

CHAPTER VI

NON-COVALENT INTERACTION BETWEEN IONIC LIQUID (1-ETHYL-3-METHYLIMIDAZOLIUM CHLORIDE-ALUMINUM CHLORIDE) AND PURE ALCOHOLS

Abstract

The present work deals with the non-covalent interactions occurring between ionic liquid namely 1-ethyl-3-methylimidazolium chloride-aluminum chloride and pure alcohols (*e.g.*, methanol, ethanol, 1-propanol, and 1-butanol). For that limiting apparent molar volume, molar refraction, and limiting apparent molar isentropic compressibility of the binary systems *viz.*, {[EMIm]Cl/AlCl₃)+methanol}, {[EMIm]Cl/AlCl₃)+ethanol}, {[EMIm]Cl/AlCl₃)+1-propanol}, and {[EMIm]Cl/AlCl₃)+1-butanol} have been calculated using physicochemical properties *i.e.*, density, refractive index, and speed of sound respectively within the temperature range $T=293.15\text{K}-318.15\text{K}$ (with 5K interval). Here, the ionic liquid strongly interacts with 1-butanol than other chosen primary alcohol at a higher temperature (318.15K). The outcomes have been discussed in terms of intermolecular forces and non-covalent interactions like hydrogen bond, ion-dipole, electrostriction, hydrophobic interactions, and structural configurations.

Keywords: 1-Ethyl-3-methylimidazolium chloride-aluminum chloride, primary alcohol, ion-solvent and ion-ion interactions, physicochemical properties

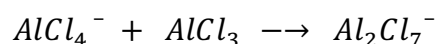
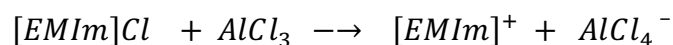
1. Introduction

Industrial and academic interest in ionic liquids (ILs) is well established. [1,2] The importance of ionic liquids in industries is reflected by the number of commercial processes and products based on these compounds currently available in the market. [3-7] Chemists, engineers, designers, and some researchers have a limited amount of available data for selecting ionic liquids in designing their product and processes, and for the use of models and correlations. The increasing number of databases and accessibility of some trustworthy databases [8] were making our task easy to correlate the thermophysical data of ionic liquids for a wide range of applications. Effect of temperatures [9-11] and effect of alcohol [12-14] on some physicochemical properties of ionic liquids are available. Thus, the knowledge of thermodynamic, physicochemical, and transport properties of ionic liquids is very useful to design products and processes.

Apparent molar volume, apparent molar isentropic compressibility, and apparent molar expansivity are important tools to determine the behaviour of solutes in solution and are being studied for various compounds. [15,16] These studies provide important information about solute-solvent interactions in solution. [17,18]

Some articles are published on 1-Ethyl-3-methylimidazolium chloride-aluminum chloride ([EMIm]Cl/AlCl₃) (a) as reaction media for acylative cleavage of ethers [19], (b) conductivities as a function of electrolyte composition and temperature for electrodepositing and surface morphology of aluminum. [20] The electrodepositions by chloroaluminate based ionic liquids give good results owing to its low viscosity and non-flammable properties, which have sufficiently wide range applications in electrochemical windows. [21] This behavior makes it an excellent solvent for Friedel-Crafts reaction [22], polymerizations of alkenes in refinery waste gas [23], catalytic hydrogenation [24,25] and stereoselective hydrogenation of aromatic compounds. [26] Ionic liquids composed of 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) and AlCl₃ is a classical chloroaluminate based electrolytes having many desired properties as non-flammability, non-volatility, low viscosity, high conductivity, and high thermal stability and chemical inertness. [27] In this electrolyte, AlCl₃ complexes with the Cl⁻ ion from

[EMIm]Cl to produce $AlCl_4^-$ and $[EMIm]^+$, and any excess $AlCl_3$ converts a portion of $AlCl_4^-$ into $Al_2Cl_7^-$, resulting in the coexistence of $AlCl_4^-$ and $Al_2Cl_7^-$:



The [EMIm]Cl/ $AlCl_3$ -based ILs have also been used as electrolytes for rechargeable metal batteries. [27,28]

On a careful survey of the literature (review), it has been found that there are no articles studied on molecular interactions between 1-ethyl-3-methylimidazolium chloride-aluminum chloride and alcohols by thermodynamic properties *viz.*, density, refractive index, and speed of sound respectively within temperature range $T=293.15K-318.15K$.

Vaz et. al. [29], investigated the solvation behaviour of different types of ionic liquids in 1-propanol for understanding the effect of anion and cation by isothermal titration calorimetry (ITC), molecular dynamics (MD) simulation and quantum chemical (QC) calculations. In this work, we have attempted to study the molecular interactions occurring in binary systems between [EMIm]Cl/ $AlCl_3$ and primary alcohols (methanol, ethanol, 1-propanol, 1-butanol). The physicochemical properties like density, refractive index, and speed of sound within the temperature range from 293.15K to 318.15K, and atmospheric pressure have been used to find out the derived parameters for interpreting the interactions occurring there. The results have been discussed in terms of ion-solvent interaction with the help of hydrogen bond, ion-dipole, London dispersion force, electrostriction, hydrophobic interaction with structural aspect, and configuration.

2. Materials and Methods

2.1. Materials

The selected ionic liquid and four primary alcohols namely: methanol, ethanol, 1-propanol, and 1-butanol were purchased from Aldrich and used as such. The chemicals

were kept in desiccators with molecular sieves to reduce evaporation and adsorption of moisture. The Metrohm 831 Karl-Fischer coulometric titrator has been used for the determination of water content. The source, CAS number, mass fraction purity, and water content of the chemicals used in this study have been given as a tabular form in Table VI.1. Apparent mole fraction of composition is $x=0.62$ for AlCl_3 and rest is for EMImCl . Where $[\text{EMIm}]$ and AlCl_4 with a charge +1 and -1 respectively act as cation and anion.

