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SLLE and SLLVE of the water + NH_4Cl + 1-propanol system at 101.3 kPa

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Highlights

- Multiphase equilibrium for water+1-propanol+ NH_4Cl
- LL, SL and SLL and LLV, SLV and SLLV equilibrium data are determined at 298.15 K and at boiling temperature
- Inconsistency of previous results is shown
- Results are compared with the equilibrium phase diagram of water + NaCl + 1-propanol
- Extended UNIQUAC modeling of three - phase equilibrium including solid

Keywords

Water; 1-Propanol; NH_4Cl ; Isobaric; Vapor-liquid-liquid-solid; Consistency, Phase diagram, extended UNIQUAC model

Abstract

The equilibrium of the ternary electrolyte system at 101.3 kPa, water + 1-propanol + ammonium chloride (NH_4Cl), has been investigated at 298.15 K and at the boiling temperature to determine the shape of equilibrium surfaces and regions on the phase diagram. The data obtained have been compared with previously published experimental data showing their inconsistency.

Moreover, the results obtained allow us to study the shape of the phase diagram of the system, to analyze the evolution with the temperature of this equilibrium diagram and to show the differences with a similar system such as water + NaCl + 1-propanol.

Finally, it has been shown that the extended UNIQUAC model for electrolytes predicts the different equilibrium regions and boiling temperatures but there are great discrepancies between experimental and calculated equilibrium concentrations.

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1. Introduction

An investigation on industrial requirements for thermodynamic and transport properties carried out by the Working Party on Thermodynamic and Transport properties of the European Federation of Chemical Engineering, EFCE [1] showed the acute need for accurate, reliable, and thermodynamically consistent experimental data.

One of the fields where the lack of experimental data is notorious is the mixed solvent electrolyte systems. This type of mixture is found in many processes including extractive distillation, crystallization, regeneration of solvents and liquid-liquid extraction of mixtures containing salts. The literature available on these systems is scant, the relatively small amount of existing experimental data is incomplete and some of them contain important inconsistencies as shown in a previous paper [2]. Consequently, the users of thermodynamic models such as the electrolyte NRTL model [3] or the extended UNIQUAC model for electrolytes [4] applied to represent these systems have difficulties to find experimental equilibrium data to calculate the model parameters.

In this sense, we previously studied the equilibrium diagram of the water + NaCl + 1-propanol system at 101.3 kPa [2] in order to examine the shapes of the various equilibrium surfaces and regions that arise in it. The electrolyte was NaCl whose solubility in water changes little with temperature: only 6.7% in 100 K (from 26.28 wt% at 273.15 K to 28.05 wt% at 373.15 K) [5]. The objective of the present paper is to extend that study to another similar system involving a salt such as NH_4Cl whose solubility in water changes a lot with temperature: 88.7% in 100 K (from 22.92 wt% at 273.15 K to 43.24 wt% at 373.15 K) [5]. This fact could make the phase diagrams of both systems and their evolution with the temperature very different.

In this work, LL, SL and SLL equilibrium data at 298.15 K and 101.3 kPa and LV, LLV, SLV and SLLV equilibrium data of the water + NH_4Cl + 1-propanol system at boiling temperature and 101.3 kPa have been determined experimentally. The results obtained permit us to carry out a study of the shape of the phase diagram of the system, show the inconsistency of previous results, compare it with that of a similar system such as water + NaCl + 1-propanol and verify the accuracy of calculations done by using a model such as the extended UNIQUAC.

2. Experimental

2.1. Chemicals

Table 1 presents the description of the chemicals used. It includes ethanol since this was used as an internal standard for quantitative chromatographic analysis. The water content of the organic compounds presented in the Table was determined by the Karl Fischer technique. Ultrapure water obtained by means of a MiliQPlus system was used. Its conductivity was lesser than $1 \mu\text{S}/\text{cm}$.

2.2. Apparatus and procedures

Phase equilibrium determinations at 298.15 K and 101.3 kPa. Equilibrium measurements were made by preparing mixtures of known overall compositions by weighing different quantities of water, alcohol and solid salt in 20 mL tubes which were placed in a thermostatic bath at a constant temperature of 298.15 K where they were stirred intensively and left to settle for 24h to ensure that equilibrium was reached. Then, the upper and lower liquid phases were separated and their compositions determined using the methods of analysis described later.

Phase equilibrium determinations at boiling temperature and 101.3 kPa. A modified vapor-liquid Fischer Labodest unit (Fischer Labor und Verfahrenstechnik) was used in the determinations. A previous paper [6] describes the equipment used which includes an ultrasonic transducer to enhance the mixing and dispersion of the phases and consequently the mass transfer between them, especially between the solid and the two liquid phases in the boiling flask. Due to the great change of solubility of NH_4Cl with temperature, unlike the equipment used in previous works, it was necessary to include a controlled heating electric resistance around the return pipe that joins the phase separator with the mixer. The resistance maintains an external temperature of 373.15 K avoiding the crystallization of the salt in the duct and its clogging by a slight cooling of the stream that flows through its interior.

