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# The salting-out effect and phase separation in aqueous solutions of electrolytes and poly(ethylene glycol)

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**Abstract**

The compositions of coexisting phases have been determined for aqueous two-phase systems containing poly(ethylene glycol) (PEG) of nominal molecular weight 8000 and a series of eight electrolytes: NaOH, $Na_2CO_3$, $Na_2SO_4$, $Na_2HPO_4$, $Na_3PO_4$, $(NH_4)_2SO_4$, $MgSO_4$, $ZnSO_4$. The salting-out effects of the electrolytes on the polymer were obtained by fitting a Setschenow-type equation to the tie line data to derive a salting-out coefficient for each electrolyte. For the sodium salts the relative effectiveness of the anions in forming biphasic mixtures follows the Hofmeister series. The relative salting-out effectiveness of the sulphate salts, however, is probably influenced by complexation of the cations by PEG. The values of the salting-out coefficients reflect the extent of preferential hydration of the ethylene oxide units in the polymer chains.

*Keywords:* Hofmeister series; Phase separation; Poly(ethylene glycol)

## 1. Introduction

Ternary aqueous solutions of poly(ethylene glycol) (PEG) and certain electrolytes separate into a PEG-rich phase and a salt-rich phase over part of the composition space. Aqueous two-phase systems of this nature are useful for the separation and purification of biomaterials where the employment of a nonpolar solvent/aqueous phase system would lead to degradation of biological activity [1,2]. The phase equilibria of aqueous solutions of PEG containing salts are also of interest per se because they manifest the ion specificity which is summarised in the well-known Hofmeister series [3]. Ananthapadmanabhan and Goddard [4], using the turbidimetric titration technique, have shown that for a series of sodium salts, two-phase formation occurs with anions such as sulphate which have a marked 'salting-out' effect on nonelectrolytes but that for large, singly-charged ions such as iodide only one phase exists. The same authors also found that for a series of sulphates, the salting-out effects of the anions are offset by cations which are believed to coordinate to the ether oxygens to produce a 'salting-in' effect. The effectiveness of salts in inducing the formation of two phases in PEG solutions also correlates with the lowering they produce in the cloud point in dilute solutions of PEG [5]. Depression of the cloud point (which is approximately equal to the lower critical solution temperature) is related to the salting-out phenomenon since water becomes a poorer solvent for PEG as the temperature is raised [6]. Salting-out effects are usually quantified by fitting solubility data to the empirical equation of Setschenow [7]:

$$\ln\frac{S_0}{S} = k_S c_S \tag{1}$$

in which $S_0$ and $S$ refer to the solubilities of the nonelectrolyte in pure water and in a salt solution of concentration $c_S$, respectively and $k_S$, the salting-out coefficient, is specific for a particular nonelectrolyte/salt pair. Ananthapadmanabhan and Goddard [4] claimed Setschenow-type behaviour for compositions on the binodal line separating the two-phase and one-phase regions in the phase diagram for PEG/salt solutions i.e. that the logarithm of the PEG concentration was a linear function of salt concentration. However, this conclusion was challenged by

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Zaslavsky et al. [8] who determined the compositions of coexisting phases for the PEG/$(NH_4)_2SO_4$/water system. These authors found that although the total binodal curve could not be fitted by a single Setschenow-type equation, the PEG-rich and salt-rich branches of the same curve were fitted by Setschenow-type equations with different parameters. The work described in this paper was undertaken in order to further explore the relationship between Setschenow-type behaviour and the phase diagrams for a number of PEG/aqueous salt systems.

## 2. Experimental

### 2.1. Materials

Ammonium sulphate (analytical grade), sodium hydroxide (analytical grade), zinc sulphate heptahydrate (analytical grade), magnesium sulphate heptahydrate, sodium carbonate monohydrate, sodium phosphate dodecahydrate, disodium hydrogen phosphate heptahydrate and sodium sulphate salts were obtained from Aldrich and used as received. PEG supplied by Aldrich had a nominal molecular weight of 8000. Vapour pressure osmometry measurements on a sample of the polymer dissolved in chloroform yielded a number-average molecular weight of 7264 ($\bar{x}_n = 165$). Aqueous solutions were prepared using purified water (resistivity 18 MΩ cm) from an Elgastat UHQ II unit.

