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Thermochimica Acta 433 (2005) 149–152
thermochimica acta
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Heat capacities of ionic liquids and their heats of solution in molecular liquids

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Received 23 November 2004; received in revised form 23 February 2005; accepted 1 March 2005
Available online 7 April 2005

Abstract

Heat capacities of ionic liquids (IL): 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMImBF_4$), 1-ethyl-3-methyl imidazolium bis((trifluoromethyl)sulfonyl) imide ($EMImN(CF_3SO_2)_2$), 1-bytyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) and *N*,*N*-methyl, propyl pyrrolidinium bis((trifluoromethyl)sulfonyl) imide ($MPPyN(CF_3SO_2)_2$) were measured from 283.15 to 358.15 K. Room temperature heat capacities have also been estimated by an additive group contribution method, based on the assumption that the heat capacity of a molecular compound equals the sum of individual atomic-group contributions. The $C_p^{293.15\,\mathrm{K}}$ estimated values are about 12% higher than experimental values. The estimates suggest that heat capacities of ionic liquids do not differ considerably from those typical for molecular liquids (ML). The heats of solution, $\Delta_{\mathrm{sol}}H$, of ionic liquids $EMImBF_4$, $BMImBF_4$ $EMImN(CF_3SO_2)_2$ and $MPPyN(CF_3SO_2)_2$ were measured in water, acetonitrile (AN) and methanol, as a function of ionic liquid concentration c_{m}. The measured $\Delta_{\mathrm{sol}}H$ values decrease with decreasing c_{m}. Enthalpies of ionic liquid transfer, $\Delta_{\mathrm{t}}H^{\circ}$, from water to methanol and acetonitrile were calculated from measured solution enthalpies. Values of $\Delta_{\mathrm{t}}H^{\circ}$ for the transfer from water to methanol are positive and those for the transfer to acetonitrile are negative.

Keywords: Heat capacity; Solution enthalpy; Transfer enthalpy; Ionic liquid

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1. Introduction

Enthalpies of dissolution of various solutes in different molecular solvents, $\Delta_{\mathrm{sol}}H$, have been measured for many systems and critically reviewed [1,2]. Much data are available in the literature on thermodynamics of individual ion solvation (or transfer) [2–5]. There is growing interest in room temperature ionic liquids (RTIL), a new class of liquid media. Both the thermodynamics and kinetics of chemical processes carried out in ionic liquids (IL) may differ considerably from those in conventional molecular liquids (ML). These new solvents are characterised by negligible vapour pressure, and hence, emit no volatile organic compounds (VOC), in contrast to molecular liquids. Chloroaluminate ionic liquids, especially 1-ethyl-3-methylimidazolium chloroaluminate ($EMImAlCl_4$), seem to have been the first extensively examined RTIL. However, ionic liquids based on the chloroaluminate anion are moisture sensitive, which limits their possible application. More recently, numerous non-chloroaluminate room temperature ionic liquids have been synthetized and studied [6–8]. There are papers reporting phase equilibria in the system molecular compound—ionic liquid [9] or describing transfer free enthalpies of single-ions from a molecular solvent to a number of ionic liquids [10,11]. However, to our knowledge, there are no systematic thermodynamic (thermochemical) studies available in the literature concerning the formation of ionic liquids and their solutions. The general aim of this paper is to investigate heats of solution of ionic liquids in molecular solvents, as well as the heat capacity of neat ionic liquids.

