Calorimetric Investigation of the Formation of Aqueous Two-Phase Systems in Ternary Mixtures of Water, Poly(ethylene oxide) and Electrolytes (Or Dextran)

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Received: February 23, 2000; In Final Form: July 31, 2000

The evolution of ternary mixtures containing water, poly(ethylene oxide) (PEO) and dextran or electrolytes (NaCl, Na_2SO_4 or Li_2SO_4), toward the formation of aqueous two-phase systems was investigated by calorimetry measuring enthalpies of solution for one of the components in water and in an aqueous solution of the other component. These values were then analyzed as enthalpies of transfer from water to aqueous solution of the second component, to probe the energy balance for the solvation of the transferred component between both states. The obtained results confirmed that enthalpic contributions are relevant to biphase formation in the presence of electrolytes, but much less important in mixtures of the two polymers. In all cases, phase separation was accompanied by an enthalpy increase, indicating that entropy increase is the driving force for aqueous two-phase systems formation. Moreover, based on enthalpy data, it was possible to assign different behavior to electrolytes capable of inducing aqueous two-phase systems formation (lithium and sodium sulfates), and sodium chloride, which does not induce phase separation. A model is proposed to account for the processes leading to phase separation in terms of electrolyte and polymer interaction.

Introduction

It has long been recognized that the mixture of aqueous solutions of some incompatible polymers (for instance, poly-(ethylene oxide) (PEO) and dextran) or of some polymers and electrolytes (for instance, PEO and Na_2SO_4) forms a stable two-phase liquid system, where the only solvent is water. This phenomenon was first reported by Beijerinck a century ago, but these systems have only started to receive greater attention after Albertsson's proposition for their use in bioseparation processes[1] in the late 50s. Since then, considerable effort has been devoted to the compilation of phase equilibrium data on these aqueous two-phase systems and on their application to purification of a variety of biomolecules. Most of these results have been thoroughly reviewed elsewhere.[2,3]

On the other hand, efforts aiming at the understanding of the underlying reasons for the formation of aqueous two-phase systems are considerably fewer, most of them dealing with theoretical efforts in modeling their phase behavior and solute partitioning.[4–8] Such studies are fundamental in designing systems for a specific purpose, which still remains mostly a trial-and-error practice. Even more limited are experimental efforts devoted to understanding the mechanism involved in this phase separation, which may provide sounder basis for the development of more realistic and effective theoretical models.

As far as their thermodynamics is concerned, the majority of the investigations on aqueous two-phase systems follow principles of polymer physical chemistry, most commonly within the framework of Flory–Huggins theory, and most of the data refers to their phase diagrams. As these studies are focused on Gibbs energies, no direct discrimination is given as to what are the separate contributions from enthalpy and entropy. Recently, Haynes and co-workers [9] proposed a set of simple analytical equations derived from Flory–Huggins theory which allow a qualitative assessment on the contributions of enthalpy and entropy to the phase separation or partitioning processes.

Our aim with the present work is to directly investigate the balance of interactions associated with aqueous two-phase systems formation and their contribution to enthalpy changes, experimentally assessed by calorimetric measurements. This study was motivated by earlier reports of Ananthapadmanabhan and Goddard,[10–12] who systematically investigated the phenomenon of aqueous biphase formation in mixtures of PEO and electrolytes in water. Those studies revealed that aqueous two-phase systems formation is very similar to phase separation observed in polyether solutions upon heating, known as clouding. In addition, their investigation also revealed different efficacy for anions and cations in inducing aqueous two-phase system formation. For univalent sodium salts, hydroxide and fluoride caused aqueous two-phase system formation, whereas sodium chloride and bromide were not capable. For a given anion, for instance sulfate, the cation efficacy followed the pattern $Na^+ > Mg^{2+} > Zn^{2+} > Li^+$. These differences have been ascribed in terms of specific interactions between polymer and the ions. On the other hand, Rogers[13] and co-workers reported a correlation between the efficacy of a series of cations in inducing aqueous two-phase system formation and their hydration enthalpies and Gibbs energies.

