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Study of the liquid–liquid equilibrium of 1-propanol + manganese sulphate and 2-propanol + lithium sulphate aqueous two-phase systems at different temperatures: Experiment and correlation

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ABSTRACT

Phase equilibrium data for 1-propanol + manganese sulphate and 2-propanol + lithium sulphate aqueous two-phase systems were measured at T = 298.15, 308.15 and 318.15 K. The salting-out effect was discussed on the bases of the salting-out coefficient of the Setschenow-type equation. Furthermore, the experimental tie-line compositions were successfully correlated to the generalized electrolyte-NRTL model for mixed solvent electrolyte system (e-NRTL), and the binary interaction parameters of the e-NRTL model were obtained. Correlation of the tie-lines data shows that the calculated values and experimental data are in good agreement and the performance of the e-NRTL model in the correlation of the tie-lines data is good.

1. Introduction

Aqueous two-phase systems (ATPS's), formed by mixing of two polymers or one polymer and one inorganic salt, are important for separation and purification of enzymes, nucleic acids and other biological processes [1]. This extraction technology offers the advantages of easy processing on any scale, high capacity, easy and precise scale up and high product yields. The salts used are usually phosphates [2], citrates [3] or sulphates [4]. In recent years many research groups have focused on the measurement of new two-phase equilibrium data for aqueous polymer + salt systems. Also, for large-scale processes, methods for recycling chemicals have been developed [5,6]. Greve and Kula [6] have described the use of some two-phase systems composed of lower aliphatic alcohols + water + inorganic salts for the extraction of salt from the primary bottom phase of the protein extraction processes in PEG + salt systems. In this respect, they have reported the detailed liquid–liquid equilibrium (LLE) data for some ternary systems composed of alcohol + salt + water [6]. Furthermore, Zafarani-Moattar and coworkers [7], Salabat and Hashemi [8], Hu et al. [9] and Taboada [10] have reported LLE of some aliphatic alcohols + salt + water systems.

In recent years several models have been developed to describe the thermodynamic properties of liquid solutions. Wilson [11], NRTL [12] and UNIQUAC [13] models, which are on the bases of the local composition concept have been used to study the thermodynamic properties of nonelectrolyte systems. Chen et al. [14] proposed the electrolyte NRTL model based on the NRTL model of Renon and Prausnitz [12] and successfully used it to represent thermodynamic properties of aqueous electrolyte solutions. The model has been extended to represent the multicomponent electrolyte solutions [15] and it gives a reasonable representation of LLE of electrolyte solutions at low salt concentrations. Recently, Chen and Song [16] generalized the electrolyte NRTL model to represent the equilibrium of mixed solvent electrolyte systems.

In this work, we have studied the LLE of 1-propanol + manganese sulphate + water and 2-propanol + lithium sulphate + water systems at T = 298.15, 308.15 and 318.15 K and the effect of temperature on the studied systems were also discussed. Furthermore, phase equilibrium data was correlated to the Setschenow-type equation introduced by Hey et al. [17] to describe the salting out effect arising from the addition of manganese sulphate or lithium sulphate to the alcohols on the studied systems. The effects were analyzed using the corresponding composition phase diagrams. Moreover, the binary interaction parameters of the generalized electrolyte-NRTL model (e-NRTL) were obtained using the binary vapor–liquid equilibrium data, and these parameters successfully used to correlate the tie-lines data.

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Table 1
Physical properties of the chemicals used in this work.

Chemical	Cass No.	Source	Purity (in mass fraction %)	Molecular mass ($g\,mol^{-1}$)	Density[a] at T = 298.15 K ($g\,cm^{-3}$)	
					This work	Ref. [28]
1-Propanol	71-23-8	Merck GR	>99.5%	60.096	0.799527	0.79954
2-Propanol	67-63-0	Merck GR	>99.7%	60.096	0.780824	0.78110
Lithium sulphate monohydrate	10102-25-7	Merck GR	>99%	127.961	–	–
Manganese sulphate monohydrate	10034-96-5	Merck GR	99–101%	169.017	–	–

[a] The density of pure alcohols were measured at T = 298.15 with a digital vibrating-tube analyzer (Anton paar Model DSA 5000, Austria) with proportional temperature controller that kept the samples at working temperature with an accuracy of ±0.001 K. The uncertainty of the density measurement is better than $\pm 3 \times 10^{-6}\,g\,cm^{-3}$.

2. Experimental

2.1. Materials

The chemicals used in this work were described in Table 1. These chemicals were used without further purification and double-distilled deionized water was used.

