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Measurement of vapor–liquid equilibria (VLE) and excess enthalpies (H^E) of binary systems with 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and prediction of these properties and γ^∞ using modified UNIFAC (Dortmund)

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Abstract

Vapor–liquid equilibria (VLE) and excess enthalpies (H^E) were measured for a variety of alkanes, alkenes, aromatics, alcohols, ketones and water in several ionic liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[EMIM]^+[BTI]^-$, 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide $[BMIM]^+[BTI]^-$, 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide $[HMIM]^+[BTI]^-$ and 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide $[OMIM]^+[BTI]^-$, covering the temperature range from 323.15 to 413.15 K. The new data were used together with the already available experimental data for imidazolium compounds to fit the required group interaction parameters for modified UNIFAC (Dortmund). The results show that in the future modified UNIFAC (Dortmund) can be applied successfully also for systems with ionic liquids.

Keywords: Ionic liquids; Vapor–liquid equilibria; Excess enthalpies; Modified UNIFAC (Dortmund)

1. Introduction

In recent years there has been an increasing interest in the thermodynamic properties of systems with ionic liquids, since ionic liquids enable application in diverse areas. They show a number of advantages: due to the negligible vapor pressure there are no solvent emissions. Furthermore it is relatively easy to separate the ionic liquid from volatile substances. Through their ionic character they show a special phase equilibrium behavior. Furthermore, ionic liquids exhibit a number of interesting properties: low melting points and a wide liquid range, good electrical conductivity and solvent transport properties, high solubility for a wide variety of inorganic, organic, and organometallic species, and wide electrochemical potential windows. Therefore, they are of interest not only as solvents for organic synthesis, but also as selective solvents for separation processes. But, they are also appropriate solvents for biphasic chemical processes, and electrochemical processes.

To describe the real behavior of multicomponent systems with ionic liquids, a reliable knowledge of the phase equilibrium behavior is indispensable. To obtain the required information, experimental measurements can be carried out. However, measurements are very time-consuming and therefore expensive. For traditional solvents, various reliable thermodynamic models for the prediction of the phase equilibrium behavior already exist, e.g. the group contribution methods UNIFAC or modified UNIFAC (Dortmund) [1–4].

With the large number of possible anions, cations, alkyl rests and functional groups there is virtually no limit in the number of feasible ionic liquids. In order to enable a problem-oriented selection from the multitude of ionic liquids, a reliable prediction method is required. Kato and Gmehling [5] have shown that modified UNIFAC (Dortmund) is well suited to describe also the thermodynamic behavior of systems with ionic liquids.

For the development of a predictive method and to obtain a better understanding for the use of ionic liquids as alternatives to conventional organic solvents e.g. for the development

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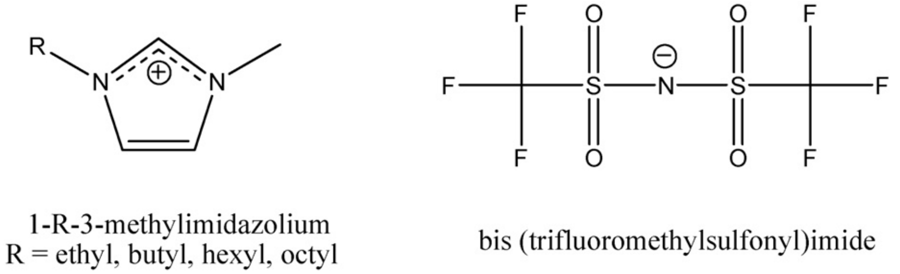

Fig. 1. Cations and anion of the investigated ionic liquids $[EMIM]^+[BTI]^-$, $[BMIM]^+[BTI]^-$, $[HMIM]^+[BTI]^-$ and $[OMIM]^+[BTI]^-$.

of chemical and separation processes, measurements of the different thermodynamic properties for binary and higher systems are required, since up till now the available data base for systems with ionic liquids is still very limited [6]. However, a sufficient data base is a prerequisite for the development and the simultaneous fitting of the required group interaction parameters for the appropriate group contribution method. Various research groups are engaged in the measurement of phase equilibrium data. This paper continues our series of systematic measurements and study of VLE, H^E and γ^∞ data [5,7–11]. In this article new experimental vapor–liquid equilibria (VLE) and excess enthalpies (H^E) for systems with the ionic liquids $[EMIM]^+[BTI]^-$, $[BMIM]^+[BTI]^-$, $[HMIM]^+[BTI]^-$ and $[OMIM]^+[BTI]^-$ are presented. The measured data, together with data stored in the Dortmund Data Bank (DDB) [6], have been used for the revision and extension of the group interaction parameters of modified UNIFAC (Dortmund). The group interaction parameters were obtained by fitting them simultaneously to the available experimental vapor–liquid equilibria (VLE), excess enthalpies (H^E) and activity coefficients at infinite dilution (γ_i^∞) for systems consisting of alkanes, alkenes, aromatics, alcohols, ketones, water and different kinds of imidazolium cations and the bis(trifluoromethylsulfonyl)imide anion. The structures of the investigated ionic liquids are given in Fig. 1.

2. Materials and purities

The purities of the organic components used and their suppliers are given in Table 1. For the VLE measurement all components were degassed and distilled at low pressure [12]. For the H^E measurements, the compounds were used without degassing. The purity was checked by gas chromatography and the water concentration (always <100 ppm) was measured by Karl Fischer titration. The ionic liquids $[EMIM]^+[BTI]^-$, $[BMIM]^+[BTI]^-$, $[HMIM]^+[BTI]^-$ and $[OMIM]^+[BTI]^-$ investigated in this work were obtained from Merck GmbH. All ionic liquids were purified by vacuum evaporation to remove traces of volatile impurities before use.

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

Component	Supplier	Purity (% GC)
Hexane	Fluka Chemie	99.8
Octane	ACROS	99.8
Nonane	Aldrich	99.8
Octene	ACROS	99.9
Acetone	J.T. Baker	99.8
Butanone	Aldrich	99.8
3-Pentanone	ACROS	99.5
Ethanol	VWR	99.9
1-Propanol	Roth	99.9
Benzene	Roth	99.9
Toluene	Roth	99.9
Methylcyclohexane	J.T. Baker	99.8

3. Experimental

3.1. Vapor–liquid equilibria

The isothermal VLE (Px) measurements were carried out with a computer-driven static apparatus. A detailed description of the measurement procedure is available in the literature [13,14]. The equipment consists of a thermostated equilibrium cell, which is connected with a Digiquartz pressure sensor (Model 245A, Paroscientific). The accuracy is approximately 0.0005% of the maximum pressure. The temperature is measured using a Pt100 resistance thermometer (Model 1506, Hart Scientific) whit a precision of ±1 mK. Via automatic valves, known quantities of thermostated, purified and degassed compounds are injected into the evacuated equilibrium cell by stepping motor-driven injection pumps. The apparatus can be applied at temperatures between 278 and 368 K and pressures up to 0.3 MPa.

3.2. Excess enthalpies

A Hart Scientific isothermal flow calorimeter (model 7501) was used for the determination of the excess enthalpy data. This apparatus allows the detection of endothermic and exothermal mixing effects. The flow of the solvents is realized with the help of two syringe pumps (modell LC 2600, ISCO). The thermostated flow cell equipped with a pulsed heater and a Peltier cooler is the heart of the calorimeter. Temperature constancy of the flow cell is achieved by balancing the pulsed heater, the Peltier cooler and the contribution of the excess enthalpy against each other. The accuracy of the heats of mixing measurements is estimated to be less than ±1%. A detailed description of the equipment and the measurement procedure can be found in literature [15].