Solid−Liquid Equilibrium and Activity Coefficients for Caprolactam + 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide and Cyclohexanone Oxime + 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide

Marina P. Shevelyova, Dzmitry H. Zaitsau, Yauheni U. Paulechka, Andrey V. Blokhin, and Gennady J. Kabo*

Chemistry Faculty and Research Institute for Physical Chemical Problems, Belarusian State University, Leningradskaya 14, Minsk 220030, Belarus

Sergey P. Verevkin and Andreas Heintz*

Department of Physical Chemistry, University of Rostock, Hermannstrasse 14, 18051 Rostock, Germany

Thermophysical properties for binary mixtures ϵ-caprolactam + 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and cyclohexanone oxime + 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide have been measured. New measurements of heat capacity for caprolactam (CL) in the temperature range of (260 to 370) K and parameters of fusion have been carried out. Mutual solubility of caprolactam (CL) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([HMIM][NTf$_2$]) in the wide concentration range and solubility of cyclohexanone oxime (CHO) in [HMIM][NTf$_2$] within x(CHO) from (0.2 to 1) were studied by a visual method. Activity coefficients of the components were estimated. Vapor−liquid equilibrium (VLE) of the binary mixture CL + [HMIM][NTf$_2$] was studied using the Knudsen method. VLE measurements were carried out over the broad concentration range at temperatures between (315.3 and 331.9) K. Activity coefficients of CL in [HMIM][NTf$_2$] have been determined from the VLE data and are described formally by using the NRTL equation. Activity coefficients in infinity dilution of CL in [HMIM][NTf$_2$] have been derived by extrapolation to the infinite dilution of CL. Activity coefficients at infinite dilution of CHO in the temperature range (364.9 to 438.0) K and CL at 427.5 K in [HMIM][NTf$_2$] have been determined by gas chromatography using the ionic liquid as the stationary phase.

Introduction

Ionic liquids (ILs) potentially have various industrial applications as extracting agents and environmentally friendly solvents and catalytic media.[1,2] Caprolactam production is one of the possible processes to be improved with the use of ILs. Ionic liquids have been proved as effective and selective reaction media for Beckmann rearrangement.[3,4] Solid−liquid equilibria (SLE) of binary mixtures (caprolactam + 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and cyclohexanone oxime + 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide) have been studied in this work. Limiting activity coefficients of caprolactam and cyclohexanone oxime in caprolactam + 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide have been obtained by a GC method.[5]

Parameters of fusion for pure cyclohexanone oxime (CHO) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide ([HMIM][NTf$_2$]) required for calculations were taken from our previous works.[6,7] Heat capacity values and parameters of fusion for [HMIM][NTf$_2$] measured in our laboratory are in good agreement with high-quality measurements by Shimizu et al.[8] New measurements of heat capacity for caprolactam (CL)

in the condensed state and parameters of fusion have been carried out.

Experimental Section

Materials. A sample of [HMIM][NTf$_2$] was synthesized by Dr. Muldoon (University of Notre Dame, USA). To remove volatile impurities, the sample was exposed to a vacuum of 0.1 Pa at T = 353 K for 4.5 h. The mole fraction of [HMIM][NTf$_2$] was determined to be x([HMIM][NTf$_2$]) = 0.9976 by the fractional-melting experiments in an adiabatic calorimeter.[7]

Commercial samples of CHO and CL with an initial mass fraction ≥ 0.95 and a mole fraction ≥ 0.995, respectively, were sublimed at p = 0.3 kPa and T = 340 K. Mole fractions of CHO and CL purified samples were x(CHO) = 0.9998[9] and x(CL) = 0.9998, as determined from the fractional-melting experiments.

Adiabatic Calorimetry. The heat capacity of CL (mass of the sample was 0.5253 g) in the temperature range (260 to 370) K and parameters of fusion were determined in a TAU-10 vacuum adiabatic calorimeter (Termis, Moscow).[7] The calorimeter and the procedure of measurements have already been described.[7] The relative uncertainty of heat capacity measurements did not exceed ± 0.4 % in the temperature range (260 to 370) K.

Mutual Solubility in Binary Mixtures Determined by a Visual Method. The glass tubes of internal volume ≈4 cm^3 and

Table 1. Mass Fraction w of Water in Saturated Solutions of Water in Cyclohexanone

$T^{\text{LLE}}/\text{K}^a$	$100\ w_{\text{lit}}^b$	$100\ w^c$	Δ^d
303.2	6.1	6.0	−1.6
313.2	6.4	6.6	3.1
323.2	7.1	7.0	−1.4
343.2	8.3	8.5	2.4

^{a} Saturation temperature. ^{b} Literature data.[9] ^{c} Data obtained in this work. ^{d} $\Delta = 100\cdot(w - w_{\text{lit}})/w_{\text{lit}}$.

diameter ≈0.6 cm were filled with mixtures of known compositions of CL + [HMIM][NTf$_2$] and CHO + [HMIM][NTf$_2$] (uncertainty of weighing ± 5·10^{-5} g; uncertainty of mole fraction ± 3·10^{-4}) in a drybox. Two or three glass beads of 1 mm diameter were added for better mixing of the components.

