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DENSITY, VISCOSITY AND SPEED OF SOUND OF BINARY MIXTURES OF (*N*-BUTYLAMMONIUM ACETATE + ALCOHOL) AT DIFFERENT TEMPERATURES AND ATMOSPHERIC PRESSURE

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Abstract. *Density, viscosity and speed of sound of solutions of n-butylammonium acetate + ethanol, or + 1-propanol have been measured over the entire composition range at (288.15, 293.15, 298.15 and 303.15) K and atmospheric pressure. Excess molar volume, viscosity deviation, isentropic compressibility and excess Gibbs energy of activation have been calculated from the data and correlated to the Redlich-Kister polynomial. For all properties, the values are negative over the entire composition range, except for the excess Gibbs energy of activation. For the system containing 1-propanol, excess molar volume presented positive values for the ionic liquid concentrations higher than 70%. Excess molar volume and isentropic compressibility deviation decrease whereas viscosity deviation and excess Gibbs energy of activation increase with increasing in temperature. The results obtained are discussed in terms of intermolecular interactions, particularly hydrogen-bonding interactions between like and unlike molecules.*

Keywords: *density, viscosity, speed of sound, ionic liquids.*

1. INTRODUCTION

Thermodynamics properties of binary and multicomponent liquid mixtures are required in many chemical engineering calculations involving fluid flow, heat and mass transfer. Their derived properties can provide valuable information about molecular interactions and structural effects.

Literature defines ionic liquids (ILs) or room-temperature ionic liquids (RTILs) as organic salts with melting point below 100 ºC, resulting from the combinations of organic cations and various anions. RTILs are viewed as a novel class of green solvents that attract attention of both industry and academy as substitute for conventional organic solvents. Due to their unique physical and chemical properties, such as low values of vapor pressure, low toxicity and chemical, electrochemical and thermal stability, they have been used in wide variety of applications including separation and manufacturing processes, in biocatalysis, as lubrificants, as working fluid of electrochemical applications and for processing biomass. Consequently, studies of thermodynamic properties of mixtures involving ionic liquids and organic solvents are gaining importance and have been studied for many authors (Singh *et al.* (2013), Matkowska and Hofman (2013), Calvar *et al.* (2012), Curra´s *et al.* (2010), Deng *et al.* (2011), Gao *et al.* (2010), Jiang *et al.* (2012)).

In the present work, density, viscosity and speed of sound of the solutions of *n*-butylamine acetate + ethanol, or + 1-propanol have been measured over the entire composition range at (288.15, 293.15, 298.15, and 303.15) K and atmospheric pressure. Both pure liquid and mixture viscosity were measured using a Stabinger viscosimeter (Anton Paar SVM 3000M). Density and speed of sound were measured using a commercial density and speed of sound analyzer (Anton Paar DSA 5000 densimeter and speed of sound analyzer). Excess molar volume, viscosity deviation, isentropic compressibility deviation and excess Gibbs energy of activation have been calculated from the data and fitted to the Redlich-Kister polynomial.

The new low-cost ionic liquids were prepared under ambient conditions by the reaction of acetic acids with *n*-butylamine. To the best our knowledge, the systems studied in the present work have not yet been published in the literature. This work enables a better opportunity to understand the behavior of the matrices in the production of ionic liquids and makes it possible to view their future application in industrial processes.

2. EXPERIMENTAL

2.1 Materials

N-butylamine (Sigma-Aldrich, purity ≥ 99,5 %) and acetic acid (Merck, purity > 99 %) were used without further purification. The reaction between these substances produced the ionic liquid *n*-butylammonium acetate, in which the acid was slowly added on the amine, once the reaction is extremely exothermic. The temperature was controlled to be lower than 15 ºC to avoid the IL degradation or even the occurrence of other reactions.

