Thermodynamic Properties of Mixtures Containing Ionic Liquids. 3. Liquid−Liquid Equilibria of Binary Mixtures of 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide with Propan-1-ol, Butan-1-ol, and Pentan-1-ol[†]

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An apparatus for measuring liquid−liquid equilibria of small samples of liquid mixtures with relatively high differences in density and viscosity was applied for studying mixtures of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and the three alcohols propan-1-ol, butan-1-ol, and pentan-1-ol. The synthetic method has been applied where cloud points at a given composition were determined by varying the temperature. The point of phase splitting was detected by light scattering. Data in the temperature range 281 K to 340 K have been obtained for the three systems.

Introduction

Ionic liquids are a most interesting new class of fluid systems having the character of molten salts which are moisture and air stable at room temperatures and in many cases stable at temperatures above 400 K. Due to their negligible vapor pressure, ionic liquids have been used widely as solvents for chemical reactions, biphase catalysis, and biocatalysis and other processes where the nonvolatility of solvents are of great advantage.[1,2] While the chemistry of ionic liquids and their utilization for chemical processes has already been studied in many publications, data of important properties such as mutual solubilities with other solvents and thermodynamic properties of mixtures containing ionic liquids are rare.

Our interest in ionic liquids is focused on providing systematic data of activity coefficients, phase equilibria, densities, viscosities, and enthalpies of mixing in mixtures with organic solvents. In continuation of our previous work on activity coefficients at infinite dilution of organic solvents in ionic liquids at different temperatures[3−5] and on excess volumes,[6] in this work we present new data of liquid−liquid equilibria of mixtures consisting of propan-1-ol, butan-1-ol, pentan-1-ol and the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][NTf$_2$]), see Figure 1.

Experimental Section

Substances. [EMIM][NTf$_2$] was synthesized according to a prescription developed in the group of Wasserscheid.[7] 1-Methylimidazole was quaternized in the 3-position using diethyl sulfate. The synthesized [EMIM][$C_2H_5OSO_3$] was hydrolyzed. Anion exchange of [EMIM]HSO_4 was obtained using Li[NTf$_2$] ,and the Li_2SO_4 was then separated by extracting it with H_2O from the desired product, which has a low solubility in water. The purity of the ionic liquid was verified by NMR spectroscopy to check for residues of the basic compounds. Signals of these compounds have not been detected, but some traces of water have. To remove the water content, the ionic liquid was dried and degassed by evacuating the sample to about 10^{-6} bar at 75 °C for 8 h. The substance was stored under Ar atmosphere to avoid absorption of water or air.

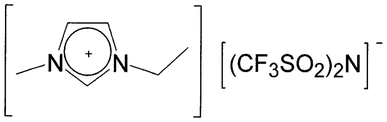

Figure 1. Structure of [EMIM][NTf$_2$].

The alcohols were supplied by Fluka, with purities of ≥99.8% (propan-1-ol), ≥99.8% (butan-1-ol), and ≥99% (pentan-1-ol) and a water content of ≤0.1%. All alcohols have been used without further purification.

Experimental Apparatus. A new apparatus designed for the determination of liquid−liquid equilibria of small amounts of samples has been constructed.[8]

The principle is based on the nephelometric observation of the phase separation. The process of phase separation is detected by measuring the intensity of scattered light, which propagates in the Tyndall cone.

The optical setup consists of a laser as light source and a photodiode as light sensor. The optical plane, defined by the axis of the optical elements, is located in the vertical center of the liquid phase (see Figures 2 and 3). The intensity of the scattered light is measured at an angle of 135° with respect to the direction of the incident laser light beam. The laser diode module emits light of 635 nm wavelength. It has an adjustable power and can be pulsed up to a frequency of 25 kHz. The detector is a photodiode with an integrated amplifier. Laser and detector are the essential parts of a phase-sensitive detector, which provides a calibrated electrical voltage proportional to the intensity of the scattered light. Due to the application of a phase-sensitive detector, the measurement is independent of ambient light. Laser and detector are mounted on a sleeve, which is fixed tightly surrounding the jacket of the liquid cell.

The voltage from the electronic circuit is fed to a data acquisition card connected to a PC. Analyzing the voltage, the PC controls an open circulator bath, which is connected

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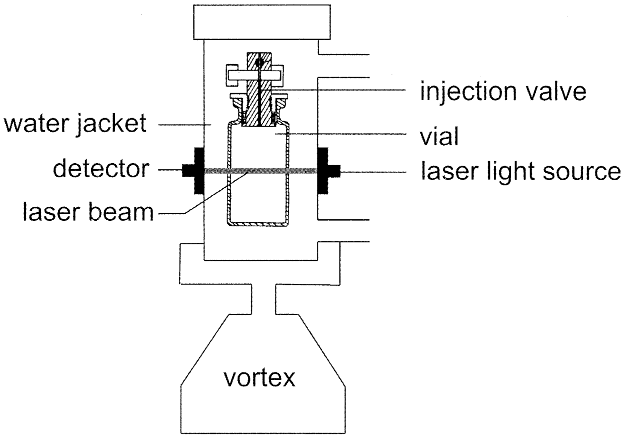

Figure 2. Experimental setup of the LLE cell.

