216\,\phi^2$. In case where both the coefficients χ_1 and χ_2 (eq. 6) are assumed to be dependent on the temperature, the $\chi(T,\phi)$ is modified as, $\chi(T,\phi)=0.377+37.79/T+(-0.567+270.13/T)\phi$. The θ-temperature found from these relationships was in the range of 34.00~34.31℃, which was well agreed with the value so far published for the same system.

INTRODUCTION

Since the lattice theory of polymer solution was known,[1,2] many expressions on the Flory-Huggins interaction parameter χ, characteristic of the interaction energy of polymer segments with solvents, have been proposed and tested against experimental results.[3~6] But few of them have achieved more than a limited success in quantitative prediction of observed phase relationships even for a quasibinary polymer solution. The difficulty is considered to be arised primarily from the fact that the interaction parameter for polymer solution depends on the molar mass of polymer molecule as well as the concentration and temperature, and hence χ for polymer solution should depend on the molar mass distribution of the polymer solute.

As many researchers have pointed out, the disparity of threshold temperature of a quasibinary solution system with critical point is entirely attributable to the molar mass heterogeneity of polymer used, and thus the use of the temperature at the maximum of the cloud point curve instead of the critical temperature for the determination of Flory theta temperature is basically incorrect for a polydisperse polymer sample dissolved in a single solvent.[7~9]

Recently, Koningsveld[3,4] proposed a method of measurement to define the conditions of critical state of a system constituted with multicomponent polymer and a single solvent, and insisted that a measurement of critical points in the same solvent of solution of different samples varying in average molar mass and molar mass distribution allowed them to calculate the concentration and temperature dependence of the interaction parameter accurately.

In this paper, it has been attempted to establish the empirical equations for the parameters of χ and mutual interaction parameter g in terms of concentration and temperature for the system of polydisperse poly(α-methylstyrene) and cyclohexane, which has never been treated in detail, by following after the procedure proposed by Koningsveld et al..[3] An estimation of the Flory theta temperature for the given system allowed us to confirm the accuracy of the χ and g fuctions derived.

EXPERIMENTAL SECTION

Polymer

The poly(α-methylstyrene)(PαMS), synthesized by anionic polymerization,[10] was dissolved in toluene, filtered, and precipitated in methanol. Two additional cycles of dissolution and precipitation were carried out for further purification. The polymer thus obtained was dried under reduced pressure.

Fractionation

The conventional non-solvent addition method was used. The initial polymer concentration prepared was 0.96% by weight. Toluene and methanol were used as the solvent-nonsolvent system.

GPC

The values of $\overline{M}_w$ and $\overline{M}_z$ and their polydispersity indices of various polymer fractions were estimated by size exclusion chromatography. Measurements were performed on Waters Associates Model 201 with toluene as the mobile phase. The elution was conducted with a flow rate of 1 ml/min. A series arrangement of μ-styragel columns with upper porosity ratings of 10^3 to 10^6 Å was employed.

Membrane Osmometry

The $\overline{M}_n$ and osmotic second virial coefficient (A_2) were determined by measuring osmotic pressure of polymer fractions in toluene at 35℃. Wescan Model 310-104 osmometer fitted with S & S AC 61 membrane was used.

Preparation of Binary Solution

A proper amount of polymer sample, being dried at 50℃ under reduced pressure for more than three days, was weighed into a cylindrical tube containing a small magnetic stirrer chip. A desired amount of purified solvent was then poured into the tube which was followed by perfect sealing with ground glass stopper. Being weighed the tube was sealed further by teflon tape.

Cloud Point

Cloud point temperatures for a series of PαMS and cyclohexane solutions were measured in a thermostated water bath by monitoring the intensity of light transmitted through the solutions. Turbidimeter employed is illustrated schematically in Fig. 1. The cylindrical tube containing test solution was suspended in the middle portion of the water bath by using a clamp. The solution was warmed up to 35~40℃ and then allowed to cool by circulation of cooling water, but in the vicinity of cloud point, being estimated by a preliminary experiment, the temperature of the bath was lowered with the rate of 0.03℃/min. A light emiting diode beam forced to pass through the test solution yielded intensity variations of the transmitted light which were monitored by photodiode. The cloud point was then determined from the break point of intensity variations of transmitted light vs. temperature curve, as illustrated in Fig. 2.