2.2 Apparatus and procedures

The binary mixtures were prepared in 10 cm³ bottles by weighing the pure components on OHAUS Adventurer with uncertainty of $1 \cdot 10^{-4}$ g. The densities and speeds of sound were measured using a densimeter and speed of sound analyzer manufactured by Anton Paar (Model DSA 5000), with uncertainties of $1 \cdot 10^{-6}$ g·cm^{-3} in densities and 0·01 m.s^{-1} in speeds of sound. The viscosities were measured using a Stabinger Viscosimeter (Model SVM 3000) with an uncertainty of $1 \cdot 10^{-4}$ mPa·s in viscosities.

2.3 The measuring principle of DSA 5000

DSA 5000 simultaneously determines two independent physical properties of the same sample. The apparatus is equipped with a density cell and sound velocity cell by combining the principle of an oscillator tube and a sound velocity measurement highly accurate. Both cells are thermally controlled by Peltier thermostat, which enables rapid measures of variation with temperature. The operating principle of a mechanical oscillation tube consists of introducing a sample into a U-shape borosilicate glass that is electronically excited to vibrate at its characteristic frequency electronically. This frequency change according to the density of the sample. Through the precise determination of the characteristic frequency, it can determine the period of oscillation of the oscillator tube and from these values, calculate the density through a mathematical equation.

The sample is introduced into the speed of sound measuring cell that is bordered by an ultrasonic transmitter on the one side, by a receiver on the other side. The transmitter sends sound waves of a known period through the sample. Thus, the sound velocity can be calculated by determining the period of the received sound waves, taking into account the distance between the transmitter and the receiver.

2.4 The measuring principle of SVM 3000/G2

SVM 3000 / G2 is a rotational viscometer cylindrical geometry. The measurement with this viscometer is based on measuring torque and rotation. Inside the SVM 3000 / G2, a magnet rotating creates a current field induced with an exact braking time and dependent on the rotation. The torque of the induced current is measured with extremely high resolution. The measuring cell contains a tube which rotates at a constant speed. The whole is filled by the sample and it floats a magnetic rotor which is centered by centrifugal forces. The viscous forces on the fluid analysis drive the rotor, leading to an equilibrium rate, which is recorded as an accurate measure of viscosity. The floating rotor and a measuring sensor without contact result in the elimination of the influences of external friction.

3. RESULTS AND DISCUSSION

The excess molar volume, viscosity deviation, isentropic compressibility deviation and excess Gibbs energy of activation were determined for the systems (*n*-butylammonium acetate + ethanol) and (*n*-butylammonium acetate + 1-propanol) over the entire composition range at 288.15, 293.15, 298.15 and 303.15 K and atmospheric pressure.

Excess molar volume (V_m^E), viscosity deviation ($\Delta\eta$), isentropic compressibility deviation ($\Delta\kappa$) and excess Gibbs energy of activation (ΔG^{*E}) were calculated using Eq. (1) to (4), respectively:

$$V_m^E = x_1 M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1} \right) + x_2 M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2} \right) \quad (1)$$

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (2)$$

$$\Delta\kappa = \kappa - (x_1\kappa_1 + x_2\kappa_2) \quad (3)$$

$$\Delta G^{*E} = RT\,[\ln(\eta V/\eta_2 V_2) - x_1 \ln(\eta_1 V_1/\eta_2 V_2)] \quad (4)$$

in which ρ is the density, η is the viscosity, κ is the isentropic compressibility and V is the molar volume of the mixture. The subscripts 1 and 2 refer, respectively, to the alcohol and the IL, and ρ_i, η_i, κ_i, V_i, M_i and x_i represent, respectively, densities, viscosities, isentropic compressibilities, molar volume, molar mass and molar fraction of pure components. R represents the gases universal constant and T is the temperature.

