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Experimental and predicted phase equilibria and excess properties for systems with ionic liquids

Vincent Liebert, Silke Nebig, Jürgen Gmehling*

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

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ABSTRACT

Vapor–liquid equilibria (VLE) for the binary systems methylcyclohexane–toluene and 1-octene–*n*-octane and the ternary systems with the ionic liquid 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide $[HMIM]^+[BTI]^-$ as entrainer were measured. The addition of the ionic liquid leads to an increase of the separation factors. Excess enthalpies (H^E) were measured for methylcyclohexane and *n*-octane in the same ionic liquid as well. Furthermore activity coefficients at infinite dilution (γ^∞) were determined for a few solutes in various ionic liquids such as 1-hexyl-3-methyl-imidazolium bis(trifluoro-methylsulfonyl)imide $[HMIM]^+[BTI]^-$, 1-hexyl-3-methyl-imidazolium trifluoro-methanesulfonate $[HMIM]^+[OTF]^-$, 1-methyl-1-octyl-pyrrolidinium bis(trifluoromethyl-sulfonyl)imide $[MOPYR]^+[BTI]^-$, 1-methyl-1-butyl-pyrrolidinium trifluoromethanesulfonate $[MBPYR]^+$ $[OTF]^-$ and 1-ethyl-3-methyl-imidazolium ethyl sulfate $[EMIM]^+[EtOSO_3]^-$. The γ^∞-values were used to determine the selectivities $S_{ij}^\infty = \gamma_i^\infty/\gamma_j^\infty$ and the capacities $k_i = 1/\gamma_i^\infty$ at infinite dilution. The experimental data with $[R_1R_2IM]^+[BTI]^-$ were compared with the predicted results using mod. UNIFAC (Do). The predicted results are in good agreement with the experimental data.

1. Introduction

Since a few years there is an increasing interest in ionic liquids (IL). This has lead to an exponential increase of publications about ionic liquids [1]. Due to the fact that the properties of the ionic liquids can be adjusted by variation of the cation and the anion, the chain length of the alkyl rests and the substituents, theoretically up to 10^{18} possible ionic liquids are designable [2]. Therefore, ionic liquids are also referred as designer solvents, hence their properties can be optimized for a specific task. The use of ionic liquids offers several advantages. They have a negligible vapor pressure, which leads to negligible solvent emissions. So volatile organic compounds (VOCs) could replace organic solvents in various industrial applications resulting in a decreasing VOC-emission. The simple regeneration of ionic liquids is another advantage, because volatile components can be removed easily. Ionic liquids are characterized by a low melting point <373.15 K and a wide liquid range [3]. They show high solubility for both polar and non-polar organic and inorganic substances. Furthermore, ionic liquids are suitable solvents for biphasic chemical processes. The biphasic acid scavenging utilizing ionic liquid-process (BASIL) from BASF is the first large-scale process forming an ionic liquid [4,5]. During the reaction a product phase is formed by the ionic liquid.

Since the measurement of the huge number of feasible systems with ionic liquids is very time-consuming and expensive, the development of a reliable prediction method would be most desirable. Kato and Gmehling [6] and Nebig et al. [7] have shown that modified UNIFAC (Dortmund) is suitable to describe the thermodynamic behavior of systems with ionic liquids. But up to now the parameter matrix for ionic liquids is still limited. Therefore, work is going on to extend the existing parameter matrix.

In this work it was investigated if ionic liquids can be used as alternative entrainers for the separation of aliphatics from aromatics or alkanes from alkenes by extractive distillation. Extractive distillation is often used when the separation factor shows values close to unity. Entrainers should influence the separation factor allowing the separation of the system. The separation of the binary systems methylcyclohexane–toluene and 1-octene–octane are investigated in this work. Besides binary vapor–liquid equilibria (VLE) data experimental VLE data of ternary systems as well as γ^∞ and H^E-data with ionic liquids are presented. Additionally activity coefficients of the separation problem ethanol and water in various ionic liquids were measured, to show how the separation factor is influenced by the presence of the selected ionic liquids.

The structures of the cations and anions of the ionic liquids investigated in this work are shown in Fig. 1.

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* 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).