To carry out an experiment, a mixture of water, 1-propanol and NH_4Cl is placed inside the boiling flask where it is heated at a pressure of 101.3 kPa that is maintained by a Fisher M101 phase equilibrium control system. The boiling temperature is measured using a Pt100 sensor coupled to a digital thermometer (Hart Scientific 5615).

When equilibrium is reached, samples of the condensed vapor are taken. Liquid phases (one or two) with or without solid in suspension are also taken from the equipment and separated at the boiling temperature.

Method of analysis. Condensed vapor phases were analyzed by gas chromatography with a Thermal Conductivity Detector (TCD). For the liquid phases, a small amount of sample is introduced into a vial with a known amount of ethanol, which serves as an internal standard. This sample is subsequently analyzed by gas chromatography with TCD to determine the water and 1-propanol content. Another aliquot of the liquid phase is collected and the amount of salt that it contains is determined by a gravimetric method at 353.15 K to avoid a loss of NH_4Cl due to its volatility.

A Shimadzu GC14B gas chromatograph with a 2 m x 3 mm 80/100 Porapack Q packed column is employed to perform the analysis. When the liquid samples are analyzed, glass wool is put inside the glass insert to avoid NH_4Cl entering the column. Helium is used as a carrier gas at a

flow rate of 25 mL/min. The temperature of the oven is set to 463.15 K while the injector and the detector are set to 483.15 K. A 100 mA current is used.

The uncertainties were obtained from a statistical calculation of repeated measurements. The temperature standard uncertainty (u) in the SLLV determinations is 0.06 K. The composition relative uncertainty ($u_r(x) = \frac{u}{x}$) is 2% for all components except for the NH_4Cl in the organic phase where the relative uncertainty is 5%.

4. Results

Experimental results.

Phase equilibrium at 298.15 K and 101.3 kPa. Water and 1-propanol are completely miscible but the presence of NH_4Cl can split the mixture into two liquid phases in equilibrium. Consequently, the phase equilibrium diagram has the following regions: one LL region, two SL regions (organic and aqueous branch) and one SLL that is invariant (3 phases, 3 components, 2 degrees of freedom = pressure and temperature). Table 2 and Figure 1 show the equilibrium data determined for each region.

On the same Figure 1, the experimental equilibrium data at 298.15 K of Chen et al [7] have been represented. They reported data of 5 tie lines of the LL region and 17 points of the solubility curve. It can be seen that their points of the organic phases of the tie lines coincide with ours. The tendency of the points of its solubility curve also coincides with the extremes of our tie lines, both in the organic layer and in the aqueous one (Figure 1 a). But the points of the aqueous layer of their tie lines differ greatly from ours and even from the points of their solubility curve (figure 1 b). Obviously, they must have committed some error.

Fig. 1. Equilibrium diagram (mole fraction) at 298.15 K for the water + NH_4Cl + 1-propanol system at 101.3 kPa. (a) Experimental data of this work and solubility curve of Chen and Song [7]. (b) Experimental data of Chen and Song [7]

Phase equilibrium at boiling point and 101.3 kPa. Equilibrium data and boiling temperature of different mixtures are shown in Table 3 corresponding to the different regions of the equilibrium diagram. Figure 2 shows some of these data: the LLVE region is represented by continuous tie lines joining the two liquid phases in equilibrium, and dashed lines joining the organic liquids with the point that is representative of the vapor phase. In the same way, the SLVE region is represented by continuous lines joining solid and liquid, and dashed lines joining the liquids with the vapor. Lastly, the SLLVE region is represented by a triangle whose three vertexes are the solid salt and the compositions of the two liquid phases that are in equilibrium with each other.

On the same Figure 2, the LL, SL and SLL regions of the system at 298.15 K have been represented with dotted lines for comparison. It can be seen that the solubility curve separating the two liquids and one liquid region are almost coincident. However, the straight line separating the LL and SLL regions has moved up making the size of the regions with two liquid phases without solid phase much larger at boiling temperature.

Fig. 2. Equilibrium diagram (mole fraction) at boiling temperature for the water + NH₄Cl + 1-propanol system at 101.3 kPa.

On the other hand, Johnson and Furter [8] studied the equilibrium of some mixtures saturated in the salt of this system and determined their effect on the SLV equilibrium. The boiling temperature and the mole fraction of 1-propanol in the vapor are shown in Fig. 3 against the composition of the liquid on a salt-free basis. On the same Figure, our data of the SLV and SLLV regions have been represented. Although the boiling temperature and composition of the vapor of all the samples in the central part of the graph should not change, since they

correspond to the SLLV region, the authors [8] report small differences of 0.5 K and 0.01 mole fraction. Considering these errors, their results agree perfectly with ours, except for the point that represents the aqueous phase of the SLLV region, which has a boiling temperature and a mole fraction of 1-propanol that is lower than the previous result.

