Phase separation of poly(ethylene glycol)-water-salt systems

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Phase separation temperatures, each corresponding to lower critical solution temperature (*LCST*) for solutions of poly(ethylene glycol) (PEG) in water–sodium chloride (NaCl) and in water–propionic acid–sodium salt (Pro–Na), have been determined for PEG with molecular weights of $M_\eta = 2.18 \times 10^3$, 8×10^3 and 719×10^3 over concentration ranges from 0–1.09 M (mol/1000 g solvent) NaCl and 1.02 M Pro–Na. The phase separation temperature decreases with an increase of salt concentration and depends on polymer molecular weight. The thermal pressure coefficient, thermal expansion coefficient, and density have been determined from 20° to approximately 60°C for ethylene glycol–water solutions over the entire concentration range and also for aqueous salt solutions over the concentration ranges from 0–1.7 M NaCl and 0–0.5 MPro–Na. The excess thermal pressure coefficient, γ_V^E, excess thermal expansion coefficient, α^E, and excess of temperature dependence of γ_V, $[(\partial\gamma_V/\partial T)_p^E]$, for the EG–water system are all positive, while the excess volume of mixing V^E is negative. The thermal pressure coefficient and thermal expansion coefficient for aqueous salt solutions water–Pro–Na and water–NaCl increase with an increase of salt concentration. The behaviour of the two polymer–salt–water solutions is discussed in terms of a thermodynamic equation of state, and a shortcoming of the usual formulation of the corresponding states theory of polymer solutions is pointed out.

INTRODUCTION

Investigations of solution properties of water soluble nonelectrolyte polymers in water and organic solvents have been made by the determination of vapour pressure[1,2], phase equilibrium[1,3] and heat of mixing[4], and by gas–liquid chromatography[5,6]. The theories of polymer solution thermodynamics due to Patterson[7,8] and Flory[9,10] have been applied to nonpolar polymer solutions[11–17] and water soluble polymer–organic solvent systems such as PEG solutions[2,3,5,6]. These theories give semiquantitatively good prediction for the phase separation behaviour at the upper critical solution temperature (*UCST*) associated with endothermic behaviour of solution and the *LCST* associated with the exothermic behaviour[3,11–16]. Pressure dependence of the *LCST* and *UCST*[18–21] associated with the excess volume of mixing can also be represented by the Patterson and Flory theories. However, these theories based on the van der Waals model for interaction between molecules and the corresponding states principle cannot explain phase separation behaviour of the 'closed loop' type with the *UCST* and *LCST* observed in aqueous polymer solutions such as poly(ethylene glycol)–water[1,3] and poly(riboadenylic acid)–water[22]. Solutions of PEG in water provide typical examples of polymer solutions in which strong association and clustering of solvent molecules may occur and in which orientation-dependent interactions are dominant. A theoretical prediction for the phase diagram of the 'closed loop' type has been suggested by Barker and Fock[23] with the introduction of molecular interactions depending on the relative orientation.

In this work we examine the salt effect on solubility of PEG in water through the phase diagram of PEG in water–NaCl solution and in water–Pro–Na solution. We also analyse the temperature and concentration dependence of γ_V, density and α for water–NaCl, water–Pro–Na and ethylene glycol–water systems, using recent theories of polymer solution thermodynamics.

EXPERIMENTAL

Poly(ethylene glycol) samples used in this work were obtained from fractionated samples[3] of Union Carbide Polyox WSR 301, Nakarai Chemicals poly(ethylene glycol) 20 000 and Wako Pure Chemical Industries poly(ethylene glycol) 4000. Reagent grade sodium chloride and propionic acid sodium salt were obtained from Wako Pure Chemicals and Nakarai Chemicals, respectively. Fractionally distilled water was obtained using a specially designed distillation apparatus, which was repeatedly washed by steam for seven years. The thermal expansion coefficients and densities for water–NaCl, water–Pro–Na, and ethylene glycol–water systems were determined using a modified dilatometer with a reservoir of about 6 cm^3 and capillary (10 cm length, 0.2 mm i.d.). The dilatometer was calibrated by making use of pure mercury over the temperature range of 20° to approximately 50°C. Values of the thermal expansion coefficient for pure water measured by the variation of meniscus height with a slight increase of temperature (0.05°–0.4°C) under the closed system with the use of pure mercury agree with literature values[24] below 30°C within 1% and within 1 to 3% at temperatures higher than 30°C. Thermal pressure coefficients (γ_V) for the salt solutions and ethylene glycol solutions have been determined over the temperature range 30°–60°C by