2.2. Methods

The experimental data of density (ρ), speed of sound (u) and refractive index (n_D) were automatically and simultaneously measured using a digital vibrating-tube density meter & speed of sound analyzer (Anton Paar DSA 5000 M) and Anton Paar RXA 156 refractometer with an accuracy of $\pm 0.001\text{K}$, $\pm 1 \cdot 10^{-6} \text{g} \cdot \text{cm}^{-3}$, $\pm 0.01 \text{m} \cdot \text{s}^{-1}$, and $\pm 2 \cdot 10^{-6}$ for temperature, density, speed of sound and refractive index, respectively. And error on both the cells and measured parameters are temperature dependent and are controlled by a built-in Peltier thermostat. The purity of the solvents has been observed by comparing it with the experimental density, speed of sound, and refractive index value with literature values (Table VI.1). The density of ethanol is slightly lower than methanol; it is due to the strong H-bond in ethanol than methanol.

Before starting each set of experiments, the cell has been cleaned (three times) with ethanol (liquid 1) and then dried with acetone (liquid 2) using a fully automatic X sample 452 Module. This module of routine cleaning of the cell (u-tube of the instrument) has been performed after each measurement. After rinse and clean the instrument after each measurement, it has been calibrated by ultra-pure water and passing dry air. The stock solution has been prepared by the weighing mass of the ionic liquid. The mass has been weighed using Ohaus Pioneer™, item-PA214 with readability 0.0001g. Then, the experimental solutions have been prepared by the dilution method of the stock solution of the ionic liquid from the sealed vial. All the prepared solutions have been tightly sealed to minimize the evaporation of solvent and absorption of atmospheric moisture, and measurements have been performed instantly after the preparation of solutions. The experimentally observed values of density, refractive index, and speed of sound have been listed in Table VI.2.

3. Results and Discussions

3.1 Apparent molar volume

The term apparent molar volume is important to analyze the solvent effect on the solute or ion-solvent interactions. [30] Therefore, we have calculated the apparent molar volumes (ϕ_V) with corresponding concentrations (m) of ionic liquid at $T = 293.15\text{K}$ to 318.15K with 5K interval of temperature and at atmospheric pressure using the equation 1

$$\phi_V = \frac{M}{\rho} - \frac{(\rho - \rho_0)}{m\rho\rho_0} \quad (1)$$

where ρ , ρ_0 , M and m are the density of the solution, solvent, molar mass of ionic liquid, and concentration in molality respectively. The apparent molar volumes (ϕ_V) have been represented in Figure VI.1 (each solvent at different temp), Figure S1 ((Supplementary Data) at a particular temp in different solvents). These apparent molar volumes (ϕ_V) have been plotted with the square root of concentration (\sqrt{m}) to obtain the limiting apparent molar volume (ϕ_V^0) (Table VI.3) with the help of the least square analysis of the Masson equation [31],

$$\phi_V = \phi_V^0 + S_V\sqrt{m} + B_Vm \quad (2)$$

where S_V , and B_V were the empirical coefficients, and the estimated values have been given in Table VI.3. ϕ_V is signifying the interactions between ion and solvent (ion-solvent interaction) into the solution. A perusal of Figure VI.1 and Table VI.3, show that the values of ϕ_V and ϕ_V^0 respectively increases (a) with rising of temperature and (b) from methanol to 1-butanol (Figure S1). This indicates the ion-solvent interaction between ionic species of ionic liquids and solvent molecules increases with (i) increasing temperature and (ii) increasing number of carbon atoms in the solvent. The coefficient, S_V is signifying the ion-ion interactions (or self-interaction of ions of the solute). For all the studied compositions and temperatures, it is observed that the magnitude of S_V is positive but very much lower than limiting apparent molar volume. This observation of S_V , means that there must have some extent of self-interactions between the ions of ionic liquid (ion-ion interactions). But it is negligible compare to the

ion-solvent interactions. The plausible forms [32] of ion-ion interactions ($[EMIm]^+ / [EMIm]^+ \text{ or } AlCl_4^- / AlCl_4^-$ and $[EMIm]^+ / AlCl_4^-$) have been shown as scheme 1.

At infinite dilution, the ions of ionic liquid are separated by the solvent molecules. The ions are located at infinite distance from each other and surrounded only by the solvent molecules. Therefore, in this situation, the interactions that occur are only between ions of solute and solvent molecules, *e.g.*, there are only ion-solvent interactions with no ion-ion interactions. Hence, we can say ion-solvent interactions are dominating over ion-ion interactions. Since, ϕ_V^o is only affected by ion-solvent interactions. So, it's value giving us the quantitative measurement of ion-solvent interactions. [33-36] Table 3 (or Figure S1) showing the values of limiting apparent molar volume, ϕ_V^o , for the ionic liquid in all the chosen solvents were positive, and the trends are increasing with rising temperature. The similar increasing trend of ϕ_V^o , has been observed if we change solvents (from methanol to 1-butanol). From this observation we can suggest the plausible two effects; there are temperature effect (at different temperatures), and solvent effect (for the structure of different solvents). We have seen that, with rising temperature the value of ϕ_V^o is increasing, which indicates the interactions between ions and solvent molecules (ion-solvent interaction) is strengthening with rising temperature. This observation can also be explained by transition state theory. [37] According to this theory, an increase in the temperature causes the molecules/ions to gain energy and become excited, and as a result, it is easy to transfer at the transition state. The formation of the transition state is coupled by the rupture of the intermolecular hydrogen bond of the alcohol and distortion of the intermolecular forces in the solvent molecules. Then these excited molecules/ions favourably interact with solvent molecules, which imply stronger ion-solvent interactions. [37]

