Fluid Phase Equilibria 338 (2013) 135–140

Contents lists available at SciVerse ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Prediction of different thermodynamic properties for systems of alcohols and sulfate-based anion Ionic Liquids using modified UNIFAC

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ARTICLE INFO

Article history:
Received 29 May 2012
Received in revised form
15 September 2012
Accepted 1 November 2012
Available online 9 November 2012

Keywords:
Ionic Liquids
Activity coefficients at infinite dilution
Vapor–liquid equilibria
Excess enthalpies
Modified UNIFAC (Dortmund)

ABSTRACT

Activity coefficients at infinite dilution in the temperature range between 303.15 K and 353.15 K, vapor–liquid equilibria at 353.15 K and excess enthalpies at 353.15 K of binary systems containing the Ionic Liquids 1-ethyl-3-methyl-imidazolium ethylsulfate $[EMIM]^+[EtSO_4]^-$, 1-ethyl-3-methyl-imidazolium methylsulfate $[EMIM]^+[MeSO_4]^-$ and 1-ethyl-3-methyl-imidazolium hydrogensulfate $[EMIM]^+[HSO_4]^-$ have been measured. The obtained experimental data are used together with literature data to fit modified UNIFAC interaction parameters between the sulfate anion and the main groups OH and CH_3OH. The predictions are compared with the experimental values. Additionally an overview about the current status of the modified UNIFAC parameter matrix for Ionic Liquids is given.

1. Introduction

Over the last couple of years there has been an increasing interest in Ionic Liquids. Because of their specific properties, e.g. negligible vapor pressure, high solubility of organic and inorganic compounds, thermal stability, etc. Ionic Liquids are discussed as alternative solvents in industrial processes, e.g. separation processes. Because of the wide range of possible anions, cations, alkyl rests and substituents the properties of the Ionic Liquids can be adjusted for a specific problem. Therefore Ionic Liquids are also called "Designer Solvents". For the selection of the best suited Ionic Liquid for a separation process the reliable knowledge of the phase equilibrium behavior is required. Because of the wide range of possible cations, anions and substituents a reliable predictive model would be desirable for the selection of the most suitable Ionic Liquid.

This was the reason to extend the modified UNIFAC model to systems with Ionic Liquids. Modified UNIFAC (Dortmund) is a group contribution model [1] for which a limited number of experimental data are needed to fit the required group interaction parameters. Even though there are some authors like Safarov et al. [2] or Sumartschenkowa et al. [3], who published thermodynamic data, the database for Ionic Liquids is still limited. To extend this database systematic measurements of activity coefficients at infinite dilution (γ^∞), vapor–liquid equilibria (VLE) and excess enthalpies (H^E) are carried out. This manuscript gives an overview about the experimental methods, comparison between experimental results and prediction using modified UNIFAC and a presentation of the current status of the modified UNIFAC parameter matrix for Ionic Liquids.

2. Experimental

2.1. Materials and purities

The investigated Ionic Liquids $[EMIM]^+[EtSO_4]^-$, $[EMIM]^+[MeSO_4]^-$ and $[EMIM]^+[HSO_4]^-$ were obtained from IOLITEC. To remove the last traces of volatile impurities, the Ionic Liquids were treated by vacuum evaporation before use. Before each dilutor experiment the purity was checked by taking a gas phase sample before the solutes were added. Normally there were no impurities or just very low (lower than the amounts of infinite diluted components) amounts of known components. The water contents of the Ionic Liquids were checked by Karl Fischer Titration (<90 ppm). $[EMIM]^+[EtSO_4]^-$ is able to react with water, but in a test this behavior was only observed at higher amounts of water and temperatures higher than 343.15 K. The investigated alcohols methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol were obtained from VWR. All components and their suppliers are listed in Table 1. For the dilutor experiments the solutes are used without further purification since impurities are separated in the column of the gas chromatograph and the

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http://dx.doi.org/10.1016/j.fluid.2012.11.003

Table 1
Supplier and purity of the chemicals used.

Component	Supplier	Purity (% GC)
Methanol	VWR	99.5
Ethanol	VWR	99.9
1-Propanol	VWR	99.9
2-Propanol	VWR	99.8
1-Butanol	VWR	99.9
2-Butanol	VWR	99.8
$[EMIM]^+[EtSO_4]^-$	IOLITEC	
$[EMIM]^+[MeSO_4]^-$	IOLITEC	
$[EMIM]^+[HSO_4]^-$	IOLITEC	

negligible amount in the measurement cell have no influence on the quality of the results [4].

The purities of ethanol and 1-propanol were checked by gas chromatography (99.9%). The water content was determined by Karl Fischer titration (<90 ppm). Additionally for the VLE measurements all components were degassed at low pressure.

2.2. Activity coefficients at infinite dilution

For the measurement of γ^∞ the dilutor technique was used. A detailed description of the equipment and procedure is given by Gruber et al. [5]. Because of their negligible vapor pressure the Ionic Liquids do not evaporate from the measurement cell, so that no additional saturation cell for the gas stream was required. The results of γ^∞ for the solutes methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol measured in the Ionic Liquids $[EMIM]^+[EtSO_4]^-$, $[EMIM]^+[MeSO_4]^-$ and $[EMIM]^+[HSO_4]^-$ are given in Tables 2–4. The relative error using this method is approximately ±2.5%.

