Theoretical prediction of the upper and lower critical solution temperatures in aqueous polymer solutions based on the corresponding states theory

S. Saeki, T. Namiki, M. Tsubokawa and T. Yamaguchi
Department of Polymer Engineering, Fukui University, Fukui 910, Japan
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The upper and lower critical solution temperatures in aqueous polymer solutions have been predicted by the Flory–Huggins theory with a particular temperature dependence of the χ parameter characterized by a parabolic-like function of temperature with a maximum. The closed-loop type of phase diagram for an aqueous polymer solution is discussed using an equation derived from the thermodynamic equation of state on the basis of the corresponding states theory, which is able to explain the particular temperature dependence of χ in aqueous polymer solutions.

(Keywords: upper and lower critical solution temperatures; aqueous polymer solution; nonpolar polymer solution; corresponding states theory)

INTRODUCTION

The phase separation behaviour in non-electrolyte aqueous polymer solutions such as poly(ethylene glycol)–water[1,2] is characterized by a closed-loop type of phase diagram with upper and lower critical solution temperatures. Although the closed-loop type of phase diagram was explained by Baker[3] using a model in which the molecular interactions depend on the relative orientation, there is no report on whether the phase diagram in aqueous polymer solutions is predicted theoretically through the thermodynamic properties of water or not. The corresponding states theory for nonpolar polymer solutions[4–7] is able to analyse the particular properties of water based on the reduced equation of state, which takes into account the thermal pressure γ_v and the expansion coefficient α_p of the liquid. One of the important differences between water and organic solvents such as n-heptane and benzene appears in temperature dependence of the thermal pressure coefficient[8]. For example, values of γ_v for water have a maximum around 150°C, while γ_v for most organic liquids decrease monotonically with increasing temperature[8].

In this work we have tried to predict the closed-loop type of phase diagram in an aqueous polymer solution using the Flory–Huggins theory with a particular temperature dependence of χ and an equation derived from the thermodynamic equation of state on the basis of the corresponding states principle. It is also discussed whether the corresponding states principle is experimentally applicable to aqueous solutions or not.

THEORETICAL BACKGROUND FOR THE CALCULATION

The phase separation behaviour in polymer solutions is often analysed using the Flory–Huggins formulation[9] for the chemical potential:

$$\mu_1 - \mu_1^0 = RT[\ln(1-v_2) + (1-r^{-1})v_2 + \chi_1 v_2^2] \qquad (1)$$

and

$$\mu_2 - \mu_2^0 = RT[\ln v_2 - (r-1)(1-v_2) + \chi_1 r(1-v_2)^2] \qquad (2)$$

where v_2 is the volume fraction of polymer, r is the ratio of the molar volume of polymer to that of solvent, χ_1 is the polymer–solvent interaction parameter, and R is the gas constant. The condition of phase equilibrium for the two phases is given by:

$$\mu_1 = \mu_1' \qquad (3)$$

and

$$\mu_2 = \mu_2' \qquad (4)$$

where the prime indicates the concentrated phase. The T vs. v_2 phase diagram is calculated by equations (1)–(4) and the χ_1 vs. T function, which is determined experimentally[9].

The corresponding states theories of nonpolar polymer solution derived by Flory[4,5] and Patterson[6,7] are very useful to be able to explain most thermodynamic properties of polymer solutions, such as the lower critical solution temperature[10–12], the excess volume of mixing[13], the concentration dependence of the χ parameter[13], and the pressure dependence of the upper and lower critical solution temperatures[14,15]. The function of the parameter χ with respect to temperature in these theories is essentially the same and is characterized by a parabolic-like function with a minimum[16]. The parameter χ in the Patterson theory[6] is expressed by:

$$\chi_1 = (-U_1/RT)\nu^2 + (C_{p,1}/2R)\tau^2 \qquad (5)$$

where the quantity $-U_1$ is the vaporization energy of the

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solvent, $C_{p,1}$ is the configurational heat capacity of the solvent and v^2 and τ^2 are molecular parameters. The corresponding states theory assumes that all liquids satisfy a universal equation of state or reduced equation of state, in which the variables are expressed in reduced form such as $\tilde{P}=P/P^*$, $\tilde{V}=V/V^*$ and $\tilde{T}=T/T^*$; the reduction parameters P^*, V^* and T^*, reflecting the intrinsic properties of the liquids, are independent of temperature and pressure. In the Patterson theory the parameter τ^2 is defined by $\tau^2=(1-T_1^*/T_2^*)^2$, while v^2 is taken to be an empirical parameter, where T_1^* and T_2^* are the temperature reduction parameters for solvent (1) and polymer (2), respectively. By using the reduced equation of state given by Flory *et al.*[4], the quantities $-U_1$ and $C_{p,1}$ are expressed as:

$$-U_1=\tilde{V}^{-1}P_1^*V_1^* \tag{6}$$

$$=(\gamma_v T-P)V \tag{7}$$

where the equation $\gamma_v T/P=1+(\tilde{P}\tilde{V}^2)^{-1}$ derived from the reduced equation of state is used to obtain equation (7) and

$$C_{p,1}=-U_1\alpha_p \tag{8}$$

$$=(\gamma_v T-P)V\alpha_p \tag{9}$$

The expression for χ_1 in equation (5) is given using equations (7) and (9) by:

$$\chi_1=[(\gamma_v T-P)V/RT]v^2+[(\gamma_v T-P)V\alpha_p/2R]\tau^2 \tag{10}$$

or in the case of negligible pressure $P\approx 0$

$$\chi_1=(\gamma_v V/R)v^2+(\gamma_v TV\alpha_p/2R)\tau^2 \tag{11}$$

It is important to point out that the expression for U_1 in equation (6) is the intermolecular energy of van der Waals type and cannot apply to the aqueous polymer solution. However, the equations (7), (9) and (10) are useful for the aqueous solution as discussed below.

It is necessary to derive an expression for χ_1 without using any models for the intermolecular energy, when we discuss the thermodynamic properties of aqueous polymer solutions in the framework of the Flory–Huggins theory. The following equation has been derived based on the thermodynamic equation of state[17]:

$$(\partial E/\partial V)_T=\gamma_v T-P \tag{12}$$

$$\approx\gamma_v T \qquad P\approx 0 \tag{13}$$

and

$$[\partial V(\partial E/\partial V)_T/\partial T]_P=\gamma_v V+\gamma_v TV\alpha_p+VT(\partial\gamma_v/\partial T)_P \tag{14}$$

Equation (14), with dimension of energy/degree, shows that variation of internal energy E due to temperature change at constant pressure consists of three terms in general if $V(\partial E/\partial V)_T$ gives the internal energy at temperature T. In the corresponding states theory the quantity χ or $\Delta H_M\simeq\Delta E_M$ at constant temperature are replaced by $E_M(\tilde{T})$ and $\partial E_M(\tilde{T})/\partial\tilde{T}$ because of differences between $\tilde{T}_1$ for solvent and $\tilde{T}_2$ for the polymer due to the difference of T_1^* and T_2^* at constant temperature. The detailed discussion on χ_1 in the corresponding states theory is given by Patterson *et al.*[7] This is the main reason why the function of χ_1 in equation (11) is the same as that in equation (14) except for $VT(\partial\gamma_v/\partial T)_P$ in equation (14). The molecular parameters v^2 and τ^2 in equation (11) are evaluated from a reduced equation of state, experimental values of the thermal pressure and the expansion coefficient, and the molar volumes for polymer and solvent. From these considerations, the general expression for χ_1 based on the corresponding states principle is given by:

$$\chi_1=(\gamma_v V/R)\alpha^2+(\gamma_v VT\alpha_p/R)\beta^2+[VT(\partial\gamma_v/\partial T)_P/R]\gamma^2 \tag{15}$$

where the parameters α^2, β^2 and γ^2 reflect the characteristic differences between polymer and solvent or water and are less than one in most cases. In this work we take these parameters as empirical parameters. Calculations of the phase diagrams for aqueous polymer solutions have been carried out by applying the corresponding states principle for aqueous polymer solutions and using equations (1)–(4) and (15).

RESULTS AND DISCUSSION

The χ_1 vs. v_2 phase diagram for a polymer solution with $r=100$ calculated by equations (1)–(4) using the same procedure given in ref. 9 is shown in *Figure* 1. The quantities $\gamma_v V/R$ and $\gamma_v VT\alpha_p/R$ for pure water in equation (15) calculated using the experimental values of γ_v, V and α_p for pure water[8] are plotted against temperature in *Figure 2*, where the temperature dependence of the χ_1 parameter for an aqueous polymer solution simulated by equation (15) with $\alpha^2=0.2$ and $\beta^2=\gamma^2=0$ is also plotted. The phase diagram for the aqueous polymer solution

