Viscosities, Vapor Pressures, and Excess Enthalpies of Choline Lactate + Water, Choline Glycolate + Water, and Choline Methanesulfonate + Water Systems

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This research has been focused on viscosities, vapor−liquid equilibria (VLE), and heat of mixing measurements for water with the following choline-based ionic liquids: choline lactate, choline glycolate, and choline methanesulfonate. Isothermal vapor−liquid equilibria were measured by means of a static VLE apparatus at (303.15, 313.15, and 323.15) K. The experimental VLE data were correlated using the NRTL and UNIQUAC models, and the root-mean-square deviations (rmsd's) are given. Furthermore, the molar excess enthalpies of water + choline glycolate and water + choline lactate ionic liquid systems have been performed at $T = (303.15, 315.15, \text{and } 323.15)$ K using a differential scanning calorimeter. The results were fitted to a Redlich−Kister equation to determine the fitting parameters and the mean relative deviations. Viscosities of the binary aqueous systems with choline glycolate and choline lactate have been measured at 293.15 K.

Introduction

Ionic liquids (ILs) are a class of low-temperature molten salts, generally comprised of an organic cation and an inorganic or organic anion. The term "room-temperature ionic liquid" (RTIL) has been introduced to describe a class of organic salts that are liquid in their pure state at or near room temperature.

The unique properties of RTILs, such as wide liquid temperature range, high chemical stability, good solvents for a wide range of organic, inorganic, and polymeric materials, negligible saturation vapor pressure, and suitable viscosity, are the focus of many recent scientific investigations[1−10] from industrial and academic communities. There is nearly no limit to the possibilities of combinations of the anionic and cationic structures. Consequently, due to their physical and chemical properties, which could be adjusted by a careful choice of the cation and the anion, ionic liquids are receiving increased attention in the elaboration of synthetic methods, in catalysis, separation processes, membrane technology, and other more specialized fields. Detailed information about the synthesis and the application of ionic liquids is available in the literature.[2]

Knowledge of ionic liquid properties will provide a fundamental insight into the particular behavior of this novel class of benign solvents, and the values of their properties are playing an important role in process design. Therefore, various research groups are involved in systematic measurements of the thermodynamic properties.[11−15]

From all applications, there is one of a practical interest concerning the aqueous solutions of ionic liquids.[16−20] Namely, ionic liquids tend in some cases to be too viscous to be useful as a reaction medium. However, their mixture with water shows reduced viscosity without jeopardizing their advantages as solvents. In other cases, extensive efforts have been orientated to remove water from ionic liquids for some specific reactions.[2] Hence, the thermodynamic information about IL−H_2O systems is important.

This paper presents a part of our ongoing systematic measurements (η, VLE, H^E) concerning the thermodynamics of aqueous systems containing ionic liquids. The influence of anion variation of cholin-based ionic liquids in the thermodynamic properties is also investigated.

In particular, these data are necessary for possible applications in absorption heat pump systems and might suggest a basis for evaluation of the affinity between an IL and water.

Materials and Purities

The ionic compounds used in this study, choline glycolate, choline lactate, and choline methanesulfonate, were prepared by mixing accurately measured equimolar amounts of the respective acid and base in aqueous solution with stirring followed by removal of the water under reduced pressure at elevated temperatures using a rotary evaporator. The materials thus obtained were further dried in a vacuum at ca. 70 °C for 60 h. The following commercially available materials were used: choline hydrogen carbonate (Aldrich, 75 % aqueous solution); glycolic acid (Aldrich, high purity, 70 % aqueous solution); lactic acid (Aldrich, 85 % aqueous solution); methanesulfonic acid (Fluka, puriss., ≥ 99.0 %). Methanesulfonic acid was diluted prior to use to give a ca. 70 % aqueous solution. The aqueous choline hydrogen carbonate, glycolic acid, lactic acid, and methanesulfonic acid solutions were assayed by standard titration methods. The ionic compounds that were found contain < 500 ppm chloride and bromide by ion chromatography using a Metrohm modular setup (709 IC pump, 732 IC detector, 733 IC separation center, 753 suppressor module, 762 IC interface, 812 valve unit). The water content of the ionic