The tubes were thermostatted at (266 to 332) K. The temperature was measured within ± 0.1 K. Saturation point temperatures, T^{SLE}, were determined visually as the temperatures when the last crystal disappeared. The temperatures T^{SLE} were determined under slow heating at a rate of 0.5 K·h^{-1} and continuous mixing. Change of composition of the mixtures caused by partial evaporation of CL and CHO into the hollow space of the tubes was shown to be negligible compared with the uncertainty of the experiment and was not taken into account.

Before each series of experiments, the solutions were kept at 247 K for 2 days to crystallize the solute. The deviation between the values of T^{SLE} for the given compositions obtained in different experiments did not exceed 0.1 K.

The validity of the method was checked in measurements of water + cyclohexanone liquid−liquid equilibria (LLE). The average deviation of our results with the literature data[10] was 2 % (Table 1).

Vapor−Liquid Equilibria (VLE) Measurements of CL + [HMIM][NTf$_2$] by the Knudsen Method. The experimental technique has already been described in detail.[11] The uncertainty of the measurements for pure substances does not exceed ± 5 %. The Knudsen cell of internal volume ≈1 cm^3 was used. Parameters of the effusion orifice were l = (84 ± 2) μm and d = (446.7 ± 0.5) μm. The temperature of the cell was maintained constant to within ± 0.03 K. The solutions under study occupied (30 to 50) vol % of the cell. The vapor pressure of [HMIM]-[NTf$_2$] is negligibly low[12] in comparison with that for CL. Therefore, the vapor over the solutions consists only of CL molecules. Mass loss of CL in the experiments was from (0.3 to 12) mg. Before each experiment, the mole fraction of CL was recounted according to mass loss during the previous one. The uncertainty of weighing was ± 5·10^{-5} g. The vapor pressure values were calculated using the following equation[11]

$$p = \frac{\Delta m}{k S_{\text{orif}} \tau} \sqrt{\frac{2\pi RT}{M}} \quad (1)$$

where p is the vapor pressure of CL; Δm is the mass loss of CL during the exposition time τ; T is the temperature of the heat carrier in the thermostat; S_{orif} is the area of the effusion orifice; k is the transmission probability coefficient through the effusion orifice; and M is the molar mass of CL (the vapor of CL was considered to be monomolecular[13]).

The k coefficient was calculated according to Wahlbeck's isotropy failure theory.[14] An effective diameter of the CL molecule, σ = 0.578 nm, was taken from ref 13. Values of the vapor pressure were referred to the average mole fraction of CL during an experiment.

GC Method for Determination of Activity Coefficients at Infinite Dilution. Because ILs have negligible vapor pressure
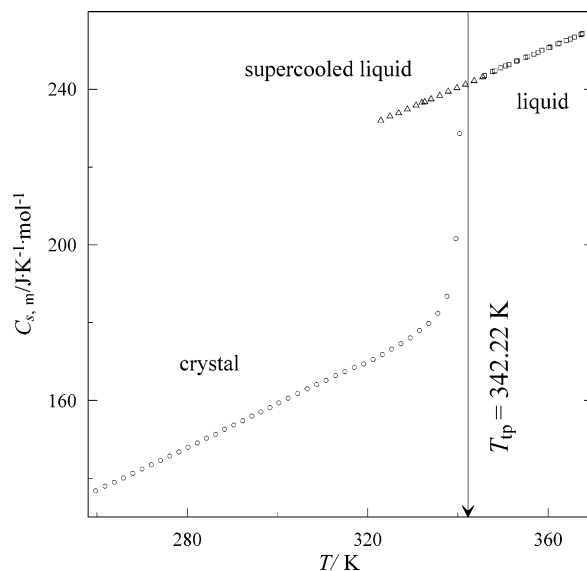

Figure 1. Experimental heat capacity of caprolactam in the range (260 to 370) K: ○, crystal; □, liquid; △, supercooled liquid.

at temperatures below 500 K, the gas−liquid chromatographic method is suitable for measuring activity coefficients at infinite dilution of volatile solutes in ionic liquids using the IL as the stationary phase.[5] The experimental procedure was described elsewhere.[15] The experiments were performed with a Varian-3600 gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. Chromosorb coated with [HMIM][NTf$_2$] was used as support material in the GC column (length of the column = 43 cm, diameter = 0.4 cm, nitrogen was used as a carrier gas). The solid support material was coated with the IL by dispersing a certain portion of chromosorb in a solution of the IL in dichloromethane followed by evaporation of the solvent using a rotating evaporator. The material was weighed before and after the coating process. The amount of stationary phase ([HMIM][NTf$_2$]) was 2.25 mmol. The mass of the stationary phase was determined with an uncertainty of ± 3·10^{-4} g. To avoid possible residual adsorption effects of the solutes on chromosorb, the amount of IL was about 50 mass percent of the support material.[15]