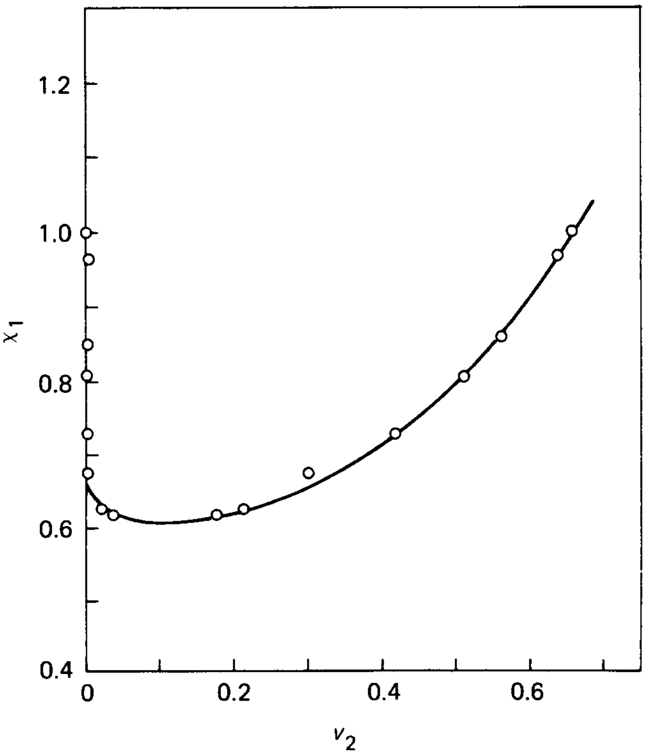

Figure 1 χ_1 vs. v_2 phase diagram for a polymer solution with $r=100$ calculated by equations (1)–(4)

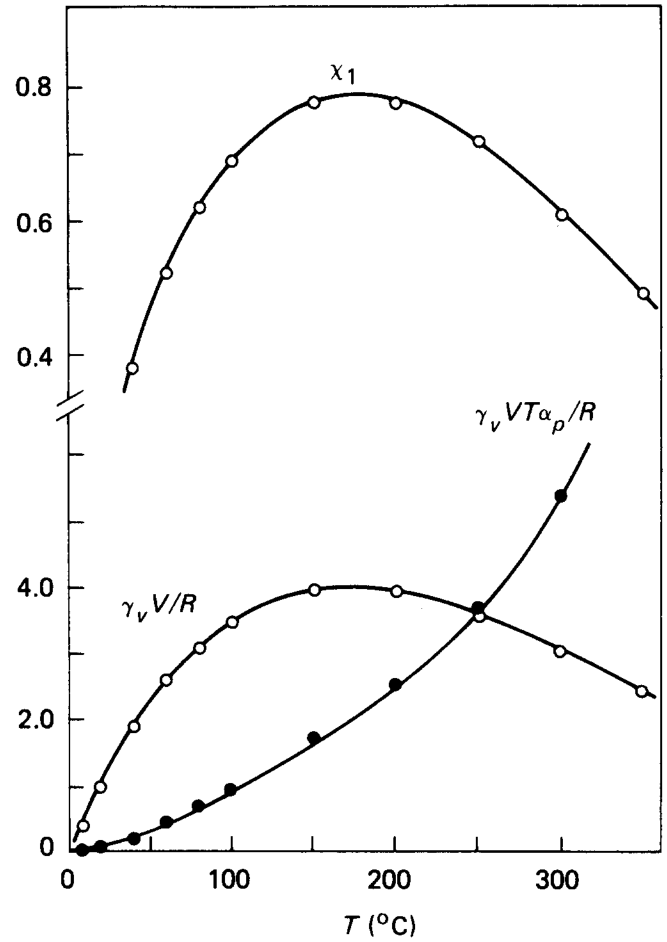

Figure 2 χ_1 vs. v Tcurve calculated by equation (15) with parameters $\alpha^2=0.2$ and $\beta^2=\gamma^2=0$ (top curve). The temperature dependence of $\gamma_v V/R$ and $\gamma_v VT\alpha_p/R$ for water (bottom curves)