### 2.2. Equilibrium phase behaviour

Stock solutions of PEG (40% w/w) and concentrated salt solutions were made up by weight. To prepare systems with compositions falling within two-phase regions, appropriate amounts of PEG and salt solutions were weighed and mixed in 50 $cm^3$ flasks. Points on the binodal curve were determined by gradually adding water from a burette to a sample until a sharp transition from a turbid mixture to a clear solution was observed. During titrations sample flasks were continually shaken in a water bath maintained at 25 °C. After an endpoint had been reached the flask was left in the water bath for a further 5 min to ensure that a stable homogeneous solution was present. The final weight of the solution was then determined. Concentrations of PEG and salt were expressed as molalities with the molar mass of the ethylene oxide subunit being used in the case of the polymer.

To determine the compositions of coexisting phases, various ratios of the stock PEG and salt solutions were weighed into 30 $cm^3$ sample tubes and water added to bring the total sample weight to approximately 25 g. The sample tubes were then capped and shaken vigorously to mix the contents. Following phase separation, the mixtures were equilibrated in a water bath maintained at 25 °C until both phases were transparent. Samples of the polymer-rich top phase were withdrawn for analysis. The remainder of the top phase was then removed before a sample of the salt-rich bottom phase was collected in order to avoid contamination by the top phase solution.

The salt concentrations in the two phases were found by means of conductivity measurements (Jenway 4010 Conductivity Meter) at 25 °C. For each salt a calibration curve was constructed from measurements of the conductivities of a series of diluted stock solutions of that particular salt. An investigation of the effect of dissolved PEG on the conductivity of single phase mixtures containing both solutes showed that in general when the PEG concentration was below ca. 5 g $dm^{-3}$, the error in the salt concentration calculated from the conductivity was less than 1% for solutions with salt concentrations below ca. 0.1 molal. Samples of the two phases were therefore diluted by known factors in order to bring them within this composition range before the final conductivity measurement. PEG concentrations in the polymer-rich top phase were obtained from refractive index measurements made with a Hilger Abbe refractometer ($n_D$, 25 °C). As the refractive index is also sensitive to the presence of salts, the contribution of the latter had to be subtracted before the PEG concentration could be calculated. Binary solution calibration curves for solutions of PEG and for each salt were determined and then the refractive indices of a series of ternary solutions were investigated. It was found that for ternary solutions with PEG concentrations less than ca. 100 g $dm^{-3}$ and salt concentrations less than ca. 0.1 molal the contributions of the two solutes to the total refractive index of the solution were additive to within the accuracy of the instrument ($\pm$ 0.0005). In order to meet this condition samples from the top phase were diluted by a factor of four before measurement. The PEG concentration could then be calculated after allowing for the effect of the salt concentration as determined by conductivity measurement. In the case of the bottom phase, however, the PEG concentration was too low ($<1\%$) to be obtained accurately by this method. Instead the concentration was estimated from the smoothed binodal curve and the previously determined salt concentration.

## 3. Results and discussion

### 3.1. Phase diagrams

Figs. 1 and 2 show both the binodal boundaries obtained from turbidimetric titrations and the tie line data for the compositions of conjugate solutions. The titration results are represented by best fit lines using polynomial functions of degree three. The positions of the binodals for the five sodium salts shown in Fig. 1 demonstrate the relative effectiveness of anions in inducing two-phase formation: $PO_4^{3-} > HPO_4^{2-} > CO_3^{2-} > SO_4^{2-} > OH^-$. Fig. 2 shows the binodal lines for the four sulphates. Here the order of effectiveness for the cations is less clear since the phase

