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ELECTROLYTIC CONDUCTIVITY AND MOLAR HEAT CAPACITY OF AQUEOUS SOLUTION OF 1-ETHYL-3-METHYLIMIDAZOLIUM DICYANAMIDE

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ABSTRACT

New measurements of electrolytic conductivity, κ, and molar heat capacity, C_P, for aqueous solutions of ionic liquid, 1-ethyl-3-methylimidazolium dicyanamide, were reported here for temperature up to 353.2 K using a commercial conductivity meter and differential scanning calorimeter for κ and C_P measurements, respectively. The estimated measurement uncertainties for κ and C_P were ±1 and ±2 %, respectively. The present κ and C_P data were reported as a function of temperature and composition. A modified empirical equation from another researcher was used to correlate the temperature and composition dependence of the present κ data and an excess molar heat capacity, C_P^E, expression using the Redlich–Kister type equation for the latter's temperature and compositional dependence was used to represent the measured C_P and C_P^E of the considered solvent systems. The applied correlations represent the κ and C_P measurements satisfactorily as shown by an acceptable overall average deviation of 7.8 and 0.1 %, respectively.

INTRODUCTION

Solutions of alkanolamines are industrially important compounds because they are effective on CO_2 removal. But the used of these compounds usually requires higher energy consumption and operational cost, and also comes with solvent pollutions. On the other hand, in recent years, there has been a new class of compound, termed as green solvents, which is now recognized as a versatile alternative to aqueous alkanolamine solutions. This class, known as room-temperature ionic liquids (RTILs) are organic salts that are liquids at ambient temperature and because of their unique properties, such as low volatility, non-flammability, high thermal stability, and high solvation capacity, [1, 2] they have attracted a number of research groups such that these groups had been doing a systematic measurement and collection of the thermophysical and transport properties of RTILs [3-13] for the last decade.

Although, RTILs have been the focus of attention of these researchers for sometime, the data bank for physicochemical properties are still wanting, as in the case of κ and C_P. Most studies reported on κ and C_P measurements are for pure system; those for mixtures including RTILs are still scarce in the open literature [14-23].

For the considered solvent systems, $[Emim][C_2N_3] + H_2O$, as far as we know, there is no available literature data for κ and C_P. Thus, in this work, κ and C_P were measured at normal atmospheric pressure and at temperatures up to 353.2 K using a DSC and a commercial conductivity meter, respectively. Both measured κ and C_P data were presented and correlated as a function of temperature and composition.

NOMENCLATURE

AAD (%)	[%]	Average absolute deviation
A_i	[-]	Empirical parameters in Eq. (1)
$b_{i,0}$, $b_{i,1}$	[-]	Determined parameters in Eq. (4)
B_i	[-]	Temperature-dependent parameters in Eq. (3)
C_P	[J/mol/K]	Molar heat capacity
C_P^E	[J/mol/K]	Excess molar heat capacity
$C_{P,i}$	[J/mol/K]	Molar heat capacity of the pure component, i
n		Number of data points
T	[K]	Absolute system temperature
x		Mole fraction
Special characters		
ε	[-]	Data (electrolytic conductivity or molar heat capacity)
κ	[S/m]	Electrolytic conductivity
Subscripts		
1		Ionic liquid, $[Emim][C_2N_3]$
2		Solvent, water
cald		Calculated
expt		Experimental
i		Pure component

MATERIALS AND METHODS

The RTIL, [Emim][C_2N_3], which was obtained from TCI Co. has a minimum purity (in mass fraction) and water content (in mass fraction) of ≥ 0.999 and ≤ 0.0005, respectively. The RTIL were used without further purification, i.e., further reduction of water content, since it would be mixed with water later to form aqueous solutions. The water used to prepare the aqueous solutions was processed in Barnstead Thermodyne (model Easy Pure 1052) to produce deionized water (Type I reagent grade) with a resistivity of 18.3 MΩ cm and TOC (total organic content) of less than 15 ppb. All weight measurements during the preparation of solutions were performed on digital balance from Mettler-Toledo (model AL204) having $\pm 1 \times 10^{-4}$ g accuracy. A Type I reagent grade deionized water and standard KCl solution (0.1 N) were used to calibrate the DSC and the conductivity meter, respectively.

