Fluid Phase Equilibria 302 (2011) 220–225

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Prediction of phase equilibria and excess properties for systems with ionic liquids using modified UNIFAC: Typical results and present status of the modified UNIFAC matrix for ionic liquids

Silke Nebig, Jürgen Gmehling*

Carl von Ossietzky Universität Oldenburg, Technische Chemie, D-26111 Oldenburg, Federal Republic of Germany

ARTICLE INFO

Article history:
Received 16 June 2010
Received in revised form 7 September 2010
Accepted 10 September 2010
Available online 17 September 2010

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

ABSTRACT

Vapor–liquid equilibria at 363.15 K, and excess enthalpies in the temperature range 363.15–413.15 K of binary systems containing the ionic liquids 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[BMPYR]^+[BTI]^-$, 1-hexyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[HMPYR]^+[BTI]^-$, and 1-octyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[OMPYR]^+[BTI]^-$, have been measured. The experimental data were used for fitting the group interaction parameters between the pyrrolidinium cation and the main groups ACH and $ACCH_2$. The experimental results are compared with the predictions of modified UNIFAC (Dortmund). Furthermore the current state of modified UNIFAC matrix for ionic liquids, typical results, and the application for process development will be presented.

1. Introduction

Because of their interesting properties, e.g. negligible vapor pressure, good solvent for organic and inorganic compounds, etc. ionic liquids are discussed as alternative solvents in chemical engineering, e.g. as solvents for separation processes such as extractive distillation, extraction, absorption and a large number of other applications. A prerequisite for the selection of the best suited ionic liquid for separation processes is a reliable knowledge of the phase equilibrium behavior. Because of the multitude of possible anions, cations, alkyl rests and substituents a predictive model would be most desirable.

This has motivated the further development of modified UNIFAC for systems with ionic liquids. For the extension of the limited database systematic measurements are carried out. In this paper besides new experimental data the current status of the parameter matrix for ionic liquids is presented.

2. Materials and purities

For the *VLE* measurement all components were degassed and distilled at low pressure [1]. For the measurements of the excess enthalpies h^E the compounds were used without degassing. Benzene and toluene were supplied by Roth and their purities, checked by gas chromatography, were 99.9%. The water concentration (always < 100 ppm) was measured by Karl Fischer titration. The investigated ionic liquids $[BMPYR]^+[BTI]^-$, $[HMPYR]^+[BTI]^-$ and $[OMPYR]^+[BTI]^-$ were obtained from Merck GmbH. To remove the last traces of volatile compounds from the ionic liquids they were treated by vacuum evaporation before use.

3. Experimental

3.1. Vapor–liquid equilibria

For the determination of the binary vapor–liquid equilibria a computer-driven static apparatus was used, described in Refs. [2,3]. In Table 1 the Px-data for the binary systems benzene (1)–$[HMPYR]^+[BTI]^-$ (2), toluene (1)–$[HMPYR]^+[BTI]^-$ (2), benzene (1)–$[OMPYR]^+[BTI]^-$ (2) and toluene (1)–$[OMPYR]^+[BTI]^-$ (2) measured at 363.15 K are given. The maximum pressure of the used pressure sensor (Keller Druckmesstechnik, type PA-25HTC/8585) is 2000 kPa. The reproducibility of the pressure measurement is 0.005% of the maximum pressure, this results in a maximum pressure error of 0.1 kPa. The temperature is measured using a Pt100 resistance thermometer (Model 1506, Hart Scientific) within ±1 mK resolution.

---

* Corresponding author. Tel.: +49 441 798 3831; fax: +49 441 798 3330.
E-mail address: gmehling@tech.chem.uni-oldenburg.de (J. Gmehling).
URL: http://www.uni-oldenburg.de/tchemie (J. Gmehling).

0378-3812/$ – see front matter
doi:10.1016/j.fluid.2010.09.021

Table 1
Vapor–liquid equilibria for different systems containing ionic liquids.

x_1	P [kPa]	x_1	P [kPa]	x_1	P [kPa]
Benzene (1)–$[\text{HMPYR}]^+[\text{BTI}]^-$ (2)		0.0587	3.502	0.4226	50.88
363.15 K		0.0677	4.020	0.5634	76.17
0.0167	1.762	0.0764	4.561	0.7272	111.1
0.0345	3.663	0.0852	5.087	0.8295	129.6
0.0487	5.155	0.1076	6.418	0.8842	134.7
0.0603	6.479	0.1477	8.881	Toluene (1)–$[\text{OMPYR}]^+[\text{BTI}]^-$ (2)	
0.0729	7.848	0.2311	14.46	363.15 K	
0.0882	9.602	0.3455	22.67	0.0162	0.7956
0.1043	11.53	0.4901	34.06	0.0288	1.435
0.1185	13.20	0.6664	47.74	0.0444	2.212
0.1418	15.98	Benzene (1)–$[\text{OMPYR}]^+[\text{BTI}]^-$ (2)		0.0559	2.813
0.1956	22.62	363.15 K		0.0708	3.571
0.2791	33.97	0.0191	1.761	0.0850	4.301
0.3931	51.45	0.0366	3.375	0.0987	5.008
0.5350	77.30	0.0523	4.933	0.1119	5.738
0.7056	113.35	0.0707	6.665	0.1370	7.123
0.8148	132.29	0.0846	8.046	0.1887	10.05
Toluene (1)–$[\text{HMPYR}]^+[\text{BTI}]^-$ (2)		0.1023	9.863	0.2719	15.09
363.15 K		0.1205	11.73	0.3853	22.70
0.0112	0.6850	0.1367	13.42	0.5255	33.33
0.0223	1.332	0.1609	16.04	0.6944	46.52
0.0301	1.817	0.2172	22.58	0.8046	52.65
0.0455	2.727	0.3053	33.68		