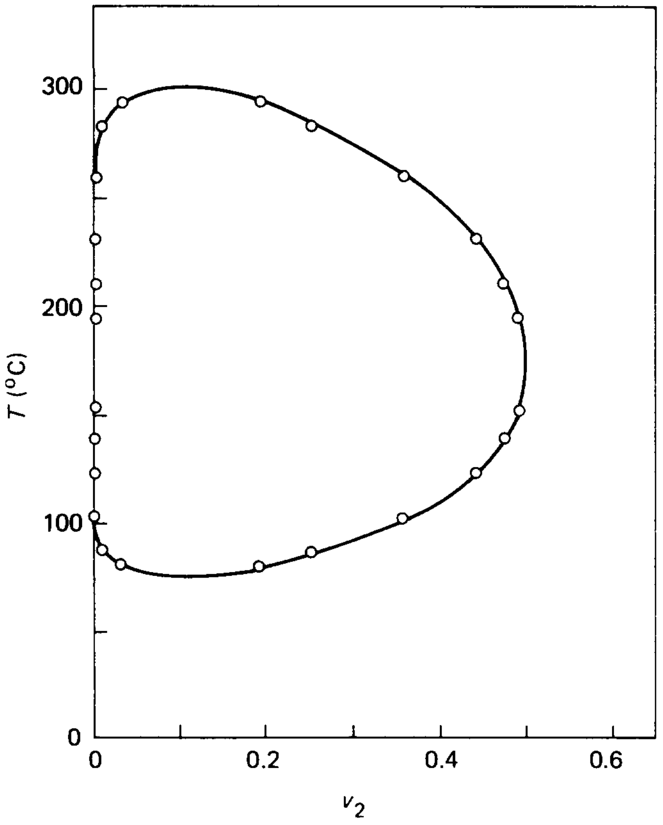

Figure 3 T vs. v_2 phase diagram for an aqueous polymer solution ($r=100$) determined using the values in *Figures 1* and *2*

$r=100$) determined using the values in *Figures 1* and *2* (χ_1 vs. T curve) is shown in *Figure 3*, where the closed-loop type of phase diagram is obtained. Various temperature dependences of χ_1 for aqueous solutions using equation (15) with suitable molecular parameters are shown in *Figure 4*, where the temperature at which the χ_1 parameter is a maximum shifts to lower values by introducing the third term or γ_2 term in equation (15). The temperature for the maximum value of χ_1 corresponds to the temperature of the centre of the closed loop (see *Figures 2* and *3*). It is observed in simple aqueous solutions, such as 2-butanone–water and s-butanol–water[8], that the temperature of the centre of the closed loop is lower than the value 200°C observed in poly(ethylene glycol)–water[1,2] and is around 70°C for 2-butanone–water, which is predicted by equation (15) with $\alpha^2=0.12$, $\beta^2=0$ and $\gamma^2=0.025$ (see *Figure 4*).

It is interesting to discuss the correlation between the phase separation behaviour for the aqueous polymer solution and that for the nonpolar polymer solution[11,12]. The quantities $\gamma_v V/R$ and $\gamma_v VT\alpha_p/R$ for n-heptane calculated by equations (7) and (9) and the experimental values[8] of γ_v, V and α_p are plotted against temperature in *Figure 5*, where the temperature dependence of χ_1 calculated by equation (5) with $v^2=0.015$ and $\tau^2=0.15$ is also included. These values of v^2 and τ^2 are comparable to those for the polystyrene–cyclohexane system[12] ($v^2=0.0159$ and $\tau^2=0.119$). The phase diagram for solution of polymer ($r=100$) in n-heptane calculated using the values in *Figures 1* and *5* is shown in *Figure 6*. It