The effect of temperature on ϕ_V^o , can be expressed by fitting ϕ_V^o data to a polynomial [30] as,

$$\phi_V^o = a_0 + a_1T + a_2T^2 \quad (3)$$

where, a_0, a_1 , and a_2 were the empirical coefficients. The nature of these coefficients depend on the type of electrolytes, solvents, and studying temperature T (K). The

calculated values of these coefficients were listed in Table VI.4. The first differentiation of Equation 3, limiting apparent molar volumes (ϕ_V^o) concerning temperature (T) at constant pressure gives the limiting molar expansibility (ϕ_E^o) [30] as follows,

$$\phi_E^o = \left(\frac{\partial \phi_V^o}{\partial T} \right)_P = a_1 + 2a_2T \quad (4)$$

The limiting molar expansibility (ϕ_E^o) have been reported in Table VI.5. The positive values of ϕ_E^o ascribed to the characteristics of solvation, electrostriction, or rearrangement of the solvent molecules at the surrounding surface of the ions. With increasing the temperature, some solvent molecules attached to the ionic liquid via hydrogen bond (scheme VI.2) may be released from the surrounding surface of the ionic liquid, as a result, the apparent molar expansibilities are increased.

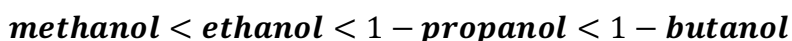
The positive attitude of ϕ_E^o , also signifies the absence of caging or packing effect of the ionic liquid in the solution system. The ϕ_E^o values in methanol and ethanol are increasing with increasing temperature, suddenly decreases in the case of 1-propanol, and increases in the case of 1-butanol. But it is a lower magnitude than the above three solvents. This may be because the 1-butanol has greater ion-solvent interaction (replace the methanol with 1-butanol in Scheme VI.2). For the similar reason of hydrogen bonding (Scheme VI.2), the ionic species have less expansibility in 1-propanol than ethanol, which in turn less than methanol. Since S_V is not making sole criteria to predict the structure breaking and making the tendency of a solute/electrolyte. Therefore, Hepler [38] introduced another view (the second derivative of ϕ_V^o concerning temperature (equation 5)) to find out the structure breaking and making nature of ions in the binary solution systems using the general thermophysical expression [30],

$$\left(\frac{\partial^2 \phi_V^o}{\partial T^2} \right)_P = \left(\frac{\partial \phi_E^o}{\partial T} \right)_P = 2a_2 \quad (5)$$

The positive and negative signs of $(\partial \phi_E^o / \partial T)_P$ implies the tendency of structure making and breaking (the tendency of order and disorder) respectively. By the inspection of Table VI.4, we have found the positive magnitude of $(\partial \phi_E^o / \partial T)_P$ of the ionic liquid in all the investigated binary solutions. These results are indicating the structure making

tendency and/or symmetric rearrangement of solvents may be with hydrogen bond, ion-dipole, London dispersion force, electrostriction, hydrophobic interactions, etc.

Solvent effect: At a particular temperature (say 298.15K), the values of limiting apparent molar volumes (ϕ_v^o) for ionic liquids increases with increasing the number of side-chain carbon atoms (increasing the chain with CH₂ group, as well as increasing the inductive effect, +I effect) from methanol to 1-butanol in the chosen alcohols (Figure S1 or Table VI.3). The consequences can also be elucidated by Friedman and Krishnan's co-sphere model [39]. According to this model, co-sphere solvation is destructive due to the effect of overlapping. Since, the effect of (i) overlapping and (ii) hydrophobic-hydrophobic interaction, decreases the limiting apparent molar volume. Therefore, the ion-hydrophobic or ion-hydrophilic interactions (chain of ionic liquids and solvent molecules or chain of solvent with central ion) will give a positive effect on stronger ion-solvent interactions. Hence, from the inspection of experimental observations of (ϕ_v^o) and the positive effect of ion-hydrophobic or ion-hydrophilic interaction (in ion-solvent interaction), increasing order of ion-solvent interaction in chosen alcohols at each temperature can be rearranged as follows,



The limiting apparent molar volumes of each part of chosen ionic liquid *i.e.*, ([EMIm]Cl/AlCl₃) also play a crucial role in ion-solvent interaction. [35,40,41] If we discuss the solvated ions in solution (at infinite dilution, ionic liquid parts are far apart from each other and only solvated by solvent molecules) concerning crystal ionic volume we can say that the solvation of ionic liquid molecules have occurred through the solvation of individual part [EMIm]⁺ and AlCl₄⁻; and they are solvated by non-covalent interaction (scheme VI.2) as ion-dipole, electrostatic interaction, and electrostriction etc. The limiting apparent molar volumes ($\phi_{v(ion)}^o$) for each part (calculated using radius ratio rule)[35], solvated radii ($r_s/\text{\AA}^3$) have been depicted in Table VI.5. A perusal of Table VI.5, we have got the limiting apparent molar volume of each ionic part, the solvated radii of cation [EMIm]⁺ and the solvated radii of anion AlCl₄⁻ are increase (a) from methanol to 1-butanol of the chosen solvents and (b) with increasing temperature. These results are indicating the ionic solvation by solvent

molecules. This ionic solvation (for both ions) is higher in the case of 1-butanol compared to the other chosen solvents. And this ionic solvation is also strengthening with rising temperatures.