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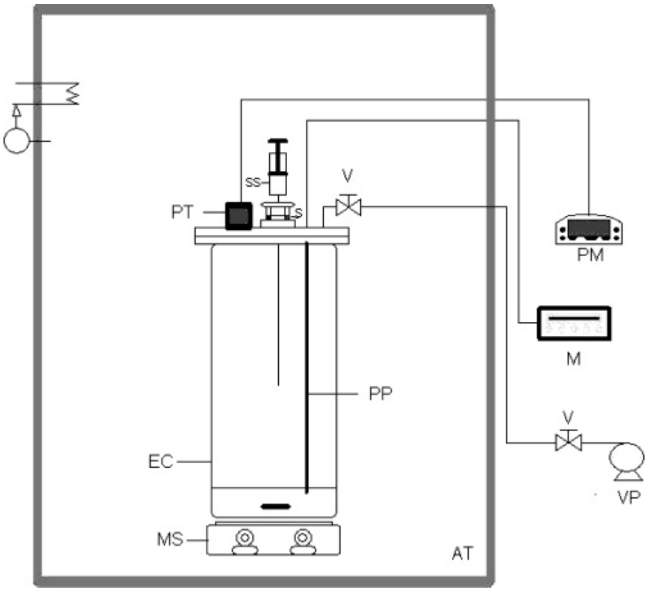


Figure 1. Scheme of the static apparatus for the measurement of VLE data: AT, air thermostat; EC, equilibrium cell; PP, platinum resistance thermometer probe; PT, pressure transducer; M, multimeter; MS, magnetic stirrer; S, septum; V, valve; SS, syringe sample; PM, pressure measurement; VP, vacuum pump.

compounds was determined by Karl Fischer titration using a Metrohm 795 KFT Titrino apparatus before each series of measurements and taken into account for the calculation of the composition of the respective binary mixtures.

Choline Glycolate (2-Hydroxyethyl-trimethylammonium 2-hydroxyethanoate) $[(CH_3)_3N^+(CH_2)_2OH][CH_2(OH)COO^-]$. This material was prepared by adding dropwise an aqueous solution (70.2 %) of glycolic acid (606.67 g, 5.60 mol) to an aqueous solution (74.8 %) of choline hydrogen carbonate (1236.72 g, 5.60 mol). It was obtained as a colorless crystalline solid.

Choline Lactate (2-Hydroxyethyl-trimethylammonium 2-hydroxypropanoate) $[(CH_3)_3N^+(CH_2)_2OH][CH_3CH(OH)COO^-]$. This material was prepared by adding dropwise an aqueous solution (83.6 %) of lactic acid (560.31 g, 5.20 mol) to an aqueous solution (74.8 %) of choline hydrogen carbonate (1148.38 g, 5.20 mol). It was obtained as a highly viscous, yellowish oil.

Choline Methanesulfonate (2-Hydroxyethyl-trimethylammonium methanesulfonate) $[(CH_3)_3N^+(CH_2)_2OH][CH_3SO_2O^-]$. This material was prepared by adding dropwise an aqueous solution (71.3 %) of methansulfonic acid (687.47 g, 5.10 mol) to an aqueous solution (74.8 %) of choline hydrogen carbonate (1126.30 g, 5.10 mol). It was obtained as a colorless crystalline solid.

Apparatus and Procedure

The viscosity of the mixtures was determined using a viscosimeter DV-E Brookfield with an adaptor for small samples. The contact time to the atmosphere during mesurement has been kept so short that evaporation or absorption of water can be neglected. Taking into account the accuracies of temperature (< 0.5 K) and mole fraction (< 0.001), the accuracy of the viscosity measurement has been estimated to be 1 %.

The apparatus for the vapor−liquid measurements (Figure 1) primarily consists of a glass equilibrium cell (EC) with an internal volume of 2.41, which is placed in an air thermostat (AT). The apparatus can be applied for $p-t$ measurements at temperatures between (293 and 340) K and at pressures up to 1.6 bar.

The temperature in the cell is measured using a platinum resistance thermometer (Pt100 sensor) with an accuracy of ± 0.05 K. The pressure measurements are performed using a WIKA pressure transducer (S-10/A-RB-1) with a maximum pressure of 1.6 bar. The accuracy guaranteed by the provider is 0.5 % of the maximum pressure. The real accuracy which has been verified measuring the vapor pressure of pure water can be estimated to be < 0.1 % of the maximum pressure (i.e., < 1.6 mbar). The reproducibility is approximately 0.01 % of the maximum pressure.

