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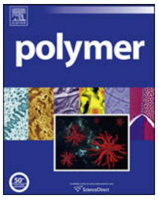

The effect of NaCl on the eutectic phase behavior of aqueous poly(ethylene glycol) solutions

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The phase behaviors of aqueous polymer solutions are known to be affected by the presence of ions even if the polymer itself does not have any charges. We studied the effect of salt (sodium chloride) on the eutectic phase behavior of non-ionic polymer, poly(ethylene glycol) (PEG) in aqueous solutions using differential scanning calorimetry. We observed that the addition of NaCl increased the liquidus temperature of PEG and decreased that of water. As a result, a steep rise (or fall) is induced in the liquidus around the eutectic point. A simple Flory–Huggins lattice model for the mixture (PEG–water–NaCl) was applied to the experimental results. The model quantitatively reproduced the change in the liquidus both with and without NaCl. The obtained interaction parameters suggest that the increase of the PEG melting temperature by NaCl can be understood as the depletion of NaCl around PEG, possibly due to the image charge repulsion.

1. Introduction

Poly(ethylene glycol) (PEG) is a simple synthetic and water soluble polymer. Because of many applications from cryoprotectant to protein purification, PEG solutions have been attracted to many scientists especially in terms of its hydration properties [1–4]. Among the many applications, protein crystallization using PEG is one of the most important uses, where proteins usually crystallize in a complex mixture of protein, water, salt, and PEG. Salt is often necessary to screen surface charges on protein molecules, whereas PEG is thought to induce required attraction between protein molecules via the depletion effect [5,6]. In fact, a lot of proteins are crystallized using combinations of PEG and some salt. The detailed interactions among constituents in the solution, however, are not fully understood yet. Especially, interaction between PEG and salt in protein solutions, and how it affects protein crystallization, have been received little attention.

The interaction between PEG and salt affects the phase behaviors of PEG itself. The melting behaviors of PEG–water mixtures have been intensively investigated previously [3,7]. The Flory–Huggins theory reproduced at least partly the phase diagram with the Flory–Huggins interaction χ-parameter. Addition of NaCl to the PEG–water mixture destabilizes the solution state of PEG, and decreases the cloud point of the solutions [8,9]. This was attributed to the so-called salting-out effect, which is thought to be caused when the salt molecules are preferentially excluded from the surface of the polymer [9]. NaCl is also known to prevent the cold crystallization of PEG in frozen solution [10]. So far, however, few studies have been reported on the effect of NaCl on the liquidus of PEG–water mixtures.

In this study, we focus on the effect of NaCl on the eutectic phase behavior of PEG–water mixtures using differential scanning calorimetry (DSC). Special attention is paid on the melting behaviors (liquidus) of water and PEG. We test a simple lattice model to reproduce the experimentally obtained liquidus curves in an attempt to understand the interaction among the constituents of this complex system. Firstly we review the lattice model and the method to construct liquidus curves. Then we suggest a simple form of the chemical potential balance with parameters experimentally tractable. Since the parameters are physically well defined in the lattice model, it is expected that it helps us to elucidate the relation between the interaction of constituents and the phase behaviors in the mixtures.

2. Methods

2.1. Experimental

PEG was purchased from Fluka Chemical and used without further purification. The molecular weight was $M_n = 35\,000$ g/mol. Aqueous solutions with different concentrations of NaCl and PEG in a powder form were mixed at an appropriate ratio in an aluminium

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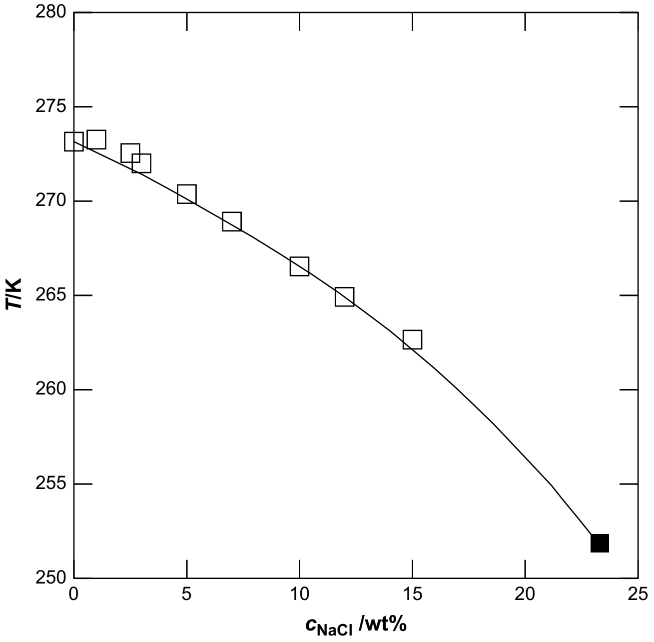

Fig. 1. Melting points of water–NaCl mixtures determined in this study, squares, and the freezing points reported by Hall et al. [13], the solid curve. The solid square represents the eutectic point.

pan with a hermetic cap. The samples were kept at 60 °C or 80 °C overnight (about 12 h) prior to measurements to ensure the homogeneity. The sample weight (10 ± 0.5 mg) was measured before and after the measurements to check water evaporation.