Activity coefficients at infinite dilution γ_i^∞ were calculated by the Cruickshank equation[16]

$$\ln \gamma_{i,3}^\infty = \ln\left(\frac{n_3 RT}{V_N p_{01}}\right) - \frac{B_{11} - V_1^0}{RT}\cdot p_{01} + \frac{2B_{12} - V_1^\infty}{RT}\cdot J p_0 \quad (2)$$

where $\gamma_{i,3}^\infty$ is the activity coefficient of component i at infinite dilution in the stationary phase (index 3); p_{01} is the vapor pressure of the pure liquid solute; n_3 is the number of moles of the stationary phase component (IL) on the column; V_N is the standardized retention volume; B_{11} is the second virial coefficient of the solute; B_{12} is the mixed virial coefficient of the solute with the carrier gas nitrogen; V_1^0 is the molar volume of pure liquid solute; and V_1^∞ is the partial molar volume of solute in the IL at infinite dilution. The computation procedure has been described in detail earlier.[15,17]

The outlet pressure p_0 was taken to be equal to the atmospheric pressure. The pressure drop ($p_i - p_0$) was varied between (143 and 215) kPa, providing sharp peaks with suitable retention times. The pressure drop was measured using a membrane manometer. The inlet vapor pressure p_i was determined with an uncertainty of ± 0.2 kPa.
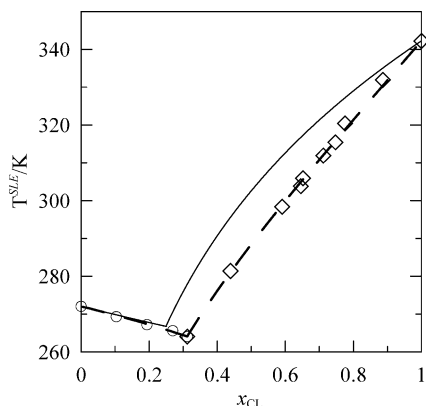
Figure 2. Experimental and ideal SLE diagrams for CL + [HMIM][NTf₂]: □, saturated solutions of CL in [HMIM][NTf₂]; ○, saturated solutions of [HMIM][NTf₂] in CL; - - -, approximation curves; —, curves of ideal solubility.
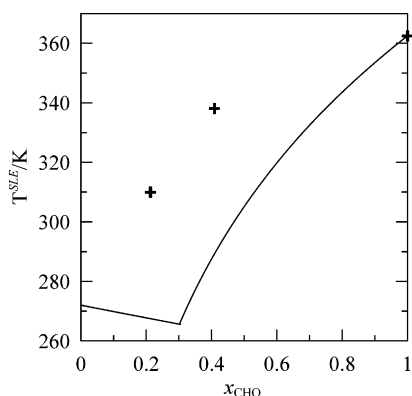

Figure 3. Experimental and ideal SLE diagrams for CHO + [HMIM]-[NTf₂]: +, saturated solutions of CHO in [HMIM][NTf₂]; —, curves of ideal solubility.

The molar volume of CHO, V_1^0, was estimated according to the Chueh and Prausnitz method,[18] and the molar volume of CL was calculated from the density of pure CL.[19] Partial molar volumes of solute at infinite dilution V_1^∞ have been assumed to be equal to V_1^0. Values of B_{11} have been estimated according to Tsonopolous' method.[18] Values of the critical pressure, p_c, the critical temperature, T_c, and the critical volume, V_c, for pure CHO were estimated using Lydersen's method.[20] Critical parameters for pure CL were available from the literature.[19] Acentric factors, ω_i, were calculated by Edminster's equation.[18] Values of B_{12} have also been estimated according to Tsonopolous' method. The mixed critical properties, p_{cij}, T_{cij}, V_{cij}, and Z_{cij}, and mixed acentric factor, ω_{ij}, were calculated by equations given in the literature.[18,20] Values of vapor pressures, p_{01}, of pure CL and CHO were taken from the literature.[13,6] The validity of the experimental procedure has been checked by comparison of our measured values of γ_i^∞ for hexane, heptane, and benzene in hexadecane with those available in the literature.[15] Values of γ_i^∞ are estimated to be accurate to within ± 3 %.

Results and Discussion

Heat Capacity, Enthalpy, and Temperature of Fusion for the Components. Experimental heat capacities for CL in the temperature range from (260 to 370) K are shown in Figure 1.

To obtain crystalline CL, the melt was cooled to a temperature of 310 K when spontaneous crystallization started. Then the melt was heated to 342.1 K and was maintained at this temperature until the heat evolution caused by the crystallization completely stopped (about 5 h).
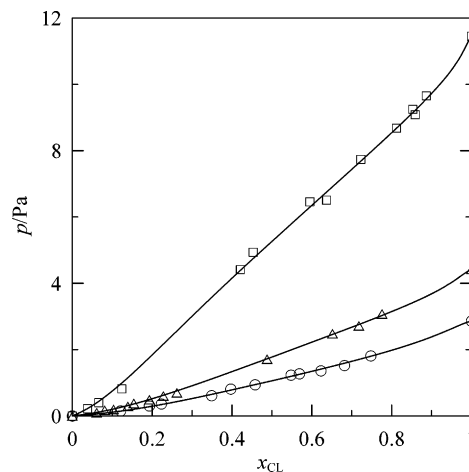

Figure 4. Vapor pressure p of CL + [HMIM][NTf₂] at different temperatures: ○, 315.3 K; △, 320.3 K; □, 331.9 K.