Table 2
Excess enthalpies for different systems containing ionic liquids.

x_1	h^E [J mol^{-1}]	x_1	h^E [J mol^{-1}]	x_1	h^E [J mol^{-1}]
Benzene (1)–$[\text{BMPYR}]^+[\text{BTI}]^-$ (2)		0.3368	−568.01	0.7939	−796.81
363.15 K, 2239 kPa		0.4184	−670.90	0.8525	−588.61
0.0815	−129.36	0.4896	−702.13	0.9204	−307.28
0.1541	−260.09	0.5523	−694.68	0.9720	−103.00
0.2191	−356.17	0.6574	−641.24	Toluene (1)–$[\text{HMPYR}]^+[\text{BTI}]^-$ (2)	
0.2777	−460.08	0.7421	−516.54	413.15 K, 2377 kPa	
0.3308	−569.59	0.8119	−393.32	0.0759	−153.23
0.3792	−646.09	0.8962	−227.17	0.1443	−294.52
0.4639	−758.12	0.9628	−75.87	0.2063	−404.69
0.5357	−848.15	Benzene (1)–$[\text{HMPYR}]^+[\text{BTI}]^-$ (2)		0.2626	−507.24
0.7758	−732.76	393.15 K, 2342 kPa		0.3140	−605.66
0.8385	−524.85	0.0899	−176.71	0.3612	−689.56
0.9121	−293.06	0.1686	−362.91	0.4448	−789.21
0.9689	−97.094	0.2380	−504.88	0.5165	−832.49
Toluene (1)–$[\text{BMPYR}]^+[\text{BTI}]^-$ (2)		0.2998	−607.07	0.5787	−848.95
413.15 K, 2342 kPa		0.3550	−740.42	0.6812	−785.79
0.0687	−121.15	0.4047	−833.20	0.7622	−633.37
0.1315	−253.29	0.4906	−950.86	0.8278	−469.76
0.1892	−364.72	0.5622	−1053.9	0.9058	−268.96
0.2423	−431.73	0.6228	−1102.2	0.9665	−108.22
0.2914	−498.62	0.7198	−985.59		

3.2. *Excess enthalpies*

Excess enthalpy data can be used to describe the temperature dependence of the activity coefficients using the Gibbs–Helmholtz relation. For the measurement of the excess enthalpies an isothermal flow calorimeter (model 7501) from Hart Scientific was used. A detailed description of the equipment and the measurement procedure can be found in the literature [4]. The accuracy of the heats of mixing measurements is estimated to be better than ±1%. The experimental excess enthalpy data for the binary systems consisting of the ionic liquids $[\text{BMPYR}]^+[\text{BTI}]^-$ and $[\text{HMPYR}]^+[\text{BTI}]^-$ with benzene and toluene are listed in Table 2.

4. Modified UNIFAC (Dortmund)

The following new main groups and subgroups have been introduced in the group contribution method modified UNIFAC (Dortmund) to describe the phase equilibrium behavior of systems with ionic liquids: the cations imidazolium $[\text{IM}]^+$, pyridinium $[\text{PY}]^+$ and pyrrolidinium $[\text{PYR}]^+$ and the anions bis(trifluoromethylsulfonyl)imide $[\text{BTI}]^-$, trifluoromethanesulfonate $[\text{OTF}]^-$ and tetrafluoroborate $[\text{BF4}]^-$ (see Fig. 1). The group interaction parameters were fitted simultaneously to binary data stored in the Dortmund Data Bank (DDB) [5] and the systemat-

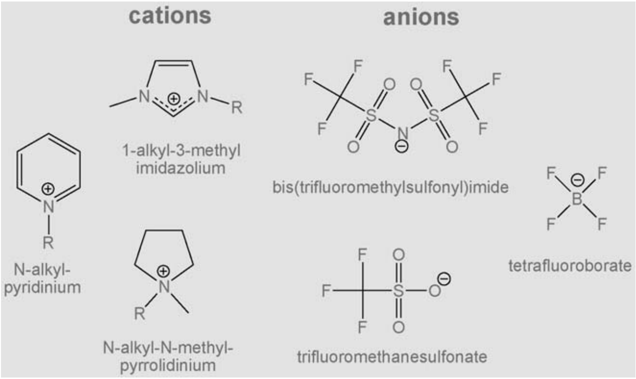

Fig. 1. Cations and anions of the investigated ionic liquids.