Isentropic compressibility and molar volume were calculated using Eq. (5) and (6), respectively, in which u is the speed of sound and M is the molar mass.

$$\kappa = \frac{1}{\rho u^2} \tag{5}$$

$$V = M/\rho \tag{6}$$

The excess properties were also fitted to the following Redlich-Kister equation (Redlich and Kister, 1948) (Eq. 7) using a least-square method, in which Y_m^E represents V_m^E, $\Delta\eta$, $\Delta\kappa$ and ΔG^{*E}, and A_j are parameters of the equation. The standard deviations (σ) were calculated using Eq. 8. Y_{cal}^E, Y_{exp}^E, N and n are, respectively, the excess properties calculated using Redlich-Kister equations, the excess properties calculated by experimental data, the number of data, and the degree of the equation.

$$Y_m^E = x_2(1-x_2)\sum_{j=0}^{j=n} A_j(1-2x_2)^j \tag{7}$$

$$\sigma = [\sum\{Y_{(expt)}^E - Y_{(cal)}^E\}^2/(N-n)]^{1/2} \tag{8}$$

The excess properties were plotted as functions of molar fraction of the ionic liquid, shown in Figs. (1) to (4).

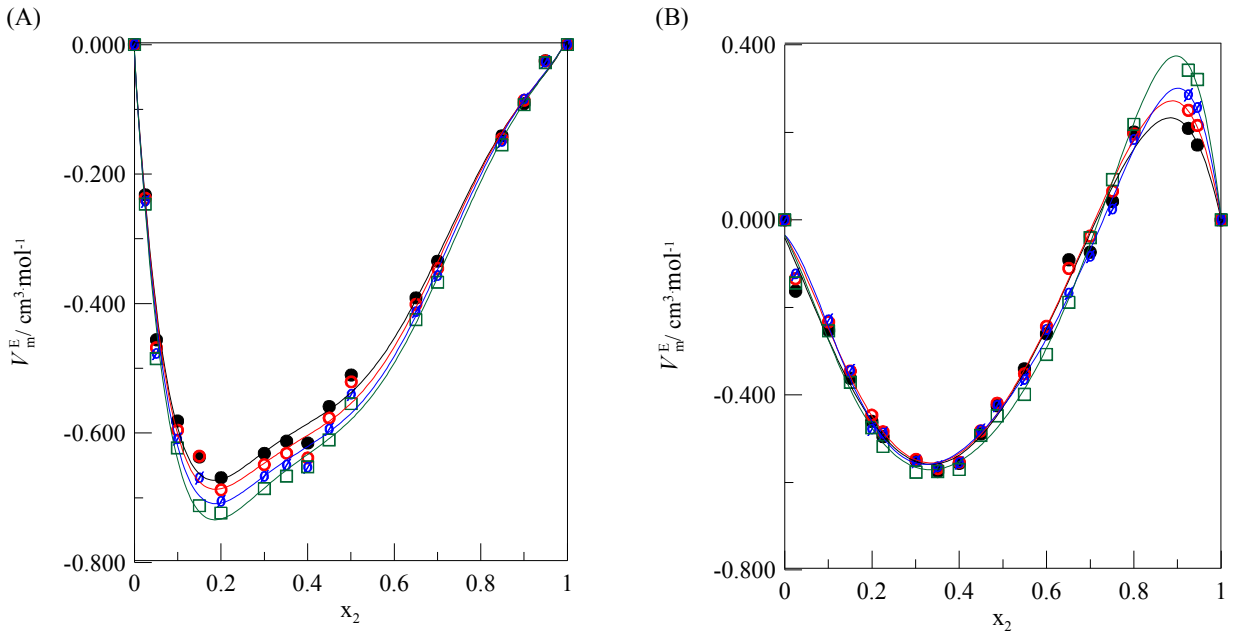


Figure 1. Excess molar volume (A) for the system {ethanol (1) + *n*-butylammonium acetate (2)}; (B) for the system {1-propanol (1) + *n*-butylammonium acetate (2)}, as a function of IL molar fraction at different temperatures and atmospheric pressure: ●, 288.15 K; ○, 293.15 K; Ø, 298.15 K; □, 303.15 K. (——) Redlich-Kister.