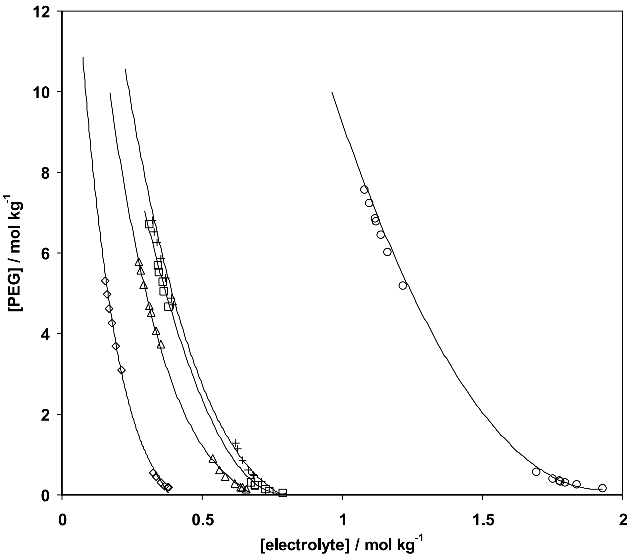

Fig. 1. Phase diagrams for aqueous solutions of PEG and various sodium salts. The positions of the coexistence curves were determined by fitting polynomials of degree three to turbidimetric titration data. Symbols show the compositions of coexisting phases for the different systems (tie lines are omitted for clarity): NaOH (○); $Na_2SO_4$ (+); $Na_2CO_3$ (□); $Na_2HPO_4$ (Δ); $Na_3PO_4$ (◇).

separation boundaries cross each other in places with the binodals for the ammonium and sodium salts having steeper gradients than those for the magnesium and zinc sulphates.

To derive a quantitative measure of salting-out in PEG solutions we first write for the chemical potential of EO units in salt solutions:

$$\mu_P = \mu_P^\theta + RT \ln f_P c_P \tag{2}$$

where $c_P$ is the molality of EO and $\mu_P^\theta$ is the limiting value of $(\mu_P - RT \ln c_P)$ as both EO and salt concentration approach zero. The excess partial molar Gibbs energy of the EO units, $RT \ln f_P$, is due to a combination of EO–EO and EO–salt interactions. At a given temperature $\ln f_P$ can be represented as a power series in $c_S$ and $c_P$ [10]. If only linear terms are important, then

$$\ln f_P = k_P c_P + k_S c_S. \tag{3}$$

A similar bilinear form was employed by Edmond and Ogston [11] to describe the effect of like and unlike polymer chains on the non-ideality of each polymer species in their analysis of phase separation in the ternary systems PEG/dextran/water and PEG/bovine serum albumin/water. The parameter $k_S$ which appears in the above equation can be identified with the empirical salting-out coefficient in Eq. (1) because for non-electrolytes with low solubilities

$$\ln\frac{f}{f_0} = \ln\frac{S_0}{S} = k_S c_S \tag{4}$$

where $f$ and $f_0$ are the activity coefficients of the solute in salt and salt-free solution, respectively. For a two-phase system at equilibrium, the chemical potential of PEG is the same in both phases. Eq. (2) then leads to

$$\ln f'_P c'_P = \ln f''_P c''_P \tag{5}$$

where single primes denote the upper phase and double primes the lower phase.

