

Excess enthalpy and excess volume for binary systems of two ionic liquids + water

Silvia Porcedda · B. Marongiu · Manuela Schirru ·
D. Falconieri · Alessandra Piras

AICAT2010 Special Chapter
© Akadémiai Kiadó, Budapest, Hungary 2010

Abstract In this work we report the experimental measurements of excess molar enthalpy and excess molar volume, at 298.15 K and atmospheric pressure, on ethylammonium nitrate (EAN) and propylammonium nitrate (PAN) + water mixtures. Positive enthalpies were found for the two systems (maximum, at x_1 around 0.37 correspond to about 700 and 900 J mol⁻¹ for EAN and PAN respectively). As the hydrophobic/hydrophilic ratio increases, along with the length of the alkyl chain in the ionic liquids, ILs, the specific interactions IL-water become less important. The excess molar volumes, V^E , are negative over the entire composition range for the two binary mixtures. They have similar values but curves exhibit a different asymmetric shape and around equimolar composition they intersect each other. This behaviour: positive H^E and negative V^E , is not very common.

Keywords Enthalpy · Ionic liquids · Volume · Water

This paper is a tribute to Dr. Henry V. Kehiaian from Prof. Bruno Marongiu and coworkers.

S. Porcedda · B. Marongiu (✉) · M. Schirru · D. Falconieri ·
A. Piras
Dipartimento di Scienze Chimiche, Università degli Studi di
Cagliari, Cittadella Universitaria, S.P. Monserrato—Sestu,
km 0,700, 09042 Monserrato, CA, Italy
e-mail: maronb@unica.it

S. Porcedda
e-mail: porcedda@unica.it

M. Schirru
e-mail: schirru.manu@tiscali.it

D. Falconieri
e-mail: danilo.falconieri@tiscali.it

A. Piras
e-mail: apiras@unica.it

Introduction

Room Temperature Ionic Liquids (RTILs) are a class of organic molten electrolytes which are liquids around room temperature [1]. They have specific properties such as negligible vapour pressures, high ionic conductivity, outstanding catalytic properties, non inflammability and often stability from room temperature up to 300 °C or more [2]. Moreover, the physical and chemical properties of RTILs can be adjusted by proper selection of the kind of anion, cation and substituting groups of the cation [3]. RTILs are also potential environmentally friendly solvents since their non volatile nature can prevent environmental pollution. There are several publications devoted to experimental and theoretical thermodynamic studies on pure ILs and their mixtures with common organic solvents [4–6], most of them concerning imidazolium-based ILs. Some works have dealt with the thermodynamic properties of (RTILs + water) binary systems [7–9], and a growing number of investigations on the thermodynamic properties of such systems is being carried out. In this work we report the experimental measurements of excess molar enthalpy and excess molar volume on ethylammonium nitrate (EAN) and propylammonium nitrate (PAN) + water mixtures. Two sources [10, 11] of density-correlated data on EAN + water system are available in literature. Data reported by Bou Malhan [11] were drawn from a previous paper [12]. No further data on thermodynamic properties concerning the system investigated were found.

Experimental section

Materials

Sources and relevant physical properties of substances employed in this study are reported in Table 1. Before using,

Table 1 Supplier, molar masses, purities express as mole fraction and densities at 298.15 K of chemicals used in the experiments

Compound	Supplier	$M^a/\text{g mol}^{-1}$	Purity	$\rho_{\text{exp}}/\text{kg m}^{-3}$	$\rho_{\text{lit}}/\text{kg m}^{-3}$	Source of exp. data
EAN	IoLiTech	108.097	0.97	1209.90	1209.06	[10]
					1210.62	[12]
PAN	IoLiTech	122.123	0.97	1150.90	1156.8 ^b	[14]
Water	–	18.0152		997.04	997.0474	[15]

^a calculated from the atomic weight of elements recommended by IUPAC [13]

^b value at 27 °C

the ILs, purchased from IOLITECH (Ionic Liquids Technologies, Denzlingen, Germany), were kept for several days in an oven set at 40 °C at reduced pressure in presence of phosphorous pentoxide as dehydrator. Water was obtained by distillation and used immediately after preparation.