Thermal analysis of PEG solutions was carried out with a differential scanning calorimetry (2920 MDSC V2.5F, TA Instruments). Samples kept either at 60 °C (for samples lower than 50 wt% of PEG) or at 80 °C (for those higher than 50 wt% of PEG) were cooled with a rate of 1 °C/min down to −50 °C. They were kept there for 2 min and then heated with the rate of 5 °C/min.

The melting temperature of a eutectic mixture is in general defined as the temperature where every part of solid melts and the heat absorption finishes, that is, the end point of a peak in heat-flow-temperature diagrams. In practice, however, the melting point does not necessarily correspond to the end point of the peak because of the finite response time of a DSC apparatus. Mraw proposed a model of DSC of heat flux type which describes the heat flows and temperature changes of both a sample and a heat bath [11]. We followed the method proposed by Toda et al. [12] who solved the equations and suggested a procedure how to estimate accurately the melting point from DSC thermograms. We chose peak points of the thermograms as the melting temperature except pure water and the NaCl solution at the eutectic point, where the onset is sharp enough to be identified as the melting point (Fig. 2b).

We tested our method by measuring the melting point of NaCl solutions. Fig. 1 shows a good agreement between our results and the freezing point of NaCl solutions in the literature [13]. The method used in this study minimizes the effect of the response time of an apparatus and does not require to test several heating rates for the extrapolation to the infinitely slow heating. Thus it is especially suitable for the study of transitions of polymer mixtures, in which the annealing effect with a slow heating cannot be avoided [14].

2.2. Model

To construct model phase diagrams, we calculate chemical potentials of PEG and water both in a liquid state and a solid state. We use the lattice model of Flory–Huggins [15] for the liquid states and Hildebrand–Scott's equations [16] for the solid states. The method is a combination of those introduced by Smith and Pennings [17] and Koningsveld and Kleintjens [18] except that in our case it is for a quaternary mixture among water, PEG, Na^+, and Cl^-. Although we firstly introduce four components represented by subscripts 1, 2, 3 and 4, we treat NaCl as one component (denoted by the subscript a) by taking the mixture between water and NaCl, or those between PEG and NaCl as the reference state for the chemical potentials.

2.2.1. Chemical potential of liquid phase

The free energy of mixing per unit volume ΔG is given as [15],

$$\frac{\Delta G}{kT} = \frac{1}{v_s}\left[\sum_i \frac{\phi_i \ln \phi_i}{N_i} + \sum_{i<j} \chi_{ij}\phi_i\phi_j\right] \qquad (1)$$

with $i = 1$–4 denoting water, PEG, Na^+, and Cl^-. k is the Boltzmann constant and T is the temperature. v_s is the volume of a segment which is set at the volume of a water molecule (18 cm^3/g). N_i represents the number of segments per molecule of each

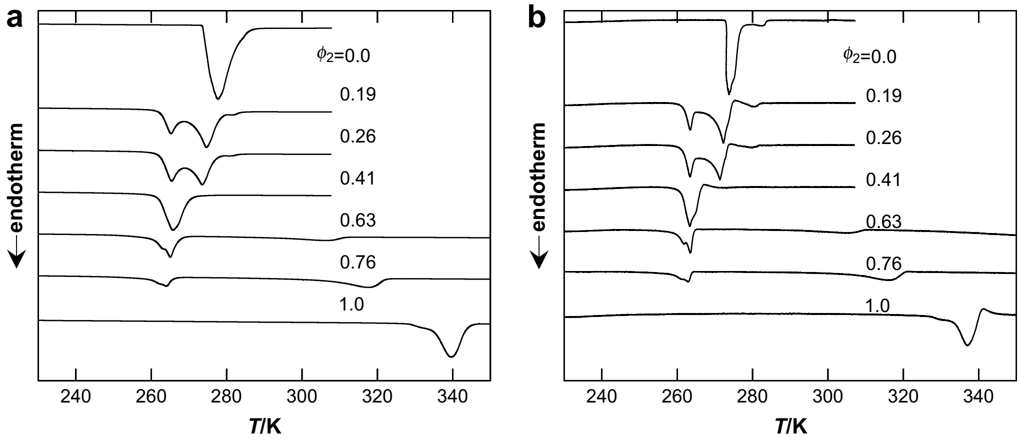

Fig. 2. DSC melting endotherms for binary PEG–water mixtures with various volume fractions of PEG, ϕ_2. The raw data (a) are corrected as shown in (b) according to the method proposed by Toda et al. [12]. The peak position is shifted and the peak width is reduced with the correction. The slight peaks seen just after the main peaks in (b) are artifacts resulted from the correction.

Table 1
The parameters obtained from the experiments.

NaCl/wt%	0	1.0	3.0	5.0
$T_1^{0'}$/K	273	273	272	270
$T_2^{0'}$/K	337	337	337	338
$\Delta h_1^{0'}$/J g^{-1}	340	329	229	226
$\Delta h_2^{0'}$/J g^{-1}	176	178	171	164
$\Delta C_1^{0'}$/J g^{-1} K^{-1}	2.1	2.0	2.1	1.9
$\Delta C_2^{0'}$/J g^{-1} K^{-1}	0.42	0.54	0.45	0.52

component. By definition, $N_1 = 1$. The number of polymer segments, N_2, is defined by the volume of a PEG molecule, v_{PEG}, as $N_2 = v_{\mathrm{PEG}}/v_s$, where v_{PEG} is calculated using the specific volume of PEG, 0.885 cm^3/g [19].