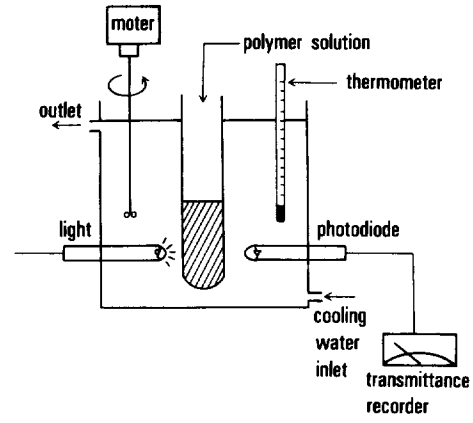

Fig. 1. Schematic diagram of turbidimeter.

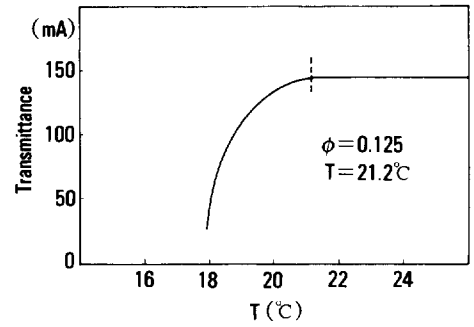

Fig. 2. Cloud point determination for poly(α-methyl styrene)(α-4) in cyclohexane.

Coexistence Curve

The phase separation experiments into dilute and concentrated phases were carried out with solutions of given concentration at temperature range between 16.2~27.4℃. Phase equilibrium was attained in a period of two to three days and the volume ratio of the upper to lower phase was determined from the height of the stationary phase boundary. Each phase was then separated. Their concentrations were determined by the dry weight method. The plot of phase separation temperatures against polymer concentration yielded the coexistence curve. A typical example is shown in Fig. 3.

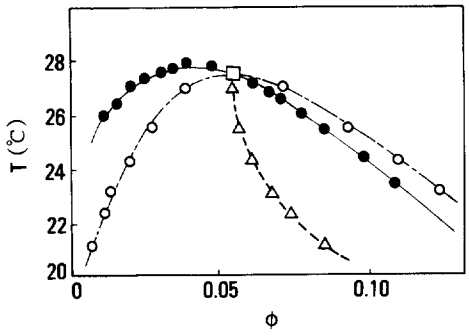

Fig. 3. Critical point determination for poly(α−methylstyrene)(α−1) in cyclohexane : (●) cloud point, (○) binodal, (△) mid point, (□) critical point, (——) cloud point curve, (−·−) coexistence curve.

RESULTS AND DISCUSSION

Critical Points

In principle, for the binary system which is constituted with strictly monodisperse polymer and a single solvent the coexistence curve should be in excellent agreement with cloud point curve, and hence the critical point(CP) is the maximum of the coexistence curve which coincides with the cloud point curve.[11] But if the mixture contains many macromolecular components differing in chain length, the cloud point curve no longer represents coexisting phases and the critical point is usually found on the right hand branch of the cloud point curve. In addition, in such cases where quasibinary mixtures are concerned, the coexistence curve are often very flat in the neighborhood of the CP, so that the determination of the exact position of the CP on the cloud point curve is very difficult.

Following Koningsveld et al.,[12] the limiting value of the phase-volume ratio at the critical temperature will equal unity, if the coexistence curve is approached by changing the temperature of a two-phase systems with an overall concentration equal to the critical one. Therefore, a necessary and sufficient criterion to predict whether or not the liquid mixture is expected to be at the critical concentration is the equality of the phase volumes measured at a temperature close to the cloud point of that concentration.