Apparatus and procedure

Calorimetry

Heats of mixing were determined by means of a flow micro-calorimeter (model 2277—LKB-producer AB, Bromma, Sweden). The apparatus and the experimental procedure are described in detail elsewhere [16]. Fully automatic burettes (ABU80—Radiometer, Copenhagen, Denmark) were used to pump the liquid into the LKB unit. The molar flow rate m_i (mol sec⁻¹), of component i flowing into the mixing cell is given by:

$$m_i = \frac{\Phi_i \rho_i}{M_i} \quad (1)$$

where Φ_i is the volumetric flow rate, ρ_i the density and M_i the molar mass.

The molar excess enthalpies have been evaluated from the formula

$$H^E = \frac{I^2 R (E/E_c)}{m_i} \quad (2)$$

where I and R are the electrical current and resistance in the electrical calibration experiment, E and E_c are the voltage readings for measurement and electrical calibration, respectively, and m is the molar flow rate of the mixture. All enthalpy measurements were carried out at 298.15 K. The accuracy of the LKB bath temperature is 0.1 K. The reliability of the apparatus and procedure adopted were checked periodically by performing H^E measurements on the test system benzene + cyclohexane. Our results concerning this system differed by <2% from reliable literature data [17] over the entire composition range.

Volumetry

The necessary density data for the determination of the molar flow in the calorimetric determinations and of the

excess molar volumes were measured with a vibrating tube densitometer (model DMA 58, Anton Paar, Graz, Austria) with a reproducibility of $1 \times 10^{-5} \text{ g cm}^{-3}$. Accuracy in the temperature was better than $\pm 1 \cdot 10^{-2} \text{ K}$ by means of an internal temperature control device that applies the Peltier principle to maintain isothermal conditions. Densitometer calibration was performed before every run using a double reference (water and dry air).

The liquid mixtures were prepared by weighing in septum-capped vials of approximately 2 mL using needles and syringes to transfer liquids.

The molar excess volumes V^E were calculated from the equation:

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (3)$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 the molar masses, ρ_1 and ρ_2 the densities of the two pure components and ρ is the density of the mixture. The procedure was checked by comparison of our experimental V^E data of the water + ethanol system with reliable literature data [18]. Our experimental data differed by less than 0.8% in the whole composition range.

The whole set of experimental data on H^E and V^E are reported in Table 2.

Experimental results and discussion

The experimental Y^E ($Y = H$ or V) data of the binary mixtures containing EAN or PAN (1) with water (2), reported in Table 2, were fitted to the smoothing Redlich–Kister equation:

$$Y^E = x_1 x_2 \sum_{i=0}^{n-1} a_i (x_1 - x_2)^i \quad (4)$$

with 3 or 4 parameters, where x_1 is the mole fraction of the RTILs and n is the number of coefficients. The values of the coefficients a_i and the standard deviation of the fit, $\sigma(Y^E)$:

$$\sigma(Y^E) = \sqrt{\frac{\sum (Y_{i,\text{calc}}^E - Y_{i,\text{exp}}^E)^2}{N - n}} \quad (5)$$

