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Aqueous biphasic formation, volumetric and compressibility behaviour in tetrabutylammonium bromide-inorganic salts aqueous systems

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Phase diagrams for several (salt + salt) aqueous biphasic systems containing tetrabutylammonium bromide and inorganic salts NaH_2PO_4, Na_2HPO_4, Na_3PO_4, Na_2CO_3, K_3Cit and Na_2SO_4 were determined at $T = (298.15, 308.15 \text{ and } 318.15)$ K. The salting-out strength of the investigated kosmotropic salts on the tetrabutylammonium bromide (chaotropic salt) in aqueous solutions follows the well established Hofmeister series, as in the case of (polymer + salt) aqueous biphasic systems. In order to obtain further evidence about the salting-out effect in these systems, volumetric and compressibility behaviour of tetrabutylammonium bromide aqueous solutions were also determined in the absence and presence of the investigated inorganic salts at different temperature. It was found that there is a relation between the relative concentration of various salts to form two-phase system with tetrabutylammonium bromide and the apparent molar volume or isentropic compressibility of transfer of tetrabutylammonium bromide from water to aqueous solution of the investigated salts.

1. Introduction

Aqueous biphasic systems (ABS) consist of two immiscible aqueous-rich phases based on polymer–polymer, polymer–salt or salt–salt combinations in which each phase contains mainly one of the compounds and a small amount of the other, with water as solvent in both phases with mass fraction (80 to 90)% in the equilibrium phases. Polymer based ABS have been widely used for the separation and purification of biomolecules such as nucleic acids and proteins [1–3]. In recent years, it was found that a new class of ABS can be formed when a hydrophilic ionic liquid (IL) and a certain water structuring inorganic or organic salt are combined with each other in aqueous solution [4–33]. Based on a compilation and analysis of the data hitherto reported about the IL based ABS, Freire *et al.* [34] published a critical review in which a judicious assessment of the available literature on the subject has been provided and the effect of temperature, pH, the IL structure and the various types of salting-out agents on the phase equilibria of ABS has been discussed. Despite the immense versatility inherent to the cation-anion permutations in ionic liquids, most of the phase diagrams of IL-based ABS have been reported for imidazolium-based ILs, whereas relatively few studies have used phosphonium-, pyridinium-, piperidinium-, ammonium-, or pyrrolidinium-based ILs [34]. Regarding to the ammonium-based IL-salt ABS, there is only a report on the binodal curves of tetrabutylammonium chloride–salt (K_3PO_4, K_2HPO_4, K_2CO_3, $(NH_4)_2SO_4$, KOH) ABS at ambient temperature by Rogers *et al.* [18]. Tetrabutylammonium bromide ($N_{4444}Br$) + $(NH_4)_2SO_4$ ABS have been used for the separation of metal ions [12,13] and microextraction of methyl orange [35]. Although studies on the thermodynamic properties of aqueous salt-salt solutions provide useful information about the molecular mechanism of the salting-out effects in these systems, however, detailed knowledge on the thermodynamic properties of $N_{4444}Br$-salt aqueous solutions is scarce in the literature. To the best of our knowledge, there is no information in the literature about the volumetric and acoustic properties of $N_{4444}Br$-salt aqueous solutions. In order to learn more about the salting-out effects in the salt–salt ABS, here we have investigated the phase diagrams, volumetric and compressibility properties of aqueous solutions of $N_{4444}Br$ in the absence and presence of inorganic salts NaH_2PO_4, Na_2HPO_4, Na_3PO_4, Na_2CO_3, K_3Cit and Na_2SO_4 at different temperatures, for which such information is not available in the literature.

2. Experimental

2.1. Materials

All purity values in the following are as mass fraction. Tetrabutylammonium bromide ($N_{4444}Br$) ($\geqslant$0.990), NaH_2PO_4 ($\geqslant$0.995), Na_2HPO_4 ($\geqslant$0.995), Na_3PO_4 ($\geqslant$0.990), Na_2CO_3 ($\geqslant$0.999) and Na_2SO_4 ($\geqslant$0.990) were purchased from Merck and used as received. The K_3Cit (>0.990) was purchased from Fluka. The salts were used without further purification. Double distilled and deionised water was used. The provenance and purity values are summarised in table 1.