Substitution of Eq. (3) into Eq. (5) gives

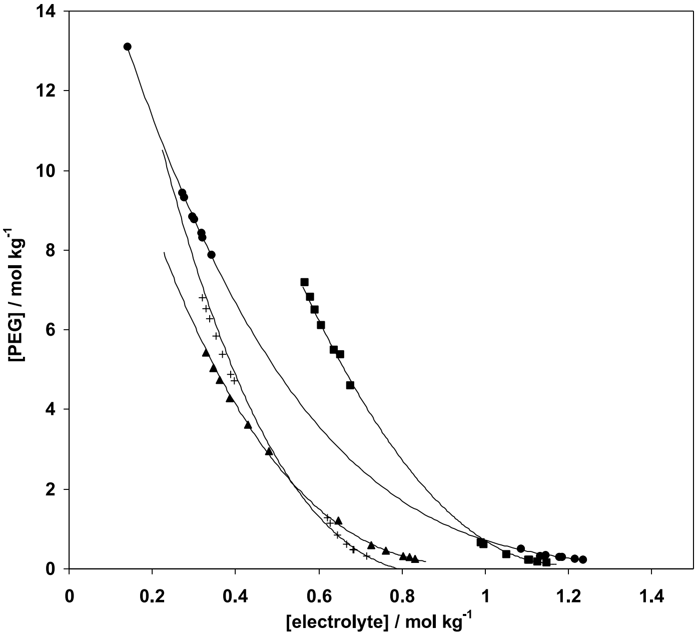

Fig. 2. Phase diagrams for aqueous solutions of PEG and various sulphates. The positions of the coexistence curves were determined by fitting polynomials of degree three to turbidimetric titration data. Symbols show the compositions of coexisting phases for the different systems (tie lines are omitted for clarity): $(NH_4)_2SO_4$ (■); $MgSO_4$ (●); $Na_2SO_4$ (+); $ZnSO_4$ (▲).

$$\ln\left(\frac{c'_P}{c''_P}\right) = k_P(c''_P - c'_P) + k_S(c''_S - c'_S). \tag{6}$$

If the first term on the right hand side of this equation is small compared to the second term, a Setschenow-type equation is obtained. This would imply that $k_P \ll k_S$ since the absolute values of $(c''_P - c'_P)$ exceed the $(c''_S - c'_S)$ values.

Fig. 3 shows a Setschenow plot of the tie line data for the eight PEG/salt systems. Linear regression indicates a very high correlation between the variables with intercepts close to the origin implying that the effect of an electrolyte co-solute is dominant in determining the activity coefficient of the polymer. The slopes of the plots give the $k_S$ values listed in Table 1 together with corresponding values of $R^2$, the goodness of fit parameter.

### 3.2. Salting-out parameters

For the sodium salts the rank order of the $k_S$ values is $OH^- < SO_4^{2-} < HPO_4^{2-} < CO_3^{2-} < PO_4^{3-}$, indicating an increasing degree of incompatibility between electrolyte and PEG. With the exception of $Na_2HPO_4$ and $Na_2CO_3$ which are reversed in order, the increase of $k_S$ is reflected in the phase diagram by a shift in the position of the binodal curve to the left corresponding to a decrease in the area representing the single-phase mixtures (Fig. 1). For solutions of $Na_2HPO_4$ and $Na_3PO_4$ the following acid–base equilibria have to be considered in specifying compositions:

$$HPO_4^{2-} + H_2O \leftrightarrow PO_4^{3-} + H_3O^+ \tag{1}$$

Table 1
Parameter values from least-squares linear fits to Setschenow plots

| Electrolyte | $k_S$/kg mol$^{-1}$ | Intercept | $R^2$ |
|---|---|---|---|
| $MgSO_4$ | 4.3 | −0.37 | 0.9628 |
| NaOH | 4.3 | 0.12 | 0.9987 |
| $ZnSO_4$ | 6.3 | 0.01 | 0.9997 |
| $(NH_4)_2SO_4$ | 7.2 | −0.32 | 0.9981 |
| $Na_2SO_4$ | 10.2 | −0.98 | 0.9993 |
| $Na_2HPO_4$ | 11.1 | −0.62 | 0.9975 |
| $Na_2CO_3$ | 11.9 | −0.87 | 0.9986 |
| $Na_3PO_4$ | 15.1[a] | 0.00 | 0.9989 |

[a] Represents an average for orthophosphate and hydrogen phosphate salts—see text.