3.2 Molar refraction

The experimental observed refractive index (n_D) and density (ρ) of solutions have been used to obtain the molar refraction (R_M) by following expression [42],

$$R_M = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) V_m \quad (6)$$

Where, the molar volume ($V_m = \frac{M}{\rho}$, where M = mol mass of solvent and ρ = solvent density) and then polarizability (α) have been calculated from R_M , using the following equation [43],

$$\alpha = \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \left(\frac{3V_m}{4\pi N_A} \right) \quad (7)$$

Where, N_A is the Avogadro's number. From the definition of the refractive index, it is a ratio of the speed of light in vacuum and through the medium (c_0/c), or more simply, it is the capacity of reflection of light when it moves from one medium to another medium, and consequently, higher the refractive index more is the refraction of light. [42,43] And more refraction of light is only possible when the substance is tightly packed or denser. Molar refraction is linearly varied with the refractive index. From the molar refraction data in Table VI.3 and Figure VI.2, it is noted that there is not too much variation with rising temperature, but it reasonably changes with changing the solvent. This fact is indicating that the ions $[EMIm]^+$ and $AlCl_4^-$ are more tightly packed in 1-butanol with respect to other chosen alcohols via non-covalent interactions. Similar results have been observed from the apparent molar volumes calculation (mentioned above).

The polarizability effect has been explained by London dispersion forces and the intermolecular forces *viz.*, hydrogen bonding, ion-dipole interactions, etc. The London

dispersion force is also an intermolecular force exhibited by the molecule and it can be expressed by polarizability. Polarizability is depended on the total number of electron and the total volume over which they were spread. The existence of a large number of electrons in large volumes over their spread, greater will be the polarizability as well as greater the dispersion force. From a scrutiny of Table VI.5, it has been seen that the polarizability (α) values increase from methanol to 1-butanol among the selected primary alcohols. This result indicates in the presence of a number of electrons, the apparent molar volume also becomes higher. This result also suggests the London dispersion forces are also responsible for ion-solvent interaction, as we have interpreted by other intermolecular forces (viz., H-bonding, ion-dipole interactions). The dominance of the London dispersion forces can also be shown from the boiling point of the solvents, more the boiling point greater the dispersion forces (64.7°C, 78.4°C, 97.0°C, 117.7°C are the boiling points of methanol, ethanol, 1-propanol, 1-butanol respectively). It is also noted that the polarizability linearly depend on molar refraction. Alternatively, both the polarizability and molar refraction follow the same trend with concentration as we observe in apparent molar volume. In the optical region, the molar refraction is in the same trend with the strength of dispersion forces. On the other hand, we measured the refractive index in the optical region, where the polarizability cannot be included as an orientation effect. [44-47] Thus, it is showing that there are negligible changes in molar refraction by orientation effect on polarizability with 5K interval of temperature.

The molar refraction and apparent molar volume can also be used to obtain the apparent molar solvated volume, $\phi_V^o(\text{solv})$, which represent the volume occupied by solvent molecules, as $\phi_V^o(\text{solv}) = (\phi_V^o - R_M)$ and reported in Table 5. This volume appearance is also used in many liquid-state models, based on the van der Waals equation-of-state. The values of $\phi_V^o(\text{solv})$ were invariant with the change of solvent indicating that the ion-solvation interaction is quite the same as found in ions (cation/anion). But the values of $\phi_V^o(\text{solv})$ increases with temperature means that the ion-solvation rises with rising the temperature. Hence, a cooperative analysis of density and refractive index provides a useful clue about the solvodynamic behaviour of a system.

3.3 Isentropic Compressibility

The values of speed of sound (u) and density (ρ) have been utilized to calculate the isentropic compressibility (β_S) for the binary systems (ionic liquid+alcohols). This β_S values have been calculated by employing the Newton-Laplace's equation [30],

$$\beta_S = 1/(\rho \cdot u^2) \quad (8)$$

Now, the isentropic compressibilities (β_S) have been plotted with corresponding concentration (m) of alcohol (Figure S2 in Supplementary Data). The magnitude of isentropic compressibility of the ionic liquid is higher in 1-butanol than 1-propanol, ethanol, and methanol at a particular temperature (say 298.15K). And this compressibility is also increasing with rising temperature (293.15K to 318.15K) in a particular solvent system (methanol). The fact can be elucidated by hydrogen bonding and dipole moments; ion-solvent interactions are more when ions can rupture the hydrogen bonds of solvent molecules. Methanol has a stronger hydrogen bond and higher dipole moment than ethanol, which in turn has a stronger H-bond than other higher alcohols; and the ions of ionic liquids cannot effectively rupture the stronger H-bond of methanol, resulting in poor ion-solvent interaction. This agrees with the findings from radial distribution functions (RDFs) analysis [32] and contact ion pair (CIP) and solvent shared ion pair (SSIP) optimization by DFT calculations. [48] For each temperature, β_S , is gradually decreasing with an increasing molality of alcohol, is due to the solvation of ions.

The isentropic compressibilities (β_S) have been used to compute the apparent molar isentropic compressibility [30] (ϕ_κ),

$$\phi_\kappa = \frac{M\beta_S}{\rho} - \frac{(\beta_o\rho - \beta_S\rho_o)}{m\rho_o} \quad (9)$$

where β_o and β_S are isentropic compressibility of pure and binaries respectively. The limiting apparent molar isentropic compressibility (ϕ_κ^o) is computed using the following relation [30],

$$\phi_\kappa = \phi_\kappa^o + S_\kappa\sqrt{m} + B_\kappa m \quad (10)$$

and listed in Table 3, where S_κ and B_κ are the empirical coefficient. ϕ_κ^o , S_κ and B_κ are similar significant as described in Equation 1 of the apparent molar volume. A perusal of

Table VI.3, the negative values of limiting apparent molar isentropic compressibility indicates that the solvated ions of ionic liquid would present greater resistance to compression. At a particular temperature (say 298.15K), the values of ϕ_k^o increases from methanol to 1-butanol (Figure 3). And for a particular solvent (say methanol) these ϕ_k^o values were also increasing with rising temperature (Figure S3). The results certify that the ion-solvent interactions are increased with both, the increase in temperature and change in solvent (from methanol to 1-butanol). Comparing the similar significant (ion-ion interaction) empirical coefficient of B_V and B_k from apparent molar volume and apparent molar isentropic compressibility is negative (Table VI.3), implies that there is no tertiary effect between the ion and solvent molecules in the studied binary solution systems.