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doi:10.1016/j.tca.2005.03.001

2. Experimental

2.1. Ionic liquids

Hexane (Merck), acetonitrile (AN) (Merck), bromoethane (Fluka), chlorobutane (Fluka, >99.5%), 1,1,1-trichloroethane (POCh Gliwice, Poland) and acetonitrile (Merck), necessary for ionic liquid synthesis, were distilled through a 60 cm long Vigreux column. An aqueous solution of silver tetrafluoroborate ($AgBF_4$) was prepared by reacting tetrafluoroboric acid, (HBF_4, Aldrich, 48% solution in water) with silver oxide (POCh Gliwice, Poland). 1-Ethyl-3-methylimidazolium bromide (EMImBr) was prepared by substitution of bromoethane to 1-methylimidazole (Fluka) in trichloroethane (POCh) [12]. 1-Ethyl-3-methylimidazolium tetrafluoroborate ($EMImBF_4$) was obtained by titration of an aqueous solution of $AgBF_4$ with an aqueous solution of EMImBr versus a silver indicating electrode [13]. 1-Ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl) imide ($EMImN(CF_3SO_2)_2$) was prepared from $LiN(CF_3SO_2)_2$ (Fluka) and EMImBr aqueous solutions [12]. 1-Butyl-3-methylimidazolium chloride (BMImCl) was prepared by reacting chlorobutane with 1-methylimidazole [14]. 1-Butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) was prepared from aqueous solutions of $NaBF_4$ and BMImCl [13]. 1-Methyl-1-propylpyrrolidinium iodide (MPPyI) was obtained by reacting propyl iodide with a solution of 1-methylpyrrolidine (Fluka) in acetonitrile [15]. 1-Butyl-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl) imide ($BMPyN(CF_3SO_2)_2$) was prepared from aqueous solutions of BMPyI and $LiN(CF_3SO_2)_2$ [15]. The water content, analysed with Karl Fischer titrant (Aldrich, Cat. No. 22,120-1), was below the detection limit (<4.5 mg H_2O/cm^3).

2.2. Solvents

Acetonitrile (Aldrich, 99.8%) and methanol (P.O.Ch. Gliwice, AR grade) were purified by distillation in a nitrogen atmosphere. Deionised, double-distilled water and organic solvents were outgassed under reduced pressure before use.

2.3. Measurements

Heats of ionic liquid dissolution in molecular solvents were measured with an isoperibol temperature-rise calorimeter. The 90 cm^3 glass calorimetric vessel was equipped with a calibration heater, a 10 kΩ thermistor in a Wheatstone bridge and a stirrer-ampoule holder. A thin-walled glass ampoule containing the substance to be dissolved was attached to the ampoule holder (the stirrer) and crushed against the bottom of the calorimetric vessel during the experiment. A temperature change of approximately 3×10^{-5} K could be detected. The calorimeter was placed in a hermetically closed brass jacket with a capacity of about 1 dm^3 and immersed in a water thermostat. The temperature stability of the thermostat was better than 1×10^{-3} K. The electrical calibration of the calorimeter was verified by a test reaction of KCl dissolution in water.

Specific heat capacities of the ionic liquids were measured with a Micro DSC III scanning calorimeter (Setaram, France) from 283.15 to 359.15 K at 0.35 K/min, according to the procedure proposed by Goralski et al. [16]. The differential heat rate was measured for: (1) an empty vessel; (2) the vessel with *n*-heptane as a reference substance; and (3) the vessel containing the ionic liquid. The experimental vessel was made of Hastelloy C276 and had a volume of ca. 1 cm^3. An alloy block was used as a reference (instead of the vessel). The accuracy of C_p determination was of the order of ±0.15%.

The samples of ionic liquids were weighed with an accuracy of 10^{-5} g using a Sartorius RC210D balance. All operations with ionic liquids were performed in a glove box in a dry nitrogen atmosphere.

3. Results and discussion

3.1. Heats of solution

Heats of solution, $\Delta_{sol}H$, of ionic liquids $EMImBF_4$ and $BMImBF_4$ in acetonitrile as a function of ionic liquid concentration c_m are collected in Table 1. The measured $\Delta_{sol}H$ decreases with decreasing IL concentration. The enthalpy of solution at infinite dilution, $\Delta_{sol}H^\circ$, was determined by linear extrapolation of measured $\Delta_{sol}H$ values to $\sqrt{c_m} = 0$. In the other systems (water and methanol), five to six independent measurements of the dissolution enthalpy were performed in each solvent. The final concentrations of ILs, c_m, ranged from 0.0015 to 0.01 mol/kg. As no concentration dependence was observed, the measured enthalpies, $\Delta_{sol}H$, were regarded as the values at infinite dilution, $\Delta_{sol}H^\circ$. Table 2 contains $\Delta_{sol}H^\circ$ values for all the systems studied.