The ionic liquids were purified by subjecting the liquid to a pressure of $< 10^{-2}$ mbar for approximately 60 min. Thus, volatile chemicals and water were removed.

The ionic liquid−water mixtures were prepared by weighing precise quantities of ionic liquids and water in glas flasks using a microbalance. The precision of the mole fraction was estimated to be $\pm\, 10^{-4}$. After mixing both components, the sample was degassed for 30 min in an ultrasonic bath at room temperature and ambient pressure. The sample solution with a volume of 30 cm^3 was injected into the equilibrium cell, which was evacuated ($< 10^{-2}$ mbar) and kept in the air thermostat. Then the sample is heated and stirred well with a magnetic stirrer to prevent superheating. At thermal equilibrium, the pressure and the temperature of the sample solution were measured.

The liquid-phase composition is obtained by solving the mass and volume balance equation also accounting for the vapor−liquid equilibrium.

The H^E measurements have been performed by using a differential scanning calorimeter (model micro-DSC VII, Setaram), which allows the choice of the isothermal calorimetry mode. The calorimetric sensitivity is ± 0.4 μW.

The calorimetrical block is made up of a double aluminum chamber, at the heart of which two cylindrical hollows have been machined to take the experimental vessels: the "measurement" vessel takes the sample, and the "reference" vessel contains an inert test piece to compensate for the thermal effect due to heating. The block's temperature control is carried out using two stages of Peltier-effect thermoelements.

Two closed, mixing vessels have been used for the evaluation of mixture heat between the investigated liquids. We used, instead of a pure IL, an already diluted aqueous IL, which has been placed on the bottom of the cell, whose lower volume is 400l μL. The upper part of the cell (μL) was designated for pure water. In this way, the difficulty associated with the high viscosity of pure ILs could be avoided.

Results and Discussion

The structures of the cations and the anions of the investigated ionic liquids are shown in Table 1.

The viscosities for the water + ionic liquid systems (Table 2) are plotted against the molar fraction x_1 of water and are shown in Figure 2.

As Figure 2 shows in the case of choline lactate, the addition of water reduces notably the viscosity, and the results suggest that water is accommodated in the ionic liquid structure in the salt region ($x_1 < 0.5$) possibly by forming hydrogen bonds with both the anion and the cation. The dramatic decrease of the viscosity indicates that the presence of water molecules reduces the electrostatic attractions between the ions. Thus, the overall cohesive energy of the system and hence its viscosity are lowered, too. A more elaborate study regarding the interactions between water and ionic liquid was presented in the literature.[4,8]

Choline glycolate and choline methanesulfonate are solids as pure compounds. Beginning at a water mole fraction of

Table 1. Investigated Ionic Liquids in This Work

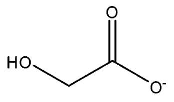
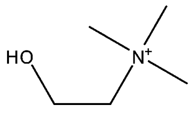
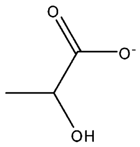
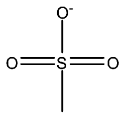
Name	Structure Cation	 Anion
Choline glycolate		
Choline lactate		
Choline methanesulfonate		

Table 2. Viscosity η of the Investigated Mixtures at T = 293.15 K

water (1) + choline glycolate (2)		water (1) + choline lactate (2)	
x_1	η/cP	x_1	η/cP
0.366	660	0.0272	5850
0.536	209	0.382	940
0.718	53.2	0.546	336
0.813	19.9	0.731	75
0.871	9.2	0.878	12.5
0.937	3.3	0.915	6.5
		0.941	3.9

approximately 0.33 in the case of choline glycolate and 0.66 in the case of choline methanesulfonate, respectively, both systems are in the liquid phase.

The experimental isothermal vapor−liquid equilibria (VLE) data for the binary systems measured at (303.15, 313.15, and 323.15) K are listed in Tables 3 to 5. The pressure data are mean values generated by fitting and interpolating the results of about 10 single measurements at various temperatures near the nominal temperature. As pointed out before, the maximum error of the pressure data has been estimated to be lower than 2 mbar.