In the present study, a series of ternary systems containing PEO and electrolytes capable or not of inducing phase separation, and containing two polymers, PEO and dextran, were investigated. Solution enthalpies for one of the components in water and in an aqueous solution of the other component were determined from low concentrations to above phase splitting, being analyzed in terms of differences caused by interactions between the components, as previously reported for other systems.[14,15]

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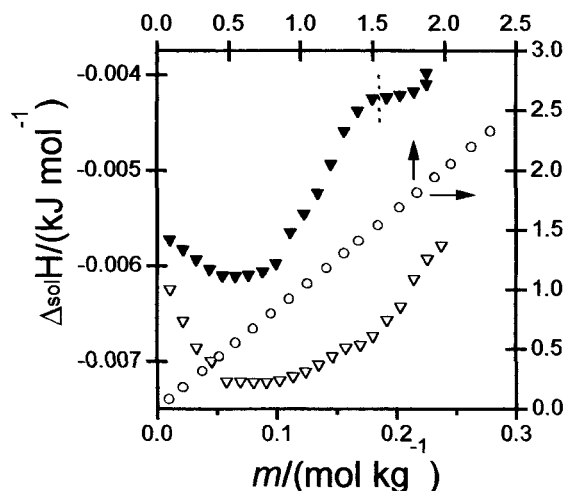
Figure 1. Differential solution enthalpies of PEO 3350 in water (○), of dextran in water (▽), and of dextran in a 7.82% (w/w) PEO 3350 solution (▼). Dashed lines indicate transition to two-phase region.

Experimental Section

Materials. Poly(ethylene oxide) with nominal molecular weight of 3350 g mol^{-1} and dextran with average molecular weight of 428 000 g mol^{-1} (provided by the supplier) were purchased from Sigma. The electrolytes used, NaCl, Na$_2$SO$_4$, Li$_2$SO$_4$, and KCl were all of analytical grade. All of these compounds were kept in a desiccator under P$_2$O$_5$ for, at least, 5 days before use.

Calorimetric Measurements. Solution enthalpies were determined in a Thermometric 2225 Precision Solution calorimeter by the ampule breaking technique. This unit was inserted into a Thermometric water bath operating at 298 K, with stability of 0.0001 degree. Operation was according to the manufacturer's instructions. Typically, between 100 and 300 mg of each material was loaded into a thin glass ampule which was inserted and broken in 0.1 dm^{-3} of water or suitable solution. With the amounts of substance used, the minimum energy measured in one experiment was 3 J, well above the energy exchanged by breaking an empty ampule. The accuracy of the equipment and of the procedure were confirmed by measuring solution enthalpies of KCl, with agreement better than 0.8% with literature data.[16] All of the reported enthalpies are averages of, at least, two independent experiments, with deviations always smaller than 1%.

All of the ternary systems were investigated prior to calorimetric measurements, and their phase separation boundaries were determined by turbidimetric titration[11] in a temperature-controlled environment.

Results and Discussion

Enthalpies of solution of NaCl, Na$_2$SO$_4$, Li$_2$SO$_4$, PEO 3350 and dextran in water were determined at 298 K. For these electrolytes, the obtained values (not shown) are in agreement with literature data,[17] presenting deviations smaller than 1% and attesting to the methodology accuracy. All of these increment enthalpies are essentially the same as obtained by the differentiation of the integral enthalpies of solution, being, therefore, called differential solution enthalpies.

Differential enthalpies of solution for PEO and dextran in water and for dextran in PEO solutions are shown in Figure 1. For polymers such as PEO, these values are known to depend on the degree of crystallinity of the solid,[18] therefore making any comparison with literature data difficult. Even so, using
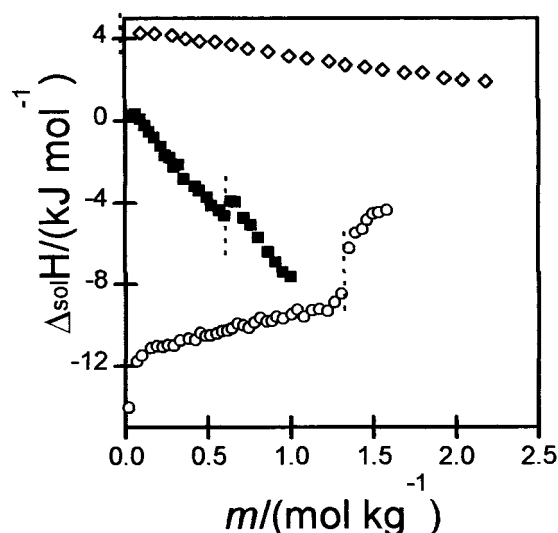