The κ was measured using SC-170 conductivity meter manufactured by Suntex, which operates with ac current of 60 Hz frequency. The temperature was monitored using digital thermometer (model 3002, CROPICO), with an uncertainty of ±0.01 K. A fixed volume of sample (3 mL) was placed in a test tube and was placed in a water bath where the temperature was controlled. The conductivity cell was first adjusted to zero in the air followed by the calibration of standard KCl solution before it was put in the sample to be measured. The conductivity cell was then washed by deionized water and ethanol to remove any adhering IL, and dried. To preserve the conductivity cell it was placed in water or in dry air before used for the next measurement.

The C_P was measured using the differential scanning calorimeter consisting of a DSC-2010 and a thermal analysis controller from TA Instruments. The DSC operating range is from the room temperature to 725 °C. Both the temperatures and the heat flow associated with transitions in materials can be easily and rapidly measured with the system. The DSC operates with a temperature repeatability of ±0.1 K. Calorimetric sensitivity is 1 μW (rms). The calorimetric precision is ±1 % based on measurements of metal samples. The purge gas was nitrogen with a flow rate of 40 mL·min^{-1}. The heating rate was set to be 5 [K/min]. By using the sample encapsulating press, the liquid sample was prepared within a hermetic sample pan. The internal volume of the hermetic pan was approximately 10 mm^3. Sample weight is in the range (15 to 20) mg. Five replicate runs were carried out for each measurement. The apparatus and the experimental procedures were the same as those described by Chiu et al. [24].

The uncertainty of the present reported κ data using the conductivity meter was estimated to be ±1 % with the calibrating solution (standard KCl solution) as the reference and on the basis of comparison with literature values for liquid water, the uncertainty of the C_p measurements is estimated to be ±2 %. The details of the calibration (validation) procedures for κ and C_P measurements were discussed in our previous works [17, 25]. All measurements were carried out in three to five replicate runs and the average values were reported.

RESULTS AND DISCUSSION

The κ data for the studied aqueous RTIL system were measured for temperatures ranging from (293.2 to 353.2) K at normal atmospheric pressure. The plots showing the present κ data and its behavior for the studied solvent system is shown in Figure 1. As shown in this figure, as expected, the κ values decrease as the concentration increase and increase as the temperature increase.

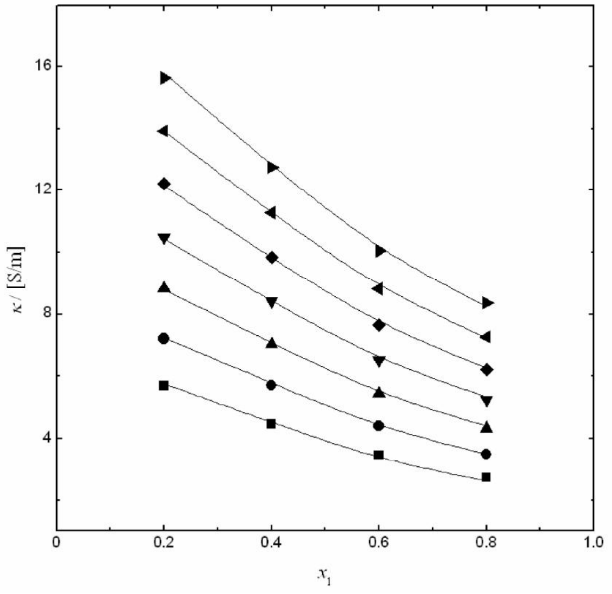

Figure 1 Electrolytic conductivity of [Emim][C_2N_3] (1) + H_2O (2): ■, 293.2 K; ●, 303.2 K; ▲, 313.2 K; ▼, 323.2 K; ◆, 333.2 K; ◀, 343.2 K; ▶, 353.2 K; and lines, calculated using Eq. (1).