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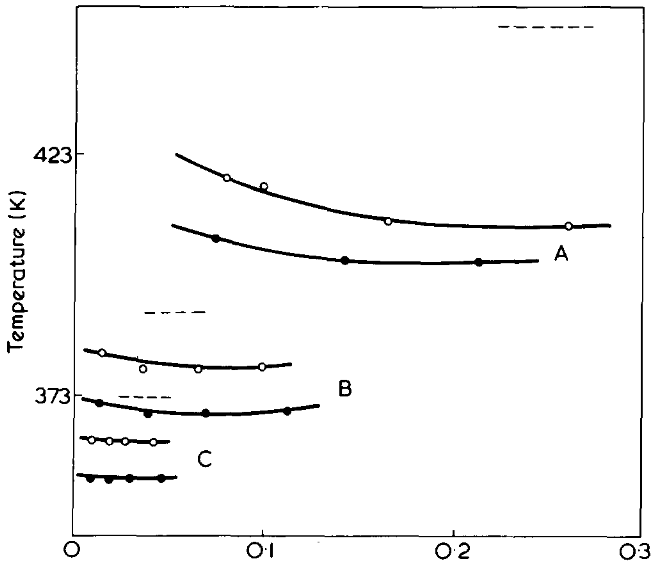

Figure 1 Temperature/weight fraction of polymer (w_2) phase diagram for the poly(ethylene glycol) samples (M_1, $M_\eta = 2.18 \times 10^3$; M_2, $M_\eta = 8 \times 10^3$; M_3, $M_\eta = 719 \times 10^3$) in water–sodium chloride (NaCl) and water–propionic acid sodium salt (Pro–Na) at salt concentrations: ○, 0.2998 M NaCl; ●, 1.015 M Pro–Na; – – –, 0.0 M salt concentration. A, M_1; B, M_2; C, M_3

the use of a constant volume thermometer described in detail elsewhere[21]. Accurate values of γ_V for these systems were obtained by correcting for the thermal expansion coefficient and isothermal compressibility of the glass cell and mercury by procedures described in detail elsewhere[21]. The values of γ_V for pure water measured in this work agree with reported values[24] within 0.8% over the temperature range of 30°–60°C. Cloud point temperatures for the solution of PEG in salt solution were determined optically with a precision of ±0.05°C as described elsewhere[13].

RESULTS

Typical phase diagrams for solutions of PEG in water–NaCl and water–Pro–Na are shown in *Figure 1*. The diagrams indicate significant variation of the *LCST* with an increase in salt concentration, without change in the shape of the phase diagrams. An upper critical phase diagram was not observed at temperatures up to 220°C in the low molecular weight PEG–water–salt systems. Although the minimum points of the cloud point curves for the solution of PEG in water–salt deviate slightly from the critical points because of polydispersity of the samples[25,26] and salt concentration, the deviations from the critical points should be quite small in relation to polydispersity because of the polymer samples being obtained by the solution fractionation technique. The θ temperature, estimated experimentally from the maximum and minimum point in the separation temperature *versus* concentration plot for the solution of poly(riboadenylic acid) of the well defined molecular weight in sodium chloride solution[22], coincides well with the value obtained from the vanishing of A_2, the second virial coefficient. Since we are mainly interested in qualitative features of miscibility, the minimum temperatures in the phase diagrams are taken as the critical solution temperatures, or *LCST*s.

The lowering of the *LCST* with an increase of salt concentration in the vicinity of zero salt concentration depends on polymer molecular weight. The *LCST* is lowered 144°C/M with Pro–Na and 364°C/M with NaCl in aqueous PEG ($M_\eta = 2.18 \times 10^3$) solution; 39°C/M with Pro–Na and 58°C/M with NaCl in aqueous PEG ($M_\eta = 8 \times 10^3$) solution, and 25°C/M with Pro–Na and 34°C/M with NaCl in aqueous PEG($M_\eta = 719 \times 10^3$) solution. The results indicate that a large variation of the *LCST* occurs with a decrease of molecular weight of polymer and that a larger variation of the *LCST* occurs in the water–NaCl system than in the Pro–Na system.