This consideration allows us to determine the critical points of the system PαMS-cyclohexane which has, so far, not been dealt with in detail. The procedure of critical point determination attempted here is rather simple than methods proposed by Koningsveld[12] and Kuwahara,[13] and starts with following simple relationship :

$$V_0\phi_0 = V_1\phi_1 + V_2\phi_2 \quad (1)$$

where V is the volume of solution phase and ϕ denotes the volume fraction of polymer in solution. The subscript zero means the original solution before phase separation, and subscripts 1 and 2 are the dilute and concentrated solution after phase separation, respectively. If volume ratio of coexistence phases is unity ($r = V_2/V_1 = 1$), then equation (1) can be written as

$$\phi_{r=1} = 1/2(\phi_1 + \phi_2) \quad (2)$$

where $\phi_{r=1}$ corresponds to the midpoint of volume fractions of two phases. Therefore, measurements of volumes and concentrations of the phases that have separated at a given temperature can yield the values of ϕ_1 and ϕ_2, and hence the value of $\phi_{r=1}$ to the cloud point curve leads to find the critical point.

Fig. 3 gives an example of such data on a sample of PαMS($\overline{M}_w = 6.04 \times 10^5$ g/mol) in cyclohexane. As is shown in Fig. 3, the coexistence curve differs from the cloud point curve and lies at right hand side of cloud point curve. This type of phenomenon is usual when polymers concerned are heterogeneous in molar mass, and the reason is also well documented.[14] The square mark in Fig. 3 defines the critical point of the system given. Likewise, treatments of phase separation data obtained from those other fractions gave values of critical points, and were summarized in Table 1 together with values of precipitation threshold points. Fig. 4 shows T versus ϕ phase diagrams for cyclohexane solutions of PαMS fractions. Each curve corresponds to a different molar mass. A comparison of the cu-

Table 1. Average Chain Lengths, Polydispersity Indices, and Values of Critical and Threshold Points for the Poly(α-methylstyrene)-cyclohexane System

sample code	$\overline{M}_w \times 10^{-5}$ (g/mol)	$P_n \times 10^{-2}$	$P_w \times 10^{-2}$	$P_z \times 10^{-2}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_z/\overline{M}_w$	ϕ_c	ϕ_{th}	T_c (℃)	T_{th} (℃)
α-0	2.57	9.1770	18.2656	34.2813	1.99	1.88	0.0830	0.0487	22.2	25.0
α-1	6.04	24.9717	43.1713	69.0600	1.73	1.60	0.0550	0.0400	27.4	28.1
α-2	4.24	22.2205	34.5441	49.8022	1.55	1.44	0.0588	0.0435	25.1	25.5
α-3	2.90	19.3283	25.4460	31.8142	1.32	1.24	0.0634	0.0532	24.6	24.8
α-4	2.27	17.2121	21.8756	26.9468	1.27	1.23	0.0679	0.0558	23.3	23.5
α-5	1.65	13.0502	15.6108	18.1997	1.20	1.17	0.0760	0.0647	22.4	22.5
α-6	1.13	6.9836	10.8283	12.1331	1.14	1.12	0.0865	0.0709	20.4	20.6

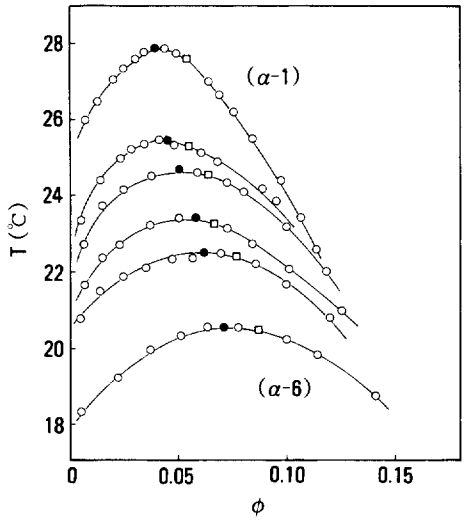

Fig. 4. Phase diagram of poly(α-methylstyrene)(α-1), (α-2), (α-3), (α-4), (α-5), and (α-6) in cyclohexane : (○) cloud point, (●) threshold point, (□) critical point.