2.2. Apparatus and procedure

For determination of the tie-lines, feed samples (about $2 \times 10^{-5}\,m^3$) were prepared by mixing appropriate amounts of alcohol, salt and water in the vessel. The samples were stirred for 1 h and were placed in the thermostated bath and allowed to settle for at least 24 h to separate into two clear phases. The temperature was controlled at a constant temperature with circulation of water using a thermostat (JULABO model MB, Germany) with an accuracy of ±0.02 K. After the separation of the two-phases, the concentration of lithium sulphate in the top and bottom phases was determined by flame photometry (JENWAY model PFP7, England). Also, the concentration of manganese sulphate, was determined by atomic absorption (Shimadzu AA-6300). The concentration of alcohol in both phases was determined by refractive index measurements performed at 298.15 K using a refractometer (Quartz RS-232, Ceti, Belgium). The uncertainty in the refractive index measurement is ±0.0001. For dilute aqueous solutions containing an alcohol and a salt, the relation between the refractive index, n_D, and the mass fractions of alcohol, w_m, and salt, w_{ca} is given by:

$$n_D = n_w^0 + a_m w_m + a_{ca} w_{ca} \tag{1}$$

where n_w^0 is the refractive index of pure water, which is set to 1.3325 at 298.15 K. a_m and a_{ca} are constants of alcohol and salt, respectively, and for each of them, the linear calibration plots of refractive index of the solution are obtained. The values of the a_m and a_{ca} for each of the studied systems are listed in Table 2. However, it should be noted that Eq. (1) is only valid for dilute solutions. Therefore, before refractive index measurements, it was necessary to dilute the samples to be in the concentration range. The uncertainty of the mass fraction of 1-propanol and 2-propanol achieved using Eq. (1) was better than ±0.002.

3. Results and discussion

3.1. Phase diagram

For the 1-propanol + manganese sulphate + water and 2-propanol + lithium sulphate + water systems the experimental tie-line compositions at T = 298.15, 308.15 and 318.15 K are given in Tables 3 and 4, respectively. However, due to large uncertainties obtained in the determination of binodal data by the cloud point method [18], these data are not reported here.

Also, Fig. 1a and b illustrates the effect of temperature on the phase forming ability of the 1-propanol + manganese sulphate + water and 2-propanol + lithium sulphate + water systems at T = 298.15, 308.15 and 318.15 K, respectively. As these figures shows, the effect of temperature on the phase forming ability of the both studied systems is insignificant within the investigated temperature range. This trend is similar to the results obtained by Zafarani-Moattar and Salabat [19], Hu at al. [9] and Taboada [10] for the aliphatic alcohols + manganese sulphate + water, aliphatic alcohols + cesium sulphate + water, and 1-propanol + lithium sulphate + water systems, respectively.

Table 2
Values of the parameters of Eq. (1) for the studied systems.

System	a_1	a_2
1-Propanol + manganese sulphate + water	0.0863	0.1834
2-Propanol + lithium sulphate + water	0.0895	0.1885

3.2. Study of the salting-out effect

Salting-out effects are usually quantified by fitting solubility data to the empirical equation of Setschenow [20]:

$$\ln\frac{S_0}{S} = k_{ca} C_{ca} \tag{2}$$

where S_0 and S refer to the solubility of a given nonelectrolyte in pure water and in a salt solution of concentration C_{ca}, respectively. k_{ca} is the salting-out coefficient specific for a particular

Table 3
Experimental tie-lines for 1-propanol (m) + manganese sulphate (ca) + water (w) system at T = 298.15, 308.15 and 318.15 K.

Top phase: organic rich phase		Temperature	Bottom phase: salt rich phase	
w_m[a]	w_{ca}[b]		w_m	w_{ca}
		T = 298.15[c]		
0.7570	0.0007		0.0210	0.2862
0.6562	0.0024		0.0353	0.2340
0.5676	0.0095		0.0847	0.1585
0.5265	0.0124		0.1031	0.1362
0.4837	0.0189		0.1310	0.1140
		T = 308.15		
0.8713	0.0011		0.0186	0.3319
0.8058	0.0018		0.0239	0.2968
0.7353	0.0025		0.0326	0.2636
0.6729	0.0059		0.0425	0.2326
0.6160	0.0096		0.0505	0.2151
		T = 318.15		
0.8784	0.0007		0.0080	0.4132
0.7938	0.0013		0.0114	0.3691
0.7508	0.0019		0.0145	0.3415
0.5982	0.0074		0.0302	0.2679
0.4886	0.0110		0.0465	0.2097

[a] The uncertainty for 1-propanol mass fraction was better than ± 0.002 using Eq. (1).

[b] The uncertainty for manganese sulphate mass fraction was better than ±0.001 using atomic absorption.

[c] The uncertainty for temperature was better than ±0.02 K.