Dissolution of ionic liquid in the molecular solvents may be either endothermic or exothermic, within a relatively narrow range of ca. +20 and −5 kJ/mol. Enthalpy of solution, $\Delta_{sol}H^\circ$, is a sum of enthalpy of solvation, $\Delta_{solv}H^\circ$, which reflects the solute–solvent interaction, and enthalpy of vapor-

Table 1
Heats of solution of ionic liquids ($EMImBF_4$ and $BMImBF_4$) in acetonitrile (AN) as a function of ionic liquid concentration; $T = 298.15$ K

$EMImBF_4$ + AN		$BMImBF_4$ + AN	
c_m (mol/kg)	$\Delta_{sol}H$ (J/mol)	c_m (mol/kg)	$\Delta_{sol}H$ (J/mol)
0.00443	−4.56 ± 0.14	0.00215	−4.86 ± 0.14
0.00580	−4.53 ± 0.14	0.00218	−4.84 ± 0.14
0.00661	−4.53 ± 0.14	0.00299	−4.80 ± 0.14
0.00736	−4.51 ± 0.14	0.00409	−4.74 ± 0.14
0.00891	−4.48 ± 0.14	0.00429	−4.74 ± 0.14
0.01011	−4.48 ± 0.14	0.00594	−4.68 ± 0.14
0.01024	−4.47 ± 0.14	0.00778	−4.59 ± 0.13
0.01291	−4.43 ± 0.14	0.00902	−4.53 ± 0.13
0.01373	−4.40 ± 0.13	0.01009	−4.50 ± 0.13
0.01868	−4.35 ± 0.13	0.01152	−4.46 ± 0.13

Table 2
Heats of solution, $\Delta_{sol}H^\circ$, of ionic liquids in molecular solvents at infinite dilution as well as enthalpy of transfer from water to methanol and acetonitrile, $\Delta_t H^\circ$; $T = 298.15$ K

Solvent	$\Delta_{sol}H^\circ$ (kJ mol^{-1})	$\Delta_t H^\circ$(W → S) (kJ mol^{-1})
$EMImBF_4$		
Water	17.33 ± 0.27	–
Methanol	19.02 ± 0.13	1.7
Acetonitrile	−4.77 ± 0.15	−22.1
$BMImBF_4$		
Water	15.81 ± 0.31	–
Methanol	18.50 ± 0.22	2.7
Acetonitrile	−5.15 ± 0.15	−21.0
$MPPyN(CF_3SO_2)_2$		
Water	4.24 ± 0.53	–
Methanol	14.51 ± 0.30	10.3
Acetonitrile	0.44 ± 0.04	−3.8
$EMImN(CF_3SO_2)_2$		
Water	7.81 ± 0.47	–
Methanol	13.73 ± 0.31	5.9
Acetonitrile	−2.18 ± 0.34	−10.0

Table 3
Estimated heats of individual ion transfer from water to methanol and acetonitrile, based on the assumption that $1/2[\Delta_t H^\circ(EMIm^+) + \Delta_t H^\circ(BMIm^+)] = \Delta_t H^\circ(BF_4^-)$; $T = 298.15$ K