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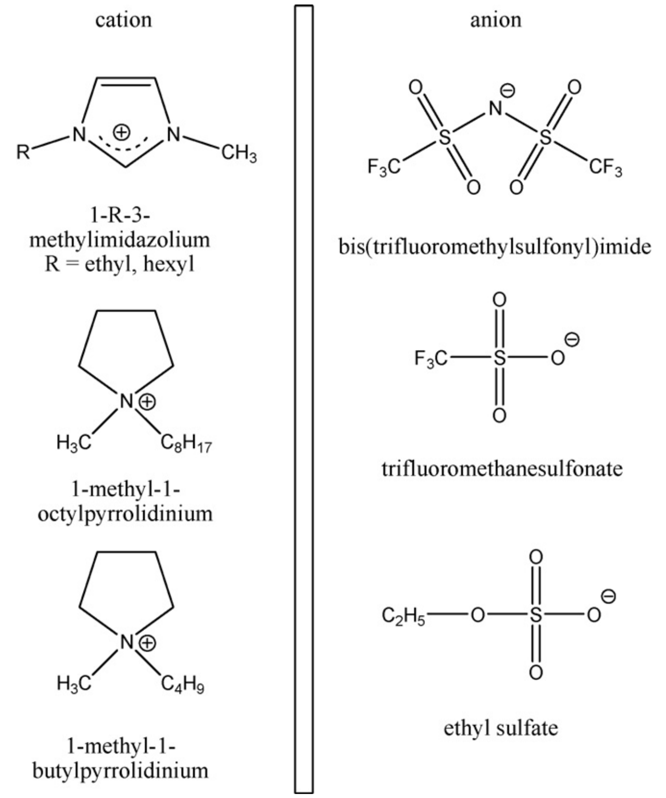

Fig. 1. Cations and anions of the investigated ionic liquids $[HMIM]^+[BTI]^-$, $[HMIM]^+[OTF]^-$, $[MBPYR]^+[OTF]^-$, $[MOPYR]^+[BTI]^-$ and $[EMIM]^+[EtOSO_3]^-$.

The new experimental data together with the data stored in the Dortmund Data Bank (DDB) [8] will be used for the extension of the group interaction parameter matrix of mod. UNIFAC (Do) for ionic liquids.

2. Materials and purities

All components in this work, except the ionic liquids, were used without degassing. The chemicals were dried over molecular sieves and the final purities were checked by gas chromatography (HP 6890 with Chemstation Rev. B.02.01-SR1). The water content was controlled for every compound including ionic liquids by Karl Fischer titration [9]. For all components investigated the water concentration determined with this method was less than 100 ppm. The purity, the supplier and the water content of the chemicals used are listed in Table 1. The applied de-ionized water was bi-distilled and used without further treatment.

Table 1
Supplier, purity, and water content of the chemicals

Component	Supplier	Purity (%)	Water content (ppm)
Methylcyclohexane	Photrex reagent	99.8	11.5
Toluene	ACROS	>99.9	5.1
1-Octene	ACROS	99.7	47.8
Octane	ACROS	99.8	29
Ethanol	VWR	99.7	15.4

The ionic liquids $[HMIM]^+[BTI]^-$, $[HMIM]^+[OTF]^-$, $[MOPYR]^+[BTI]^-$, $[MBPYR]^+[OTF]^-$ and $[EMIM]^+[EtOSO_3]^-$ investigated in this work were obtained from Merck GmbH. At the beginning of the measurement all ionic liquids were purified by vacuum evaporation to remove the last traces of volatile compounds.

3. Experimental section

3.1. VLE

Isothermal VLE (*xy*) measurements were carried out with a static apparatus. In this case a new headspace sampler (HS-sampler) from Agilent Technologies (G1888 Network Headspace sampler) was used. The underlying analytical technique is called as “static headspace gas chromatography”. The term “headspace” refers to the vapor space above the liquid sample placed in a vial. The experimental procedure is described in detail by Liebert [10]. A 70-sample vial tray is located on top of the HS-sampler. The 20-ml vials move from this sample tray into an oven, in which the vials can be heated to a specified temperature between 313 K and 503 K. The temperature is controlled with a Pt100 resistance thermometer (Model 1502A, Fluke) with an accuracy of ±6 mK. After reaching equilibrium between the liquid and the vapor phase, the vapor phase of the respective vial is analyzed by gas chromatography (Model 6890N, Agilent Technologies) with the help of a flame ionization detector (FID). While for the system methylcyclohexane–toluene a HP-1701 capillary column from Hewlett–Packard (30.0 m × 320 μm × 0.25 μm) was used, for the other system 1-octene–*n*-octane a HP-INNOWAX capillary column of J&W Scientific (60.0 m × 320 μm × 0.25 μm) was applied. The HS-sampler and the gas chromatograph are connected via a transfer line. This line can be heated up to 523 K. Since ionic liquids have no measurable vapor pressure, they do not disturb the measurement.

Table 2
Molar excess enthalpies for methylcyclohexane and *n*-octane with $[HMIM]^+[BTI]^-$

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
Methylcyclohexane (1)–$[HMIM]^+[BTI]^-$ (2) 363.15 K and 1617 kPa		*n*-Octane (1)–$[HMIM]^+[BTI]^-$ (2) 363.15 K and 1548 kPa	
0.0612	192.0	0.0486	203.6
0.1180	385.0	0.0950	369.2
0.1708	553.3	0.1392	449.8
0.2202	695.4	0.1814	483.5
0.2663	735.3	0.2217	462.9
0.3096	723.4	0.2603	443.1
0.3885	643.7	0.3327	401.1
0.4586	569.3	0.3993	367.0
0.5213	502.5	0.4608	331.0
0.6288	394.6	0.5707	266.3
0.7176	302.1	0.6660	202.2
0.7922	219.8	0.7495	160.8
0.8840	112.5	0.8568	95.1