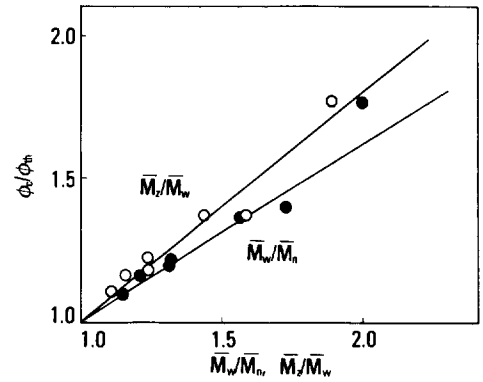

Fig. 5. The plot of ϕ_c/ϕ_{th} vs. polydispersity indices ($\overline{M}_w/\overline{M}_n$, $\overline{M}_z/\overline{M}_w$).

rves suggests that the critical temperatures(T_c) are elevated to higher temperature, while the critical concentration(ϕ_c) moves to lower region of volume fraction as the molar mass increases. In addition, the curves of low molar mass fractions differ markedly in their width from the high molar mass fraction. This feature is also known[15] as the typical one for systems consisting of a multicomponent polymer fraction in a single solvent. The significant aspect of Fig. 4, on the other hand, is the considerable deviation of critical point from its threshold point. This can be explicable in terms of the disparity in molecular size of polymer chains contained in the given sample of fraction. Some of theoretical and experimental studies[16~18] have also been offered the same corroborating evidences for quasibinary polymer solution systems.

According to Solc[17] and Tsuyumoto,[18] the ratio of critical volume fraction at threshold point(ϕ_c/ϕ_{th}) is dependent only on $\overline{M}_z/\overline{M}_w$, and hence the critical and threshold behavior have nothing to do with $\overline{M}_n$. In disagreement with this conclusion, however, it is observed that the system under consideration shows the value of ϕ_c/ϕ_{th} is not only correlated with $\overline{M}_z/\overline{M}_w$ but also with $\overline{M}_w/\overline{M}_n$, as Fig. 5 exhibits. This behavior allows us to suggest that the $\overline{M}_n$ too has an important meaning for making interpretations on phase characteristics for poly-

mers having the polydispersity indices within the range cited here.

Evaluation of Interaction Parameters

As is known well, the Gibbs free energy of mixing for the quasibinary solution is given by

$$\Delta G_m/RT = \phi_0 \ln\phi_0 + \Sigma\phi_i P_i^{-1} \ln\phi + \chi\phi_0\phi \quad (3)$$

where RT has the usual meaning, and ϕ_0 and ϕ_i are the volume fractions of solvent and polymer i, respectively. The relative chain length of polymer i is denoted by P_i and the total volume fraction of the polymer solute by ϕ, which can be written as :

$$\phi = \Sigma\phi_i = 1 - \phi_0 \quad (4)$$

Accordingly, the appropriate partial defferentiations of ΔG_m in equation give chemical potentials equation for the solvent,

$$\Delta\mu_0/RT = \ln(1-\phi) + (1-P_n)^{-1} + \chi\phi^2 \quad (5)$$

where P_n is the number-average relative chain length of the polymer mixture, and χ is the well known Flory-Huggins(F-H) interaction parameter, which is, in general, a function of the state variables T, P, ϕ_1, ϕ_2, ϕ_3,$\cdots\phi_i$, but the conventional assumption so far adopted in the phenomenonlogical approach to polymer solutions is that the parameter χ does depend on the total volume fraction ϕ, and hence can be expanded in integral powers of ϕ : [13,14,16,19]

$$\chi = \chi_1 + \chi_2\phi + \chi_3\phi^2 + \cdots \quad (6)$$

In the meantime, for polymer solutions the F-H equation has long been known to be unsatisfactory when it comes to quantitative comparison with experiment. Thus, an empirical concentration dependence of a new mutual interaction parameter g(T, ϕ) was introduced by Tompa.[18] By substitution of χ with g, equation (3) can be rewritten as :

$$\Delta G_m/RT = \phi_0 \ln\phi_0 + \Sigma\phi_i P_i^{-1} \ln\phi_i + g(T,\phi)\phi_0\phi \quad (7)$$