	$\Delta_t H^\circ$ (kJ/mol)	
	Methanol	Acetonitrile
BF_4^-	1.1	−10.8
$EMIm^+$	0.6	−11.3
$BMIm^+$	1.6	−10.2
$MPPy^+$	5.0	−4.3
$N(CF_3SO_2)_2^-$	5.3	0.5

ization, $\Delta_{vap}H^\circ$, to form an ideal gas by the solute molecules. Ionic liquids are characterised by negligible vapour pressure, and therefore, the $\Delta_{vap}H^\circ$ values are not experimentally accessible. As a consequence, splitting the measured enthalpy of solution into both components ($\Delta_{solv}H^\infty$ and $\Delta_{vap}H^\circ$), in order to obtain the enthalpy of solvation, is not possible. However, it is possible to determine the difference in the solvation enthalpy of the same IL in two different solvents, $\Delta_t H^\circ$, by subtracting the enthalpies of solution:

$$\Delta_t H^\circ(A \to B) = \Delta_{sol} H^\circ(B) - \Delta_{sol} H^\circ(A)$$

Enthalpies of transfer from water to methanol and acetonitrile are listed in Table 2. Values of $\Delta_t H^\circ$ for the transfer from water to methanol are positive and those for the transfer to acetonitrile negative. From the molecular point of view, the enthalpy of solute solvation, $\Delta_{solv}H$, is the sum of three components: (i) enthalpy of disconnecting the ion aggregates in the theoretical gas phase (endothermic effect); (ii) enthalpy of formation of a cavity in the solvent (endothermic effect) as well as (iii) the enthalpy of solute–solvent interaction (exothermic effect). As can be seen from Table 2, IL dissolution in aprotic acetonitrile is associated with slightly exothermic total effect, while in the case of protic solvents (water and methanol), the total effect is endothermic.

3.2. Single ion transfer enthalpies

Single-ion solvation enthalpies or single-ion transfer enthalpies are necessary for further understanding of the IL interaction with a molecular solvent. While the enthalpies of IL transfer from one medium to another can be derived directly on the basis of strict thermodynamics, the single-ion enthalpies require an extra-thermodynamic assumption. Methods for estimation of single-ion properties are based on the idea that large cations and anions of low charge density, e.g. Ph_4As^+ and BPh_4^-, should be solvated similarly in different solvents. Thus, the assumption that the transfer enthalpy of the electrolyte is the sum of equal cation and anion contributions, i.e. $\Delta_t H^\circ(Ph_4As^+) = \Delta_t H^\circ(BPh_4^-)$, may be used for the estimation of single-ion transfer enthalpies. Ionic liquids consist, in general, of large ions having a low charge density, which reduces the lattice energy of the salts and hence lowers their melting point. From this perspective, some of them, especially those consisting of relatively large and symmetrical anions, can be regarded as reference electrolytes, for example, $EMImBF_4$ or $BMImBF_4$. Assuming that $\Delta_t H^\circ(EMIm^+) \approx \Delta_t H^\circ(BF_4^-)$ and $\Delta_t H^\circ(BMIm^+) \approx \Delta_t H^\circ(BF_4^-)$, which is equivalent to $\Delta_t H^\circ(BF_4^-) = 1/2[\Delta_t H^\circ(EMIm^+) + \Delta_t H^\circ(BMIm^+)]$, the value of $\Delta_t H^\circ(BF_4^-,\ W \to MeOH) = 1.1 \pm 0.3$ kJ/mol for the BF_4^- transfer from water to methanol may be estimated from the $EMImBF_4$ and $BMImBF_4$ transfer enthalpies listed in Table 2. This value agrees very well with the literature data (1.2 kJ/mol) derived from Ph_4AsBPh_4 assumption [2]. The agreement suggests that $EMImBF_4$ and $BMImBF_4$ salts can be treated as reference electrolytes, similar to the Ph_4AsBPh_4 salt, leading to $\Delta_t H^\circ(BF_4^-,\ W \to \text{acetonitrile}) = -10.8 \pm 0.6$ kJ/mol. The $\Delta_t H^\circ(BF_4^-)$ transfer enthalpies lead to the transfer enthalpies of the remaining ions in Table 3. Transfer from water to methanol has a positive enthalpy change in the case of all ions. The transfer of all cations and BF_4^- to acetonitrile is exothermic, while the transfer of the imide anion is slightly positive. The transfer enthalpies of individual ions, estimated using any method, cannot be proved or disproved. However, they provide useful information about differences in solvation enthalpies of ions in different solvents.

