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Influence of the addition of Tween 20 on the phase behaviour of ionic liquids-based aqueous systems

María S. Álvarez, Ana Mateo, Francisco J. Deive *, M. Ángeles Sanromán, Ana Rodríguez *

Department of Chemical Engineering, Universidade de Vigo, P.O. Box 36310, Vigo, Spain

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ABSTRACT

The addition of a non-ionic surfactant (Tween 20) to 1-ethyl-3methyl imidazolium alkylsulfate ($C_2C_1imC_nSO_4$)-based aqueous biphasic systems was investigated in this work. The solubility curves of the systems $\{(C_2C_1imC_nSO_4\ (n = 2\text{ and }8) + \text{Tween }20) + \text{high charge density salt }(K_3PO_4/K_2CO_3/K_2HPO_4) + H_2O\}$ were carried out at $T = 298.15$ K. The obtained experimental data were correlated by using three empirical equations. The molar Gibbs free energy of hydration ($\Delta_{hyd}G$) is a valuable parameter to analyse the segregation capacity provided by the inorganic salts. Additionally, the efficiency of the separation capacity was discussed in terms of the salting out potential of the selected salts and the presence of Tween 20. Othmer–Tobias and Bancroft equations have been used to correlate the experimental tie-line data.

1. Introduction

Currently, the hunt for more competitive and greener processes has led to the application of ionic liquids, neoteric solvents with outstanding properties such as their negligible volatility and tunability [1,2], in a range of fields such as electrochemistry, analytical chemistry, or chemical engineering, to name a few [3]. In this sense, one of the areas that has benefitted from the presence of these molten salts is the separation of compounds with industrial interest by means of (liquid + liquid) equilibrium [4–6].

Among the existing alternatives, the segregation of phases in systems containing aqueous solutions of ionic liquids is a field with booming interest since 2003, when Gutowski and co-workers published the first work on the capacity of hydrophilic ionic liquids to form aqueous biphasic systems (ABS) [7]. This separation strategy generally consists in adding an inorganic salt to aqueous solutions of ionic liquids, thus triggering phase disengagement: an upper aqueous phase mainly composed of ionic liquid and a lower aqueous layer rich in inorganic salt [8]. In this work, 1-ethyl-3-methyl imidazolium ethylsulfate and octylsulfate have been selected as model ionic liquids to be salted out in aqueous solutions, since they are reasonably cheap, they can be easily synthesized in an atom-efficient and halide-free way, they display relatively low viscosities and melting points [9], and they belong to one of the most representative families (1-ethyl-3methyl imidazolium) already synthesized at levels higher than one ton per year [10].

Different types of ABS have been described in the literature, such as those exclusively formed by a polymer and a salt, a polymer and a polymer, an ionic liquid and a salt, an ionic liquid and a polymer, and a surfactant and a salt [11–15]. The latter has been reported to be advantageous in terms of cost, availability at bulk quantities, biodegradability, lower interface tension, mild operation temperatures and wider immiscibility window. Thus, in this study, the phase segregation capacity of different potassium-based inorganic salts was studied in aqueous mixtures of ionic liquids and a model non-ionic surfactant (Tween 20). This family is commonly used in industrial biotechnology, for instance in enzyme production processes or bioremediation studies, and has been reported to act even as nutrient in culture media [16,17].

In recent research works, the suitability of this kind of non-ionic surfactants (Tween 20) to extract biomolecules [18], industrial dyes [19] and metals [20] has already demonstrated. Additionally, the applicability of $C_2C_1imC_nSO_4$ has also been concluded for enzyme separation [8,21]. Therefore, in this study we intend to shed light on the ABS behaviour of both compounds mixed (non-ionic surfactants and ionic liquids at ratios 25:75 and 75:25, respectively) in the presence of the inorganic salts K_3PO_4, K_2HPO_4 and K_2CO_3. These salts are well-known salting out agents, as predicted by the Hofmeister series, so their segregation capacity was discussed in this work by analysing the solubility curves at $T = 298.15$ K and the molar Gibbs free energy of hydration ($\Delta_{hyd}G$). Three empirical equations were employed to correlate the

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* Corresponding authors. Tel.: +34 986 81 87 23.
E-mail addresses: deive@uvigo.es (F.J. Deive), aroguez@uvigo.es (A. Rodríguez).

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experimental solubility data. The segregation capacity was also evaluated in terms of tie-line data, tackling the slope (*S*) and the tie-line length (*TLL*). Othmer–Tobias and Bancroft models were used to evaluate the consistency of the tie-line data [22].

2. Experimental

2.1. Chemicals

The ionic liquids 1-ethyl-3-methyl imidazolium ethylsulfate ($C_2C_1imC_2SO_4$) and 1-ethyl-3-methyl imidazolium octylsulfate ($C_2C_1imC_8SO_4$) were provided by Merck. They were subjected to vacuum of $P = 10^{-1}$ Pa and temperature $T = 330.15$ K for several days in order to remove moisture and possible traces of organic volatile compounds. The inorganic salts K_3PO_4, K_2HPO_4 and K_2CO_3 were supplied by Sigma–Aldrich and were used as received, without further purification. The non-ionic surfactant Tween 20, polyethoxylated sorbitan monolaurate was purchased from Sigma–Aldrich. All the data concerning chemicals purities and provenance are shown in table 1.

2.2. Experimental procedure

The solubility curves were empirically ascertained by means of the cloud point titration method [23] in a jacketed glass vessel containing a magnetic stirrer at atmospheric pressure, 101.33 kPa. The temperature was controlled at $T = 298.15$ K with a F200 ASL digital thermometer with an uncertainty of $T = \pm 0.01$ K. Known amounts of Tween 20 and $C_2C_1imC_nSO_4$ in aqueous solution were introduced to a vessel, and the immiscibility window was mapped by sequential additions of inorganic salt (K_3PO_4, K_2HPO_4 and K_2CO_3) and water, until the detection of a turbid and clear solution, respectively.