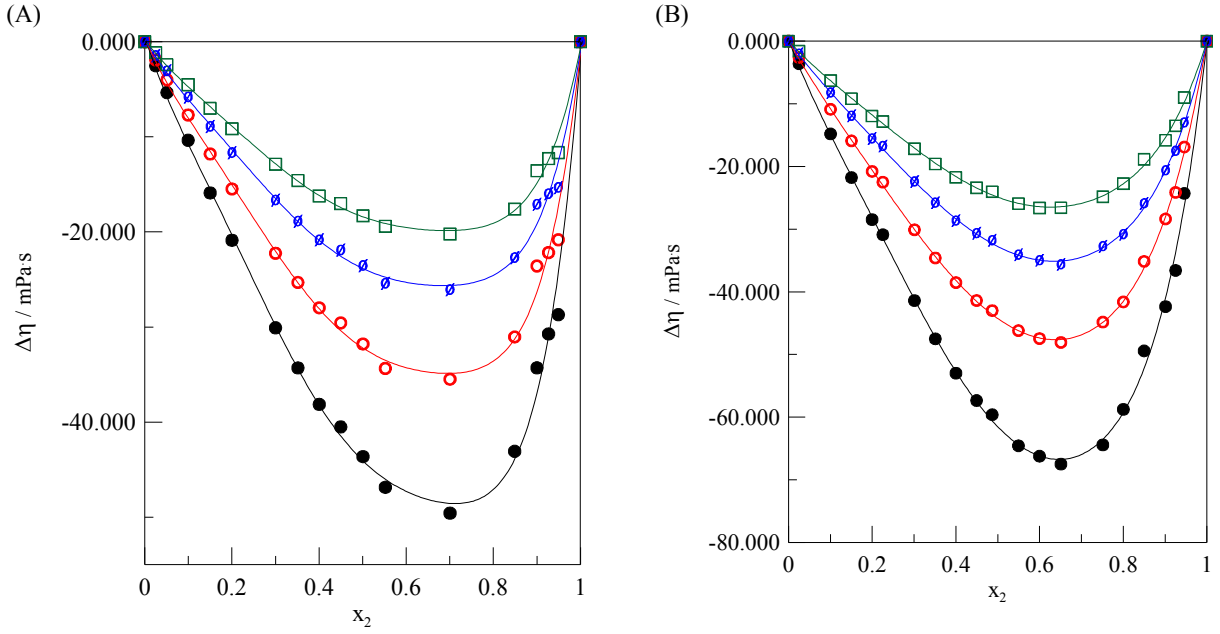


Figure 2. Viscosity deviation (A) for the system {ethanol (1) + *n*-butylammonium acetate (2)}; (B) for the system {1-propanol (1) + *n*-butylammonium acetate (2)}, as a function of IL molar fraction at different temperatures and atmospheric pressure: ●, 288.15 K; ○, 293.15 K; Ø, 298.15 K; □, 303.15 K. (——) Redlich-Kister.