Table 2. Parameters of Fusion for the Substances

| | T_{tp} | $\Delta_{fus}H_m^o$ | $\Delta_{fus}C_p^o$ | |
substance	K	kJ·mol⁻¹	J·K⁻¹·mol⁻¹	source
[HMIM][NTf₂]	272.03 ± 0.01	28.09 ± 0.08	114.1 ± 0.6	ref 7
caprolactam	342.22 ± 0.01	16.16 ± 0.02	53.5 ± 0.3	this work
cyclohexanone oxime	362.5 ± 0.3	12.70 ± 0.30	52.2 ± 0.3	ref 6

The triple-point temperature, $T_{tp} = (342.22 \pm 0.01)$ K, for CL was determined from the fractional-melting experiments. The enthalpy of fusion, $<\Delta_{fus}H_m^o> = (16157 \pm 17)$ J·mol⁻¹, was determined as the average of five experiments. The heat capacity of crystalline CL in the range (316 to 335) K was fitted by the equation

$$\{C_{p,m}(\text{crystal})/\text{J·K}^{-1}\cdot\text{mol}^{-1}\} = 1288.5 - 7.537\cdot(T/\text{K}) + 1.263\cdot10^{-2}\cdot(T/\text{K})^2 \quad (3)$$

The heat capacity of liquid and supercooled liquid in the range (323 to 368) K was fitted by the linear equation

$$\{C_{p,m}(\text{liquid})/\text{J·K}^{-1}\cdot\text{mol}^{-1}\} = 72.47 + 0.4948\cdot(T/\text{K}) \quad (4)$$

These equations were used for calculating the difference between the heat capacities of liquid and crystalline CL, $\Delta_{fus}C_p^o(T_{tp})$ (Table 2). The values of $T_{tp,i}$, $\Delta_{fus}H_{m,i}^o(T_{tp,i})$, and $\Delta_{fus}C_{p,i}^o(T_{tp,i})$ for CL, CHO, and [HMIM][NTf₂] used in this work are presented in Table 2.

SLE for CL + [HMIM][NTf₂] and CHO + [HMIM][NTf₂]. The mutual solubility of CL + [HMIM][NTf₂] and CHO + [HMIM][NTf₂] was calculated theoretically in accordance with the well-known equation[21]

$$\ln(x_i/x_i(T_{tp,i})) = A[(1/T_{tp,i}) - (1/T^{SLE})] + B[(T_{tp,i}/T^{SLE}) - 1 - \ln(T_{tp,i}/T^{SLE})] \quad (5)$$

where $x_i = x_i^{id}$ is the mole fraction of solute i in the saturated solution at the temperature T^{SLE} and $T_{tp,i}$ is the triple-point temperature. If a liquid solution is assumed to be the ideal one and the components are mutually insoluble in the crystalline state, the coefficients make sense as follows: $A = \Delta_{fus}H_{m,i}^o(T_{tp,i})/R$; $B = \Delta_{fus}C_{p,i}^o(T_{tp,i})/R$.

The eutectic points for CL + [HMIM][NTf₂] and CHO + [HMIM][NTf₂] were found as the intersections of the ideal solubility curves:
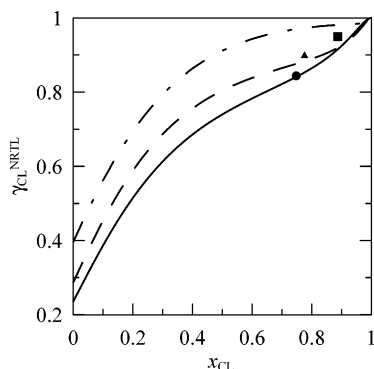
Figure 5. Activity coefficients γ of CL in CL + [HMIM][NTf$_2$]: —, 315.3 K; − −, 320.3 K; − · − · − ·, 331.9 K; ●, ▲, ■, γ of CL obtained from SLE data.

CL + [HMIM][NTf$_2$]: T(eutectic, theor.) = 265.9 K, x_{CL} = 0.245

CHO + [HMIM][NTf$_2$]: T(eutectic, theor.) = 264.4 K, x_{CHO} = 0.297.

SLE diagrams in the ideal solution approximation for the systems are shown in Figures 2 (CL + [HMIM][NTf$_2$]) and 3 (CHO + [HMIM][NTf$_2$]) with solid lines.

Experimental mole fractions in the CL + [HMIM][NTf$_2$] and CHO + [HMIM][NTf$_2$] systems at the saturation temperatures, T^{SLE}, are presented in Tables 3 and 4 and Figures 2 and 3, respectively. The mutual solubility of [HMIM][NTf$_2$] and CHO below $x_{CHO} = 0.2$ was too low to be determined with the method used.

The solubility curves for CL and CHO in [HMIM][NTf$_2$] appreciably differ from the ideal ones. However, the solubility of [HMIM][NTf$_2$] in CL is close to that calculated from eq 5. The activity coefficients γ_i of the solutes i were calculated according to

$$\gamma_i = \frac{x_i^{id}}{x_i^{SLE}} \quad (6)$$

where x_i^{id} and x_i^{SLE} are the mole fractions of the solute i in the ideal and real saturated solutions, respectively, at T^{SLE}. The values of γ_i for CL and [HMIM][NTf$_2$] are presented in Table 3, and that for CHO is presented in Table 4.