Finally, Abu Al-Rub et al. [9] determined isothermal VL equilibrium data at 333.15 K of this system using the headspace gas chromatography (HSGC) technique. But their data are thermodynamically incomplete. For example, the value of the pressure for each set of data is not given and therefore no comparison is possible.

Fig. 3. Boiling temperature (a) and composition of the vapor (b) for samples saturated with salt (SLV and SLLV).

By interpolation in Table 3, the diagrams of boiling temperature isotherms and iso-composition of phase vapor have been drawn in Figures 4 and 5. In a three-component system, according to the phase rule, the SLLV region is invariant for a determined pressure as shown previously in Fig. 3. Also, the isotherms and the vapor iso-composition lines of the SLV and LLV regions are straight lines. It can be observed that the shape of these phase diagrams at boiling temperatures is very similar to that of the water + NaCl + 1-propanol system [1] in spite of the great differences in the changes in solubility with temperature. In both systems, there are very small differences in the boiling temperatures of some of the characteristic points of the system such as the binary azeotrope water+1-propanol, the plait point of the LLV region and the invariant SLLV mixture. This feature makes a great part of the mixtures in the system boil within a very narrow range of temperatures of only 1 K.

Fig. 4. LLV, SLV, SLLV and LV isotherms for the water + NH_4Cl + 1-propanol ternary system at 101.3 kPa. Parameter of the curves = boiling temperature (K).

Fig. 5. Curves of iso-concentration of 1-propanol in the vapor phase for the water + NH_4Cl + 1-propanol system at 101.3 kPa. Parameter of the curves = mole fraction of 1-propanol in the vapor.

Extended UNIQUAC model

Finally, the equilibrium of the system has been calculated using the extended UNIQUAC model employing the parameters provided [4]. It is important to point out that these parameters were obtained from the correlation of the previously discussed SLV data of Johnson and Furter [8]. LLV data were not used in the fitting of parameters. Therefore it can be considered that the model has been used as predictive rather than correlative.

The results obtained are shown in Figure 6 comparing them with our experimental results. Although the model and parameters correctly predict the shape of the different regions and even the boiling temperatures, the results were not concurrent, as unexpectedly less salt would be needed to form a two-phase mixture. Thus, it is recommended to review the thermodynamic parameters in the model using reliable experimental data.

Fig. 6. Experimental and calculated by using the extended UNIQUAC model [4] equilibrium diagram for the water + NH₄Cl + 1-propanol system (mole fraction) at 101.3 kPa. Boiling temperatures are shown on each tie line.

4. Conclusions

The phase equilibria of the water + NH₄Cl + 1-propanol system at 101.3 kPa have been studied at 298.15 K and at the boiling temperatures. The data obtained have been compared with previously published experimental data showing their inconsistency.

The equilibrium diagrams at 298.15 K and at the boiling points show a smaller size of the equilibrium region with two liquids without solid phase at 298.15 K; a consequence of the great change of the NH_4Cl solubility in water with temperature.

For the system at the boiling temperature, the isotherms curves and the iso-concentration curves of 1-propanol in the vapor have the same shape as those for the system with NaCl which is less soluble in water. Therefore the solubility of the salt has not too much influence in the shape of these curves.

Finally, it has been shown that the extended UNIQUAC model by Thomsen et al. [4] predicts the different equilibrium regions and boiling temperatures. However, there are great discrepancies in the size of the regions, especially on the organic side.

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References

- [1] G. M. Kontogeorgis, R. Dohrn, J. C. de Hemptinne, I. G. Economou, L. F. Žilnik, V. Vesovic; Industrial Requirements for Thermodynamics and Transport Properties. *Ind. Eng. Chem. Res.*, 49(22), (2010), 11131–11141
- [2] J. Garcia-Cano, V. Gomis, J. C. Asensi, A. Gomis, A. Font, Phase diagram of the vapor-liquid-liquid-solid equilibrium of the water + NaCl + 1-propanol system at 101.3 kPa. *J. Chem. Therm.* 116 (2018) 352-362
- [3] C.C. Chen, Y. Song. Generalized electrolyte-NRTL model for mixed-solvent electrolyte system. *AIChE J.* 50 (2004) 1928-1941
- [4] K. Thomsen, M. C. Iliuta, P. Rasmussen, Extended UNIQUAC model for correlation and prediction of vapor-liquid-liquid-solid equilibria in aqueous salt systems containing non-electrolytes. Part B. Alcohol (ethanol, propanols, butanols)-water-salt systems. *Chem. Eng. Sci.* 59 (2004) 3631-3647
- [5] D. R. Lide. *CRC Handbook of Chemistry and Physics*. 83rd Ed. CRC Press, Boca Raton, Florida, 2002
- [6] V. Gomis, F. Ruiz, J. C. Asensi. The application of ultrasound in the determination of isobaric vapour-liquid-liquid equilibrium data. *Fluid Phase Equilib.* 172 (2000) 245–259
- [7] J. Chen, Y. Zhong, J. Han, M. Su, X. Shi, Liquid-liquid equilibria for water + 1-propanol (or 1-butanol) + potassium chloride + ammonium chloride quaternary systems at 298.15 K. *Fluid Phase Equilib.* 397 (2015) 50–57
- [8] A.I. Johnson, W. F. Furter, Salt Effect in Vapor-Liquid Equilibrium, Part II. *Can. J. Chem. Eng.*, June, (1960) 78-86