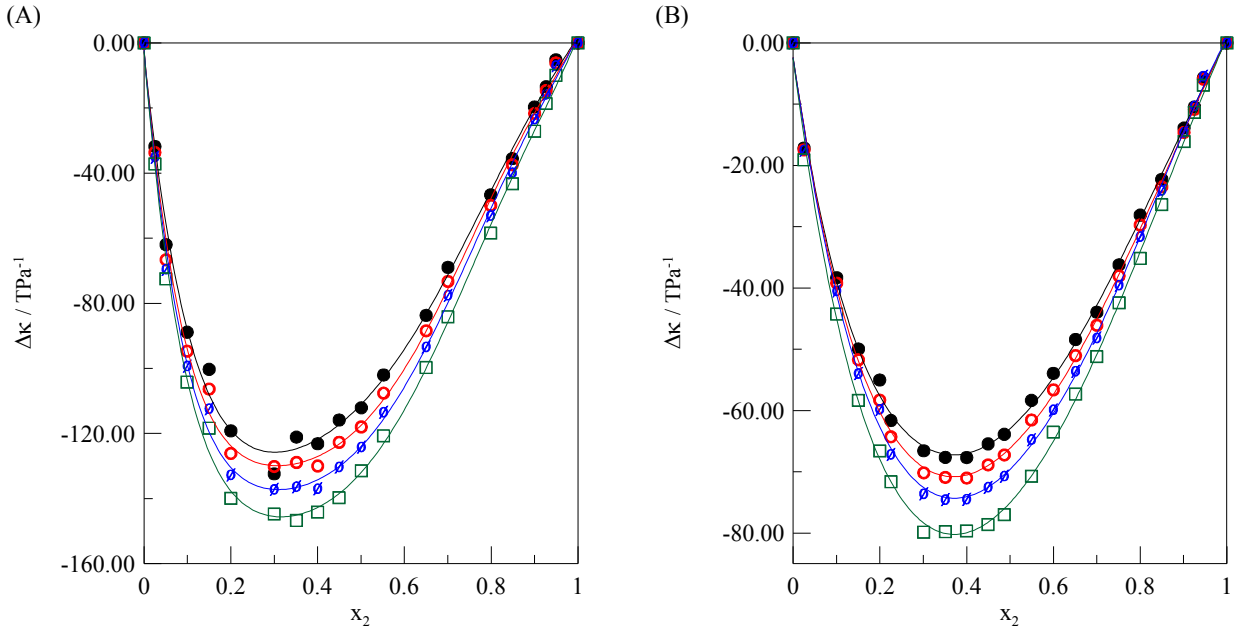
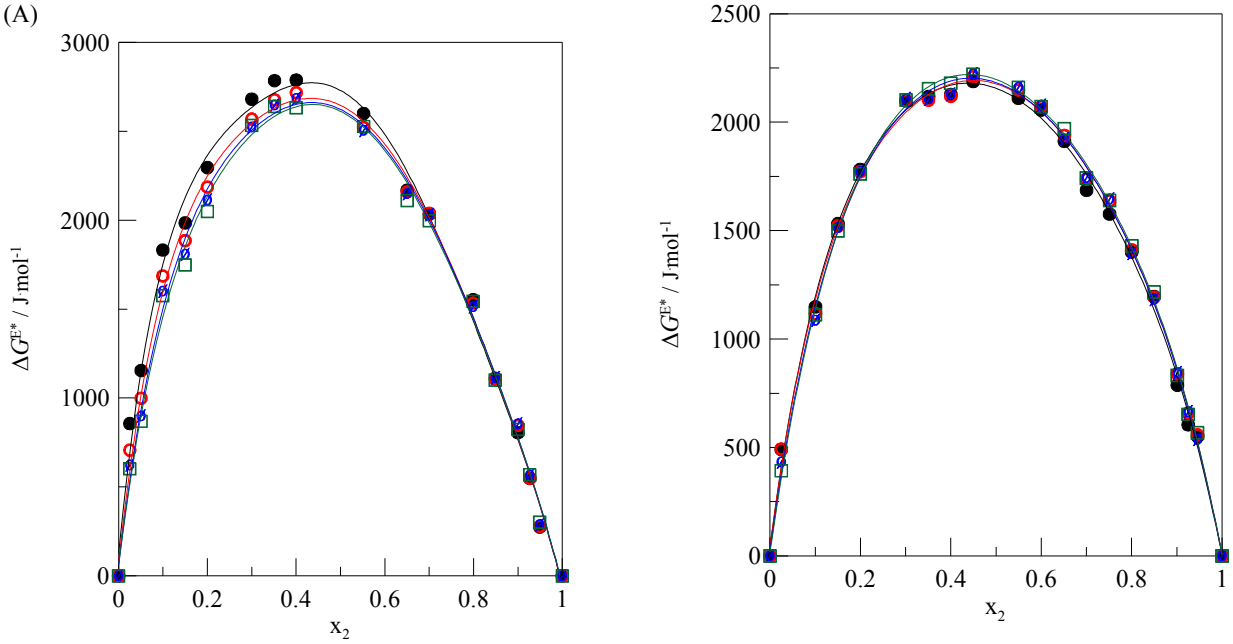