Figure 2. Differential solution enthalpies of salts in a 7.82% (w/w) PEO 3350 solution: (■) Na$_2$SO$_4$, (○)Li$_2$SO$_4$, (◇) NaCl. Dashed lines indicate transition to two-phase region.

data reported by Maron and Filisko[18] on the dissolution of PEO 6000, from a different supplier, within the concentration range that we used, the enthalpies expressed on monomer basis are in very good agreement. To the best of our knowledge, no such data are available for dextran, but some measurements of dilution enthalpies[19] have already revealed much smaller energy changes for dextran in comparison with PEO aqueous solutions, in line with the presently reported data.

Figure 1 shows that enthalpy of solution for dextran, at lower concentrations, becomes slightly more negative, reaches a plateau region and then, close to 0.1 mol kg^{-1} (expressed on monomer basis), abruptly increases, but the process remains exothermic. This increase may arise from changes in the polymer conformation and/or from the appearance of polymer−polymer interaction, both associated to enthalpy increase. The behavior observed for the solution enthalpies of dextran in PEO solutions, also shown in Figure 1, is similar, only that all values are less negative and that the enthalpy increase seems more abrupt. This enthalpy increase ceases with phase splitting, which may be explained by the mutual segregation between the polymers upon phase separation. These features suggest that the presence of the second polymer increases the tendency for dextran−dextran interaction in relation to aqueous solutions, in accordance with the behavior expected for a poorer solvent. The small enthalpy changes observed associated with the solution and phase separation processes indicate that the latter should be directed by entropic contributions, which is in line with current propositions, for instance, those based on excluded volumes.[6,20]

Figure 2 shows the differential solution enthalpies for electrolytes in a 7.8% (w/w) PEO solution. For Li$_2$SO$_4$ and Na$_2$SO$_4$, these data display a clear discontinuity at the region were phase separation is observed in independent experiments (turbidimetric titration). The same feature appears in Figure 1, indicating that this is a general behavior associated with aqueous two-phase system formation. In all cases, this discontinuity reveals that the system enthalpy increases upon phase separation, therefore indicating that this process must be driven by entropy changes. In the case of Na$_2$SO$_4$, this enthalpy increase slightly affects the trend of more negative solution enthalpies, which remains dominated by the contribution arising from the electrolyte dissolution in water. For NaCl, the values monotonically
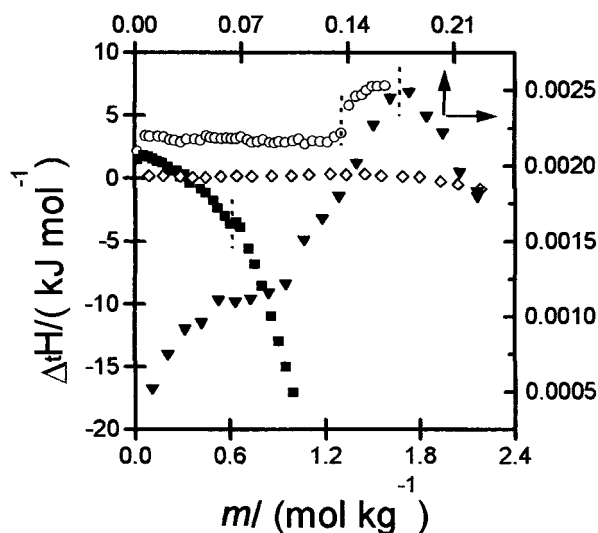
Figure 3. Differential transfer enthalpies of salts and dextran from water to 7.82% (w/w) PEO 3350 solution: (■) Na₂SO₄, (○) Li₂SO₄, (◇) NaCl, (▼) dextran. Dashed lines indicate transition to two-phase region.

decrease, in agreement with its incapacity in inducing aqueous two-phase system formation.