- [9] F. A. Abu Al-Rub, F. A. Banat, J. Simandl, Isothermal vapour-liquid equilibria of 1-propanol + water + salt mixtures. Chem. Eng. J. 74 (1999) 205-210

TABLES

Table 1.

Specifications of chemical compounds.

Chemical	Provider	Initial purity (mass %)	Water content KF ^a (mass %)	Purification method	Analysis method
NH ₄ Cl	Acros Organics	> 99.6		none	
1-propanol (1P)	Merck	> 99.5	0.09	none	GC ^b
Ethanol	VWR	> 99.8	0.02	none	GC ^b

^a KF = Karl Fischer Technique^b GC = Gas chromatography**Table 2.**Equilibrium data (mole fraction) of the water + NH₄Cl + 1-propanol (1P) system at 298.15 K and 101.3 kPa.

Solid		Aqueous layer			Organic layer	
NH ₄ Cl	Water ¹	NH ₄ Cl ²	1P ¹	Water ¹	NH ₄ Cl ²	1P ¹
SLL						
1	0.857	0.106	0.037	0.482	0.034	0.484
LL						
	0.866	0.064	0.070	0.649	0.036	0.315
	0.869	0.081	0.050	0.564	0.034	0.403
	0.863	0.094	0.043	0.518	0.034	0.448
SL						
1				0.357	0.020	0.622
1				0.258	0.012	0.731
1				0.157	0.0072	0.836
1				0.054	0.0043	0.942

T is in K with a standard uncertainty of 0.5 K, the pressure standard uncertainty is 2 kPa

The composition relative standard uncertainty is $u_r(x) = \frac{u}{x}$ is 2% except for the NH₄Cl in the organic phase where the relative standard uncertainty is 5%.¹ obtained by GC-TCD² obtained by gravimetric analysis

Table 3.

Equilibrium data (mole fraction) of the water + NH₄Cl + 1-propanol (1P) system at the boiling temperature (T) and 101.3 kPa.

Solid		Liquid phase. Aqueous layer			Liquid phase. Organic layer			Vapor phase	
T/K	NH ₄ Cl	Water ¹	NH ₄ Cl ²	1P ¹	Water ¹	NH ₄ Cl ²	1P ¹	Water ¹	1P ¹
SLLV									
362.82	1	0.810	0.171	0.020	0.379	0.037	0.584	0.446	0.554
LLV									
361.55		0.851	0.061	0.089	0.724	0.038	0.238	0.518	0.482
361.60		0.876	0.081	0.044	0.603	0.032	0.364	0.509	0.491
361.67		0.873	0.092	0.035	0.556	0.032	0.412	0.498	0.502
361.85		0.864	0.105	0.031	0.523	0.032	0.444	0.489	0.511
362.05		0.856	0.119	0.025	0.487	0.033	0.481	0.476	0.524
362.39		0.829	0.149	0.021	0.428	0.035	0.537	0.457	0.543
SLV									
362.95	1				0.322	0.0237	0.656	0.424	0.576
363.29	1				0.259	0.0184	0.723	0.390	0.610
363.95	1				0.192	0.0116	0.797	0.347	0.653
366.25	1				0.090	0.0057	0.904	0.217	0.783
368.44	1				0.033	0.0036	0.963	0.105	0.895
369.89	1				0.008	0.0030	0.988	0.030	0.970
369.43	1				0.015	0.0028	0.981	0.044	0.956
LV									
361.37					0.893	0.028	0.081	0.613	0.387
361.39					0.888	0.049	0.065	0.544	0.456
361.32					0.708	0.030	0.266	0.564	0.436
361.62					0.556	0.026	0.422	0.498	0.502
361.90					0.446	0.020	0.536	0.473	0.527

T is in K with a standard uncertainty of 0.06 K, the pressure standard uncertainty is 0.1 kPa and composition relative standard uncertainty $u_r(x) = \frac{u}{x}$ is 2%

¹obtained by GC-TCD

²obtained by gravimetric analysis