The experimental VLE data for the binary systems were correlated with the excess Gibbs energy models NRTL[21] and UNIQUAC.[22] The parameters were fitted using the Simplex−Nelder−Mead method. Several authors have used these models to describe their measurements of vapor−liquid equilibria with ionic liquids.[11−13]

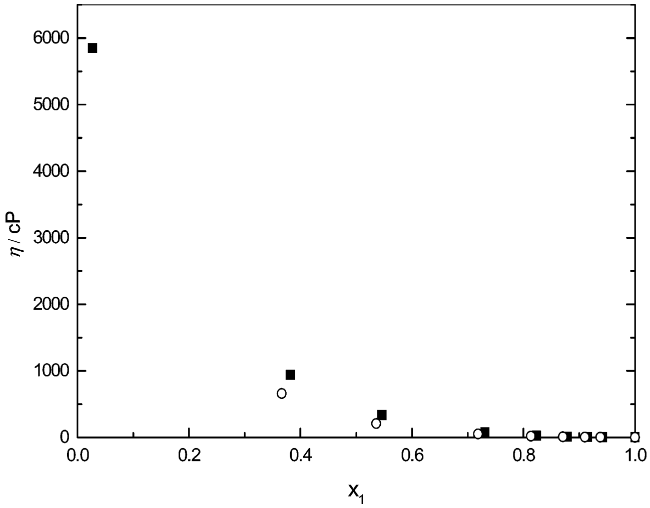


Figure 2. Viscosity of water−IL mixtures vs mole fraction x_1 of water: ■, water−choline lactate mixtures at T = 293.15 K; ○, water−choline glycolate mixtures at T = 293.15 K.

Table 3. Vapor−Liquid Equilibria for Water (1) with Choline Glycolate, Choline Lactate, and Choline Methanesulfonate at 303.15 K

water (1) + choline glycolate (2)		water (1) + choline lactate (2)		water (1) + choline methanesulfonate (2)	
x_1	p/mbar	x_1	p/mbar	x_1	p/mbar
0.3379	1.2	0.1978	2.2	0.6603	9.3
0.3987	1.6	0.2776	3.7	0.6788	10.2
0.4460	2.1	0.3449	4.1	0.6957	11.0
0.5026	2.4	0.4196	5.3	0.7092	12.0
0.5571	3.6	0.4818	6.5	0.7247	13.1
0.6300	4.9	0.5720	9.6	0.7653	15.5
0.6951	6.6	0.6591	13.5	0.7969	18.2
0.7580	9.8	0.7309	17.4	0.8303	21.5
0.8286	15.2	0.8135	23.4	0.8727	26.9
0.9216	29.1	0.9175	34.4	0.9374	36.1
0.9669	38.1	0.9698	40.6	0.9716	40.8
1.0000	42.4	1.0000	42.4	1.0000	42.4

Table 4. Vapor−Liquid Equilibria for Water (1) with Choline Glycolate, Choline Lactate, and Choline Methanesulfonate at 313.15 K

water (1) + choline glycolate (2)		water (1) + choline lactate (2)		water (1) + choline methanesulfonate (2)	
x_1	p/mbar	x_1	p/mbar	x_1	p/mbar
0.3369	2.1	0.1974	3.0	0.6590	18.5
0.3988	2.9	0.2772	4.4	0.6782	20.0
0.4458	3.7	0.3439	6.7	0.6950	21.6
0.5024	4.7	0.4188	9.0	0.7087	22.7
0.5569	5.9	0.4807	11.4	0.7242	25.0
0.6300	8.9	0.5710	15.8	0.7650	29.7
0.6951	12.6	0.6583	21.8	0.7967	34.2
0.7580	18.5	0.7301	28.5	0.8301	40.1
0.8286	28.1	0.8130	39.4	0.8727	48.6
0.9216	52.1	0.9174	59.3	0.9374	63.8
0.9669	67.0	0.9698	70.0	0.9716	70.8
1.0000	73.8	1.0000	73.8	1.0000	73.8

