



Toward an understanding of aqueous biphasic formation in polymer–polymer aqueous systems



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ABSTRACT

Aiming at gathering further evidence about the molecular-level mechanisms of the polymer–polymer aqueous biphasic systems (ABSs), systematic studies on the vapor–liquid and liquid–liquid equilibria of several ternary aqueous solutions of two water soluble polymers capable or not of inducing phase separation were performed at 298.15 K. It was found that the hydrophilicity of the investigated polymers follows the order PEGs \approx PEGDMEs > PVP \gg PPG400 and the aqueous solutions of PPG400 form ABS with PEG, PEGDME, and PVP however other investigated systems don't form ABS. The ability of PPG400-polymer solutions to form ABS increases by increasing temperature and polymer molar mass. It was also found that, the constant water activity lines of the ternary systems which capable and not of inducing phase separation respectively have the concave (or plane) and convex slopes. Therefore, from the slopes of the isopiestic constant water activity lines one can predict the phase forming abilities of the corresponding systems.

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1. Introduction

Ternary aqueous solutions of two different water soluble polymers are separated into two aqueous phases above a certain concentration in which each phases will be enriched in one of the polymers. The aqueous nature of two coexisting phases along with their different properties makes the aqueous two-phase systems possible to use them for the separation and partitioning of different biomaterials such as enzymes, cells, proteins, organelles [1–3], etc. Although both polymers are water-soluble, their aqueous solutions separate into two coexisting phases with same components but with different concentrations. Thus aqueous biphasic formation is an unusual phenomenon. Although the aqueous biphasic system (ABS) formation is well documented, its molecular level mechanism isn't still clear. During the past decade, aiming to achieve a deeper understanding about the molecular-level mechanisms of ABS formation, the salting-in and -out effects of solute 1 in solute 2 aqueous media have been theoretical and experimentally studied for salt-polymer [4,5], salt-ionic liquid [6–12], ionic liquid-polymer [13–15], amino acids-ionic liquid [16,17], and carbohydrate-ionic liquid [17,18] systems. Although the polymer–polymer ABS are the oldest ABS in relative to the other types of ABS mentioned

above, the experimental and theoretical efforts in order to the understanding of their mechanism are considerably fewer and there remains considerable uncertainty regarding to the details of the mechanism of the phase separation in these systems. According to the effects of salts on the solubilities of ionic liquids in aqueous solutions and also based on the ^1H NMR and molecular dynamic evidence, it was found that [7,9,10] the salting-out effect is an entropically driven phenomena which is a consequence of the formation of hydration complexes and the increase of the surface tension of cavity formation, but the salting-in effect is resulting from the direct binding of the ions to the hydrophobic part of the ionic liquid. The activities of different components in a solution are important for the understanding of interactions in solutions. The water activity is determined by the formation of the bond between water and solutes. Thus if the mechanism of different salting effects involves solutes dehydration or solute–solute interactions, the water activity would be expected to be strongly dependent on the different types of solutes. The isopiestic method, which is a simple experimental method for determination of solvent activity in solutions, is based on the phenomenon that different solutions connected through their vapor spaces, approach equilibrium by transferring solvent mass by distillation. The different solutions under isopiestic equilibrium have the uniform temperature, pressure and solvent chemical potential and therefore there are no concentration gradients in the same liquid phase. In the present

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paper, in order to obtain further details about the mechanisms of polymer (1) – polymer (2) ABS formation as well as a correlation between the liquid–liquid equilibria (LLE) and vapor–liquid equilibria (VLE) behavior of the polymer–polymer ABS, the isopiestic equilibrium measurements for several aqueous polymer (1) –polymer (2) solutions capable or not of inducing phase separation were performed at 298.15 K. In order to cover a range of hydrophilic and hydrophobic behaviors, the polymers polyethylene glycol 200 (PEG200), polyethylene glycol 400 (PEG400), polyethylene glycol 2000 (PEG2000), polyethylene glycol 4000 (PEG4000), polyethylene glycol 6000 (PEG6000), polyethylene glycol 10000 (PEG10000), polyethylene glycol dimethyl ether 250 (PEGDME250), polyethylene glycol dimethyl ether 500 (PEGDME500), polyethylene glycol dimethyl ether 2000 (PEGDME2000), polyvinyl pyrrolidone 10000 (PVP) and polypropylene glycol 400 (PPG400) were investigated. PEGs, PPGs, PEGDMEs and PVPs are the most important and nontoxic water soluble polymers which have been used extensively for the formation of different polymer–polymer and polymer-salt ABS, so that, these polymers have been used in the more than 95% of the polymer-based ABS. In order to study the effect of structure of the polymers, the polyethers PEG, PEGDME and PPG were selected. PEG and PEGDME have similar repeating units with different end groups (OH in the case of PEG and OCH₃ in the case of PEGDME). PPG and PEG have similar end groups with different repeating units so that, PPG contains a side chain methyl group which hinders hydrogen bonding between water molecules and the ether oxygen atoms. Both of repeating unit and end groups for PVP are different with those for the investigated polyethers.