Plots of γ_V against weight fraction of ethylene glycol (w_2) for water–ethylene glycol and against (M) for the water–NaCl and water–Pro–Na solutions are shown in *Figure 2*. The γ_V of the ethylene glycol–water system at concentrations higher than 40–60 wt % is larger than that of pure ethylene glycol, so γ_V^E is positive and large. The γ_V values of both salt solutions increase monotonically with an increase of concentration. It was also observed that the temperature functionality of γ_V for the water–Pro–Na system at concentrations lower than 0.079 M is expressed by a nearly parabolic temperature dependence with a maximum similar to that for pure water. On the other hand, the functionality of γ_V in the water–Pro–Na system for concentrations higher than 0.26 M and in the water–NaCl system for the concentration range of 0.27 to 1.42 M is expressed by a nearly parabolic temperature dependence with a minimum.

In *Figure 3*, the thermal expansion coefficients for the water–NaCl, water–Pro–Na and water–ethylene glycol solutions are plotted against salt concentration (M) and against weight fraction EG over the temperature range 25°

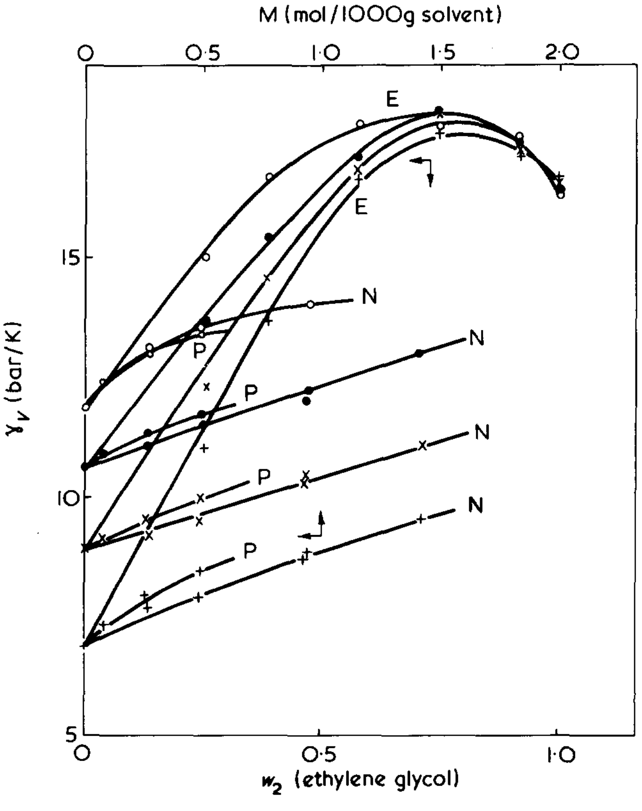

Figure 2 Concentration dependence of thermal pressure coefficient of water–ethylene glycol (E), water–NaCl (N), and water–Pro–Na (P) systems at various temperatures: ○, 60°C; ●, 50°C; X, 40°C; +, 30°C