The parameters χ_{ij} $(i<j)$ represent the interaction between segments of i and j. In general, it is known that the parameter χ_{12} which represents the interaction between solvent and polymer is a function of both the temperature and volume fraction of polymer, $\chi_{12}(T, \phi_2)$ [15,18,20]. On the other hand, we ignore any concentration dependence for the interaction parameters between salt and water or salt and PEG. For simplicity, we further assume $\chi_a = \chi_{13} - \chi_{23} = \chi_{14} - \chi_{24}$ and ignore the difference in the specific volume of Na$^+$ and Cl$^-$ with defining $\phi_a/2 = \phi_3 = \phi_4$ and $N_a = N_3 = N_4$.

These assumptions neglect the difference between Na$^+$ and Cl$^-$. This crude approximation is partly supported by the fact that NaCl does not form any complex with PEG [8]. In this study, we do not identify which of the two types of ions has dominant effects on the phase behaviors of PEG solutions. Moreover, the long range nature of the electrostatic interactions is hard to be captured with a lattice model when the concentration of electrolytes is high. Therefore our model is considered valid only for dilute salt solutions.

By differentiating Eq. (1) the chemical potentials of water and PEG are given as

$$\frac{\mu_1^l - \mu_1^0}{kT} = \ln\phi_1 + 1 - \phi_1 - \frac{\phi_2}{N_2} - \frac{\phi_a}{N_a} + \chi_{12}(1-\phi_1)\phi_2 - \chi'_{12}\phi_1\phi_2^2 + \chi_a\phi_2\phi_a + \frac{1}{2}\left(\chi_{13} + \chi_{14} - \frac{\chi_{34}}{2}\right)\phi_a^2 \qquad (2)$$

$$\frac{\mu_2^l - \mu_2^0}{kT} = \frac{\ln\phi_2}{N_2} + \frac{1-\phi_2}{N_2} - \phi_1 - \frac{\phi_a}{N_a} + \chi_{12}\phi_1(1-\phi_2) + \chi'_{12}\phi_1\phi_2(1-\phi_2) - \chi_a\phi_1\phi_a + \frac{1}{2}\left(\chi_{23} + \chi_{24} - \frac{\chi_{34}}{2}\right)\phi_a^2 \qquad (3)$$

where

$$\chi'_{12} = \left(\frac{\partial\chi_{12}}{\partial\phi_2}\right)_T. \qquad (4)$$

μ_i^l and μ_i^0 represent the chemical potential of water or PEG in a mixture and that of pure materials, respectively. From the assumption of incompressibility, the volume fraction ϕ_i must satisfy the relation,

$$\phi_1 + \phi_2 + \phi_a = 1. \qquad (5)$$

Eqs. (2) and (3) can be further simplified for our system. Since our system is not symmetric, that is, the concentration of NaCl is not high (5 wt% at maximum), it is treated as an additive. Therefore the chemical potentials of the two binary mixtures, water + NaCl (without PEG) $\mu_1^{0'}$, and PEG + NaCl (without water) $\mu_2^{0'}$ can be chosen as the references of the chemical potentials. They are given as

$$\frac{\mu_1^{0'} - \mu_1^0}{kT} = \ln(1-\phi_a) + \phi_a - \frac{\phi_a}{N_a} + \frac{1}{2}\left(\chi_{13} + \chi_{14} - \frac{\chi_{34}}{2}\right)\phi_a^2 \qquad (6)$$

$$\frac{\mu_2^{0'} - \mu_2^0}{kT} = \frac{\ln(1-\phi_a)}{N_2} + \frac{\phi_a}{N_2} - \frac{\phi_a}{N_a} + \frac{1}{2}\left(\chi_{23} + \chi_{24} - \frac{\chi_{34}}{2}\right)\phi_a^2 \qquad (7)$$

Substituting Eqs. (6) and (7) from Eqs. (2) and (3) gives

$$\frac{\mu_1^l - \mu_1^{0'}}{kT} = \ln\left(\frac{\phi_1}{1-\phi_a}\right) + \left(1 - \frac{1}{N_2}\right)\phi_2 + \chi_{12}(1-\phi_1)\phi_2 - \chi'_{12}\phi_1\phi_2^2 + \chi_a\phi_2\phi_a \qquad (8)$$

$$\frac{\mu_2^l - \mu_2^{0'}}{kT} = \frac{1}{N_2}\ln\left(\frac{\phi_2}{1-\phi_a}\right) - \left(1 - \frac{1}{N_2}\right)\phi_1 + \chi_{12}\phi_1(1-\phi_2) + \chi'_{12}\phi_1\phi_2(1-\phi_2) - \chi_a\phi_1\phi_a. \qquad (9)$$