Additionally, a mixture with known mass fraction at the biphasic region was prepared to determine the tie-lines (*TLs*), in accordance with the protocol defined by Merchuk [24]. Briefly, after a vigorous stirring, the mixture was left to settle for 24 h to allow a complete phase separation. Top and bottom layers were then separated and weighted, and the level arm rule was used to determine each *TL* composition. The estimated uncertainty associated with the determination of the surfactant (top) and salt (bottom) phases mass compositions is ±2%. All the samples were weighed in an analytical Sartorius Cubis MSA balance (125P-100-DA, $\pm 10^{-5}$ g).

3. Results and discussion

3.1. Phase diagrams determination and correlation

Up to our knowledge, this is the first time that the ABS resulting from the combination of the non-ionic surfactant Tween 20 with an ionic liquid and a high charge density inorganic salt is investigated. Thus, (liquid + liquid) de-mixing was characterised for the systems $\{(C_2C_1imC_nSO_4\ (n = 2\ \text{and}\ 8) + \text{Tween 20}) + (K_3PO_4\ \text{or}\ K_2CO_3\ \text{or}\ K_2HPO_4) + H_2O\}$ at $T = 298.15$ K. The experimental solubility data are collected in tables 2 and 3, and they are plotted in figures 1 and 2.

TABLE 1
Purities and suppliers of chemicals.[a]

Chemical	Supplier	Mass fraction purity
K_3PO_4	Sigma–Aldrich	0.98
K_2CO_3		0.99
K_2HPO_4		0.98
Tween 20		0.98
$C_2C_1imC_nSO_4$	Merck	0.98

[a] Deionised water was used in all the experiments.

The data obtained can be analysed in the light of the surfactant addition, the alkyl chain length in the ionic liquid anion, and the salting out potential of the selected inorganic salt. These factors have proven to be crucial to achieve phase segregation. The formation of an upper (ionic liquid/surfactant)-rich phase is observed, in line with previous investigations by Wang *et al.* (2004), who concluded that ionic liquids and surfactants form an organised moiety: not only does the ionic liquid act as a specific solvent, but also as a co-surfactant [25]. Additionally, it becomes patent that the increase of the surfactant concentration from 25% to 75% entails immiscibility regions closer to the origin, no matter the ionic liquid or inorganic salt employed. The comparison of the obtained data with the systems containing the pure surfactant (100% Tween 20) and ionic liquid (100% $C_2C_1imC_nSO_4$), reported by Álvarez *et al.* [22] and Deive *et al.* [26], respectively, reveals a close agreement with the observed trends. The explanation of this behaviour may be related to the increased hydrophobicity provided by the non-ionic surfactant. Thus, the competition between the mixture ionic liquid/surfactant and the inorganic salt for the water molecules is easily won when the first is more hydrophobic, due to they establish weaker hydrogen-bonds with water. This is coincident with other types of ABS involving ionic liquids and PEG [14,27]. The observed trends pose undoubted advantages related to the process economy and supply logistics.

TABLE 2
Binodal data in mass fraction for $\{(C_2C_1imC_2SO_4 + \text{Tween 20})\ (1) + \text{salt}\ (2) + H_2O\ (3)\}$ two-phase systems for different surfactants concentrations at $T = 298.15$ K, $P = 101.33$ kPa.[a]

K_3PO_4		K_2HPO_4		K_2CO_3	
100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1
25% $C_2C_1imC_2SO_4$ + 75% Tween 20					
2.83	51.43	2.21	53.74	4.07	46.42
3.53	46.06	6.95	19.35	4.98	38.90
4.32	42.48	7.63	15.85	5.96	33.71
4.84	38.73	8.06	12.32	6.45	28.43
5.40	35.58	8.43	10.21	6.93	24.77
5.92	32.41	8.65	8.36	7.33	20.48
6.24	28.34	8.89	6.56	7.43	18.54
6.74	25.66	9.24	4.75	7.69	16.22
7.06	22.72	9.44	3.58	8.01	13.26
7.49	20.79	3.44	47.75	7.16	23.22
8.00	17.14	4.33	41.93	7.92	10.99
8.13	15.28	4.98	37.26	8.64	6.40
8.50	13.39	5.48	33.48	8.31	9.09
8.89	10.87	5.84	31.17	8.87	3.24
9.17	9.37	6.15	28.62	9.20	1.80
9.31	8.00	6.43	26.21		
9.66	5.66	7.00	22.15		
9.97	3.45				
10.02	2.54				
75% $C_2C_1imC_2SO_4$ + 25% Tween 20					
10.36	25.96	8.30	32.48	8.65	29.98
10.57	23.03	8.88	28.56	8.75	26.16
10.80	20.14	9.15	25.10	9.02	22.55
10.95	17.57	9.38	23.11	9.04	20.32
11.02	15.32	9.49	18.68	9.07	17.37
11.01	13.41	9.64	17.10	9.02	15.02
11.03	8.21	9.45	20.29	9.07	13.42
11.05	6.99	9.69	15.19	9.22	10.76
11.09	5.61	9.70	12.49	9.09	8.73
11.00	11.32	9.65	9.90	9.54	4.83
10.94	9.74	9.78	7.53	8.37	33.38
11.01	13.41	9.79	5.88	9.90	2.58
11.37	3.17	9.99	3.02		
11.71	1.96				

[a] Standard uncertainties are $u(w) = \pm 0.0002$, $u(T) = \pm 0.01$ K; $u(P) = \pm 0.03$ kPa.