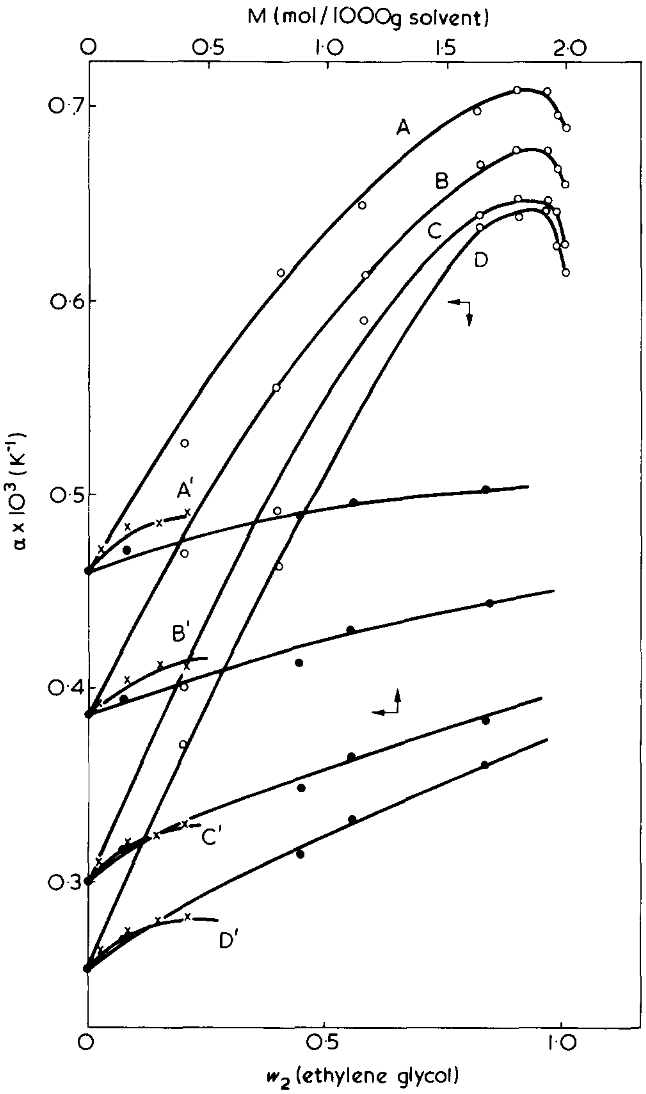

Figure 3 Concentration dependence of thermal expansion coefficient of water–ethylene glycol (○), water–NaCl (●) and of water–Pro–Na (X) at various temperatures: A, A', T_1 = 50°C; B, B', T_2 = 40°C; C, C', T_3 = 30°C; D, D', T_4 = 25°C

to approximately 50°C. The values of α for the ethylene glycol–water system have maximum values at about 90 wt % ethylene glycol. The α values are larger than the α values of pure ethylene glycol. This indicates that the excess thermal expansion coefficient (α^E) for EG–water system is positive and large. The value of α in both salt solutions increases with an increase in salt concentration.

The plot of solution specific volume (cm^3/g) against concentration of EG is shown in *Figure 4* and is a nearly parabolic curve with a minimum corresponding to a negative excess volume of mixing in the EG–water system over the temperature range of 30°–60°C. The values of V^E (cm^3/g) for EG–water at a concentration of 60 wt % EG are −0.0080 to −0.0095 (cm^3/g) over the temperature range of 60°–30°C. These results compare with the V^E values of −0.021 (cm^3/g) at 65°C and concentration of 60 wt % PEG observed in the poly(ethylene glycol) (M_η = 5000)–water system[1]. It was also observed that the plots of aqueous solution specific volume against concentration (M) of Pro–Na and NaCl shown in *Figure 4* are nearly parabolic curves with maxima; the maximum deviation from the straight line is 0.0035 (cm^3/g) for NaCl and 0.0020 (cm^3/g) for Pro–Na.

DISCUSSION

The Prigogine–Patterson[7,8] and Flory theories[10] of polymer solution thermodynamics lead to essentially the same expression for the polymer–solvent interaction parameter χ_1 as a function of temperature. The Patterson theory[7,8] yields:

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

The term $-U_1$ is the energy of vaporization of the solvent, $C_{P,1}$ is solvent configurational heat capacity, and R is the gas constant. The ν^2 parameter is related to the difference of cohesive energy and segmental size between the solvent molecules (notation 1) and polymer segments and therefore is related to the difference of specific volume and thermal pressure coefficient of the two components. The τ parameter reflects the free volume change which occurs on mixing the dense polymer with relatively expanded solvent and is related to the difference of the thermal expansion coefficient of the polymer and solvent.

It is convenient to rewrite equation (1) when applying it to polymer solutions and discussing the phenomenon of solubility using a thermodynamic equation of state or the difference between the heat capacities at constant pressure (C_P) or at constant volume (C_V):

$$-U_1 = \gamma_{V,1} V_1 T \qquad (2)$$

$$C_{P,1} = \gamma_{V,1} V_1 T \alpha_1 \qquad (3)$$

where $\gamma_V\,[(\partial P/\partial T)_V]$, $\alpha[1/V(\partial V/\partial T)_P]$ and V are the thermal pressure coefficient, thermal expansion coefficient, and specific volume, respectively. According to the corresponding states theory of Patterson, the solubility of two components would be good if the P–V–T behaviour of the two