Here g is defined by

$$g = (1-\phi)^{-1} \int_0^1 \chi \, d\phi \quad (8)$$

This relation is converted to express χ in terms of g, yielding

$$\chi = g - (1-\phi)(\partial g/\partial\phi) \quad (9)$$

If it is proposed that the parameter g can also be expanded in integral powers of ϕ, as is shown in eq.(10)

$$g(T,\phi) = g_0 + g_1\phi + g_2\phi^2 + \cdots \quad (10)$$

where the temperature dependence of g is restricted to g_0 for simplicity and is supposed to be the usual linear function of 1/T, namely :

$$g_0 = g_{00} + g_{01}/T \quad (11)$$

then, by substitution of those power series of χ and g into eq.(9) g parameter can be related to χ by

$$\chi_{k+1} = (k+1)(g_k - g_{k+1}), \; k = 1, 2, 3, 4, \cdots \quad (12)$$

On the other hand, Koningsveld et al.[3] have derived the following equations by applying the spinodal and critical conditions to the system obeying the F-H expression with g dependent on ϕ :

$$2g_0 = (1-\phi_c)^{-1} + (\phi_c P_w)^{-1} + 2g_1(1-3\phi_c) + 6g_2(1-2\phi_c)\phi_c \quad (13)$$

for the spinodal and

$$g_1 - g_2 + 4g_2\phi_c = 1/6[(1-\phi_c)^{-2} - P_z/P_w^2\phi_c^2] = Y \quad (14)$$

for the critical state. In eq.(14), ϕ_c is the volume fraction of polymer at critical point, and P_z and P_w are z-average and mass-average relative chain lengths of the polymer mixture, respectively. Thus, using eq.(14) one can evaluate the values of g_1 and g_2, and in turn g_0 can also be obtainable by employing eq.(13). A further treatment of g_0 thus obtained with 1/T yields the value of g_{00} and g_{01} from the plot of g_0 vs. 1/T. In this way, we can derive an expression for the g(T, ϕ) function.

Values found for g_1 and g_2 with the aid of data listed in Table 1 were 0.223 and 0.072, respectively. In Fig. 6 is illustrated the critical concentration dependence of Y defined in eq.(14). The circ-

les in Fig. 6 denoting the values of Y against critical volume fraction are fitted by a straight line. The temperature dependence of g_0 and the extrapolation to where $g_0-g_1=0.5$ are shown in Fig. 7. The points are also fitted by a straight line.

In this way, we obtain

$$g(T,\phi)=0.508+66.00/T+0.223\phi+0.072\phi^2 \quad (15)$$

which leads to $T_\theta=34.11$℃.

In analogy with the treatment of Koningsveld et al.,[3] expressions for the spinodal and critical state in terms of χ parameter can be derived from eq. (5) in the forms of eq.(16) and eq.(17) :

$$\chi_1=1/2[(1-\phi_c)^{-1}+(P_w\phi_c)^{-1}]-(3/2)Z\phi_c+2\chi_3\phi_c^2 \quad (16)$$

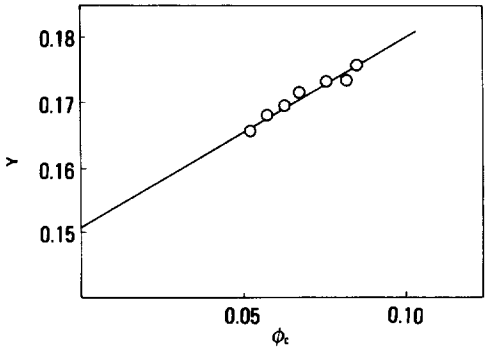

Fig. 6. Critical concentration dependence of Y for poly (α-methylstyrene) in cyclohexane.