The temperature and composition dependence of the present κ data was represented using a modified form of empirical equation previously used by Graber *et al.* [26], which was originally used for ternary aqueous solutions containing poly(ethylene) glycol (PEG). The new form of the equation is

$$\kappa = x_1 \exp\left[A_1 + A_2 T^{0.5} + A_3 x_1^{0.5}\right] + A_4 + A_5 T^{0.5} + A_6 x_1^{0.5} \qquad (1)$$

Where κ is the electrolytic conductivity in [S/m], x_1 the mole fraction of RTIL, T the absolute temperature in K, and A_i the empirical parameters. The parameters A_i were determined by fitting the κ data from this work using Eq. (1). Table 1 presented the determined parameters A_i. As seen in this table, the determined parameters A_i represented very well the present κ data as shown by an overall average absolute deviation (AAD) of about 7.8 % for a total of 52 data points. This satisfactory result using Eq. (1) was also shown in Figure 1, via the smoothed solid lines for each isotherm.

Table 1 Parameters of Eq. (1) for the considered solvent system

i	parameters A_i	No. of data points	AAD (%) [a]
1	0.98147	52	7.8
2	0.31160		
3	-5.3194		
4	-38.933		
5	1.8151		
6	7.4488		

[a] $\mathrm{AAD}\,(\%) = \frac{100}{n}\times\sum_{i=1}^{n}\left|\left(\varepsilon_{\mathrm{calcd}}-\varepsilon_{\mathrm{expt}}\right)/\varepsilon_{\mathrm{expt}}\right|_i$

Table 2 Molar heat capacities of the considered solvent system

	molar heat capacity, C_p, and excess molar heat capacity, C_p^E, in [J/mol/K]							
	$x_1 = 0.20$		$x_1 = 0.40$		$x_1 = 0.60$		$x_1 = 0.80$	
T / K	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E	C_p	C_p^E
303.2	131.1	5.3	182.2	5.9	229.5	2.6	275.6	-1.8
308.2	131.8	5.5	183.4	6.1	230.8	2.4	277.2	-2.2
313.2	132.5	5.8	184.6	6.3	232.1	2.3	279.0	-2.4
318.2	133.3	6.0	185.8	6.4	233.3	1.9	280.6	-2.8
323.2	134.0	6.2	186.9	6.6	234.7	1.9	282.2	-3.1
328.2	134.8	6.6	188.0	6.7	236.0	1.8	283.6	-3.6
333.2	135.7	6.9	189.2	7.0	237.3	1.6	285.1	-4.0
338.2	136.5	7.2	190.3	7.2	238.7	1.6	286.6	-4.4
343.2	137.2	7.4	191.5	7.4	240.0	1.5	288.1	-4.7
348.2	137.8	7.6	192.8	7.7	241.3	1.5	289.5	-5.1
353.2	138.5	7.8	193.8	7.8	242.5	1.3	290.8	-5.5

The C_p for the considered system were measured for temperature range of (303.2 to 353.2) K and at normal atmospheric pressure. Table 2 presented the C_p measurements from this work along with the calculated excess molar heat capacity C_P^E of the studied solvent system. As presented in this table, the C_p data increases as the temperature and composition (RTIL concentration) increases.

Here, the expression for C_P^E, defined by Lide and Kehiaian [27] was applied

$$C_P^E = C_P - \sum_i x_i C_{P,i} \tag{2}$$

Where $C_{p,i}$ is the molar heat capacity of the pure component, i. The molar heat capacity of the pure component, i.e. for H_2O and [Emim][C_2N_3], were determined from Osborne *et al.* [28], Yu *et al.* [25], respectively. As shown in Figure 2 and as also presented in Table 2, the behavior of the determined C_P^E values is a total opposite for the first ($0 \le x_1 \le 0.53$) and second region ($0.53 \le x_1 \le 1$) of the composition range. For the first region of the composition ($0 \le x_1 \le 0.53$), the C_P^E values increases with an increase in temperature and the values converge to a common point ($x_1 \approx 0.53$ and $C_P^E \approx 4.0$ J/mol/K) while for the composition range ($0.53 \le x_1 \le 1$), starting from the point of convergence in the first region of composition range, the C_P^E values decreases with temperature.