Table 2 Experimental values of the molar excess enthalpies, H^E and of the molar excess volumes, V^E , of binary mixtures of ionic liquid (1) + water (2) at 298.15 K

x_1	$H^E/\text{J mol}^{-1}$	x_1	$H^E/\text{J mol}^{-1}$	x_1	$H^E/\text{J mol}^{-1}$
EAN + water					
0.0166	85.7	0.1683	550.3	0.4473	651.7
0.0247	116.3	0.2125	621.2	0.5484	582.3
0.0482	221.1	0.2329	648.5	0.6182	502.4
0.0919	375.7	0.2881	685.8	0.6693	441.4
0.1189	457.8	0.3778	697.7	0.7083	388.3
PAN + water					
0.0208	95.3	0.2035	780.9	0.5767	658.3
0.0408	189.2	0.2541	852.0	0.6300	582.1
0.0785	355.7	0.3381	895.5	0.6714	516.3
0.1133	504.8	0.4052	860.8	0.7187	443.3
0.1455	625.5	0.5054	758.3	–	–
x_1	$V^E/\text{cm}^3 \text{ mol}^{-1}$	x_1	$V^E/\text{cm}^3 \text{ mol}^{-1}$	x_1	$V^E/\text{cm}^3 \text{ mol}^{-1}$
EAN + water					
0.00640	–0.0363	0.2138	–0.537	0.6179	–0.441
0.02434	–0.123	0.2966	–0.570	0.7474	–0.338
0.05001	–0.224	0.2978	–0.570	0.8188	–0.254
0.07296	–0.302	0.3735	–0.569	0.9075	–0.122
0.08697	–0.340	0.4426	–0.552	0.9112	–0.134
0.12493	–0.424	0.4557	–0.540	0.9554	–0.107
0.1602	–0.480	0.4967	–0.529	–	–
PAN + water					
0.01254	–0.0773	0.2044	–0.5739	0.5998	–0.448
0.01849	–0.111	0.2748	–0.599	0.6990	–0.350
0.05229	–0.275	0.3130	–0.604	0.7986	–0.247
0.07420	–0.357	0.4236	–0.575	0.8380	–0.203
0.1154	–0.464	0.4642	–0.546	0.9667	–0.0356
0.1857	–0.560	0.4975	–0.523	–	–

obtained by un-weighted least squares treatment, where N is the number of experimental points, are given in Table 3.

Experimental excess molar enthalpies, H^E , are represented in Fig. 1. Positive enthalpies were found for the two systems (maximum, at x_1 around 0.37 corresponds to about 700 and 900 J mol^{–1} for EAN and PAN respectively). Therefore, taking into account that the positive excess

enthalpy implicates weaker interaction upon mixing, it can be stated that the forces between the same kind of ions or molecules (IL–IL and water–water interactions) are stronger than those of among dissimilar ones. As the hydrophobic/hydrophilic ratio increases, along with the length of the alkyl chain in the ILs, the specific interactions IL–water become less important.

Table 3 Values of the coefficients, a_i and standard deviations, σ (V^E), values at equimolar composition, $V^E(0.5)$, of molar excess enthalpies, H^E and molar excess volumes, V^E , at 298.15 K, for ionic liquid (1) + water (2) mixtures

Mixtures	$a_0/\text{J mol}^{-1}$	$a_1/\text{J mol}^{-1}$	$a_2/\text{J mol}^{-1}$	$a_3/\text{J mol}^{-1}$	σ (H^E)/J mol ^{–1}	$H^E(0.5)/\text{J mol}^{-1}$
EAN + water	2474.5	–1714.2	859.4	0	5.5	+619
PAN + water	3132.8	2448	214.2	0	18	+783
Mixtures	$a_0/\text{cm}^3 \text{ mol}^{-1}$	$a_1/\text{cm}^3 \text{ mol}^{-1}$	$a_2/\text{cm}^3 \text{ mol}^{-1}$	$a_3/\text{cm}^3 \text{ mol}^{-1}$	σ (V^E)/cm ³ mol ^{–1}	$V^E(0.5)/\text{cm}^3 \text{ mol}^{-1}$
EAN + water	–2.075	1.0149	–1.2794	0.79664	0.012	–0.519
PAN + water	–2.0786	–1.2126	–1.3992	–1.4871	0.0085	–0.520