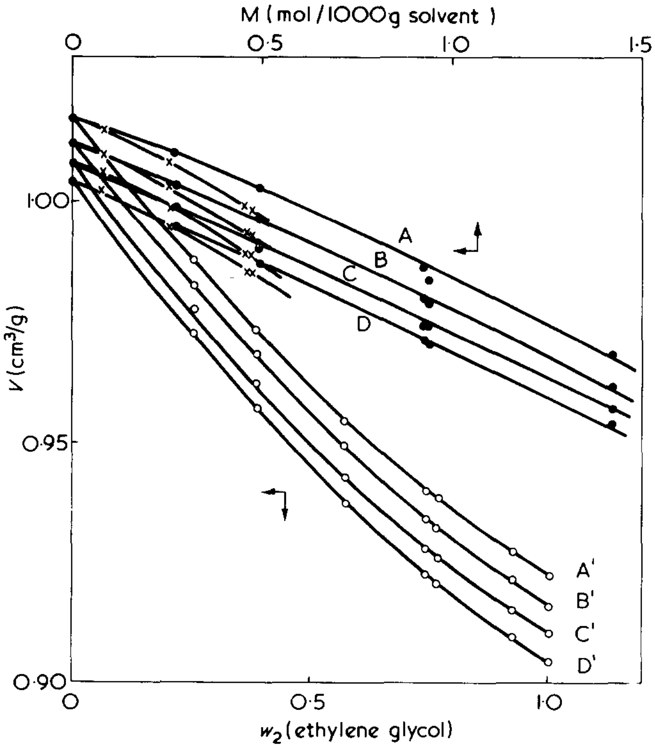

Figure 4 Concentration dependence of specific volume of water–ethylene glycol (○), water–NaCl (●) and of water–Pro–Na (X) at various temperatures: A, A', T_1 = 60°C; B, B', T_2 = 50°C; C, C', T_3 = 40°C; D, D', T_4 = 30°C

components is such that values of γ_V, α and V of two components are quite similar to each other, because the parameters υ^2 and τ^2 approach zero, and the value of χ_1 then would approach zero.

The values of γ_V in most organic liquids decrease monotonically and isothermal compressibility, β_T, and α increase with increasing temperature, which is in agreement with the theoretical prediction from the reduced equation of state of the van der Waals model. However, the mechanical properties of pure water[24], such as γ_V, β_T and α, are in extreme contrast with those of many organic liquids. For example, the temperature dependence of γ_V for pure water is expressed by a parabolic-like temperature dependence with a maximum at ~150°C, and the temperature dependence of β_T is given by a parabolic-like temperature dependence with a minimum in the vicinity of 45°C. The value of α for pure water is very small compared with that of most organic solvents and has a negative value in the vicinity of 4°C. It would be unjustified to use equation (1) in discussing solubility or phase separation of aqueous polymer solutions because equation (1) applies only to non-polar solutions.

It is of interest to discuss the phenomenon of solubility of any type of polymer solution, including the system in which orientation-dependent interactions are dominant, with the aid of the temperature derivative of the thermodynamic equation of state. From thermodynamics:

$$dE = TdS - PdV + \sum_i \mu_i dN_i \tag{4}$$

where μ_i and N_i are chemical potential and number of molecules of component i. Now,

$$(\partial E/\partial V)_{T,N_i} = T(\partial S/\partial V)_{T,N_i} - P \tag{5}$$

Taking the limit as pressure goes to zero

$$(\partial E/\partial V)_{T,N_i} \cong T\left(\frac{\partial S}{\partial V}\right)_{T,N_i} = T\left(\frac{\partial P}{\partial T}\right)_{V,N_i} \tag{6}$$

But $\gamma_V = (\partial P/\partial T)_{V,N_i}$, so at low pressure the thermodynamic equation of state is:

$$V(\partial E/\partial V)_{T,N_i} \cong VT\gamma_V \tag{7}$$

and its temperature derivative is:

$$\left[\frac{\partial V(\partial E/\partial V)_{T,N_i}}{\partial T}\right]_{P,N_i} = \gamma_V V + \gamma_V T(\partial V/\partial T)_{P,N_i} + VT(\partial\gamma_V/\partial T)_{P,N_i} \tag{8}$$

$$T\left[\frac{\partial V(\partial E/\partial V)_{T,Ni}}{\partial T}\right]_{P,N_i} = \gamma_V TV(1 + \alpha T) + VT^2(\partial\gamma_V/\partial T)_{P,N_i} \tag{9}$$

where $\alpha = 1/V(\partial V/\partial T)_{P,N_i}$.