2.3. Vapor–liquid equilibria

A computer-driven static apparatus, as described before [6], was used to measure the binary vapor–liquid equilibria. The Px-data for the binary systems ethanol (1)–$[EMIM]^+[EtSO_4]^-$ (2) and 1-propanol (1)–$[EMIM]^+[EtSO_4]^-$ (2) at 353.15 K are listed in Table 5. The repeatability and hysteresis of the pressure sensor are approximately 0.005% of the maximum pressure. The temperature was measured by a Hart Scientific 1506 thermometer using a Pt100 resistance sensor with a resolution of ±1 mK.

Table 2
Experimental activity coefficients at infinite dilution of different alcohols in $[EMIM]^+[EtSO_4]^-$.

Solute	T (K)	γ_i^∞	Solute	T (K)	γ_i^∞
Methanol	303.15	0.537	2-Propanol	303.15	1.477
	313.15	0.419		313.15	1.307
	323.15	0.406		323.15	1.247
	333.15	0.410		333.15	1.043
	343.15	0.389		343.15	1.008
	353.15	0.339		353.15	0.966
Ethanol	303.15	0.866	1-Butanol	313.15	1.934
	313.15	0.783		323.15	1.651
	323.15	0.703		333.15	1.386
	333.15	0.600		343.15	1.367
	343.15	0.554		353.15	1.187
	353.15	0.534	2-Butanol	303.15	2.065
1-Propanol	303.15	1.306		313.15	1.829
	313.15	1.204		323.15	1.686
	323.15	1.029		333.15	1.565
	333.15	0.914		343.15	1.618
	343.15	0.855		353.15	1.394
	353.15	0.803			

Uncertainty of the activity coefficients at infinite dilution approx. ±2.5%.

Table 3
Experimental activity coefficients at infinite dilution of different alcohols in $[EMIM]^+[MeSO_4]^-$.

Solute	T (K)	γ_i^∞	Solute	T (K)	γ_i^∞
Methanol	323.15	0.257	2-Propanol	323.15	1.334
	333.15	0.203		333.15	1.172
	343.15	0.178		343.15	1.006
	353.15	0.105		353.15	0.840
Ethanol	323.15	0.449	1-Butanol	323.15	2.617
	333.15	0.398		333.15	2.403
	343.15	0.349		343.15	2.046
	353.15	0.303		353.15	1.744
1-Propanol	323.15	1.053	2-Butanol	323.15	4.017
	333.15	0.975		333.15	3.109
	343.15	0.839		343.15	2.576
	353.15	0.705		353.15	2.243

Uncertainty of the activity coefficients at infinite dilution approx. ±2.5%.

2.4. Excess enthalpies

Using the Gibbs–Helmholtz equation partial molar excess enthalpy data can be used to describe the temperature dependence of the acitvity coefficients. An isothermal flow calorimeter from Hart Scientific (model 7501) was used for the measurement of the excess enthalpies. In the literature [7] a detailled description of the apparatus and the measurement procedure can be found. The experimental results for the excess enthalpies of the binary systems ethanol (1)–$[EMIM]^+[EtSO_4]^-$ (2) and ethanol (1)–$[EMIM]^+[MeSO_4]^-$ (2) are given in Table 6. The uncertainty of the experimental excess enthalpies is approximately ±1%.

3. Modified UNIFAC

Up to now for the cations imidazolium $[RMIM]^+$, pyridinium $[RPY]^+$ and pyrrolidinium $[RMPYR]^+$ and the anions bis(trifluoromethylsulfonyl)imide $[BTI]^-$, trifluoromethanesulfonate $[OTF]^-$, tetrafluoroborate $[BF_4]^-$, hexafluorophosphate $[PF_6]^-$ and sulfate $[RSO_4]^-$ parameters are available for modified UNIFAC (Dortmund) (see Fig. 1). The group interaction parameters were fitted simultaneously to binary experimental data (VLE, γ^∞, H^E, etc.) stored in the Dortmund Data Bank [8] and the systematically measured data using the Simplex–Nelder–Mead method [9]. The database was used for revision and extension of the existing parameters [10,11]. Fig. 2 shows the present status of the modified UNIFAC parameter matrix for Ionic Liquids. The parameters used for the following discussions are given in Table 7. In Table 8 the required van der Waals-values R_k and Q_k are listed. The complete revised parameter matrix for Ionic Liquids will be available soon [12].

Table 4
Experimental activity coefficients at infinite dilution of different alcohols in $[EMIM]^+[HSO_4]^-$.

Solute	T (K)	γ_i^∞	Solute	T (K)	γ_i^∞
Methanol	323.15	0.087	2-Propanol	323.15	0.577
	333.15	0.078		333.15	0.356
	343.15	0.058		343.15	0.278
	353.15	0.041		353.15	0.223
Ethanol	313.15	0.426	1-Butanol	323.15	0.758
	323.15	0.269		333.15	0.620
	333.15	0.177		343.15	0.430
	343.15	0.130	2-Butanol	323.15	1.219
	353.15	0.116		333.15	0.760
1-Propanol	323.15	0.431		343.15	0.566
	333.15	0.338		353.15	0.452
	343.15	0.233			
	353.15	0.196			

Uncertainty of the activity coefficients at infinite dilution approx. ±2.5%