Table 5. Vapor−Liquid Equilibria for Water (1) with Choline Glycolate, Choline Lactate, and Choline Methanesulfonate at 323.15 K

water (1) + choline glycolate (2)		water (1) + choline lactate (2)		water (1) + choline methanesulfonate (2)	
x_1	p/mbar	x_1	p/mbar	x_1	p/mbar
0.3272	4.5	0.1973	4.6	0.6561	30.0
0.3917	5.3	0.2771	7.4	0.6755	33.3
0.4413	6.9	0.3442	10.0	0.6932	35.6
0.5000	9.1	0.4185	13.5	0.7074	38.1
0.5556	11.6	0.4806	17.2	0.7232	40.4
0.6293	16.8	0.5709	24.3	0.7644	49.2
0.6947	23.5	0.6582	33.7	0.7964	57.2
0.6947	23.5	0.6582	33.7	0.7964	57.2
0.6947	23.5	0.6582	33.7	0.7964	57.2
0.8286	50.2	0.8129	63.3	0.8725	81.3
0.9216	89.2	0.9173	97.5	0.9374	106.4
0.9669	112.8	0.9697	116.7	0.9716	117.7
1.0000	123.4	1.0000	123.4	1.0000	123.4

Figures 3 to 5 show the VLE results ($P-x$ diagrams) of the three binary investigated systems together with the correlation results of the NRTL model. At the moment, no vapor pressure data for the ionic liquids are available. Consequently, for the correlation of the experimental $P-x$ data, a small vapor pressure of 0.1 mbar was assumed for all ionic liquids.

Concerning the UNIQUAC model, the relative van der Waals properties r_i and q_i for the ionic liquids were estimated according to Bondi.[23] All the values of r_i, q_i, and υ_i used for the correlation are listed in Table 6.

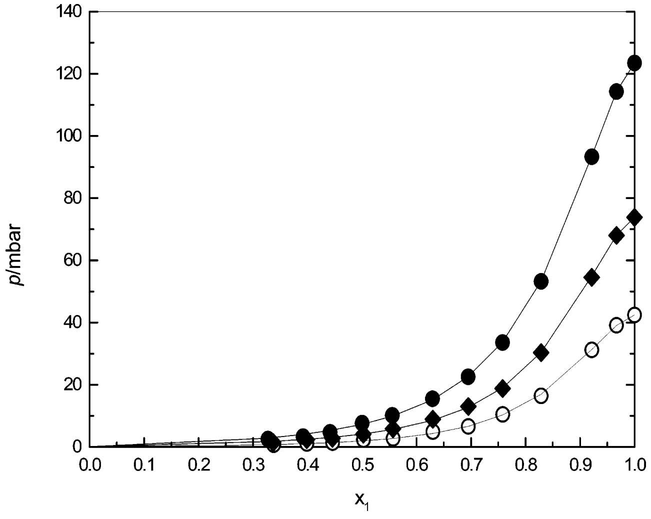


Figure 3. Vapor pressure vs mole fraction x_1 of water for water + choline glycolate at three temperatures: ○, 303.15 K; ◆, 313.15 K; ●, 323.15 K; —, calculated data, NRTL.

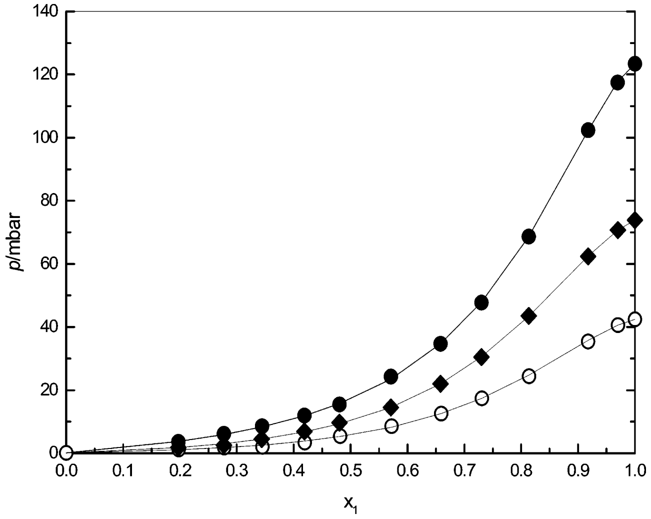


Figure 4. Vapor pressure vs mole fraction x_1 of water for water + choline lactate at three temperatures: ○, 303.15 K; ◆, 313.15 K; ●, 323.15 K; —, calculated data, NRTL.