Another way of analyzing these data is through calculation of the enthalpies of transfer, $\Delta_t H$, of one of the components by subtracting its enthalpy of solution in the presence of the other component from the enthalpy of solution in its aqueous solution. Therefore, $\Delta_t H$ represents the energy balance between the solvation of the transferred component in water and in the solution, being especially useful in analyzing partitioning processes.[21,22] For the systems under investigation, considering the small amounts of the transferred component (differential enthalpies), hence, disregarding its effects on the state of the solution,[14] $\Delta_t H$ would reflect any interaction occurring between PEO and salt or dextran, in relation to salt/dextran interaction with water which was then replaced. This balance would then be represented by

$$\Delta_t H = (\Delta H)_{PEO/W} - (\Delta H)_W \qquad (1)$$

where ΔH represents the enthalpy content related to interactions of the transferred component in both phases, PEO solution and water, respectively.

The enthalpies of transfer for electrolyte/dextran from water to a PEO solution are shown in Figure 3. For dextran, these positive values have been already ascribed to increased dextran–dextran interactions. After phase separation, the two polymers are enriched in different phases owing to mutual segregation, and the enthalpies of transfer start to decrease but still remain positive. Also, analyzing these data, it is possible to confirm that the transfer of NaCl, which is not capable of inducing phase separation, is associated with an almost negligible enthalpy change (constant at ca. 0.2 kJ mol⁻¹, within the studied concentration range), as if this electrolyte, or rather its cation and anion, sensed no difference in solvation in both phases. However, for the transfer of sodium and lithium sulfates differences are observed. For the latter, the enthalpy of transfer is always positive, remaining close to 3 kJ mol⁻¹ until the phase splitting when it raises above 7 kJ mol⁻¹, whereas with the former, these values start positive, then decrease and become continuously more negative at concentrations higher than 0.3 mol kg⁻¹. As these two electrolytes present a common anion, these differences must arise from interaction involving their cations, sodium and lithium.

In fact, both cations are known to interact with PEO resembling, in some sense, their binding to crown-ethers.[23] On the basis of a series of conductometric measurements in methanol solutions of PEO and salts, Ono and co-workers [24] attributed the observed conductivity decrease with increased PEO concentration to cation binding to the polymer. The binding strength remained virtually constant regardless the extent of occupancy, indicating no interaction between neighbor sites, and followed the sequence Li⁺ < Na⁺ < K⁺ < Cs⁺ < Rb⁺. In another related investigation, Quina et al.,[25] following the fluorescence quenching of free and polymer-bound chromophore by several salts in methanol, observed that with iodide and thiocyanate as anions, quenching was observed only with the polymer and followed the same order reported above. Moreover, when these experiments were repeated with NaCl and KCl, no quenching was observed, indicating that it was due to the anion and, hence, revealing an increased local concentration of the anion in the vicinity of the polymer. In addition, the same group has performed other investigations in aqueous solutions, using ultrafiltration techniques and measurements with ion-selective electrodes, which confirmed this electrolyte-polymer binding.[26] Therefore, any interaction between electrolytes and PEO is shown to involve both cations and anions.

According to the balance represented by eq 1, positive enthalpies of transfer would indicate predominance of polymer and electrolyte dehydration steps (which are endothermic processes) in relation to electrolyte interaction with the polymer (exothermic). Lithium sulfate would be associated to more positive values for its smaller cation, involving a more energetic hydration step in comparison with the same process for sodium sulfate.[27] The enthalpy of transfer for Li₂SO₄ being constant over the studied concentration range (until phase splitting), Figure 3, indicates that no significant perturbation of the polymer conformation is produced by its interaction with this electrolyte. The behavior displayed by Na₂SO₄ is different in this respect, because its enthalpies of transfer are positive at low concentration and decrease, becoming even more negative as concentration increases, a trend which is more accentuated after phase separation. This trend indicates that this electrolyte affects polymer conformation in a way to produce a more exothermic net effect.