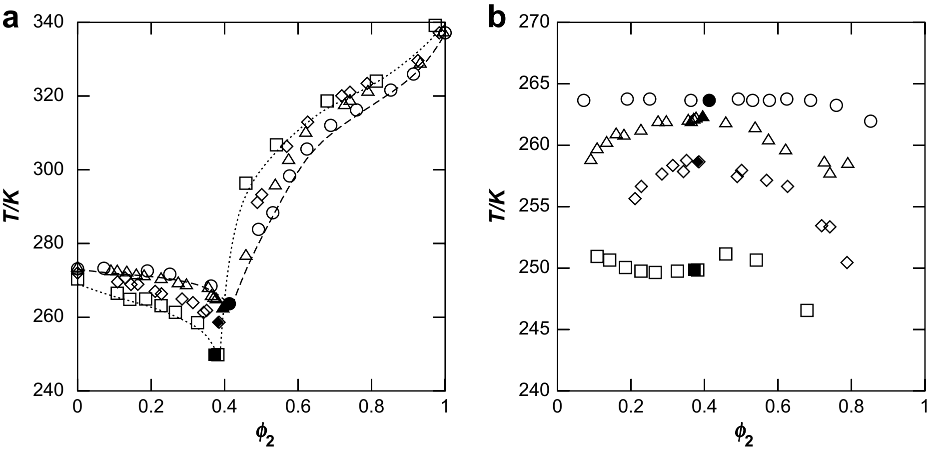

Fig. 3. Melting points of the PEG–water–NaCl systems measured by DSC. The liquidus, (a), and the solidus, (b). Symbols represent: without NaCl, circles; NaCl 1 wt%, triangles; 3 wt%, diamonds; 5 wt%, squares. Filled symbols represent the eutectic points. The broken and dotted curves are guide to eye.

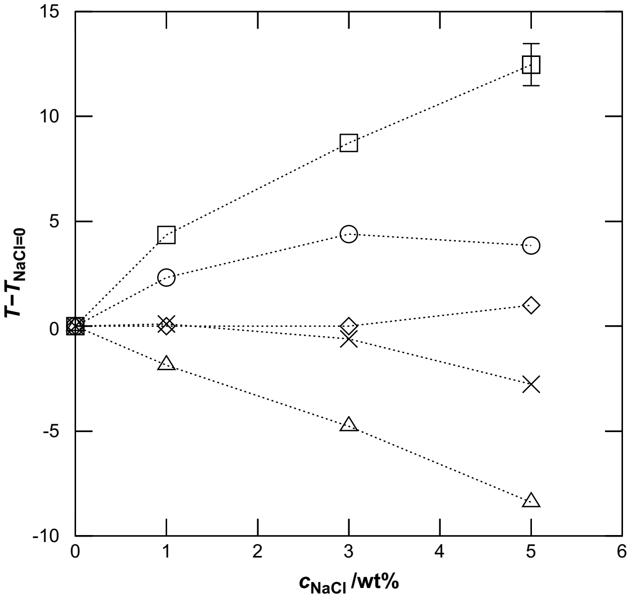

Fig. 4. The change of the melting temperature induced by NaCl at a fixed amount of PEG. The values were estimated using polynominal interpolation, and subtracted by the values at NaCl 0 wt%. Symbols represent: without PEG, crosses; $\phi_2 = 0.2$, triangles; $\phi_2 = 0.6$, squares; $\phi_2 = 0.8$, circles; without water, diamonds. The dotted lines are guide to eye.

Now the six interaction parameters, χ_{ij} are reduced to only two, χ_{12} and χ_a. The expressions in Eqs. (8) and (9) allow us to use experimentally available parameters of the binary mixtures such as the melting temperatures of ice and PEG in the presence of NaCl.

The effective interaction parameter χ_{12}^{eff} is defined as [18,20]

$$\chi_{12}^{\mathrm{eff}} = \chi_{12} - \chi'_{12}(1 - \phi_2), \tag{10}$$

with which we can keep the connection between the interaction parameter and the chemical potential of solvent without additive ($\phi_a = 0$) available in the literature as

$$\frac{\mu_1^l - \mu_1^0}{kT} = \ln \phi_1 + \left(1 - \frac{1}{N_2}\right)\phi_2 + \chi_{12}^{\mathrm{eff}}\phi_2^2. \tag{11}$$

To proceed further, we must assume a function form for $\chi_{12}(T, \phi_2)$. We use the one proposed by Koningsveld and Kleintjens [18],

$$\chi_{12}(T, \phi_2) = a + \frac{b + cT_1^0/T}{1 - d\phi_2} \tag{12}$$

where a–d are dimensionless parameters determined using PEG–water mixtures. T_1^0 is the melting temperature of pure water. We further assume that χ_{12} is not changed by the addition of NaCl.

For $\chi_a = \chi_{13} - \chi_{23} = \chi_{14} - \chi_{24}$, we assume

$$\chi_a = e + fT_1^0/T \tag{13}$$

where e and f are again dimensionless parameters determined using PEG–water–NaCl mixtures.

Table 2
The eutectic points for each solution.

NaCl/wt%	0	1.0	3.0	5.0
ϕ_2^{ep}	0.41	0.40	0.39	0.38
w_2^{ep}	0.44	0.42	0.41	0.40
T_{ep}/K	264	262	259	250
n_{max}	3.1	3.4	3.5	3.7