Equations (8) and (9) give a general formulation for the energy of the solution, apart from the energy due to ideal entropy of mixing or to combinatorial contributions, and also for the energy of pure liquids. The excess energy or excess heat of vaporization estimated from the values of $\gamma_V VT$, $\gamma_V VT^2\alpha$ and $VT^2(\partial\gamma_V/\partial T)_P$ using equation (9) would be consistent with the value of χ or excess chemical potential $[(\mu_1 - \mu_1^0)^E/RT\phi_2^2]$. The first and second term (derived with γ_V constant) in equation (8), or the first term in equation (9), correspond to the two terms in equation (1) coupled with equations (2) and (3). The last term in equations (8) and (9), originating from the temperature derivative of γ_V, is new. The disappearance of the $(\partial\gamma_V/\partial T)_P$ term in equation (1) is caused by the assumption that the intermolecular energy can be expressed by a van der Waals type of volume dependence ($-U \propto 1/V$). This means that the energy taken into account in the expression for χ is restricted to a volumetric contribution characterized by the internal pressure contribution ($\gamma_V TV$) and by a volume expansion term ($\gamma_V TV T\alpha$), or the first term in equation (9). The third energy term in equation (8) is directly related to the temperature derivative of γ_V. The contribution of $(\partial\gamma_V/\partial T)_P$ to vaporization energy or negative configurational energy is negative for most organic liquids and for water at temperature higher than ~150°C. On the other hand, that of $(\partial\gamma_V/\partial T)_P$ for water is positive below ~150°C. The contribution of the second term $\gamma_V VT\alpha$ in equation (8) for water is a much smaller positive value than for most organic liquids below ~150°C and is negative in the vicinity of 4°C. The behaviour of water at temperatures lower than ~150°C can be ascribed to strong orientational interactions such as hydrogen bonding. The positive value of $(\partial\gamma_V/\partial T)_P$ is related to the energy of orientational ordering or orientation-dependent interaction energy, which cannot be taken into account in the van der Waals model.

It is useful to examine the variation of γ_V, α, and $(\partial\gamma_V/\partial T)_P$ in the systems EG–water, Pro–Na–water and NaCl–water and compare them with the behaviour of *LCST* phase separation in the PEG–water–salt system. In the EG–water system the excess thermal pressure coefficient, γ_V^E, and excess thermal expansion coefficient, α^E, are positive, while the excess volume of mixing, V^E, is negative. The values of $(\partial\gamma_V/\partial T)_P$ for the EG–water and aqueous salt solutions are plotted against concentration in *Figure 5*. The values of $(\partial\gamma_V/\partial T)_P$ for EG–water form a nearly parabolic curve with a maximum at EG concentrations (w_2) of less than 0.6–0.8, while at the higher concentrations than 0.6–0.8 the values of $(\partial\gamma_V/\partial T)_P$ are almost zero and become negative (–0.01 bar/(deg)^2) for pure ethylene glycol. The behaviour of $(\partial\gamma_V/\partial T)_P$ at concentrations higher than 0.6–0.8 corresponds to the result that the values of γ_V at concentrations higher than 0.4–0.6 are larger than those for pure ethylene glycol (shown in *Figure 2*).

The excess vaporization energy for EG–water system, determined from plots of $\gamma_V VT$, $\gamma_V VT^2\alpha$, and $VT^2(\partial\gamma_V/\partial T)_P$ against concentration of EG according to equation (9), is positive because all excess terms are positive. For example, the calculated excess values of $\gamma_V VT$, $\gamma_V VT^2\alpha$ and $VT^2(\partial\gamma/\partial T)_P$ for the EG–water system at an ethylene glycol concentration of $w_2 = 0.3$ and temperature of 50°C are 6.6 x 10^2 bar cm^3/g for $(\gamma_V VT)^E$, 1.9 x 10^2 for $(\gamma_V VT^2\alpha)^E$ and 17 x 10^2 for $[VT^2(\partial\gamma_V/\partial T)_P]^E$. The value of $[VT^2(\partial\gamma_V/\partial T)_P]^E$ is much larger than the others. The temperature dependence of the excess vaporization energy, estimated from the temperature dependence of $(\gamma_V VT)^E$, $(\gamma_V VT^2\alpha)^E$ and $[(\partial\gamma_V/\partial T)_P VT^2]^E$, is positive and dominated by the strong temperature dependence of $[(\partial\gamma_V/\partial T)_P VT^2]^E$ and $(\gamma_V VT^2\alpha)^E$.