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2.2. Experimental procedures

The density and sound velocity of the mixtures were measured at different temperatures with a digital vibrating-tube analyzer (Anton Paar DSA 5000, Austria) with proportional temperature control that kept the samples at working temperature within $\pm 10^{-3}$ K. The apparatus was calibrated with double distilled deionised, and degassed water, and dry air at atmospheric pressure according to the instrument catalogue. Densities and sound velocities can be measured with a precision of $\pm 10^{-6}\ \mathrm{g \cdot cm^{-3}}$ and $\pm 10^{-2}\ \mathrm{m \cdot s^{-1}}$, respectively. All the solutions for volumetric determination were prepared by mass on a Sartorius CP225D balance precisely within $\pm 1 \times 10^{-5}$ g. The experimental uncertainty of density and sound velocity measurements was $\pm 3 \times 10^{-6}\ \mathrm{g \cdot cm^{-3}}$ and $\pm 10^{-1}\ \mathrm{m \cdot s^{-1}}$, respectively.

The binodal curves were established at atmospheric pressure through the cloud point titration method [36]. A glass vessel, provided with an external jacket in which water at constant temperature was circulated using a thermostat, was used to carry out the phase equilibrium determinations. Phase diagram was determined by repetitive drop wise addition of an aqueous $N_{4444}Br$ solution with known concentration to an aqueous salt solution with known concentration or vice versa until the detection of a cloudy solution (biphasic region), followed by the drop wise addition of water until the formation of a clear solution (monophasic region). The composition of the mixture was determined by mass using an analytical balance (Sartorius CP124S) with a precision of $\pm 1 \times 10^{-4}$ g. The uncertainty was found to be 0.001 in determining the mass fraction of both $N_{4444}Br$ and salt by using the titration method used.

3. Results and discussion

In this work, two sets of experiments were carried out in order to studying of the salting-out effects in the salt-salt ABS. In the first set of experiments, Phase diagrams for ($N_{4444}Br + NaH_2PO_4$, Na_2HPO_4, Na_3PO_4, Na_2CO_3, K_3Cit and Na_2SO_4 ABS) were determined at temperatures (298.15, 308.15 and 318.15) K. In the second part, density and sound velocity measurements at (293.15, 298.15, 303.15, 308.15, 313.15 and 318.15) K were carried out for the aqueous solutions of $N_{4444}Br$ in the absence and presence of $0.1\ \mathrm{mol \cdot kg^{-1}}$ investigated salts. The experimental binodal, density and sound velocity data are given in tables 2 and 3.

3.1. Aqueous biphasic formation properties

For the investigated systems, the measured binodal data were correlated to the following empirical nonlinear expression developed by Merchuk [37]:

$$m_1 = a \exp\left(b m_2^{0.5} + c m_2^3\right), \tag{1}$$

were m_i is the molality of component i, a, b and c are fit parameters and subscripts 1 and 2 stand for $N_{4444}Br$ and salt, respectively. The obtained parameters a, b and c are given in table 4.

TABLE 1
Provenance and purity of the compounds investigated.

Compound	Supplier	Mass fraction supplier
Tetrabutylammonium bromide ($N_{4444}Br$)	Merck	$\geqslant 0.990$
NaH_2PO_4	Merck	$\geqslant 0.995$
Na_2HPO_4	Merck	$\geqslant 0.995$
Na_3PO_4	Merck	$\geqslant 0.990$
Na_2CO_3	Merck	$\geqslant 0.999$
Na_2SO_4	Merck	$\geqslant 0.990$
K_3Cit	Fluka	>0.990