The following objective function F was used for fitting the required UNIQUAC parameters

$$F = \sum_{i=1}^{n} \left(\frac{p_{\text{calcd}} - p_{\text{exptl}}}{p_{\text{exptl}}} \right)^2 \qquad (1)$$

where n is the number of data points. The fitted binary NRTL and UNIQUAC parameters are summarized in Table 7 together with the root-mean-square deviations (rmsd's). The values of the rmsd have been calculated with the following equation

$$\text{rmsd} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (p_{i\text{calcd}} - p_{i\text{exptl}})^2} \qquad (2)$$

The calculated temperature dependence of the water activity coefficient ln γ_1 indicates that ln γ_1 increases with increasing temperature. However, the temperature dependence of ln γ_1 is not significant enough to derive the excess enthalpies H^E and to compare them with our H^E measurements.

The VLE correlations show a very good agreement with the experimental findings as can be seen in Figures 3 to 5 and in the values of rmsd's.

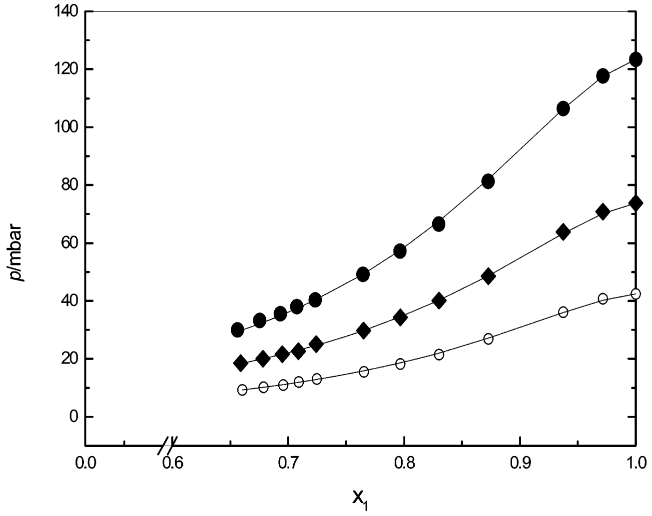


Figure 5. Vapor pressure vs mole fraction x_1 of water for water + choline methanesulfonate at three temperatures: ○, 303.15 K; ◆, 313.15 K; ●, 323.15 K; — , calculated data, NRTL.

Table 6. Relative van der Waals Parameters for UNIQUAC

component	r_i	q_i	v_i
choline glycolate	13.5	13.56	92.11
choline lactate	13.49	13.44	94.29
choline methanesulfonate	13.5	12.87	87.51
water	0.92	1.4	18.07

Table 7. Binary NRTL and UNIQUAC Parameters Fitted to Experimental VLE Data

NRTL

system	T / K	Δg_{12} / cal·mol^{-1}	Δg_{21} / cal·mol^{-1}	a_{ij}	rmsd
water (1) + choline glycolate (2)	303.15	46.7	−1835.1	0.55	0.11
	313.15	−96.5	−1822.6	0.55	0.14
	323.15	9.3	−1815.6	0.55	0.40
water (1) + choline lactate (2)	303.15	894.8	−1372.4	0.55	0.30
	313.15	1088.2	−1483.0	0.55	0.37
	323.15	1130.1	−1589.6	0.55	0.23
water (1) + choline methanesulfonate (2)	303.15	−311.5	−1452.7	0.55	0.27
	313.15	−75.1	−1372.7	0.60	0.28
	323.15	1408.8	−2192.2	0.33	0.55

UNIQUAC

system	T / K	Δu_{12} / cal·mol^{-1}	Δu_{21} / cal·mol^{-1}	a_{ij}	rmsd
water (1) + choline glycolate (2)	303.15	46.2	−111.7		0.18
	313.15	40.7	−103.2		0.11
	323.15	47.7	−104.0		0.19
water (1) + choline lactate (2)	303.15	65.1	−76.7		0.28
	313.15	62.1	−77.6		0.15
	323.15	69.5	−89.8		0.13
water (1) + choline methanesulfonate (2)	303.15	55.9	−93.7		0.25
	313.15	50.7	−82.4		0.31
	323.15	−38.6	0.3		0.18

Additionally, mixing enthalpies were measured for the systems water (1) + choline glycolate (2) and water (1) + choline lactate (2). The results are presented in Tables 8 to 10.