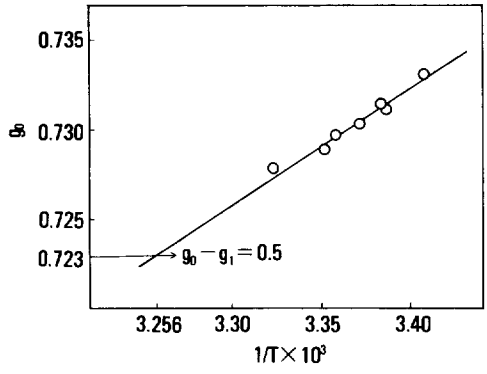

Fig. 7. Temperature dependence of g_0 and extrapolation to θ-state where $g_1-g_2=0.5$.

$$\chi_2+(8/3)\chi_3\phi_c=1/3[1-\phi_c)^{-2}+P_z/P_w^2\phi_c^2]=Z \quad (17)$$

Values evaluated for both the χ_2 and χ_3 where 0.302 and 0.216, respectively, and the critical concentration dependence of Z was also found to be linear, as is shown in Fig. 8. The plot of χ_1 against 1/T, Fig. 9, and its extrapolation to where $\chi_1=0.5$ yield χ_{10} and χ_{11} as 0.290 and 64.56, and thus, we obtain

$$\chi(T,\phi)=0.290+64.56/T+0.302\phi+0.216\phi^2 \quad (18)$$

which leads to $T_\theta=34.31$℃.

As the eq.(12) indicates, g does not equal χ and the corresponding coefficients of the $g(T,\phi)$ and $\chi(T,\phi)$ functions are not equal : namely, $\chi_1=g_0-g_1$ and $\chi_2=2(g_1-g_2)$. Comparisons of coefficients

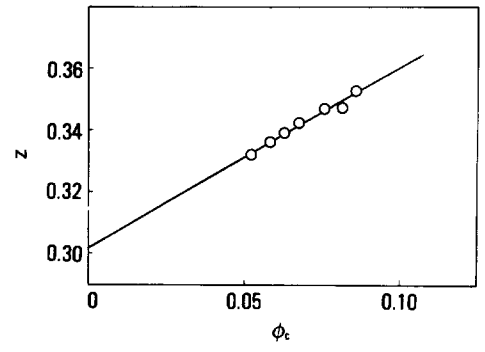

Fig. 8. Critical concentration dependence of Z for poly (α-methylstyrene) in cyclohexane.

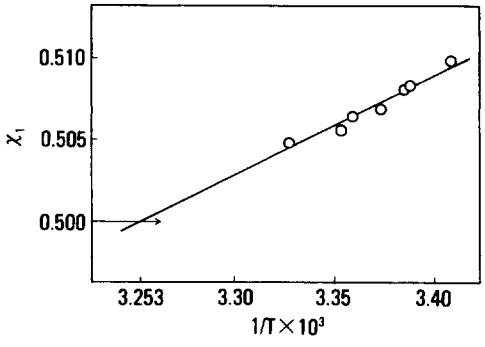

Fig. 9. Temperature dependence of χ_1 and extrapolation to θ-state where $\chi_1=0.5$.

appeared in eq.(15) and eq.(18) allow us to confirm that the data obtained here follow fairly well to what the eq.(12) reveals. In addition, the agreement between the two θ-temperatures is also quite good. Those results so far obtained, however, are derived on the basis of an assumption that only the χ_1 and g_0 are temperature dependent. This means that the temperature dependence of coefficients appeared in the power series of χ and g functions are neglected. But, from the point of view that an equation of state with virial coefficients is closely related with χ_1, χ_2, etc.[20] and those virial coefficients are functions of temperature,[21] coefficients of the power series of χ(eq.6) are supposed to be temperature dependent. Therefore, an effort is attempted to compute χ in terms of χ_1 and χ_2 under the condition that both of them are dependent on temperature.