Differences between sodium and lithium must arise either from their different sizes or strengths of interaction. Regarding this last point, the literature studies cited above already indicate that sodium salts interact more strongly with PEO than lithium salts. The trend in efficacy of their sulfates in inducing aqueous two-phase systems also conforms to these previous observations, in that the sodium salt causes phase splitting at lower concentration. The different behavior revealed by their enthalpies of transfer, however, indicates that the mechanism by which phase separation is accomplished may be different. The presently determined enthalpies of transfer for Li₂SO₄ are always positive, indicating that any occurring interaction must be followed by an increase in entropy, which drives the process. Such a finding is not uncommon, as revealed by an investigation of recent reviews on the thermodynamics of cation coordination by crown-ethers in aqueous solutions.[28,29] Interestingly, positive enthalpies of coordination seem more common with lithium than with sodium or potassium salts. This predominant entropy increase has been ascribed to the release of water molecules that were involved in cation and polymer solvation.

Therefore, the picture that arises from these data is that, when PEO and lithium salts are mixed, the cation and the polymer

interact, releasing some water molecules that were solvating them, in a process driven by this entropy increase. This cation binding continues as more electrolyte is added, until a saturation point (in this case, the ratio of total lithium cations per EO monomer is 1.5), after what no more entropy gain may be attained and the phase splitting becomes more favorable. After this saturation point, the addition of more salt would lead to a higher concentration in the bulk than around the polymer, which has been already proposed in the literature to explain salting-out effects, described as ion depletion.[30]

The same binding process should occur with sodium sulfate. The difference is that the enthalpy change associated to this process starts positive, but as the electrolyte concentration increases, it becomes negative. Enthalpies of solution and dilution of sodium sulfate in water show the same behavior that has been ascribed to increased cation−anion interaction at greater concentrations, and which is not observed for lithium sulfate at this concentration range. As the measured enthalpies of transfer reflect the balance between interaction in the presence of PEO and in pure water, these negative values indicate that ion pair interactions are greater around the polymer, possibly owing to an increased ion concentration, as suggested by the investigations cited before.[26] Again, a saturation point is reached, and phase separation becomes more favorable owing to a great enthalpic contribution due to the exothermic character of increasing sodium sulfate concentration. For sodium sulfate, phase separation occurs at an electrolyte/EO monomer ration of ca. 0.7. One has to bear in mind that these estimated ratios assume total electrolyte concentration, and that their actual values are, therefore, smaller and dependent on the extent of electrolyte binding to the polymer. As lithium salts are expected to interact to a lesser extent with PEO, the actual saturation ratio should be even smaller than the estimated ones.

The proposition that phase separation occurs in association with saturation of the electrolyte-polymer binding may sound contradictory to features of the binodal curves for aqueous two-phase systems, which point out that at lower concentrations of one component, more of the other is necessary to induce phase splitting. At this point, it is important to stress that this saturation does not mean physical saturation of the binding sites around the polymer, but that a significant amount of electrolyte is left in solution, without interacting with the polymer, destabilizing the system and, hence, leading to phase separation. This apparent discrepancy may be understood by taking into account earlier findings that this binding strength displays a strong concentration dependency, as revealed by Sartori et al.[26] These observed variations are too large to be ascribed to simple deviation from ideality, being attributed to changes in the polymer conformation and/or in the number/affinity of the binding sites. According to that investigation, the binding strength was found to increase as the ratio between salt and polymer concentrations increased. Therefore, at high polymer concentration, the binding constant is reduced and only a small fraction of the electrolyte is bound to the polymer, leaving a large fraction in solution, reaching more easily the amount of free electrolyte necessary to cause phase separation. At low polymer concentration, as more salt is added, the binding increases as well as the fraction of bound electrolyte. Therefore, more salt is needed in order to reach a level of free salt that causes destabilization and phase splitting. From the literature data on phase equilibria in aqueous two-phase systems containing PEO and these electrolytes, [11] the electrolyte/(EO monomer) ratios at the binodal curve in the region diluted in polymer present their larger values, close to 3.
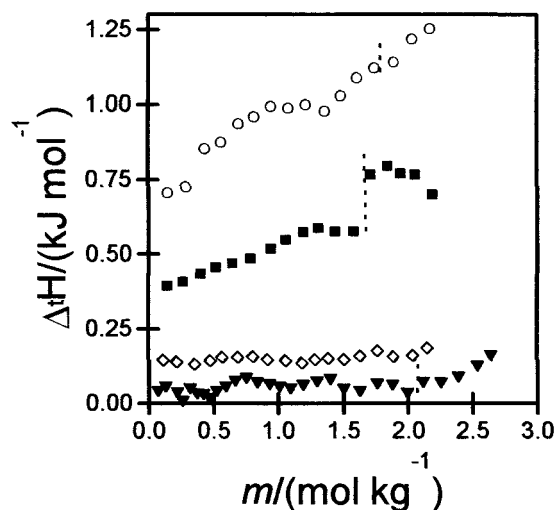