2.2.2. *Chemical potential of solid phase*

Following the method by Hildebrand and Scott [16], we start from the Gibbs–Helmholtz equation,

$$\frac{\mu_i^s - \mu_i^{0'}}{T} = -\int_T^{T_i^{0'}} \frac{\Delta h_i}{T^2}\mathrm{d}T, \tag{14}$$

where μ_i^s is the chemical potential of a segment in the solid state. Since we set the binary mixture of water + NaCl or PEG + NaCl as the reference for the chemical potential, $T_i^{0'}$ is their melting temperature. Δh_i is the latent heat approximated as [16]

$$\Delta h_i = \Delta h_i^{0'} + \Delta C_i^{0'}\left(T - T_i^{0'}\right) \tag{15}$$

where $\Delta h_i^{0'}$ and $\Delta C_i^{0'}$ are the latent heat of the binary mixture and its specific heat difference between the liquid and solid phase, respectively. The parameters $T_i^{0'}$, $\Delta h_i^{0'}$, and $\Delta C_i^{0'}$ are determined by the experiments. Substituting Eq. (15) into (14) gives the chemical potential of the solid phase,

$$\frac{\mu_1^s - \mu_1^{0'}}{kT} = -\frac{\Delta h_1^{0'}}{kT}\left(1 - \frac{T}{T_1^{0'}}\right) + \frac{\Delta C_1^{0'}}{k}\left\{\frac{T_1^{0'}}{T} - 1 - \ln\left(\frac{T_1^{0'}}{T}\right)\right\} \tag{16}$$

$$\frac{\mu_2^s - \mu_2^{0'}}{kT} = -\frac{\Delta h_2^{0'}}{kT}\left(1 - \frac{T}{T_2^{0'}}\right) + \frac{\Delta C_2^{0'}}{k}\left\{\frac{T_2^{0'}}{T} - 1 - \ln\left(\frac{T_2^{0'}}{T}\right)\right\}. \tag{17}$$

2.2.3. *Construction of the phase diagrams*

By equating Eqs. (8), (9) and (16), (17) we have equations with which the melting temperature (liquidus) of water, T_1 and PEG, T_2 can be calculated,

$$\begin{aligned} &\ln\left(\frac{\phi_1}{1 - \phi_a}\right) + \left(1 - \frac{1}{N_2}\right)\phi_2 + \chi_{12}(1 - \phi_1)\phi_2 - \chi'_{12}\phi_1\phi_2^2 \\ &\quad + \chi_a\phi_2\phi_a = -\tilde{h}_1^{0'}(x_1 - 1) + \tilde{C}_1^{0'}(x_1 - 1 - \ln x_1) \end{aligned} \tag{18}$$

$$\begin{aligned} &\frac{1}{N_2}\ln\left(\frac{\phi_2}{1 - \phi_a}\right) - \left(1 - \frac{1}{N_2}\right)\phi_1 + \chi_{12}\phi_1(1 - \phi_2) \\ &\quad + \chi'_{12}\phi_1\phi_2(1 - \phi_2) - \chi_a\phi_1\phi_a = -\tilde{h}_2^{0'}(x_2 - 1) \\ &\quad + \tilde{C}_2^{0'}(x_2 - 1 - \ln x_2) \end{aligned} \tag{19}$$

where all parameters are defined as dimensionless,

$$x_1 = \frac{T_1^{0'}}{T_1}, \quad x_2 = \frac{T_2^{0'}}{T_2} \tag{20}$$

$$\tilde{h}_1^{0'} = \frac{\Delta h_1^{0'}}{kT_1^{0'}}, \quad \tilde{h}_2^{0'} = \frac{\Delta h_2^{0'}}{kT_2^{0'}} \tag{21}$$

$$\tilde{C}_1^{0'} = \frac{\Delta C_1^{0'}}{k}, \quad \tilde{C}_2^{0'} = \frac{\Delta C_2^{0'}}{k}. \tag{22}$$

Solving numerically Eq. (18) for x_1 and Eq. (19) for x_2, we obtain liquidus curves in the phase diagrams. It should be noted that the unknown parameters in the model are $\chi_{12}(T, \phi_2)$ and χ_a, which are determined by the non-linear-fitting procedure, and the rest are all experimentally obtainable.