4. Conclusions

From the experimental results and derived parameters of the studied binary system *viz.*, {[EMIm]Cl/AlCl₃)+methanol}, {[EMIm]Cl/AlCl₃)+ethanol}, {[EMIm]Cl/AlCl₃)+1-propanol}, and {[EMIm]Cl/AlCl₃)+1-butanol}, we concluded that the ion-solvent interaction signifying parameters *e.g.*, limiting apparent molar volume, molar refraction, limiting apparent molar isentropic compressibility increases with rising the side chain of the studied alcohols and with increasing temperature. On the other hand, ion-ion interaction indicating parameters (S_V and S_k) decreases with the same. The study also attributed that ion-solvent interactions are dominant over the ion-ion interactions. The molecular interactions occurring between the ionic liquid and solvent molecules are due to the structure-making capacity that causes by intermolecular forces and non-covalent interactions.

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Conflict of interest

There is no conflict of interest.

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TABLES

■ **Table VI.1.** Chemical name, CAS number, the mass fraction of purity and water content of the chemicals used[†]

Chemical name	CAS Number	Mass fraction purity [†]	water content(%)
[EMIm]Cl/AlCl ₃ [§] (x _{AlCl₃} =0.62)	742872-100G [‡]	0.990	0.1062
Methanol	67-56-1	≥0.999	0.6723
Ethanol	67-17-5	≥0.998	0.8745
1-Propanol	71-23-8	≥0.995	0.8976
1-Butanol	71-36-3	>0.990	0.9612

[†]purification method-used as procured and analytical method Gas Chromatography;

[‡]Confirmed by the supplier; [§]1-ethyl-3-methylimidazolium chloride-aluminum chloride;

[‡]Product number

■ **Table VI.2.** Density (ρ), refractive index (n_D) and speed of sound (u) of ionic liquid (x_{AlCl₃}=0.62) and pure solvents at $T = 293.15\text{K}$ to 318.15K and at atmospheric pressure^a

Solvent	T (K)	$\rho \times 10^{-3}(\text{kg m}^{-3})$		n_D		u (m s ⁻¹)	
		Experimental	Literature	Expt	Lit	Expt	Lit
[EMIm]Cl/AlCl ₃	293.15	1.354472	-	1.480628	-	1417.07	-
	298.15	1.350003	-	1.479027	-	1410.99	-
	303.15	1.345556	-	1.477393	-	1404.46	-
	308.15	1.341135	-	1.475788	-	1398.13	-
	313.15	1.336735	-	1.474198	-	1391.75	-
	318.15	1.332360	-	1.472574	-	1385.62	-
methanol	293.15	0.792136	0.791218 ^b 0.791243 ^c	1.329146	1.32843 ^d	1120.27	1118.83^c 1119.49^e
	298.15	0.786613	0.78661 ^f 0.786710 ^e	1.327200	1.32645 ^d	1104.01	1102.98^e
	303.15	0.782717	0.781778 ^b 0.781813 ^c	1.325247	1.32410 ^g 1.3241 ^d	1087.22	1085.99^c 1086.46^e
	308.15	0.777974	0.777028 ^b	1.323244	1.32223 ^g	1069.17	1068.90^g
	313.15	0.773204	0.772238 ^b	1.321216	1.32018 ^g	1054.25	1053.55^c

			0.772287 ^c		1.32048 ^d		1053.97^e
	318.15	0.768399	0.767326 ^b	1.318681	1.31759 ^g	1038.14	1037.30^g
ethanol	293.15	0.789420	0.789386 ^h 0.79091 ⁱ	1.361503	1.36125 ^d	1162.97	1161.97^j
	298.15	0.785133	0.785096 ^h 0.78660 ⁱ	1.359482	1.35941 ^g 1.35922 ^d	1146.37	1145.44^j 1143.50^e
	303.15	0.780815	0.780779 ^h 0.78228 ⁱ	1.357377	1.35680 ^d	1129.49	1128.77^j
	308.15	0.776463	0.776431 ^h 0.77794 ⁱ	1.355298	1.35451 ^g	1114.26	1112.14^j
	313.15	0.772077	0.772044 ^h 0.77356 ⁱ	1.353195	1.35245 ^g 1.35303 ^d	1096.99	1095.49^j
	318.15	0.767646	0.768166 ^j 0.76915 ⁱ	1.351061	1.35015 ^g	1080.51	1078.79^j
1-propanol	293.15	0.804479	0.803516 ^h 0.80384 ⁱ	1.385257	1.38484 ^d 1.38578 ^k	1224.45	1223.00^d
	298.15	0.800461	0.799506 ^h 0.79985 ⁱ	1.383276	1.38307 ^d 1.38364 ^k	1207.47	1206.54^l
	303.15	0.796413	0.795476 ^h 0.79581 ⁱ	1.381227	1.38104 ^d 1.38153 ^k	1190.48	1188.64^l
	308.15	0.792332	0.791406 ^h 0.79174 ⁱ	1.379177	1.37918 ^m 1.37929 ^k	1173.58	1171.81^l
	313.15	0.788212	0.787296 ^h 0.78764 ⁱ	1.377078	1.37676 ^d 1.37702 ^k	1156.78	1150.0ⁿ
	318.15	0.784043	0.78355 ⁱ	1.374934	1.37483 ^k	1140.01	1139.4ⁿ
1-butanol	293.15	0.809607	0.809660 ^h 0.80953 ⁱ	1.399479	1.39924 ^d 1.39932 ^k	1256.34	1257.5ⁿ
	298.15	0.805792	0.805845 ^h 0.80570 ⁱ	1.397563	1.39702 ^d 1.39730 ^k	1239.61	1239.28^l
	303.15	0.801951	0.802004 ^h 0.80186 ⁱ	1.395530	1.39521 ^d 1.39523 ^k	1222.82	1223.41^l
	308.15	0.798078	0.798133 ^h 0.79799 ⁱ	1.393478	1.39318 ^k	1206.13	1206.83^l
	313.15	0.794169	0.794222 ^h 0.79410 ⁱ	1.391442	1.39090 ^d 1.39110 ^k	1189.53	1192.6ⁿ
	318.15	0.790220	0.79018ⁱ	1.389374	1.38901^k	1173.01	1169.6ⁿ