The experimental data of $\ln x_i^{SLE} = f(T)$ were approximated with eq 5, where $A = \Delta_{sol}H_m^{SLE}(T_{tp,i})/R$; $B = \Delta_{sol}C_{p,m}^{SLE}(T_{tp,i})/R$; and the values $\Delta_{sol}H_{m,i}^{SLE}$ and $\Delta_{sol}C_{p,m,i}^{SLE}$ are the change of the enthalpy and the heat capacity during formation of the saturated solution containing 1 mol of i at temperature $T_{tp,i}$. The coefficients of eq 5 for the systems CL + [HMIM][NTf$_2$] and CHO + [HMIM][NTf$_2$] as well as the values of $\Delta_{sol}H_{m,i}^{SLE}$ and $\Delta_{sol}C_{p,m,i}^{SLE}$ are given in Table 5. The experimental eutectic point for CL + [HMIM][NTf$_2$] was found as the intersection of the curves $\ln x_{CL}^{SLE} = f(T)$ and $\ln(1 - x_{[HMIM][NTf_2]}^{SLE}) = f(T)$ (Table 3). The molar enthalpies of mixing for the solutes $\Delta_{mix}H_{m,i}(T_{tp,i})$ were calculated as follows

$$\Delta_{mix}H_{m,i}(T_{tp,i}) = \Delta_{sol}H_{m,i}^{SLE}(T_{tp,i}) - \Delta_{fus}H_{m,i}^{o}(T_{tp,i}) \quad (7)$$

The values of $\Delta_{mix}H_{m,i}(T_{tp,i})$ are given in Tables 3 and 4.

The system CHO + [HMIM][NTf$_2$] shows considerable positive deviation from the ideality: the activity coefficient of CHO in the saturated solution of [HMIM][NTf$_2$] increases from 1 at the triple-point temperature $T_{tp} = 362.5$ K to 2.5 at 310 K (Table 4). The molar enthalpy of mixing, $\Delta_{mix}H_{m,i}(T_{tp,i})$, of CHO is 16.4 kJ·mol^{-1} at T_{tp}. The system CL + [HMIM][NTf$_2$] shows

Table 3. Saturation Temperatures, T^{SLE}, Mole Fractions of CL, x_{CL}^{SLE}, Activity Coefficients of the Solute, γ_i^{SLE}, in CL + [HMIM][NTf$_2$] Saturated Solutions, and Molar Enthalpies of Mixing for the Solute $\Delta_{mix}H_{m,i}(T_{tp,i})$

T^{SLE}					$\Delta_{mix}H_{m,i}(T_{tp,i})^d$
K	x_{CL}^{SLE}	γ_i^{SLE}(exptl)^a	γ_i^{SLE}(calcd)^b	Δ^c	kJ·mol^{-1}
		Caprolactam			
342.2^e	1.00	1.00	1	0.0	−6.9
331.9	0.8867	0.95	0.93	2.1	
320.4	0.7756	0.89	0.87	2.2	
315.4	0.7475	0.84	0.85	−1.2	
311.9	0.7117	0.83	0.83	0.0	
305.9	0.6520	0.82	0.81	1.2	
303.8	0.6457	0.79	0.81	−2.5	
298.4	0.5911	0.78	0.79	−1.3	
281.4	0.4389	0.76	0.76	0.0	
264.1^f	0.312^f	0.76	0.76	0.0	
		[HMIM][NTf$_2$]			
264.1^f	0.312^f	1.01	1.01	0.0	
265.6	0.2692	1.02	1.00	2.0	
267.2	0.1934	0.99	1.00	−1.0	
269.3	0.1034	0.98	1.00	−2.0	
272.0^e	0.00	1.00	1.00	0.0	−0.1

^{a} γ_i^{SLE}(exptl) $= x_i^{id}/x_i^{SLE}$(exptl), where x_i^{SLE}(exptl) is the experimental mole fraction of the solute in the saturated solution. ^{b} γ_i^{SLE}(calcd) $= x_i^{id}/x_i^{SLE}$(calcd), where x_i^{SLE}(calcd) is the fitted mole fraction of the solute in the saturated solution calculated with eq 5 using the parameters from Table 5. ^{c} $\Delta = 100 \cdot (\gamma_i^{SLE}$(exptl) $- \gamma_i^{SLE}$(calcd))/γ_i^{SLE}(exptl). ^{d} Molar enthalpy of mixing for the solute at $T_{tp,i}$. ^{e} Triple-point temperature of the pure solute. ^{f} Extrapolated values, eutectic point

Table 4. Saturation Temperatures, T^{SLE}, Mole Fractions of CHO, x_{CHO}^{SLE}, Activity Coefficients of CHO, γ_{CHO}^{SLE}, in CHO + [HMIM][NTf$_2$] Saturated Solutions, and Molar Enthalpy of Mixing for CHO, $\Delta_{mix}H_{m,CHO}(T_{tp,i})$