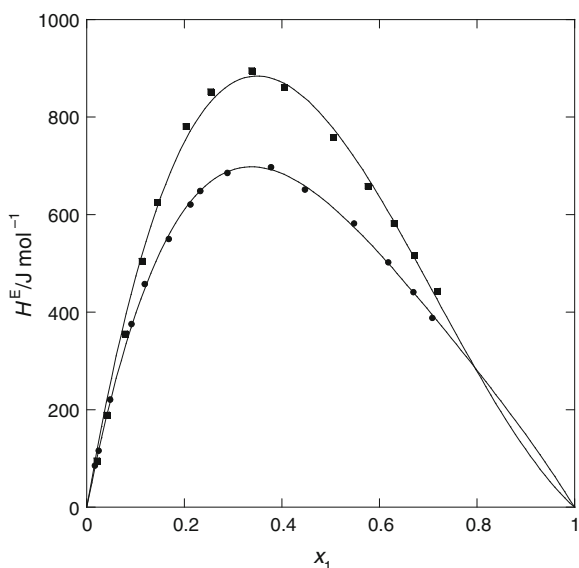


Fig. 1 Experimental molar excess enthalpies, H^E , at 298.15 K, of ionic liquid (1) + water (2) mixtures versus x_1 , the mole fraction of component (1); lines represents the 3-parameters Redlich–Kister equation, points experimental results: *filled circle*, EAN; *filled square*, PAN

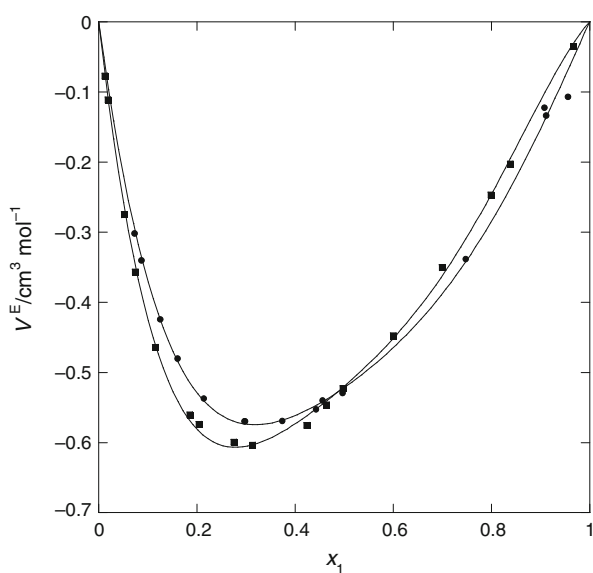


Fig. 2 Experimental molar excess volumes, V^E , at 298.15 K, of ionic liquid (1) + water (2) mixtures versus x_1 , the mole fraction of component (1); lines represents the 4-parameters Redlich–Kister equation, points experimental results: *filled circle*, EAN; *filled square*, PAN

The excess molar volumes V^E for EAN and PAN + water binary mixtures are shown in Fig. 2. V^E are negative over the entire composition range for the two binary mixtures. They have similar values but curves exhibit a different asymmetric shape and around equimolar composition they intersect each other. The minimum is around

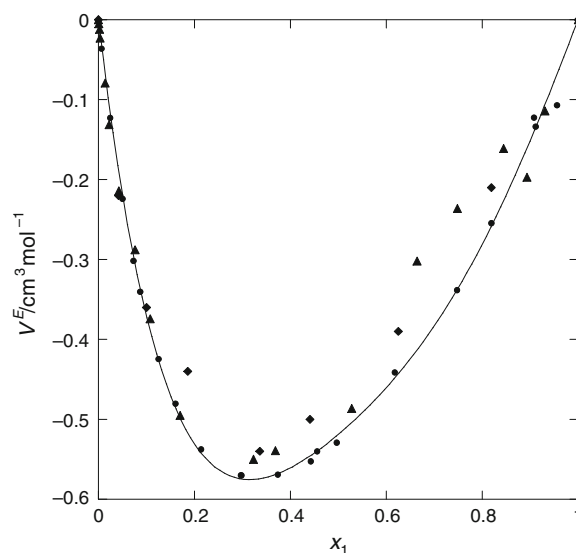


Fig. 3 Experimental molar excess volumes, V^E , at 298.15 K, EAN (1) + water (2) mixtures versus x_1 , the mole fraction of component (1), comparison with literature data: *filled circle*, this work; *filled diamond*, [11]; *filled inverted triangle*, [10]