The positive excess vaporization energy and the increase

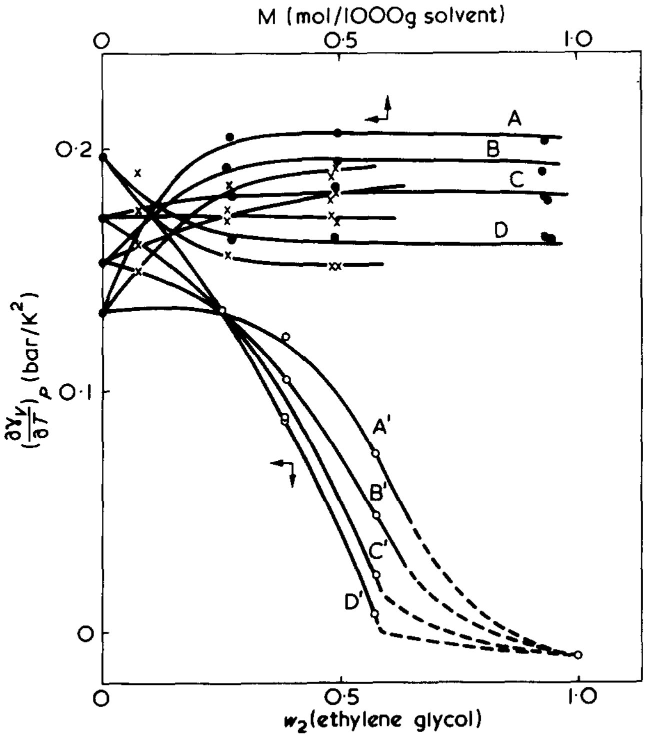

Figure 5 Concentration dependence of $(\partial\gamma_V/\partial T)_P$ of water–ethylene glycol (O), water–NaCl (●) and of water–Pro–Na (X) at various temperatures: A, A', T_1 = 55°C; B, B', T_2 = 50°C; C, C', T_3 = 45°C; D, D', T_4 = 35°C

of excess vaporization energy of the system with an increase of temperature estimated from equation (9) suggest that the system changes to a more stable state or lower energy than estimated from additivity of energy upon mixing EG and water and that the positive excess vaporization energy increases with an increase of temperature. On the other hand the excess heat of mixing of the poly(ethylene glycol)–water system over the entire concentration range at 80.3°C is negative[1], and phase separation behaviour of the *LCST* sort is also observed in the PEG–water system. There is a strong correlation between the positive excess vaporization energy calculated from the values of $V\gamma_V T$, $\gamma_V V T^2\alpha$ and $VT^2(\partial\gamma_V/\partial T)_P$ by equation (9) and the negative heat of mixing or phase separation behaviour of the *LCST*.

The great increase of $\gamma_V[=(\partial S/\partial V)_T]$ with an increase of temperature at constant concentration or with an increase of concentration at constant temperature in the Pro–Na–water and NaCl–water, as shown in *Figure 2*, indicates that the ratio of entropy change to enlargement of volume increases greatly in the salt solutions (as compared to pure water) as temperature or concentration increases. In *Figure 5*, the values of $(\partial\gamma_V/\partial T)_P$ for both solutions increase with an increase of concentration at 55°C, while the values decrease at a temperature of 35°C. This behaviour is consistent with a contribution to the entropy originating from a break down of the structure of water caused by temperature or salts and is related to the lowering of the *LCST* observed in PEG–water–salt systems. There is a clear difference in phase separation behaviour in aqueous solutions of NaCl and PEG and in aqueous solutions of Pro–Na and PEG. We cannot at this time explain quantitatively the reasons for the differences in behaviour.

CONCLUSIONS

In this work we have examined the phase separation behaviour of the *LCST* and the lowering of the *LCST* in the poly(ethylene glycol)–water system by adding salts and taking into account the thermodynamic and mechanical properties of the ethylene glycol–water system and of water–sodium chloride and water–propionic acid sodium salt systems. We discussed the phase separation behaviour of the *LCST* in the poly(ethylene glycol)–water salt systems with the aid of the χ_1 expression derived by Patterson and the thermodynamic equation of state and its temperature derivatives in which the contribution of the term $(\partial\gamma_V/\partial T)_P$ to the vaporization energy is taken into account.

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