T^{SLE}					$\Delta_{mix}H_{m,CHO}(T_{tp,i})^d$
K	x_{CHO}^{SLE}	γ_{CHO}^{SLE}(exptl)^a	γ_{CHO}^{SLE}(calcd)^b	Δ^c	kJ·mol^{-1}
310.0	0.2127	2.50	2.73	−9.1	
338.2	0.4087	1.84	1.50	18.1	
362.5^e	1.0	1.00	1.00	0.0	16.4

^{a} γ_{CHO}^{SLE}(exptl) $= x_{CHO}^{id}/x_{CHO}^{SLE}$(exptl), where x_{CHO}^{SLE}(exptl) is the experimental mole fraction of CHO in the saturated solution. ^{b} γ_{CHO}^{SLE}(calcd) $= x_{CHO}^{id}/$(calcd), where x_{CHO}^{SLE}(calcd) is the fitted mole fraction of CHO in the saturated solution calculated with eq 5 using the parameters from Table 5. ^{c} $\Delta = 100 \cdot (\gamma_{CHO}^{SLE}$(exptl) $- \gamma_{CHO}^{SLE}$(calcd))/γ_{CHO}^{SLE}(exptl). ^{d} Molar enthalpy of mixing for CHO at T_{tp}. ^{e} Triple-point temperature of the pure CHO.

negative nonideality on the contrary. The activity coefficient of CL increases from 0.76 at the eutectic-point temperature 264.1 K to 1 at the triple-point temperature $T_{tp} = 342.2$ K. The molar enthalpy of mixing, $\Delta_{mix}H_{m,i}(T_{tp,i})$, of CL is −6.9 kJ·mol^{-1} at the triple-point T_{tp}. The activity coefficient of [HMIM][NTf$_2$] in the saturated solution of CL is close to 1 in the temperature range (264.7 to 272.0) K. The molar enthalpy of mixing of [HMIM][NTf$_2$] was negligible within the experimental uncertainty.

VLE for the System CL + [C$_6$mim][NTf$_2$]. The experimental vapor pressures of CL + [HMIM][NTf$_2$] are given in Table 6 and Figure 4. The values of vapor pressure for pure CL used for the calculation of the activity coefficients have been obtained earlier.[13] The vapor pressure of liquid and supercooled CL, p_0, in the temperature range from (264 to 342) K was calculated by the equation where $A = (3761.1 \pm 0.1)$ K; $B = (5299 \pm$

$$\ln(p_0/p^o) = A/\theta + B[(1/\theta) - (1/T)] + C[(\theta/T) - 1 + \ln(T/\theta)] + D[(\theta/2)[(T/\theta) - (\theta/T) - 2\ln(T/\theta)]] \quad (8)$$

Table 5. Parameters of Equation 5 for Nonideal Solutions CL + [HMIM][NTf$_2$] and CHO + [HMIM][NTf$_2$]

	A			$\Delta_{sol}H_m(T_{tp,i})$	$\Delta_{sol}C_{p,m,i}(T_{tp,i})$
	K	B		kJ·mol^{-1}	J·K·mol^{-1}
CL/[HMIM][NTf$_2$]	1119 ± 41	−5.4 ± 1.6		9.30 ± 0.34	−45 ± 14
[HMIM][NTf$_2$]/CL	3365 ± 116	0^a		28.0 ± 1.0	0^a
CHO/[HMIM][NTf$_2$]	3495 ± 303	0^a		29.1 ± 2.5	0^a

^{a} Assumed.

Table 6. Experimental Vapor Pressures, p^{exptl}, and Activity Coefficients of CL, γ_{CL}^{NRTL}, in CL + [HMIM][NTf$_2$]

	p^{exptl}	p^{NRTL}			p^{exptl}	p^{NRTL}			p^{exptl}	p^{NRTL}	
x_{CL}	Pa	Pa	γ_{CL}^{NRTL}	x_{CL}	Pa	Pa	γ_{CL}^{NRTL}	x_{CL}	Pa	Pa	γ_{CL}^{NRTL}
	315.3 K				320.3 K				331.9 K		
1.00	2.86	2.86	1.00	1.00	4.42	4.42	1.00	1.00	11.44	11.44	1.00
0.748	(1.82^a)	1.80	0.84 (0.85^a)	0.776	(3.05^a)	2.98	0.88 (0.87^a)	0.887	(9.44^a)	9.96	0.98 (0.93^a)
0.682	1.52	1.58	0.81	0.718	2.72	2.76	0.87	0.853	9.25	9.56	0.98
0.623	1.36	1.41	0.79	0.652	2.48	2.45	0.85	0.796	9.19	8.92	0.98
0.569	1.27	1.25	0.77	0.488	1.71	1.73	0.80	0.723	7.74	8.02	0.97
0.548	1.23	1.19	0.76	0.262	0.70	0.75	0.65	0.595	6.46	6.40	0.94
0.458	0.94	0.94	0.72	0.228	0.60	0.62	0.62	0.453	4.94	4.61	0.89
0.397	0.81	0.77	0.68	0.193	0.49	0.49	0.58	0.421	4.41	4.24	0.88
0.349	0.61	0.65	0.65	0.154	0.38	0.36	0.53	0.171	1.17	1.29	0.66
0.223	0.36	0.34	0.54	0.139	0.29	0.31	0.51	0.124	0.82	0.85	0.6
0.193	0.30	0.28	0.51	0.081	0.17	0.15	0.42	0.066	0.40	0.39	0.51
0.121	0.15	0.15	0.42	0.061	0.10	0.11	0.39	0.038	0.22	0.20	0.46
0.00		0.24		0.00		0.28		0			0.40