$$H_2PO_4^{2-} + H_2O \leftrightarrow HPO_4^{2-} + H_3O^+. \tag{2}$$

The measured pH for solutions of disodium hydrogen phosphate with concentrations between 0.272 and 0.683 molal was 9.3 ± 0.02.Since $pK_a = 7.21$ for $H_2PO_4^{2-}$ at 25 °C [12], application of the Henderson–Hasselbalch equation predicts $[HPO_4^{2-}]/[H_2PO_4^-] \approx 100$ in these solutions. The calculated salting-out coefficient of 11.12 molal$^{-1}$ can therefore be assigned to $Na_2HPO_4$. Solutions of sodium phosphate with concentrations between 0.065 and 0.411 molal were found to have a pH of 11.93 ± 0.04. Using a value of 12.67 for the $pK_a$ of $HPO_4^{2-}$ in aqueous solutions at 18 °C [12], $[PO_4^{3-}]/[HPO_4^{2-}] \approx 0.18$ in these solutions. If the value of 15.15 molal$^{-1}$ found for $k_S$ in solutions containing sodium orthophosphate is assumed to be a weighted average for the $PO_4^{3-}$ and $HPO_4^{2-}$ salts, then an estimate of $k_S = 33$ molal$^{-1}$ is obtained for the true effect of the $PO_4^{3-}$ salt. Sodium carbonate solutions contain both $CO_3^{2-}$ and $HCO_3^-$ ions because of the equilibrium:

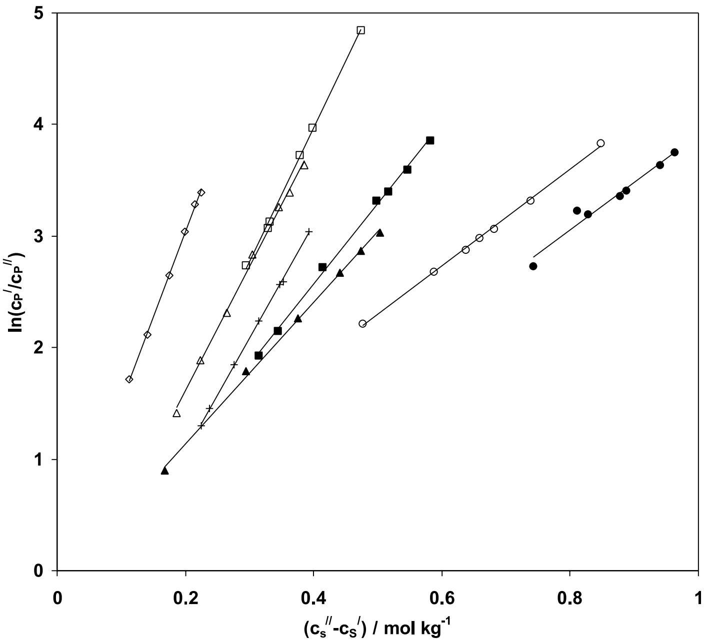

Fig. 3. Setschenow-type plots for the tie line data shown in Figs. 1 and 2.Upper phase concentrations are denoted by single primes and lower phase concentrations by double primes: $MgSO_4$ (●); NaOH (○); $ZnSO_4$ (▲); $(NH_4)_2SO_4$ (■); $Na_2SO_4$ (+); $Na_2HPO_4$ (Δ); $Na_2CO_3$ (□); $Na_3PO_4$ (◇).

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+ \tag{3}$$

In solutions with concentrations between 0.297 and 0.952 molal the measured pH was 11.59 ± 0.04, which when combined with a $pK_a$ value of 10.33 for $HCO_3^-$ in aqueous solutions at 25 °C [12] implies a value of 18.4 for the ratio $[CO_3^{2-}]/[HCO_3^-]$. The observed $k_S$ value of 11.93 $\text{molal}^{-1}$ can therefore be taken to be a good approximation to the value for the carbonate salt.