$x_1 = 0.3$ for EAN and 0.25 for PAN. More negative values are reached by the PAN-containing mixtures in the water-rich region, on the contrary at high IL-rich concentration more exothermic effects are attributable to EAN. In Fig. 3 are reported our V^E data of the EAN + water system along with other similar results. Data of Hadded et al. [12] were get from the paper of Bou Malham et al. [11] that reports the desired V^E values in explicit form. The V^E attributed to Allen [10] were calculated from the partial molar volumes reported in the paper. The agreement is good only at very low concentration of IL. Our results are more negative with respect to those reported in ref 10 of about 9% at equimolar composition. Data of Allen et al. [10] appear quite scattered especially at high values of mole fraction of component 1. The V^E values result from the chemical physical and structural characteristics of liquids. Usually the difference in size and shape of the two components and the loss of dipolar association leads to expansion in volume. The physical interaction between unlike molecules such as dipole–dipole and ion–dipole interactions results in contraction in volume. This behaviour: positive H^E and negative V^E , is not very common but possible (usually the above mentioned properties have the same sign). Similar trends are typical, for example, in n-alkane + alcohols mixtures [8]. In that case the negative value of the V^E was ascribed to the accommodation of the alkane in the interstices of the hydrogen bonded structure of the alcohol. A similar hypothesis, in our case the accommodation of the IL in the structure of the water, should be confirmed by a structural investigation.

References

1. Welton T. *Chem Rev.* 1998;99:2071–84.
2. Rogers RD, Seddon KR. *Science.* 2003;302:792–3.
3. Li RX. *Green solvents: synthesis and applications of ionic liquids.* Beijing: Chemistry Technology Press; 2004.
4. Kandil ME, Marsh KN, Goodwin ARH. *J Chem Eng Data.* 2007;52:2382–7.
5. Diedrichs A, Gmehling J. *Fluid Phase Equilib.* 2006;244:68–77.
6. Gomez E, Gonzales B, Calvar N, Tojo E, Dominguez A. *J Chem Eng Data.* 2006;51:2096–102.
7. Guan W, Li L, Wang H, Tong J, Yang JZ. *J Therm Anal Cal.* 2008;94:507–10.
8. Garcia-Miaja G, Troncoso J, Romani L. *J Chem Thermodyn.* 2009;41:161–6.
9. Rodriguez H, Brennecke JF. *J Chem Eng Data.* 2006;51:2145–55.
10. Allen M, Evans DF, Lumry R. *J Solut Chem.* 1985;14:549–60.
11. Bou Malham I, Letellier P, Mayaffre A, Turmine M. *J Chem Thermodyn.* 2007;39:1132–43.
12. Hadded M, Biquard M, Letellier P, Shaal R. *Can J Chem.* 1985;63:565–70.
13. Weiser ME. *Pure Appl Chem.* 2006;78:2051–66.
14. Greaves TL, Drummond CJ. *Chem Rev.* 2008;108:206–37.
15. Riddick JA, Bunger WB, Sakano TK. *Organic solvents, physical properties and methods of purification.* New York: Wiley; 1986.
16. Monk P, Wadsö I. *Acta Chem Scan.* 1968;22:1842–52.
17. Marsh KN. *Int Data Ser Sel Data Mix Ser A* 1973;1–5.
18. Marsh KN, Richards AE. *Aust J Chem.* 1980;33:212132.