^{a} Vapor pressure was calculated as $p^{exptl} = \gamma_{CL}^{SLE} \cdot p_0 \cdot x_{CL}$, where γ_{CL}^{SLE} is the activity coefficient for CL calculated as $\gamma_{CL}^{SLE} = x_{CL}^{id}/x_{CL}^{SLE}$ and x_{CL}^{SLE} was calculated by fitted eq 5 using the parameters from Table 5.

Table 7. Parameters of the NRTL Equation for CL + [HMIM][NTf$_2$]

T	$g_{12} − g_{22}$	$g_{21} − g_{11}$	
K	kJ·mol^{-1}	kJ·mol^{-1}	α
315.3	−7.29	−3.11	−0.853
320.3	−8.58	−2.91	−0.944
331.9	−16.00	−2.51	−0.999

126) K; $C = -18.9 \pm 0.6$; $D = (0.0113 \pm 0.0006)$ K^{-1}; $p^o = 1$ Pa; and $\theta = 442$ K.[13]

The empirical $\ln \gamma_{CL} = f(x_{CL})$ dependence at the studied temperatures was described using the NRTL (nonrandom two-liquid) model[22]

$$\ln \gamma_1^{NRTL} = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (9)$$

where $\gamma_1^{NRTL} = \gamma_{CL}^{NRTL}$; $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$; $\tau_{ij} = (g_{ij} - g_{jj})/RT$; and $\alpha_{ij} = \alpha_{ji} = \alpha$ ($i,j = 1,2$; $i \neq j$). The parameters $(g_{ij} - g_{jj})$ and α were obtained with the minimization of the function

$$F = \sum_{i=1}^{n} [p_i^{exptl} - p_i^{NRTL}]^2$$

where n is the number of experimental points; $p^{NRTL} = \gamma_{CL}^{NRTL} \cdot p_0 \cdot x_{CL}$; p^{exptl} is the vapor pressure of CL above a solution; p_0 is the vapor pressure of pure CL; and x_{CL} is a mole fraction of CL. The parameters α and $(g_{ij} - g_{jj})$ obtained by the fitting procedure are contained in Table 7.

The deviation of the experimental data from the smoothing curve does not exceed ± 10 % (Figure 4). The plots of eq 9 for CL with [HMIM][NTf$_2$] are shown in Figure 5. Values of activity coefficients for CL in the system CL + [HMIM][NTf$_2$] estimated from VLE and SLE measurements are in good agreement. The activity coefficient of CL decreases with a decrease in both mole fraction, x_{CL}, and temperature.

Table 8. Experimental Results of γ^∞ for Caprolactam and Cyclohexanone Oxime in [HMIM][NTf$_2$]

substance	T	γ^∞	$\langle T \rangle$	$\bar{H}_i^{E,\infty}(\langle T \rangle)$	$\bar{C}_{p,m,i}^{E,\infty}(\langle T \rangle)$
	K		K	kJ·mol^{-1}	J·K·mol^{-1}
caprolactam	427.5	0.49	−	−	−
cyclohexanone	364.9	2.61	403.3	13.3 ± 0.3	175 ± 29
oxime	375.4	2.41			
	386.0	2.22			
	396.5	2.03			
	407.0	1.84			
	417.1	1.67			
	417.6	1.61			
	427.5	1.51			
	438.0	1.28			

Activity coefficients at infinite dilution γ^∞ for CL at 427 K as well as those for CHO in the temperature range (365 to 438) K in [HMIM][NTf$_2$] were determined by GC. The values are listed in Table 8. The values of retention time t_r for CL below 423 K were too high and exceeded the limits of repeatability of GC, so we could measure γ_{CL}^∞ only at one temperature.

The values of γ^∞ for CHO in the range (365 to 438) K have been approximated by the equation

$$\ln(\gamma^\infty/\gamma^\infty(\theta)) = A[(1/T) - (1/\theta)] - B[(\theta/T) - 1 + \ln(T/\theta)] \quad (10)$$

where $\theta = 403.3$ K, $A = (1595 \pm 40)$ K, and $B = 21 \pm 4$. The excess partial molar enthalpy $\bar{H}_m^{E,\infty}$ and heat capacity $\bar{C}_{p,m}^{E,\infty}$ at infinite dilution for CHO were calculated as $\bar{H}_m^{E,\infty} = AR$ and $\Delta \bar{C}_{p,m}^{E,\infty}(\theta) = BR$ (Table 8). The big temperature gap between the GC data points and the SLE and VLE ones of γ_{CL}^∞ impedes interpolation, but it is evident that two of the data lumps do not contradict one another.