The effectiveness of anions in salting-out macromolecules is generally highest for small, multivalent ions, as illustrated by the five sodium salts in this study. In increasing effectiveness the sequence is $OH^-(7.52) < SO_4^{2-}(8.70) < HPO_4^{2-}(8.40) < CO_3^{2-}(10.81) < PO_4^{3-}(12.61)$ where the figure in brackets is the charge number divided by the ionic radius in nanometres [13].

The $k_S$ values for the four sulphate salts increase in the sequence $Mg^{2+} < Zn^{2+} < NH_4^+ < Na^+$. This ranking is almost certainly due in part to the complexation of $Mg^{2+}$ and $Zn^{2+}$ ions with the ether oxygens of the polymer. Schott and co-workers [14–17] have amassed abundant evidence from studies of the effects of inorganic salts on the cloud points, critical micelle concentrations and surface tensions of nonionic surfactants in aqueous solution to show that polyoxyethylene chains act as polydentate ligands in the complexation of di- and trivalent cations, leading to a salting-in effect which opposes the salting-out associated with the sulphate ions. This may also be the reason for the decreased curvatures of the binodals for mixtures containing magnesium sulphate or zinc sulphate compared to those for the sodium and ammonium salts (Fig. 2). For the non-complexing ammonium and sodium ions the ranking ($NH_4^+ < Na^+$) is in accord with the standard Hofmeister series for cations [9].

The $k_S$ values shown in Table 1 represent the specific effects of salts on the free energy of transfer of 1 mole of EO units from aqueous solution to a 1 molal salt solution. The mechanism underlying this specificity is uncertain but thermodynamic arguments require a salting-out electrolyte to be preferentially excluded from the surface of the EO units [18–20]. Differing extents of depletion for different electrolytes then account for the observed ion specificities. Salting-out effects are thus related to a reduction in entropy resulting from the exclusion of ions from volume elements immediately adjacent to the solute molecules.

Experimental evidence for the entropic origin of the salting out of poly(vinylpyrrolidone) by $(NH_4)_2SO_4$ was obtained by Garvey and Robb [21] from measurements of heats of dilution. Evidence of electrolyte depletion around PEG chains comes from a study by Florin et al. [22] in which a small increase was found for the salt/water ratio in the polymer-poor phase after phase separation of several PEG solutions brought about by the addition of alkali metal halides. Kabalnov et al. [23] reported a similar effect for sodium halides added to a Winsor III microemulsion system consisting of water, pentaethylene glycol mono-*n*-dodecyl ether ($C_{12}E_5$) and decane. The middle phase in this system consists of a bicontinuous microemulsion in which the oil and water domains are separated by a monolayer of $C_{12}E_5$. Analysis of the co-existing water and middle phases shows that for NaF, NaCl and NaBr the salt/water ratio in the microemulsion phase is lower than for the aqueous phase whilst for NaI and NaSCN it is higher. The redistribution of electrolyte was interpreted as a depletion of the former group at the EO groups of the surfactant and an enrichment of the latter group. The authors made the observation that the more polarisable the anion, the stronger its tendency to adsorb. More recently, Boström et al. [24] have argued that short range dispersion forces are responsible for specific ion effects.

### 3.3. Preferential hydration

The exclusion of solute from the environs of a polymer molecule can be described in terms of a local excess of water molecules, in analogy with the Gibbs surface excess defined in connection with macroscopic interfaces [25]. For solutions sufficiently dilute in polymer for polymer–polymer interactions to be negligible, the Gibbs–Duhem equation requires that changes in polymer chemical potential be linked to changes in the water chemical potential by:

$$d\mu_P = -N_{ew} d\mu_{ew} \tag{7}$$

where $N_{ew}$ is the excess number of water molecules per macromolecule in the salt-depleted region. $N_{ew}$ is related to the actual number of water molecules $N_w$ in this region by:

$$N_{ew} = N_w \left(1 - \frac{n_w/n_s}{N_w/N_s}\right) \tag{8}$$

where $n_w/n_s$ and $N_w/N_s$ represent water/electrolyte ratios from regions unaffected by and influenced by polymer, respectively.