Figure 3. Isentropic compressibility deviation (A) for the system {ethanol (1) + *n*-butylammonium acetate (2)}; (B) for the system {1-propanol (1) + *n*-butylammonium acetate (2)}, as a function of IL molar fraction at different temperatures and atmospheric pressure: ●, 288.15 K; ○, 293.15 K; Ø, 298.15 K; □, 303.15 K. (——) Redlich-Kister.



(B)

Figure 4. Excess Gibbs energy of activation (A) for the system {ethanol (1) + *n*-butylammonium acetate (2)}; (B) for the system {1-propanol (1) + *n*-butylammonium acetate (2)}, as a function of IL molar fraction at different temperatures and atmospheric pressure: ●, 288.15 K; ○, 293.15 K; Ø, 298.15 K; □, 303.15 K. (——) Redlich-Kister.

The parameters of Redlich-Kister equation and the standard deviations are present in Tabs. 1 and 2.

Table 1. Parameters of Redlich-Kister equation and standard deviations for the system {ethanol (1) + *n*-butylammonium acetate (2)}.

Temperature	Property	A_0	A_1	A_2	A_3	A_4	σ
T = 288.15 K	V_m^E / cm³·mol^{-1}	-2,1606	-0,8767	-0,2813	-4,4215	-3,5157	0,0273
	$\Delta\eta$ / mPa·s	-176,74	32,272	34,735	257,81	-271,50	2,6680
	ΔG^{*E} / J·mol^{-1}	11541	-987,00	-7127,5	14809	17970	134,37
	Δk / TPa^{-1}	-447,31	-206,38	-95,69	-472,36	-240,34	4,682
T = 293.15 K	V_m^E / cm³·mol^{-1}	-2,2395	-0,8855	-0,0698	-4,5550	-3,8054	0,0315
	$\Delta\eta$ / mPa·s	-129,34	15,951	38,772	192,19	-212,02	2,1654
	ΔG^{*E} / J.mol^{-1}	10936	-313,39	-2913,6	11354	10527	143,70
	Δk / TPa^{-1}	-469,22	-203,58	-99,03	-517,92	-278,22	4,142
T = 298.15 K	V_m^E / cm³·mol^{-1}	-2,2947	-0,9594	-0,2301	-4,5969	-3,6683	0,0282
	$\Delta\eta$ / mPa·s	-95,917	9,1811	31,607	141,61	-158,68	1,6572
	ΔG^{*E} / J·mol^{-1}	10705	201,41	-1357,4	9042,3	7247,1	120,06
	Δk / TPa^{-1}	-495,04	-219,79	-112,76	-525,01	-279,48	4,167
T = 303.15 K	V_m^E / cm³·mol^{-1}	-2,3190	-1,0263	-0,6582	-4,6226	-3,2657	0,0237
	$\Delta\eta$ / mPa·s	-73,973	9,3140	16,664	105,05	-112,22	1,1353
	ΔG^{*E} / J·mol^{-1}	10674	295,48	-1858,7	8405,2	7486,7	123,51
	Δk / TPa^{-1}	-529,05	-234,74	-87,339	-516,65	-354,75	4,097

Table 2. Parameters of Redlich-Kister equation and standard deviations for the system {1-propanol (1) + *n*-butylammonium acetate (2)}.