Conclusion

Physical chemical parameters of equilibrium in the binary mixtures caprolactam + 1-hexyl-3-methylimidazolium bis-

(trifluoromethylsulfonyl)imide and cyclohexanone oxime + 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide have been obtained. The parameters may be used when estimating the possibility of 1-hexyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide application for caprolactam production improvement. The results show that the solubility of caprolactam in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide noticeably differs from the solubility of cyclohexanone oxime.

Acknowledgment

Literature Cited

(1) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH Verlag, GmbH&Co. KGaA: Weinheim, 2003.

(2) Welton, T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem. Rev.* **1999**, *99*, 2071−2083.

(3) Ren, R. X.; Zueva, L. D.; Ou, W. Formation of ϵ-caprolactam via Catalytic Beckmann Rearrangement Using P$_2$O$_5$ in Ionic Liquids. *Tetrahedron Lett.* **2001**, *42*, 8441−8443.

(4) Gui, J.; Deng, Y.; Hu, Z.; Sun, Z. A Novel Task-Specific Ionic Liquid for Beckmann Rearrangement: A Simple and Effective Way for Product Separation. *Tetrahedron Lett.* **2004**, *45*, 2681−2683.

(5) Young, C. L.; Conder, J. R. *Physicochemical Measurements by Gas Chromatography*; Wiley: New York, 1979.

(6) Kozyro, A. A.; Kabo, G. J.; Krouk, V. S. et. al. Thermodynamic Properties of Cyclohexanone Oxime. *J. Chem. Thermodyn.* **1992**, *24*, 883−895.

(7) Blokhin, A. V.; Kabo, G. J.; Paulechka, Y. U. Thermodynamic Properties of [C$_6$mim][NTf$_2$] in the Condensed State. *J. Chem. Eng. Data* **2006**, *51*, 1377−1388.

(8) Shimizu, Y.; Ohte, Y.; Yamamura, Y.; Saito, K.; Atake, T. Low-Temperature Heat Capacity of Room-Temperature Ionic liquid, 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. *J. Phys. Chem. B* **2006**, *110*, 13970−13975.

(9) Kabo, G. J.; Zaitsau, Dz. H.; Paulechka, Y. U.; Blokhin, A. V.; Verevkin, S. P.; Heintz, A.; Emel'yanenko, V. N. *Comprehensive Study of Thermodynamic Properties of Cyclohexanone Oxime*, 19th International Conference on Chemical Thermodynamics, Boulder, Colorado, U.S.A., July 30−August 4, 2006; Book of Abstracts, p 628.

(10) Gorodetski, I. Ya.; Morachevski, A. G.; Olevski, V. M. Vapor−Liquid Equilibrium and Mutual Solubility in Cyclohexanone−Water System. *Vestn. Leningr. Univ.* **1959**, (22), 136−139.

(11) Zaitsau, Dz. H.; Verevkin, S. P.; Paulechka, Y. U.; Kabo, G. J.; Sevruk, V. M. Comprehensive Study of Vapor Pressures and Enthalpies of Vaporization of Cyclohexyl Esters. *J. Chem. Eng. Data* **2003**, *48*, 1393−1400.

(12) Zaitsau, Dz. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; Tschersich, A.; Verevkin, S. P.; Heintz, A. Experimental Vapor Pressures of 1-Alkyl-3-methylimidazolium Bis(trifluoromethanesulfonyl) Imides and a Correlation Scheme for Estimation of Vaporization Enthalpies of Ionic Liquids. *J. Phys. Chem. A* **2006**, *110*, 7303−7306.

(13) Zaitsau, Dz. H.; Paulechka, Y. U.; Kabo, G. J.; Kolpikau, A. N.; Emel'yanenko, V. N.; Heintz, A.; Verevkin, S. P. Thermodynamic of the Sublimation and of the Vaporization of ϵ-Caprolactam. *J. Chem. Eng. Data* **2006**, *51*, 130−135.

(14) Wahlbeck, P. G. Effusion. VII. The Failure of Isotropy of a Gas in an Effusion Cell and the Transition Region. *J. Chem. Phys.* **1971**, *55*, 1709−1715.

(15) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. Thermodynamic Properties of Mixtures Containing Ionic Liquids. 1. Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkylbenzenes in 4-Methyl-*N*-butylpyridinium Tetrafluoroborate Using Gas−Liquid Chromatography. *J. Chem. Eng. Data* **2001**, *46*, 1526−1529.

(16) Cruickshank, A. J. B.; Windsor, M. L.; Young, C. L. The Use of Gas−Liquid Chromatography to Determine Activity Coefficients and Second Virial Coefficients of Mixtures. *Proc. R. Soc.* **1966**, *A295*, 259−270.

(17) Grant, D. W. *Gas−Liquid Chromatography*; Van Nostrand Reinhold Company: London, 1971.

(18) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice Hall: New York, 1986.

(19) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. Measurements of Vapor Pressure, Heat Capacity, and Density along the Saturation Line for ϵ-Caprolactam, Pyrazine, 1,2-Propanediol, Triethylene Glycol, Phenyl Acetylene, and Diphenyl Acetylene. *J. Chem. Eng. Data* **2002**, *47*, 689−699.

(20) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

(21) Walas, S. M. *Phase Equilibria in Chemical Engineering*; Butterworth Publishers: Boston, 1985

(22) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *12*, 135−144.