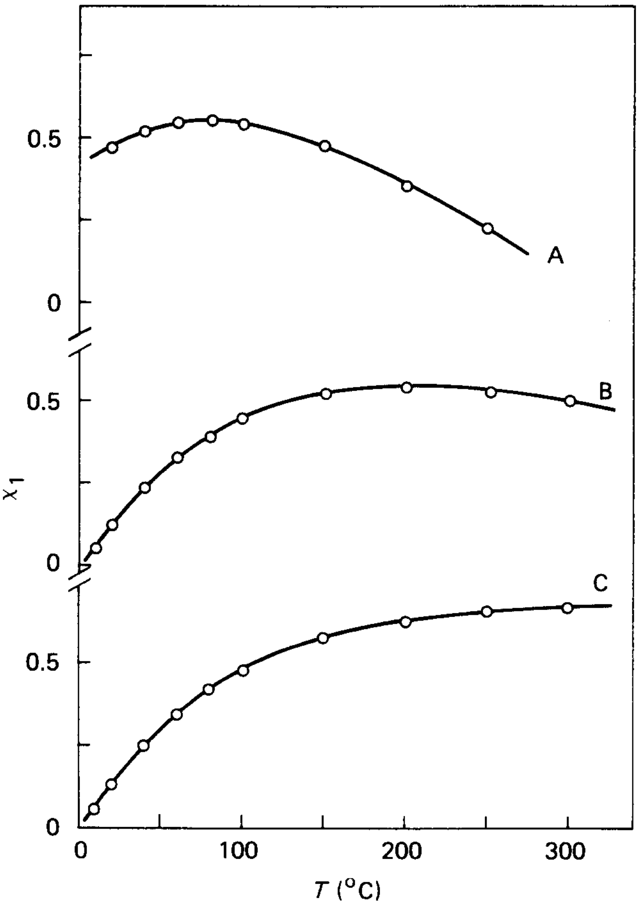

Figure 4 Various temperature dependences of χ_1 for aqueous polymer solutions calculated by equation (15) with following parameters: curve A, $\alpha^2=0.12$, $\beta^2=0$, $\gamma^2=0.025$; curve B, $\alpha^2=0.12$, $\beta^2=0.025$, $\gamma^2=0$; curve C, $\alpha^2=0.12$, $\beta^2=0.06$, $\gamma^2=0$

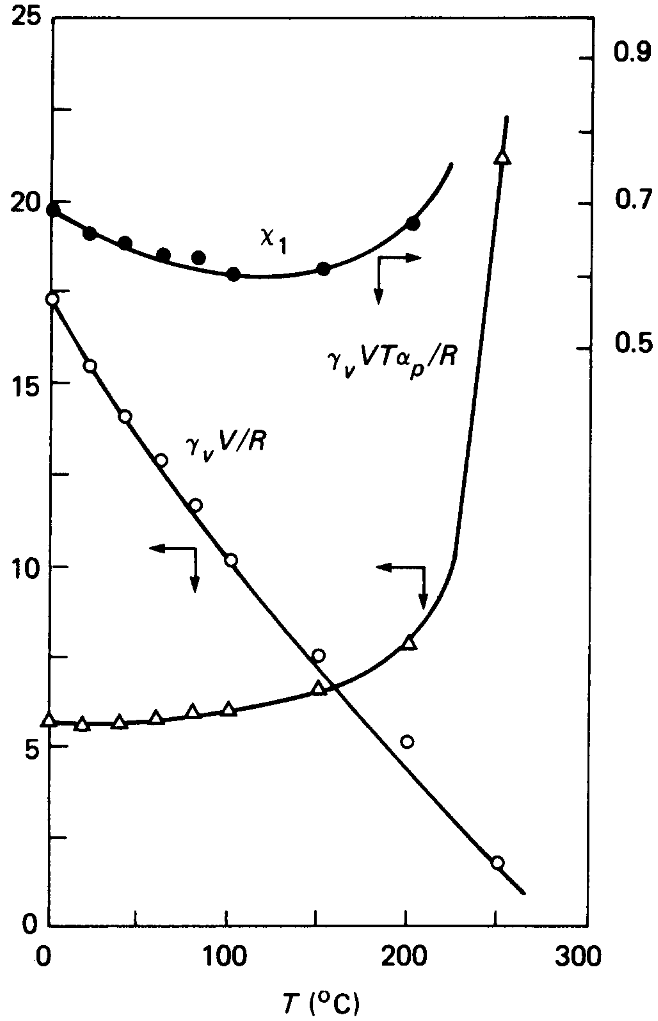

Figure 5 χ_1 vs. T curve for solution of polymer in n-heptane calculated by equation (11) with parameters $\nu^2=0.015$ and $\tau^2=0.15$ (top curve). The temperature dependence of $\gamma_v V/R$ and $\gamma_v VT\alpha_p/R$ in equations (7) and (9) (bottom curves)

is obvious that the parabolic-like temperature dependence of χ_1 with a minimum leads to a mirror image type of phase diagram, while the parabolic-like temperature dependence of χ_1 with a maximum leads to a closed-loop type of phase diagram in polymer solutions.

It is very important to examine whether aqueous polymer solutions satisfy the corresponding states principle or not, or in other words whether water and polymers satisfy the same equation of state or not. It has been recognized that most nonpolar organic solvents and polymers satisfy the reduced equation of state derived by Flory *et al.*[4] and that water and aqueous solutions are considered as an exceptional case. However, it is noteworthy that the closed-loop type of phase diagram is observed in non-aqueous solutions such as *m*-toluidine–glycerol[18] and that the special temperature dependence of γ_v with a maximum at 150°C for water is considered to be a more general behaviour of γ_v because it includes the decrease of γ_v with increasing temperature, which is observed in most nonpolar liquids. In this work we assume that the corresponding states principle is applicable to water and aqueous polymer solutions. One experimental result supporting this assumption is that the values of γ_v for poly(ethylene glycol)–water solutions increase with increasing temperature in the same way as that of pure water over the concentration range $w_2<0.5$ where w_2 is the weight fraction of poly(ethylene glycol)[17]. It may be true that an aqueous polymer solution exhibits the same P–V–T behaviour as that of pure water over the moderately concentrated range.