Temperature	Property	A_0	A_1	A_2	A_3	A_4	σ
T = 288.15 K	V_m^E / cm³·mol^{-1}	-1,9333	-2,1610	5,5406	-3,1625	-5,4301	0,0637
	$\Delta\eta$ / mPa·s	-244,41	133,37	-66,637	82,481	-53,836	1,3547
	ΔG^{*E} / J·mol^{-1}	8932,8	337,62	-2277,5	4502,5	10400	83,17
	Δk / TPa^{-1}	-260,78	-64,693	114,89	-235,15	-311,57	3,237
T = 293.15 K	V_m^E / cm³·mol^{-1}	-1,8737	-2,2192	4,7380	-3,1279	-3,2527	0,0519
	$\Delta\eta$ / mPa·s	-176,15	92,211	-43,132	47,105	-27,943	0,5910
	ΔG^{*E} / J·mol^{-1}	9028,3	67,021	-2712,0	4458,9	11112	82,66
	Δk / TPa^{-1}	-273,91	-71,238	111,72	-231,65	-300,11	3,290
T = 298.15 K	V_m^E / cm³·mol^{-1}	-1,8857	-1,8803	3,7014	-3,9254	-1,1210	0,0522
	$\Delta\eta$ / mPa·s	-130,75	64,130	-23,659	39,901	-34,097	0,3963
	ΔG^{*E} / J·mol^{-1}	8943,7	670,42	-835,50	2807,5	7430,6	60,73
	Δk / TPa^{-1}	-287,13	-75,353	102,13	-238,11	-265,13	3,300
T = 303.15 K	V_m^E / cm³·mol^{-1}	-2,0147	-1,7894	4,6790	-5,2405	-1,7501	0,0528
	$\Delta\eta$ / mPa·s	-98,955	48,543	-20,439	24,681	-19,253	0,4751
	ΔG^{*E} / J·mol^{-1}	8932,6	1153,8	393,58	1468,6	5264,9	42,45
	Δk / TPa^{-1}	-309,33	-86,32	111,16	-246,93	-303,74	3,387

Both systems presented negative values in excess molar volume, viscosity deviation and isentropic compressibility deviation, except from concentrated solutions in the ionic liquid, in which the system containing 1-propanol resulted in positive values. Excess Gibbs energy of activation resulted in positive values for the two systems over the entire range of composition.

Negative values of excess molar volume are related to chemical and structural effects, in which there may be specific interactions between the ionic liquid and the alcohols. Differences in molar volume and free volume between components may also contribute to these negative values. The molar volume of IL is twice the value of alcohols, which leads to alcohol molecules positioning between IL molecules. The positive values observed in concentrated solutions of ionic liquid in the system containing 1-propanol may be due to a break in alcohol structure prevailing compared to chemical and structural effects. The contraction effect increases as temperature increases.

Negative values of viscosity deviation mean the viscosity of solution is lower than viscosity of ideal solution, which suggests that the interactions between components in solutions are less intense compared with interactions observed in pure components. These values decrease when temperature increases and when alcohol size decreases.

Positive values in excess Gibbs energy of activation indicate specific interactions between components mainly through hydrogen bonds. Apparently, temperature does not show a significant effect in this property. Nevertheless, the decrease in alcohol size increases these values.

Isentropic compressibility deviation resulted in negative values, which means the solution is less compressible than pure components. This effect becomes more intense with an increasing in temperature. When the value of compressibility decreases, the molecules acquire more mobility, which eases the speed of sound spread.

4. CONCLUSION

In the present study, excess molar volume, viscosity deviation, isentropic compressibility and excess Gibbs energy of activation of *n*-butylammonium acetate + ethanol, or + 1-propanol over the entire composition range at (288.15, 293.15, 298.15 and 303.15) K and atmospheric pressure have been calculated from density, viscosity and speed of sound data. According to the behavior of the experimental properties, the chemical and structural effects appear to outweigh the physical effects for the systems studied in the present work.

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