^aStandard uncertainties u are $u(\rho) = 0.00005 \text{ g cm}^{-3}$ & $u(u) = 0.05 \text{ m s}^{-1}$ with $u(T) = 0.01\text{K}$ and $u(n_D) = 0.00003$ with $u(T) = 0.01\text{K}$ (with 0.68 level of confidence) and the estimated expanded uncertainties U are $U(\rho) = 0.00010 \text{ g cm}^{-3}$ & $U(u) = 0.10 \text{ m s}^{-1}$ and $U(n_D) = 0.00006$ (with 0.95 level of confidence ($k=2$)); ^b[ref. 49], ^c[ref. 50], ^d[ref. 51],

^e[ref. 52], ^f[ref. 53], ^g[ref. 54], ^h[ref. 55], ⁱ[ref. 56], ^j[ref. 57], ^k[ref. 58], ^l[ref. 59], ^m[ref. 60], ⁿ[ref. 61]

■ **Table VI.3.** Limiting apparent molar volume, ϕ_V^o , coefficients (S_V and B_V), molar refraction (R_M), apparent molar isentropic compressibility (ϕ_K^o), coefficients (S_K and B_K) of ionic liquid [emimCl]₂[AlCl₃]₃ (x_{AlCl_3} =0.62) in solvents at $T = 293.15\text{K}$ to 318.15K and at atmospheric pressure^a

T (K)	$10^6 \cdot \phi_V^o$ ($\text{m}^3 \text{mol}^{-1}$)	$10^6 \cdot S_V$ ($\text{m}^3 \text{mol}^{-3/2} \text{kg}^{1/2}$)	$10^6 \cdot B_V$ ($\text{m}^3 \text{mol}^{-2} \text{kg}$)	$10^6 \cdot R_M$ ($\text{m}^3 \text{mol}^{-1}$)	$10^{-11} \cdot \phi_K^o$ ($\text{m}^3 \text{mol}^{-1} \text{Pa}^{-1}$)	$10^{-11} \cdot S_K$ ($\text{m}^3 \text{mol}^{3/2} \text{kg}^{1/2} \text{Pa}^{-1}$)	$10^{-11} \cdot B_K$ ($\text{m}^3 \text{mol}^2 \text{kg Pa}^{-1}$)
[EMIm]Cl/AlCl ₃ +methanol							
293.15	839.20	17.59	-443.42	172.89	-229.6	12.28	-19.36
298.15	842.61	17.09	-440.76	173.03	-223.0	11.96	-18.91
303.15	847.55	16.61	-442.46	173.14	-214.2	11.40	-17.86
308.15	852.92	16.23	-446.14	173.26	-207.1	11.03	-17.36
313.15	857.47	15.81	-445.42	173.40	-195.6	10.27	-15.99
318.15	862.40	15.42	-445.09	173.60	-186.3	9.83	-15.29
[EMIm]Cl/AlCl ₃ +ethanol							
293.15	844.71	15.13	-404.48	189.46	-194.1	11.10	-18.09
298.15	848.12	14.69	-404.39	189.53	-187.7	10.76	-17.48
303.15	853.60	14.26	-403.99	189.66	-181.3	10.37	-16.78
308.15	857.42	13.86	-408.90	189.88	-176.5	10.10	-16.28
313.15	862.10	13.44	-410.23	190.07	-169.7	09.74	-15.76
318.15	866.73	13.03	-410.24	190.27	-160.9	09.17	-14.72
[EMIm]Cl/AlCl ₃ +1-propanol							
293.15	852.61	13.13	-381.78	202.05	-0.69	3.46	-5.71
298.15	855.49	12.61	-379.40	202.13	-0.66	3.41	-5.46
303.15	859.82	12.24	-382.13	202.37	-0.64	3.32	-5.31
308.15	863.06	11.81	-380.13	202.59	-0.61	3.18	-5.07
313.15	866.42	11.48	-380.34	202.90	-0.57	2.97	-4.69
318.15	869.60	11.02	-377.97	203.19	-0.54	2.80	-4.40
[EMIm]Cl/AlCl ₃ +butanol							
293.15	858.11	10.85	-362.52	209.85	-0.15	0.45	-0.65
298.15	860.54	10.31	-365.99	210.11	-0.14	0.43	-0.63
303.15	863.62	9.84	-364.47	210.38	-0.13	0.38	-0.55
308.15	866.71	9.40	-364.23	210.60	-0.12	0.35	-0.51
313.15	870.68	9.01	-364.01	210.86	-0.11	0.30	-0.44
318.15	874.52	8.64	-360.72	211.13	-0.10	0.27	-0.34

^a Standard uncertainties u are $u(\phi_V^o) = (0.13-0.96) \cdot 10^6 \text{ m}^3 \text{ mol}^{-1}$, $u(R_M) = 0.21 \cdot 10^6 \text{ m}^3 \text{ mol}^{-1}$, and $u(\phi_K^o) = (0.09-0.97) \cdot 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ Pa}^{-1}$ (with 0.68 level of confidence), and $u(T) = 0.001 \text{ K}$.