Figure 4. Differential transfer enthalpies of PEO 3350 in different solutions of salts and dextran: (■) Na$_2$SO$_4$ (0.72 mol kg^{-1}), (○) Li$_2$SO$_4$ (1.19 mol kg^{-1}), (◇) NaCl (1.75 mol kg^{-1}), (▼) dextran (0.15 mol kg^{-1}). Dashed lines indicate transition to two-phase region.

The limitation of NaCl in inducing phase separation must be related to its anion. Earlier reports[26] already suggest that NaCl interacts less strongly with PEO than Na$_2$SO$_4$ or Li$_2$SO$_4$. The presently described enthalpies of transfer for NaCl, in addition, reveal that its interaction with PEO does not involve significant disturbance of either polymer of electrolyte hydration. Therefore, neither entropy gain due to release of bound water molecules nor enthalpy decrease caused by increased ion-pairing around the polymer are observed and the alternative of a homogeneous system prevails in relation to the biphasic one.

The enthalpies of transfer for PEO 3350 between water and electrolyte or dextran solutions are shown in Figure 4. All values are positive and their absolute values are significantly smaller than the ones determined for the transfer of electrolytes (Figure 3). Bearing in mind that these differential values are assumed to reflect only solvation effects of the transferred component, the enthalpy increase in the presence of dextran or electrolyte is mainly ascribed to increased EO−EO interactions, considering that PEO−dextran interactions would be negligible and that PEO hydration is exothermic. Also in accordance with the results discussed above, the values for NaCl solutions are much smaller than those determined for Na$_2$SO$_4$ and Li$_2$SO$_4$ solutions, and phase separation is followed by an increase in the system enthalpy due to increased polymer concentration caused by phase splitting. Interestingly, for Li$_2$SO$_4$ solutions, the increase in the differential enthalpy of transfer starts before the visual observation of phase separation, which may reflect changes in polymer conformation or interactions preceding the system splitting.

In conclusion, this study revealed that all of the aqueous two-phase system formation processes investigated are endothermic, with much smaller energy changes for the system with two polymers in relation to those containing electrolytes. Therefore, these processes must be driven by entropy increase. The derived enthalpies of transfer allowed the identification of specific interaction between PEO and the electrolytes capable of inducing aqueous two-phase system formation, whereas for NaCl (which does not cause phase separation), this interaction was not observed. These findings led to the proposition that the initial mixture of polymer and electrolytes involves the interaction between these two components, resulting in an entropy increase associated with the release of water solvation molecules. As this interaction vanishes (owing to saturation), the additional

Two-Phase Systems of Water and Incompatible Polymers

J. Phys. Chem. B, Vol. 104, No. 43, 2000 **10073**

ions are no longer able to interact with the polymer, increasing the system Gibbs energy and turning the two-phase alternative more favorable, producing phase separation. In addition, this investigation stresses the importance of direct calorimetric measurements in revealing insights related to specific contributions that influence the aqueous two-phase system formation process.

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