Since it is impossible to compute the temperature dependences of χ_2 and χ_3 simultaneously, χ_3 is neglected. In Fig. 10 is illustrated the plot of χ_2, computed from eq.(17) with excluding the term concerned with χ_3, against 1/T, which shows good linearity with temperature. From this relation, χ_{20} and χ_{21} were found as -0.567 and 270.13, respectively. Again, with eq. (16) which expelled the χ_3 term, χ_1 values are obtained and plotted against 1/T, as is shown in Fig. 11. Data analysis on this basis of assumption yields

$$\chi(T, \phi) = 0.377 + 37.79/T + (-0.567 + 270.13/T)\phi \quad (19)$$

which leads to $T_\theta = 34.00$℃. From a brief comparison with the values of χ_1 and χ_2 appeared in above equation we may conclude that χ_2 is more temperature dependent, which is inconsistent with the hypothesis proposed by Koningsveld et al..

According to the two-parameter theory, second and third virial coefficients vanish at the θ-temperature, and hence χ_θ can be expanded as :

$$\chi_\theta = 0.50 + 0.333\phi + 0.250\phi^2 \quad (20)$$

where χ_θ denotes χ at $T = \theta$.

With their respective T_θ values inserted into eq.

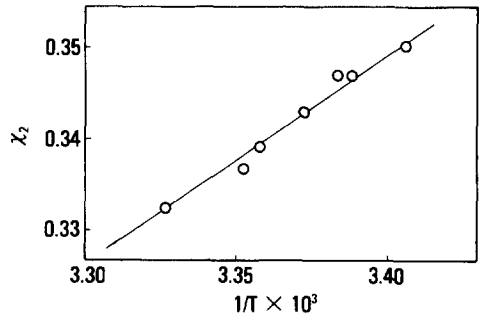

Fig. 10. Temperature dependence of χ_2.

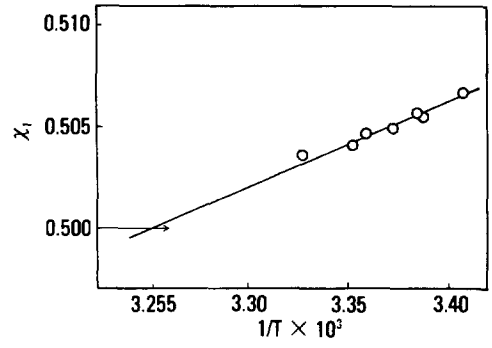

Fig. 11. Temperature dependence of χ_1.

(18) and eq.(19), respectively, two empirical expressions for χ_θ can be obtained :

$$\chi_\theta = 0.50 + 0.302\phi + 0.216\phi^2 \quad (21)$$

and

$$\chi_\theta = 0.50 + 0.312\phi \quad (22)$$

Evidently, the value of 0.312 in eq.(22) is appeared as much closer to the theoretical value 0.333 in eq.(20), which implies that the empirical expression for χ is more reliable when the coefficient χ_2 is treated as temperature depended, even it has a shortcoming that χ_3 can not determined.

The agreement of T_θ found here is fairly good and the range 34.00~34.31℃ is quite close to the value 34.5℃ obtained by Noda[23] for the same system.

CONCLUSION

The present calculation, based on the method of Koningsveld et al. for the determination of concentration dependences of interaction parameters for the system of heterogeneous PαMS-cyclohexane, has led to the formulation of empirical expressions for χ and g, which are believed essentially to be accurate. The good agreement of T_θ obtained here with the value so far known is one of the powerful evidences for the accuracy.

For the expression, in terms of critical point data alone it is hard to sort out which method of data analysis is preferable, but it is considered that a more accurate expression may be attainable when the coefficient of χ is treated too as temperature depended, even it is unable to afford the values of higher order of coefficients.

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