■ **Table VI.4.** Empirical coefficient (a_0, a_1, a_2) of equation 3, $(\partial\phi_E^o/\partial T)_p$ for ionic liquid in chosen solvents

Solvent	$10^6 \cdot a_0$ ($\text{m}^3 \text{ mol}^{-1}$)	$10^6 \cdot a_1$ ($\text{m}^3 \text{ mol}^{-1} \text{ K}^{-1}$)	$10^6 \cdot a_2$ ($\text{m}^3 \text{ mol}^{-1} \text{ K}^{-2}$)	$10^6 \cdot (\partial\phi_E^o/\partial T)_p$ ($\text{m}^3 \text{ mol}^{-1} \text{ K}^{-2}$)
Methanol	963.249	-1.689	0.0043	0.0086
Ethanol	776.592	-0.376	0.0021	0.0042
1-Propanol	491.173	-1.731	0.0047	0.0094
1-Butanol	1371.315	-3.972	0.0076	0.0152

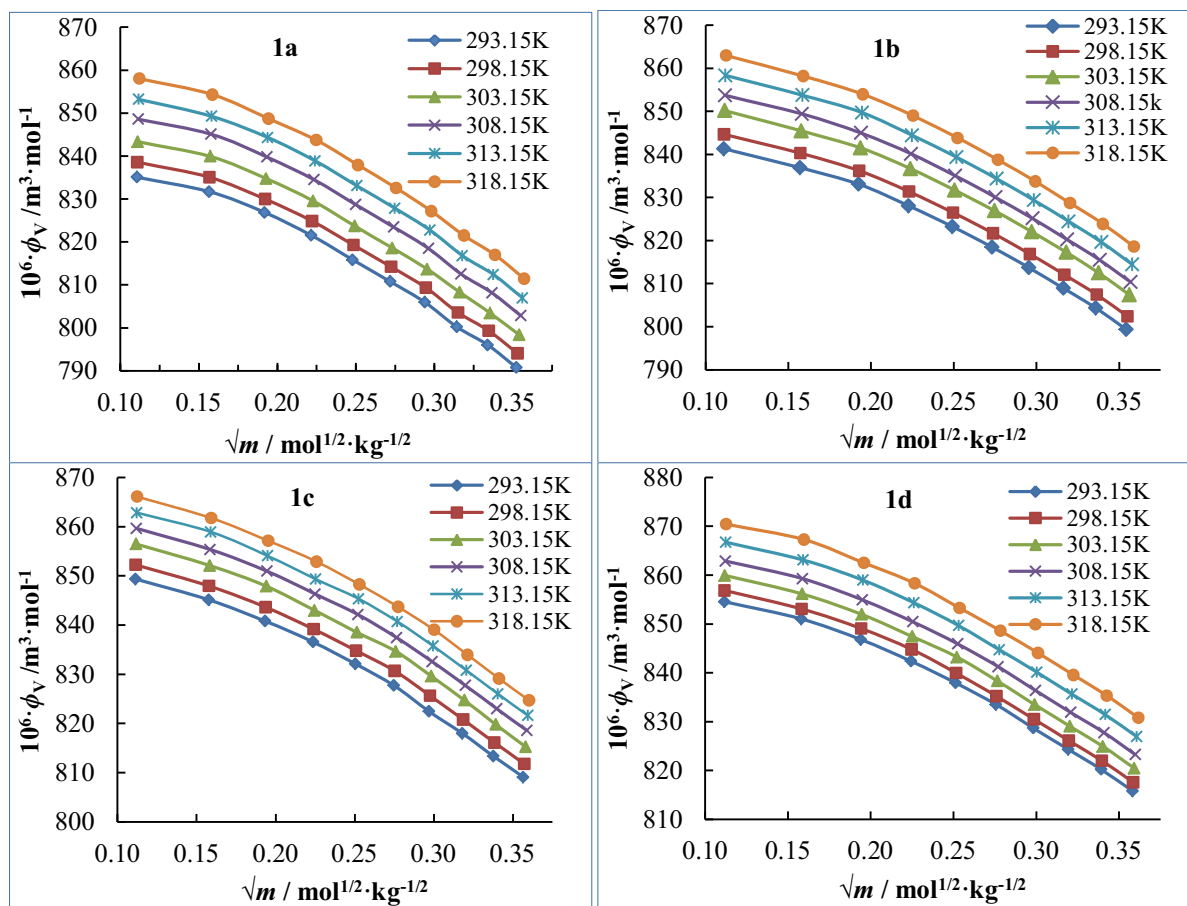
■ **Table VI.5.** Limiting apparent molar expansibility (ϕ_E^o), $\sigma(\phi_E^o)$, ionic limiting apparent molar volume ($\phi_{V(ion)}^o$) solvated volume including ions (r_s) polarizability (α), solvated volume by solvents ($\phi_V^o(\text{solv})$) in methanol, ethanol, 1-propanol, and 1-butanol