2. Experimental section

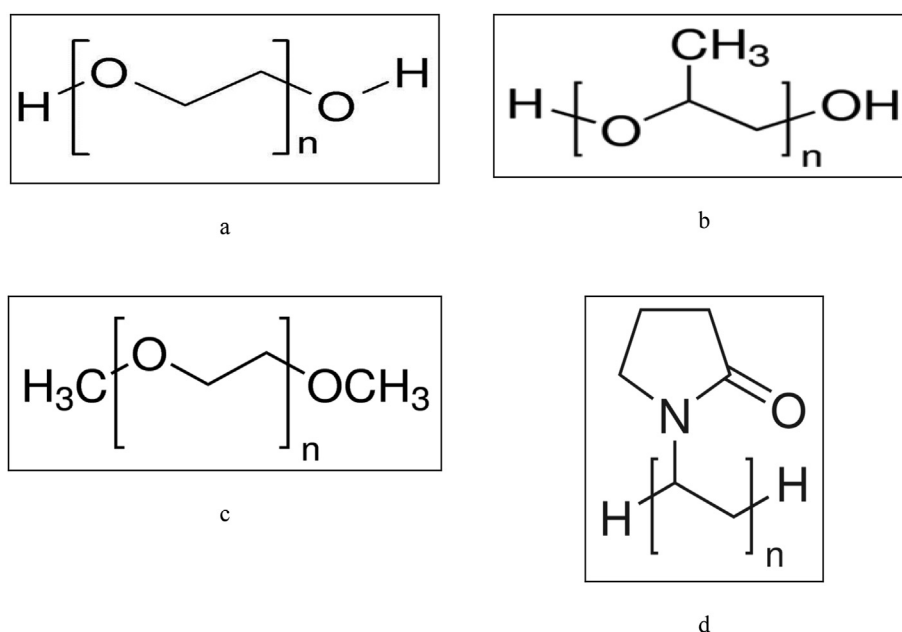
2.1. Materials

PPG400 was obtained from Fluka. PEGs, PEGDMEs and PVP were obtained from Merck. The polymers were used as received and doubly distilled and deionized water was used in the preparation of the all solutions. The structures of the investigated polymers have been presented in [Scheme 1](#).

2.2. Experimental procedures

The solutions were prepared on a mass basis using an analytical balance (Sartorius CP124S) with an accuracy of $\pm 1 \times 10^{-7}$ kg. The binodal curves were determined in a glass vessel, volume 50 cm³ [3], using the cloud point titration method at atmospheric pressure, as previously described [19]. The vessel was provided with an external jacket in which water circulated at the certain temperature (± 0.05 K) using a Julabo water thermostat. Briefly, in the glass vessel containing an aqueous polymer 1 solution of known concentration, an aqueous polymer 2 solution of known mass fraction was added drop wise or vice versa, until the appearance of a cloudy solution (biphasic region), then a known mass of water was added to make the mixture clear (monophasic region) again. All the additions occurred under constant stirring. This procedure was repeated to obtain sufficient data for the construction of a complete phase diagram.

The details of isopiestic apparatus and the procedure used in this work have been described previously [4]. In this method, the vapor space of different solutions, which connected through the vapor space, is evacuated and the volatile component is transported through the vapor phase until the solutions reach equilibrium. At isopiestic equilibrium, the solvent chemical potentials in each of the solutions within the isopiestic apparatus are identical. Since the activity of solvent in one solution (standard solution) at different temperatures and concentrations is known, therefore the solvent activity for other solutions in the isopiestic apparatus can be known. The used isopiestic cells have 7 or 8 sample cups uniformly distributed at the bottom. Known masses of pure anhydrous NaCl (two cups), pure polymer 1 (one cup), pure polymer 2 (one cup), and polymer 1 + polymer 2 mixture with a certain composition (two or three cups) were added to each isopiestic sample cup and the central cup was used as a water reservoir. These sample cups were then placed in the isopiestic apparatus, air was removed, and the apparatus was held in a constant-temperature bath for period 5–9 days (depending on the solutes concentration) at 298.15 K to within ± 0.05 K. Water is transferred from the central cup into the other cups containing the dry samples through the vapor phase until the central cup is dried. The chamber containing the solutions



Scheme 1. The structures of the investigated polymers: a, PEG; b, PPG; c, PEGDME and d, PVP.

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