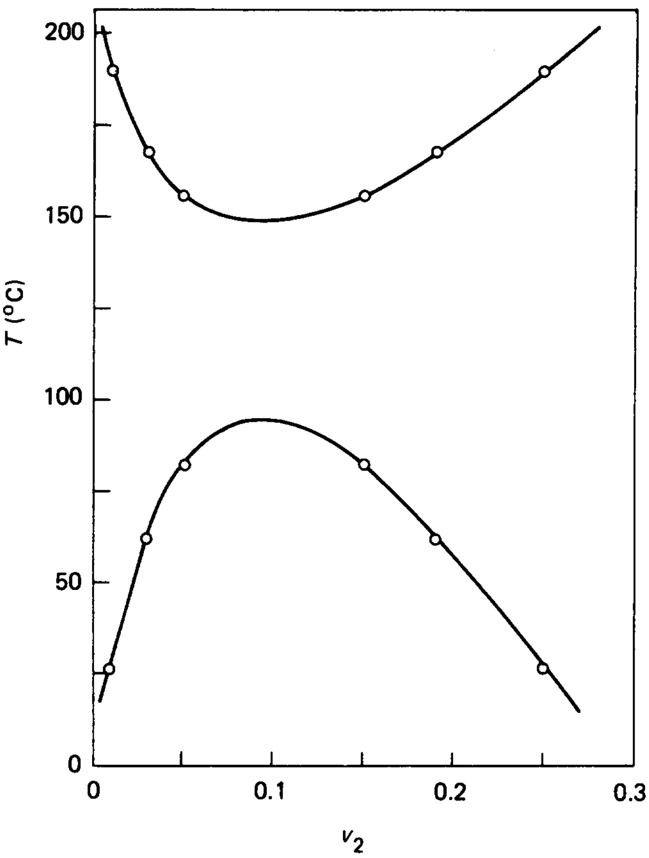

Figure 6 T vs. v_2 phase diagram for polymer solution ($r=100$) in n-heptane determined using the values in *Figures 1* and *5* (χ_1 vs. T curve)

REFERENCES

1 Malcolm, G. N. and Rowlinson, J. S. *Trans. Faraday Soc.* 1957, **53**, 921
2 Saeki, S., Kuwahara, N., Nakata, M. and Kaneko, M. *Polymer* 1976, **17**, 685
3 Baker, J. A. J. and Fock, W. *Discuss. Faraday Soc.* 1953, **15**, 188
4 Flory, P. J., Orwoll, R. A. and Vrij, A. *J. Am. Chem. Soc.* 1964, **86**, 3507
5 Flory, P. J. *J. Am. Chem. Soc.* 1965, **87**, 1833
6 Patterson, D. and Delmas, G. *Trans. Faraday Soc.* 1969, **61**, 708
7 Patterson, D. and Delmas, G. *Discuss. Faraday Soc.* 1970, **49**, 98
8 Rowlinson, J. S. 'Liquid and Liquid Mixtures', 2nd Edn., Butterworths, London, 1969
9 Flory, P. J. in 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953
10 Cowie, J. M. G., Maconnachie, A. and Ranson, R. J. *Macromolecules* 1971, **4**, 57
11 Siow, K. S., Delmas, G. and Patterson, D. *Macromolecules* 1972, **5**, 29
12 Saeki, S., Kuwahara, N., Konno, S. and Kaneko, M. *Macromolecules* 1973, **6**, 246
13 Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.* 1968, **64**, 2035
14 Saeki, S., Kuwahara, N. and Kaneko, M. *Macromolecules* 1976, **9**, 101
15 Saeki, S., Kuwahara, N., Hamano, K., Kenmochi, Y. and Yamaguchi, T., to be published
16 Saeki, S., Konno, S., Kuwahara, N., Nakata, M. and Kaneko, M. *Macromolecules* 1974, **7**, 521
17 Saeki, S., Kuwahara, N., Nakata, M. and Kaneko, M. *Polymer* 1977, **18**, 1027
18 Timmermans, J. 'Les Solutions concentrées', Paris, 1936