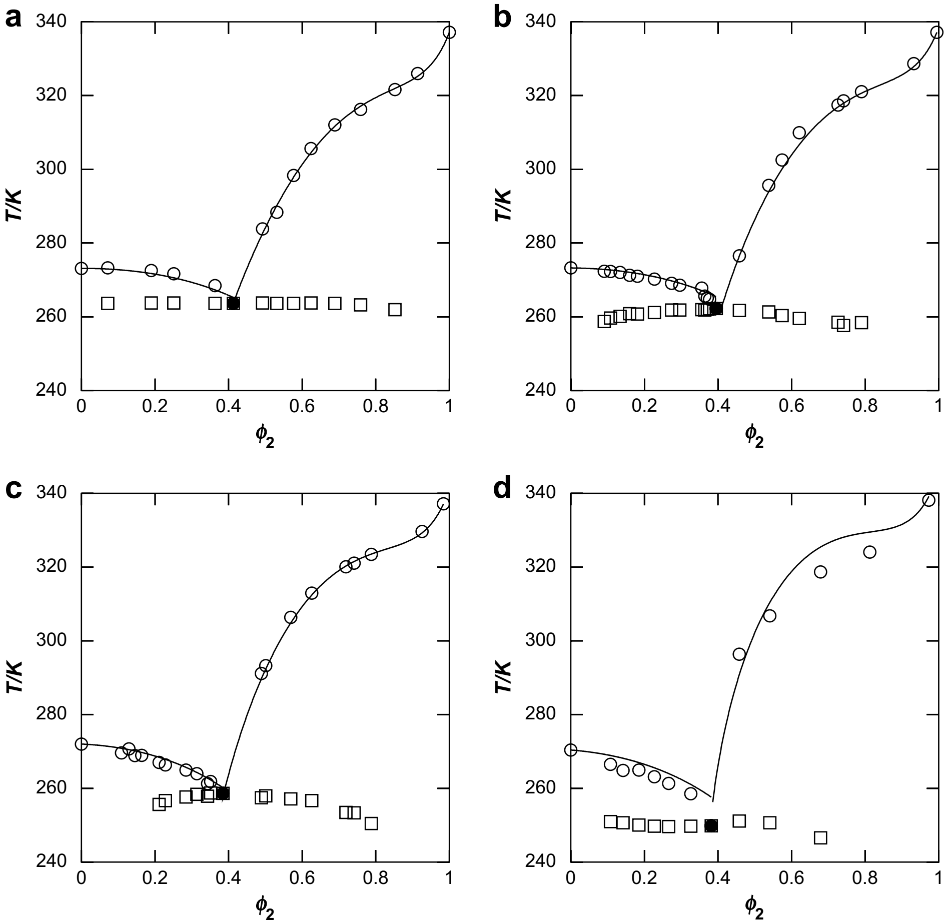

Fig. 5. Experimentally determined liquidus and solidus with liquidus predicted by the model. Open circles are the ice and PEG melting points (liquidus). The squares are the solidus. Closed circles represent the eutectic points. The solid curves are results of the lattice model. The concentration of NaCl is (a) 0 wt%, (b) 1.0 wt%, (c) 3.0 wt%, and (d) 5.0 wt%.

3. Results and discussion

Fig. 2 is the melting endotherms obtained using DSC for binary PEG–water mixtures. The raw data (Fig. 2a) and corrected ones (Fig. 2b) with the method by Toda et al. [12] are shown. In the region of low ϕ_2 ($0 < \phi_2 < 0.41$), we observed two peaks corresponding to the solidus (eutectic melting) and liquidus (ice melting). At $\phi_2 = 0.41$, there was only one peak, assigned as the eutectic point. In the region of high ϕ_2 ($0.41 < \phi_2$) there were two peaks corresponding again to the solidus (eutectic melting) and liquidus (PEG melting). In the highest region, however, we did not observe the solidus peak. In Table 1, the values of parameters obtained from the experiments, which are used in the model below, are listed.

Fig. 3 shows the measured liquidus (a) and the solidus (b) of ice and PEG. In Fig. 3a, the melting points of ice decreased with the increase of PEG volume fraction ϕ_2, whereas those of PEG increased. They met at the eutectic point where both solid phases melt simultaneously.

The addition of NaCl has opposite effects on the liquidus of water and PEG. The NaCl-induced changes in the liquidus temperature picked up at a fixed amount of PEG are shown in Fig. 4. The liquidus of water (crosses and triangles) decreases whereas that of PEG (squares, circles and diamonds) increases with the increase of NaCl. Moreover, the change depends on the amount of PEG. PEG enhances the effect of NaCl for the water liquidus. In contrast, the effect of NaCl diminishes for the PEG liquidus as the PEG volume fraction increases, and there is almost no effect in PEG–NaCl mixtures without water (see also the values of $T_2^{0'}$ in Table 1).

The decrease of the water liquidus with NaCl corresponds to the usual freezing point depression [13]. Since salt in aqueous state is known to decrease the chemical potential of water molecules in general, the liquid state of water is stabilized by the presence of salt. This leads to the freezing point depression. The presence of PEG enhances this effect. Thus it seems that PEG also stabilizes water molecules in solutions, which is consistent with the results reported by Zobrist et al [21].

The liquidus of PEG, on the other hand, was increased by the addition of NaCl. This is usually called a salting-out phenomenon [9]. Furthermore, the smaller the ϕ_2 was (closer to the eutectic point), the larger the effect became as shown in Figs. 3a and 4. In combination with the decrease of the water liquidus, as a result, NaCl makes a steep rise and fall close to the eutectic points in the liquidus.

The effectiveness to induce the salting-out phenomena generally depends on the salt species, known as the Hofmeister series. Moreover, the anions have larger effect than cations. It is expected that a stronger water-structure breaker than NaCl such as sodium thiocyanate or sodium iodide induces larger increase in the PEG liquidus. On the other hand, the freezing point depression depends only on the molar concentration of ions and is independent of the salt type in the first order approximation. The effectiveness depending on the salt type to induce the steep change in the liquidus curve around the eutectic point should be studied in detail, which remains as a future work.

Fig. 3b shows the effect of NaCl on the solidus curves. The vertical position of the solidus (thus the temperature of the eutectic

Table 3
The parameters obtained by the fitting.

a	b	c	d	e	f
0.0731	1.37	−0.998	0.749	−15.2	13.0

points) was lowered significantly by the addition of NaCl. However, the composition (the horizontal axis) of the eutectic points was not changed much by the presence of NaCl. It may be worth noting that the solidus curves went down with the increase of ϕ_2, likely due to the non-equilibrium effect. It was suggested that the small ice crystals of possibly nanometer size melt at the lower temperature than its equilibrium melting point [3]. It is also noted that water does not freeze readily in a polymer solution [21] or when confined in a small pore [22].