Table 8. H^E Data for Water (1) with Choline Glycolate and Choline Lactate (2) at 303.15 K

water (1) + choline glycolate (2)		water (1) + choline lactate (2)	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.3483	−3092	0.1585	−3923
0.4300	−3932	0.2269	−6323
0.4573	−4087	0.3051	−8527
0.5174	−4642	0.3528	−10059
0.6020	−5375	0.4853	−14022
0.6513	−5689	0.6710	−17243
0.7001	−6245	0.8719	−18290
0.7959	−6319	0.9078	−14847
0.8916	−5820	0.9751	−7845
0.9543	−4195	0.9878	−2529

Table 9. H^E Data for Water (1) with Choline Glycolate and Choline Lactate (2) at 313.15 K

water (1) + choline glycolate (2)		water (1) + choline lactate (2)	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.3400	−2018	0.1687	−3023
0.3792	−2268	0.2123	−4595
0.4264	−2438	0.3065	−6560
0.4739	−2574	0.3943	−8836
0.5268	−2954	0.5019	−10885
0.6185	−3247	0.6030	−12137
0.7391	−3534	0.7380	−13791
0.8041	−3718	0.8794	−14581
0.9032	−1500	0.9535	−10331
0.9330	−1002	0.9769	−6484
0.9748	−472		

Table 10. H^E Data for Water (1) with Choline Glycolate and Choline Lactate (2) at 323.15 K

water (1) + choline glycolate (2)		water (1) + choline lactate (2	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.3425	−993	0.1600	−1541
0.3674	−1151	0.2662	−2716
0.4192	−1294	0.3310	−3583
0.5692	−1721	0.5059	−6469
0.6811	−2005	0.6257	−8997
0.7740	−2207	0.7785	−10864
0.8726	2377	−0.8805	8764
0.9543	−1992	0.9555	−4596
0.9816	−1151	0.9884	−1001

Table 11. Parameters of the Redlich Kister Equation

T	B^0	B^1	B^2	B^3	B^4	RD
			water (1) + choline glycolate (2)			
313.15	−11373.7	11793.8	−121124	−4405.8	16150.5	7.39
			water(1) + choline lactate (2)			
303.15	−53811.5	39414.3	−58142.4	99269	−29083.5	7.28
323.15	−27288.7	45228.8	−31516.6			6.4

Some of the H^E data have been fitted to a Redlich Kister-type equation:

$$H^E = x_1(1 - x_1)\sum_{k=0}^{m} B_k(1 - 2x_1)^k \qquad (3)$$

The fitting parameters are given in Table 11 together with the mean relative deviations, calculated according to

$$\mathrm{RD} = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{H^{E,\mathrm{exptl}} - H^{E,\mathrm{calcd}}}{H^{E,\mathrm{exptl}}}\right)100\ \% \qquad (4)$$

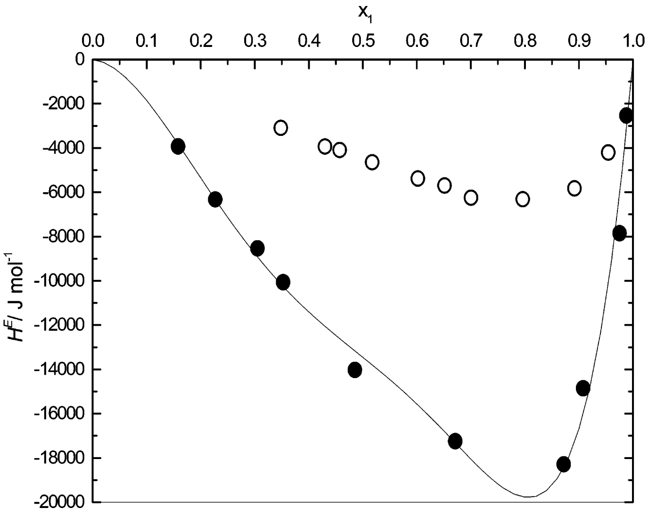


Figure 6. Excess molar enthalpy H^E plotted against the mole fraction of water at 303.15 K for the binary systems: ○, water (1) + choline glycolate (2); ●, water (1) + choline lactate (2); —, calculated data with the Redlich Kister equation.