The temperature and compositional dependence of the calculated C_P^E values was correlated using the Redlich–Kister type equation, which is given as

$$C_P^E/[\mathrm{J/mol/K}] = x_1 x_2 \sum_{i=1}^{n} B_i \left(x_1 - x_2\right)^{i-1} \tag{3}$$

Where B_i is assumed to follow the equation

$$B_i = b_{i,0} + b_{i,1}\left(T/\mathrm{K}\right) \tag{4}$$

The parameters $b_{i,0}$ and $b_{i,1}$ for the considered binary were determined by fitting the C_p data from this work using Eq. (3). Table 3 presented the obtained parameters. The number of terms (B_i), in Eq. (3), which should be used to represent the C_P^E data, depends on the degree of complexity of the binary systems.

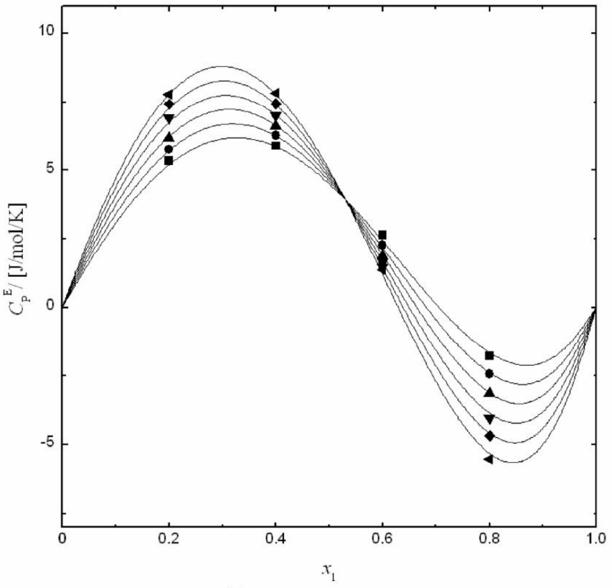

Figure 2 Determined C_P^E values of [Emim][C_2N_3] (1) + H_2O (2): ■, 303.2 K; ●, 313.2 K; ▲, 323.2 K; ▼, 333.2 K; ◆, 343.2 K; ◀, 353.2 K; and lines, calculated using Eq. (3).

Here, only three terms in Eq. (3) were found to satisfactory correlate the present measurements as shown by a reasonable overall AAD of 0.1 and 2.5 % for C_p and C_P^E calculations, respectively, for a total of 44 data points. Thus, Eq. (3) successfully represented the temperature and compositional dependence of the C_P^E data for the studied solvent system, as also shown in Figure 2 via the solid lines.

Table 3 Parameters of Eq. (3) for the considered solvent system

	parameters		No. of data	AAD (%)	
i	$b_{i,0}$	$b_{i,1}$	points, n	C_P	C_P^E
1	5.4129	0.041974	44	0.1	2.5
2	164.03	-0.66061			
3	74.473	-0.31072			

CONCLUSION

The κ and C_P of the solvent system [Emim][C_2N_3] + H_2O were measured over the temperature range from (303.2 to 353.2) K and (293.2 to 353.2) K, respectively, over a complete composition range. The present measurements of κ and C_P were then presented as a function of temperature and composition. An excess molar heat capacity expression using the Redlich–Kister equation and a modified empirical equation proposed by other researcher were used to correlate the temperature and compositional dependence of the present κ and C_P data, respectively. Both correlations yield satisfactory results. The κ and C_P values presented in this work are, in general, of sufficient accuracy for most engineering-design calculations.

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