In Table 2 the temperature T_{ep} and composition ϕ_2^{ep} at the eutectic points are listed. The eutectic point for the binary PEG–water mixture is comparable to those reported so far for the similar molecular weight of PEG [3,7]. It is considered that the lower the temperature, the larger the amount of water associating with PEG. Thus the largest possible hydration of PEG in the liquid state happens at the eutectic point, the lowest possible temperature for PEG–water liquids. If we assume that the amount of water and PEG is balanced stoichiometrically at the eutectic point [7], the following relation holds for the maximum hydration number per repeating unit of PEG, n_{max},

$$w_2^{ep} = \frac{44}{44 + 18n_{max}} \tag{23}$$

where w_2^{ep} is the weight fraction of PEG at the eutectic points. Note that n_{max} only estimates the upper bound of the hydration number. The calculated values of n_{max} are listed in Table 2. The values are similar to those reported by Huang and Nishinari [7], but larger than those of 1–2 being most frequently reported [4,3,19]. Thus these values of n_{max} calculated from the above assumption likely overestimate the actual hydration number.

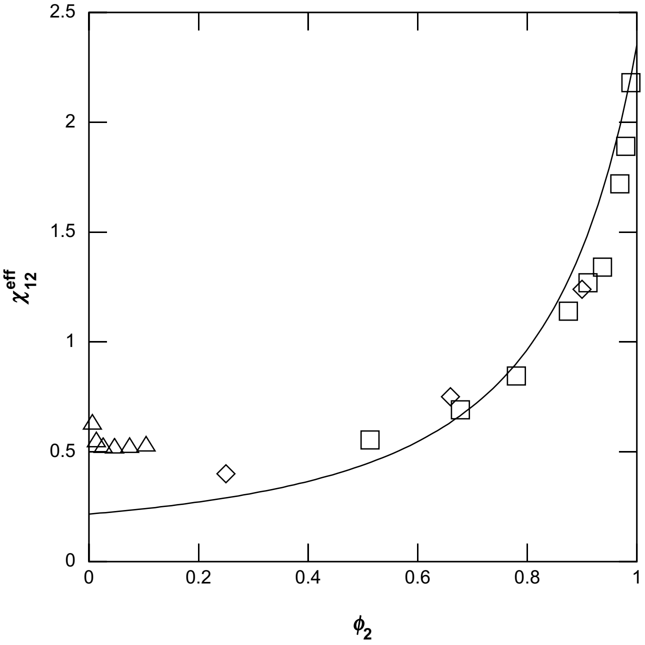

Fig. 6. The ϕ_2 dependence of the effective interaction parameter χ_{12}^{eff} (solid curve). The values reported by Malcolm and Rowlinson (diamonds) [23], Bae et al. (squares) [24], and Venohr et al. (triangles) [25] are also presented.

Now let us proceed to apply the lattice model. Fig. 5 shows the results of the model (solid curves) with experimental data. The points of experimental data are the same with those in Fig. 3. Firstly we fit the data without NaCl (Fig. 5a) with the parameter χ_{12} in Eq. (12). There is no need of χ_a without NaCl. The fitting result is shown in Table 3. As shown in Fig. 5a, the model represents the experimental points quantitatively including a small inflection at high ϕ_2. Similar inflection was observed also in the mixture between PEG and deuterium oxide [3].

The effective interaction parameter between PEG and water has been reported so far by several groups using the vapor pressure measurements [23], the liquid–liquid phase equilibria [24], or the light scattering [25]. Fig. 6 shows the ϕ_2 dependence of χ_{12}^{eff} at $T = 343$ K estimated using Eq. (10) (solid curve) with the values of χ-parameter in these references. The increase of χ-parameter with ϕ_2 like the one shown in Fig. 6 has been observed in many different systems often in the case of poor solvent [18,26]. The so-called two-state model was proposed to interpret the ϕ_2 dependence of χ-parameter [27]. Our results shown in Fig. 6 agree well with the values in the literature in the region of high ϕ_2. On the other hand, they deviate somewhat in the region of low ϕ_2.

The increase of χ_{12}^{eff} with ϕ_2 indicates that the interaction between PEG and water becomes more repulsive with the increase of ϕ_2. The repulsion between water and PEG in the high ϕ_2 region costs the chemical potential, and destabilizes the liquid state of PEG. On the other hand, the number of repulsively interacting sites decreases with the decrease of ϕ_1. This effect stabilizes the liquid state of PEG with the increase of ϕ_2. These two competing effects may be the reason for an inflexion seen at $\phi_2 \sim 0.8$ (Fig. 5).

Next, we fix the value of χ_{12} and adjust e and f in χ_a (Eq. (13)) for the data with NaCl. Using the values listed in Table 3, the model reproduces quantitatively all the change in the points of liquidus except at NaCl 5 wt% as shown in Fig. 5b–d. This success of the model strongly suggests that the mean-field treatment in the lattice model is a good approximation of the system and it is useful for the study of complex polymer mixtures.

Relatively large deviation is seen in the model at NaCl 5 wt%, where the model underestimates the decrease in the liquidus of water and overestimates the increase in the liquidus of PEG. In this way the model was unable to catch up the steep rise around the eutectic point. Since the conflicting effects of NaCl on the both water and PEG liquiduses are maximum at the eutectic point as mentioned above, it is possible that there is a non-linear effect in the interaction between components, such as a specific structure formation, which cannot be counted in a simple lattice model. Moreover, it is possible that the concentration of salt is too high for the lattice model to deal with the long range nature of the electrostatic interactions. A further study is necessary to elucidate the mechanism of the sudden change in the liquidus enhanced by the addition of NaCl.