From Eqs. (2) and (3) in Section 3.1 a differential change in polymer chemical potential at constant polymer concentration is related to a differential change in electrolyte concentration by:

$$d\mu_P = RTk_S dc_S. \tag{9}$$

Combination of Eqs. (7) and (9) then gives:

$$RTk_S dc_S = -N_{ew} d\mu_w. \tag{10}$$

Since the chemical potential of water in the environment of the polymer chains is equal to the chemical potential of water in the bulk solution, $d\mu_w$ can be related to a differential change in water activity in the solution:

$$d\mu_w = RT d \ln a_w. \tag{11}$$

The water activity depends on the concentration of electrolyte according to:

Table 2
Excess numbers of water molecules per PEG chain

| Electrolyte | $k_S/\nu$ (kg mol$^{-1}$) | $d(\varphi c_S)/dc_S$ | $N_{ew}$ |
|---|---|---|---|
| NaOH | 2.17 | 0.96 | 125 |
| $Na_2SO_4$ | 3.40 | 0.62 | 303 |
| $MgSO_4$ | 2.14 | 0.51 | 233 |
| $ZnSO_4$ | 3.15 | 0.46 | 380 |
| $(NH_4)_2SO_4$ | 2.40 | 0.62 | 215 |

$$\ln a_w = -\frac{\nu 18 \phi c_S}{1000} \tag{12}$$

where $\nu$ is the number of moles of ions in a fully dissociated mole of electrolyte and $\varphi$ is the molal osmotic coefficient [26]. Therefore, by substituting

$$d\mu_w = -\frac{RT\nu 18}{1000} d(\phi c_S) \tag{13}$$

in Eq. (10) and rearranging, we obtain

$$\frac{k_S}{\nu} = 0.018 N_{ew} \frac{d(\phi c_S)}{dc_S}. \tag{14}$$

Data quoted in Appendix 8.10 of Ref. [26] allow plots of $\varphi c_S$ against $c_S$ to be made for five of the electrolytes studied. The plots are generally linear for concentrations up to about 1 molal and values for the derivative $d(\varphi c_S)/dc_S$ range from 0.46 for $ZnSO_4$ to 0.96 for NaOH. Substitution of these values into Eq. (14) along with the experimental values for $k_S/\nu$ leads to the estimates of $N_{ew}$ shown in Table 2. In the limiting condition that $N_S$ is negligible, i.e. that the hydration shell of the polymer completely excludes electrolyte ions, these $N_{ew}$ values become equal to $N_w$, the actual numbers of water molecules around the polymer chains. For the PEG used in the study with a number-average degree of polymerisation of 165, the $N_{ew}$ values per EO repeat unit fall in the range 0.75–2.3 with an average value of 1.5.The magnitude of this result suggests that $N_w$ could be interpreted as the average hydration number of the EO repeat unit, since each unit contains one site (–O–) capable of forming two hydrogen bonds. Some support for this interpretation comes from differential scanning calorimetry studies of PEG/$D_2O$ mixtures [27,28] and PEG/$H_2O$ mixtures [29] in which estimates of maximum hydration numbers vary between 0.9 and 3.3 according to molecular weight of the polymer.

## 4. Conclusions

Tie line data from aqueous two-phase systems consisting of PEG and various salts can be used to derive a salting out parameter for the electrolyte for EO groups. Previous workers have tried to use the Setschenow equation to rationalise the phase diagrams of PEG/salt solutions but with only limited success. In the present work we have derived an equation that allows tie line data to be used in a Setschenow-type plot to obtain a characteristic parameter for the salting out effect of an electrolyte on EO groups in PEG. The magnitude of this parameter for a given electrolyte can be related to an excess number of water molecules adjacent to the ethylene oxide repeat units.

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