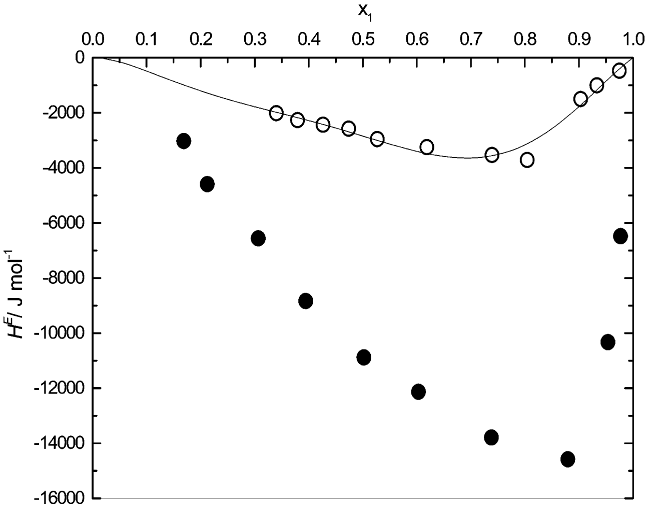


Figure 7. Excess molar enthalpy H^E plotted against the mole fraction of water at 313.15 K for the binary systems: ○, water (1) + choline glycolate (2); ●, water (1) + choline lactate (2); —, calculated data with the Redlich Kister equation.

Figures 6 to 8 show the fitted curves as well as H^E experimental values against the water mole fraction x_1 of the binary systems water + choline glycolate and water + choline lactate at T = (303.15, 313.15, and 323.15) K. As can be seen, the excess molar enthalpy is a negative function of composition over the entire composition range. For both systems, the excess molar enthalpy decreases with the temperature and exhibits a minimum at a water mole fraction of approximately 0.8 in the case of the water + choline glycolate system and of 0.85 for the water + choline lactate system.

Conclusion

In this work, η, VLE, and H^E data for three systems consisting of water with ionic liquids were measured at three temperatures. The experimental VLE data were correlated with NRTL and UNIQUAC models, and the results show that common g^E models can be successfully applied also for aqueous systems with ionic liquids.

Thermodynamic properties, in particular, VLE data, are required also for development of reliable predictive models for systems with ionic liquids. This will be desirable for the selection of the most suitable ionic liquid for extractive

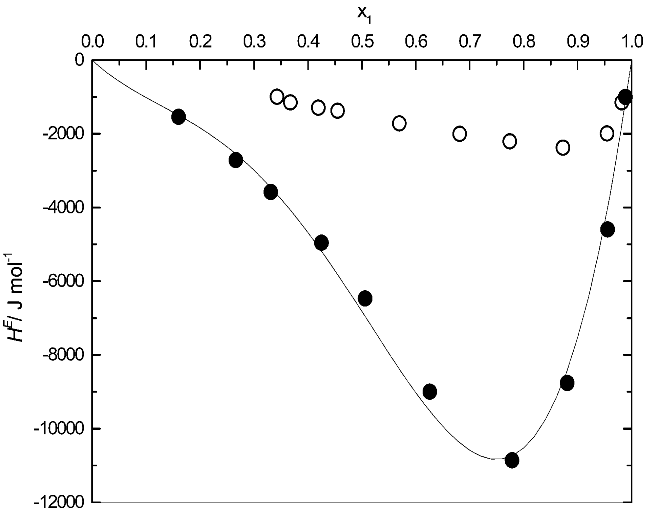


Figure 8. Excess molar enthalpy H^E plotted against the mole fraction of water at 323.15 K for the binary systems: ○, water (1) with choline glycolate (2); ●, water (1) with cholinelactate (2); —, calculated data with the Redlich Kister equation.

distillation, extraction, and for other applications in industrial chemistry.

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