Let us lastly discuss the result of $\chi_a = \chi_{13} - \chi_{23} = \chi_{14} - \chi_{24}$. The fitting shows that χ_a is negative (Table 3) suggesting $\chi_{13} < \chi_{23}$ or $\chi_{14} < \chi_{24}$. This means that NaCl is more attracted by water than PEG, which is consistent with a picture of salting-out phenomena where NaCl is depleted around PEG [9].

The dielectric constant of PEG is much lower than that of water [28,29]. The image charge repulsion between ions and a low dielectric material is thought to be the origin of the depletion and thus many salting-out phenomena. The entropic cost of the depletion drives polymer to aggregate so that the depletion zones overlap, which destabilizes the state of liquid and enhances the solidification. Furthermore, this is consistent with the fact that NaCl does not affect the PEG liquidus close to $\phi_2 = 1$ discussed above ($T_2^{0'}$ in Table 1 and Fig. 4). Since the higher the PEG concentration the lower the concentration difference between solid and liquid states, the gain in the free energy obtained by overlapping the depletion zones becomes smaller in the higher ϕ_2. In fact, if we can assume that the density of pure PEG liquid is the same as that of PEG solid, there is no gain with the solidification concerning the depletion zones.

Thus using the lattice model, the effect of salt to induce the change in the liquidus curves can be evaluated quantitatively. It is interesting to study how the property of salt (such as the Hofmeister series) affects the change in the liquidus curves. This work should be done in the future.

4. Conclusions

The phase diagrams of PEG–water–NaCl mixtures were constructed using differential scanning calorimetry. We showed that the addition of NaCl decreased the liquidus of water and increased that of PEG, thus it created a large jump at the eutectic point. A simple lattice model was applied to the liquidus curves. The model could reproduce quantitatively the experiments, which showed a mean-field nature of the system and usefulness of the model for the study of phase behaviors of polymer solutions. The model suggests that the interaction becomes repulsive with increasing the volume fraction of PEG. The model also suggested that NaCl was more attracted by water than PEG, which conformed to an image charge repulsion between ions and polymers. It was also consistent with the fact that NaCl did not affect the liquidus when the volume fraction of PEG was high, since the depletion zones of ions around polymer does not decrease with the solidification if there is no difference in the density between solid and liquid states of the polymer.

References

[1] Hager SL, Macrury TB. J Appl Polym Sci 1980;25:1559–71.
[2] Kjellander R, Florin E. J Chem Soc Faraday Trans 1981;77:2053–77.
[3] Hey MJ, Ilett SM. J Chem Soc Faraday Trans 1991;87(22):3671–5.
[4] de Vringer T, Joosten JG, Junginger HE. Colloid Polym 1986;264:623–30.
[5] Kulkarni A, Zukoski C. J Cryst Growth 2001;232:156–64.
[6] Tanaka S, Ataka M. J Chem Phys 2002;117(7):3504–10.
[7] Huang L, Nishinari K. J Polym Sci Part B 2001;39:496–506.
[8] Armstrong JK, Leharne SA, Stuart BH, Snowden MJ, Chowdhry BZ. Langmuir 2001;17:4482–5.
[9] Hey MJ, Jackson DP, Yan H. Polymer 2005;46:2567–72.
[10] Izutsu K, Aoyagi N. Int J Pharm 2005;288:101–8.
[11] Mraw SC. Rev Sci Instrum 1982;53(2):228–31.
[12] Toda A, Hikosaka M, Yamada K. Polymer 2002;43:1667–79.
[13] Hall DL, Sterner SM, Bodnar RJ. Econ Geol 1988;83:197–202.
[14] Wunderlich B. Macromolecular physics, vol. 3. New York: Academic Press; 1976.
[15] Flory PJ. Principles of polymer chemistry. New York: Cornell Univ Press; 1953.
[16] Hildebrand JH, Scott RL. Regular solutions. New Jersey: Prentice Hall; 1962.
[17] Smith P, Pennings AJ. Polymer 1974;15:413–9.
[18] Koningsveld R, Kleintjens LA. Macromolecules 1971;4(5):637–41.
[19] Bordi F, Cametti C, Di Biasio A. J Phys Chem 1988;92:4772–7.
[20] Qian C, Mumby SJ, Eichinger BE. Macromolecules 1991;24:1655–61.
[21] Zobrist B, Weers U, Koop T. J Chem Phys 2003;118(22):10254–61.
[22] Pearson RT, Derbyshire W. J Colloid Interface Sci 1974;46(2):232–48.
[23] Malcolm GN, Rowlinson JS. Trans Faraday Soc 1957;53:921–31.
[24] Bae YC, Shim JJ, Soane DS, Prausnitz JM. J Appl Polym Sci 1993;47:1193–206.
[25] Venor H, Fraaije V, Strunk H, Borchard W. Eur Polym J 1998;34:723–32.
[26] Gundert F, Wolf BA. In: Brandrup J, Immergut EH, editors. Polymer handbook. 3rd ed. New York: Wiley; 1989. p. 173–82.
[27] Baulin VA, Halperin A. Macromolecules 2002;35:6432–8.
[28] Koizumi N, Hanai T. J Phys Chem 1956;60:1496–500.
[29] Arnold K, Herrmann A, Pratsch L, Gawrisch K. Biochim Biophys Acta 1985;815:515–8.