The binodal curves can be used to illustrate the salting-out strength of the investigated salts on the $N_{4444}Br$ aqueous solutions and the results at $T = 318.15$ K are presented in figure 1. The observed shifts in the binodal curves follow the Hofmeister series for the strength of the salting-out effects of electrolytes: $Na_3PO_4 \gg K_3Cit$ (for high salt concentration) $> Na_2HPO_4 > Na_2CO_3 > Na_2SO_4 \gg NaH_2PO_4$. In fact, the anions with higher valence are more effective than anions with lower valence in the salting-out of $N_{4444}Br$ to form the ABS. Formation of ABS in these systems is an entropically-driven process which is mainly a result of the creation of water-kosmotropic salt complexes that cause the dehydration of the chaotropic salt. The addition of a high charge-density salt (such as Na_3PO_4) to an aqueous solution of a low charge-density salt ($N_{4444}Br$) leads to liquid–liquid de-mixing due to a preferential hydration of the high charge density salt over $N_{4444}Br$, leading therefore to the salting-out (exclusion) of $N_{4444}Br$ to the $N_{4444}Br$-rich phase [33,34]. In figure 2, the comparison between the binodal curves of {[C_4mim][Br] + K_3Cit} [33] and {$N_{4444}Br + K_3Cit$ ABS} has been made at $T = 298.15$ K. As can be seen, the two-phase aria of {[C_4mim][Br] + K_3Cit ABS} is very smaller than those of {$N_{4444}Br + K_3Cit$ ABS}. Cation N_{4444}^+ is more hydrophobic than cation C_{4mim}^+ and therefore $N_{4444}Br$ is easier to salt-out than [C_4mim][Br]. In order to more comparison between the hydrophobic properties of $N_{4444}Br$ and [C_4mim][Br], the plot of the water activity against solute molality for the binary aqueous solutions of $N_{4444}Br$ (data taken from reference [33]) was compared with those of [C_4mim][Br] (data taken from reference [38]). It was found that, the plot for [C_4mim][Br] shows markedly larger negative slope of the water activity against molality, which implies that [C_4mim][Br]–water interactions are stronger than $N_{4444}Br$–water interactions.

Although in the case of ($N_{4444}Br + K_3Cit$) ABS system, the two-phase area in the whole concentration range is expanded with temperature, however for all the systems containing the investigated sodium salts, the binodal curve isotherms have been intersected in a certain concentration and the binodal curves for the corresponding concentration are independent of temperature. As shown in figure 3, in the $N_{4444}Br$-rich region, an increase in temperature caused the expansion of the one-phase area; while, for the salt-rich region, expansion of the two-phase area was observed with increase in temperature. The similar behaviour has also been observed for the polymer–sodium salt ABS [36–40]. However in the case of [$C_n$mim][X]-salt ABS [32,33], the one-phase area in the whole concentration range is expanded with temperature. Therefore we may conclude that the temperature behaviour of the $N_{4444}Br$-salt ABS is similar to those of the polymer–salt ABS. In fact, the results obtained for the sodium salts investigates show that in the $N_{4444}Br$-rich and salt-rich regions, the salting-out strength of the investigated salts on the $N_{4444}Br$ aqueous solutions respectively decreases and increases by increasing temperature. (Vapour + liquid) equilibria behaviour of the binary $N_{4444}Br$ aqueous solutions shows that the vapour pressure depressions of the ($N_{4444}Br + H_2O$) system decrease by increasing temperature which implies that $N_{4444}Br$ becomes more hydrophobic with increasing temperature [41]. Therefore we expect that at higher temperatures, $N_{4444}Br$ can be more easily salted-out by a salting-out-inducing ion. Since the temperature has a slight effect on the (vapour + liquid) equilibria properties of aqueous inorganic salt solutions, then we may conclude that the solute–water interaction is not the only factor governing the observed salting-out effects. But the phase behaviour in the $N_{4444}Br$-salt ABS is controlled by the net result of competition between the ability of the solutes to interact with water and the favourable (or non-favourable) interactions that occur between the $N_{4444}Br$ and salts to a large extend.