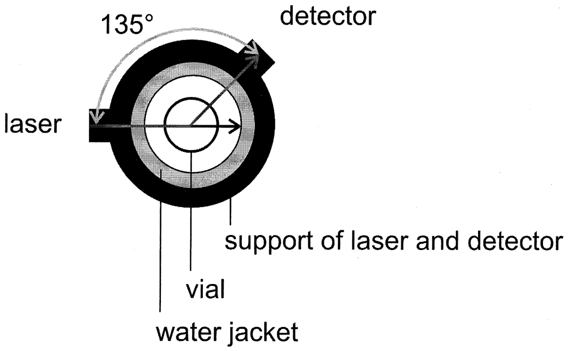

Figure 3. Arrangement of laser and detector.

to the jacket of the liquid cell. A computer program enables us to define the stepwise increase or decrease of temperature.

Starting in the homogeneous region of the mixture studied, the temperature is decreased until the cloud point is observed at a given composition. The approach to the determination of the cloud point is controlled by the PC, which enables a semiautomatic registration of the cloud point temperature.

The mixtures are prepared by injecting directly the two components into a probe vial of 4 mL. To avoid loss of substance by evaporation, the sample is injected by a closed syringe through a narrow tube in the Mininert valve, which forms the cap of the vial. The composition is determined gravimetrically. The relative error of the mass fraction was estimated to be less than 2×10^{-4}.

The vial is mounted inside the temperature-controlled jacket. It turned out that insufficient results were obtained by using various conventional stirring devices because of the relatively high differences of viscosity and density of the two phases. Therefore, the complete jacket with the vial and the optical setup is shaken with a vortex mixer, which leads to a much more effective generation of small droplets at the onset of phase splitting, resulting in a sharper and more reproducible change of the scattered light intensity. This method also speeds up the adjustment of the temperature equilibrium and suppresses the formation of homogeneous layers of the pure components after decomposition into two phases. Cloud point temperatures can be determined with an accuracy of ±0.1 K near the UCST, and with ±0.3 K near the edge of the curves.

Results and Discussion

Results of binodal curves of mixtures containing [EMIM][NTf$_2$] and propan-1-ol, butan-1-ol, or pentan-1-ol, respectively, are shown in Figure 4. All systems show an UCST. All systems show nearly symmetrical binodal curves when the results are plotted versus the mass fraction. Using mole fraction as units shifts the maximum (UCST) to the left, resulting in more unsymmetrical curves (not shown here). Numerical results are presented in Tables 1−3.

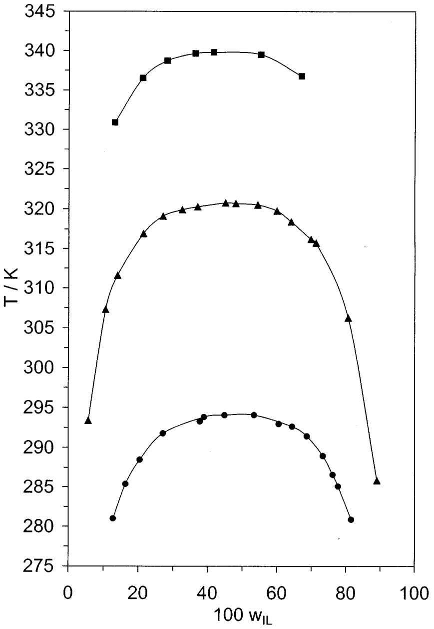

Figure 4. LLE coexistence curves for [EMIM][NTf$_2$] + propan-1-ol, ●, butan-1-ol, ▲, and pentan-1-ol, ■, at atmospheric pressure. w_{IL} is the mass fraction of [EMIM][NTf$_2$].

Table 1. Experimental Cloud Point Results for the System [EMIM][NTf$_2$] + Propan-1-ol as a Function of Mass Fraction w_{IL} of the Ionic Liquid

$100w_{IL}$	T/K	$100w_{IL}$	T/K
12.78	281.0	60.49	293.0
16.36	285.4	64.38	292.7
20.46	288.5	68.64	291.5
27.10	291.8	73.31	289.0
37.71	293.3	76.16	286.6
38.93	293.8	77.71	285.1
44.85	294.1	81.51	280.9
53.38	294.1		

Table 2. Experimental Cloud Point Results for the System [EMIM][NTf$_2$] + Butan-1-ol as a Function of Mass Fraction w_{IL} of the Ionic Liquid

$100w_{IL}$	T/K	$100w_{IL}$	T/K
5.67	293.4	47.99	320.7
10.56	307.3	54.34	320.6
13.98	311.6	59.87	319.8
21.39	317.0	64.02	318.5
27.01	319.1	69.75	316.3
32.56	319.9	71.21	315.8
37.02	320.3	80.58	306.3
45.05	320.8	89.05	285.9

Table 3. Experimental Cloud Point Results for the System [EMIM][NTf$_2$] + Pentan-1-ol as a Function of Mass Fraction w_{IL} of the Ionic Liquid

$100w_{IL}$	T/K	$100w_{IL}$	T/K
13.14	330.9	41.50	339.8
21.11	336.6	55.16	339.5
28.15	338.8	66.96	336.8
36.23	339.7		

The data show an increasing UCST with increasing size of the alkyl chain of the alcohols. It is obvious that with decreasing polar character in the order propan-1-ol, butan-

1-ol, pentan-1-ol the tendency of demixing in mixtures with [EMIM][NTf_2] increases. This fact corresponds to the results of activity coefficients at infinite dilution of alcohols in [EMIM][NTf_2], which increase also with increasing chain length of the alcohols.[4]

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