3.3. Heat capacities of ionic liquids

Heat capacities of neat ionic liquids at 5 K intervals are shown in Table 4. The heat capacity increases linearly with temperature. Room temperature heat capacities of ionic liquids have also been estimated with an additive group contribution method. The method is based on the assumption that the heat capacity equals the sum of individual atomic-group contributions. Such data are available [17] for C_p calculation for $MPPyN(CF_3SO_2)_2$ and $EMImN(CF_3SO_2)_2$. The estimated $C_p^{293.15\,K}$ values are approximately 12% higher than

Table 4
Ionic liquid heat capacities C_p (expressed in J/g/K and J/mol/K)

T (K)	$EMImBF_4$		$BMImBF_4$		$EMImN(CF_3SO_2)_2$		$MPPyN(CF_3SO_2)_2$	
	J/g/K	J/mol/K	J/g/K	J/mol/K	J/g/K	J/mol/K	J/g/K	J/mol/K
283.15	1.532	303.4	1.583	357.8	1.274	502.3	1.333	544.2
288.15	1.540	304.9	1.593	360.2	1.280	504.6	1.341	547.5
293.15	1.548	306.5	1.604	362.5	1.285	506.9	1.349	550.7
298.15	1.556	308.1	1.614	364.8	1.291	509.2	1.357	554.0
303.15	1.565	309.8	1.624	367.2	1.297	511.5	1.365	557.3
308.15	1.573	311.5	1.635	369.5	1.303	513.8	1.373	560.6
313.15	1.582	313.2	1.645	371.9	1.309	516.1	1.381	563.9
318.15	1.591	315.0	1.656	374.3	1.315	518.5	1.389	567.2
323.15	1.600	316.8	1.666	376.6	1.321	520.9	1.397	570.5
328.15	1.610	318.7	1.677	379.0	1.327	523.3	1.405	573.8
333.15	1.619	320.6	1.688	381.4	1.333	525.7	1.413	577.2
338.15	1.629	322.5	1.698	383.9	1.339	528.1	1.422	580.5
343.15	1.639	324.5	1.709	386.3	1.345	530.5	1.430	583.9
348.15	1.649	326.5	1.720	388.7	1.352	533.0	1.438	587.2
353.15	1.660	328.6	1.731	391.2	1.358	535.5	1.446	590.6
358.15	1.670	330.7	1.741	393.6	1.364	538.0	1.455	594.0

$EMImBF_4$: 1-ethyl-3-methylimidazolium tetrafluoroborate; $EMImN(CF_3SO_2)_2$: 1-ethyl-3-methyl imidazolium bis((trifluoromethyl)sulfonyl) imide; $BMImBF_4$: 1-bytyl-3-methylimidazolium tetrafluoroborate; $MPPyN(CF_3SO_2)_2$: *N*,*N*-methyl, propyl pyrrolidinium bis((trifluoromethyl)sulfonyl) imide.

experimental values. For $EMImN(CF_3SO_2)_2$, a heat capacity ($C_p^{293.13\,K}$) of 562.2 J/mol/K is calculated, while the experimental value 506.9 J/mol K is circa 55 J/mol/K lower. Similarly, the estimated $C_p^{293.15K}$ value for $MPPyN(CF_3SO_2)_2$ (623.6 J/mol/K) is approximately 70 J/mol/K higher than the experimental value ($C_p^{293.15\,K} = 550.7$ J/mol/K). The group-contribution method was constructed from data for molecular liquids where the agreement between experimental and estimated C_p value was generally within 2–3% and almost always within 5%. The estimates for ILs suggest that the heat capacities of ILs are greater than those for molecular liquids because of ion–ion interactions.

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