T(K)	$10^6 \cdot \phi_E^o$ ($\text{m}^3 \text{ mol}^{-1} \text{ K}^{-1}$)	$10^6 \cdot \sigma(\phi_E^o)$ ($\text{m}^3 \text{ mol}^{-1} \text{ K}^{-1}$)	$10^6 \cdot \phi_{V(ion)}^o$ ($\text{m}^3 \text{ mol}^{-1}$)		$r_s(\text{\AA}^3)$	$10^{23} \cdot \alpha$ ($\text{m}^3 \text{ mol}^{-1}$)	$10^6 \cdot \phi_V^o(\text{solv})$ ($\text{m}^3 \text{ mol}^{-1}$)
			$[EMIm]^+$	$AlCl_4^-$			
methanol							
293.15	0.83	0.0015	337.36	501.84	11.170	6.854	666.31
298.15	0.88	0.0016	338.73	503.88	11.185	6.859	669.58
303.15	0.92	0.0017	340.72	506.83	11.207	6.864	674.41
308.15	0.96	0.0017	342.87	510.05	11.230	6.869	679.66
313.15	1.00	0.0018	344.70	512.77	11.250	6.874	684.07
318.15	1.05	0.0019	346.68	515.72	11.272	6.882	688.80
ethanol							
293.15	0.86	0.0017	339.57	505.14	11.194	7.511	655.25
298.15	0.88	0.0018	340.94	507.18	11.209	7.514	658.59
303.15	0.90	0.0018	343.15	510.45	11.233	7.519	663.94
308.15	0.92	0.0018	344.68	512.74	11.250	7.527	667.54
313.15	0.94	0.0019	346.56	515.54	11.270	7.535	672.03
318.15	0.96	0.0019	348.43	518.30	11.291	7.543	676.46

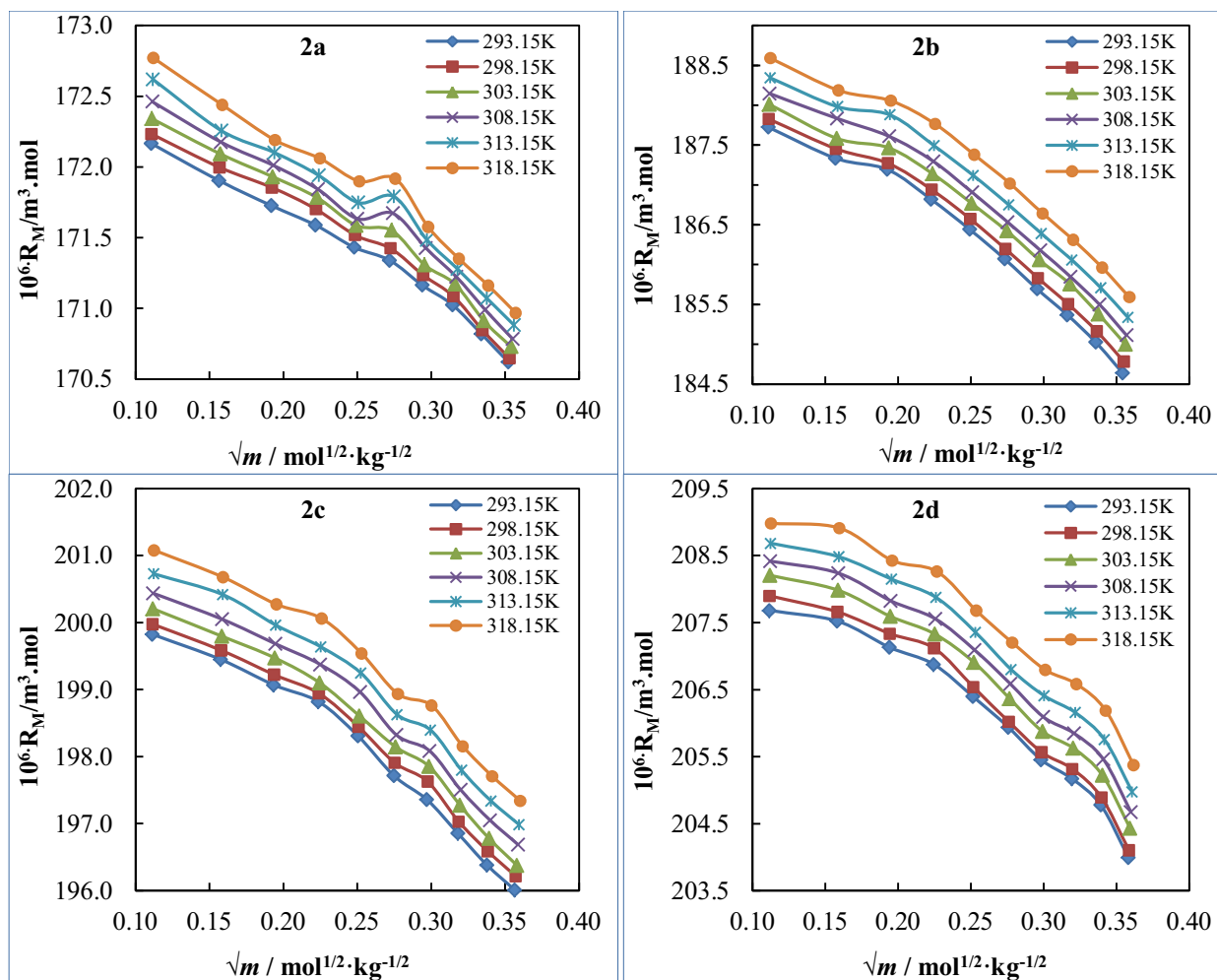
1-propanol							
293.15	0.73	0.0014	342.75	509.86	11.229	8.010	650.56
298.15	0.72	0.0014	343.91	511.58	11.242	8.013	653.36
303.15	0.70	0.0013	345.65	514.17	11.260	8.023	657.45
308.15	0.68	0.0013	346.95	516.11	11.275	8.031	660.47
313.15	0.67	0.0013	348.30	518.12	11.289	8.044	663.52
318.15	0.65	0.0012	349.58	520.02	11.303	8.055	666.41
1-butanol							
293.15	0.48	0.0001	344.96	513.15	11.253	8.319	648.26
298.15	0.56	0.0002	345.94	514.60	11.264	8.329	650.43
303.15	0.64	0.0002	347.18	516.44	11.277	8.340	653.24
308.15	0.71	0.0002	348.42	518.29	11.290	8.349	656.11
313.15	0.79	0.0002	350.01	520.67	11.308	8.359	659.82
318.15	0.86	0.0003	351.56	522.96	11.324	8.370	663.39

FIGURES

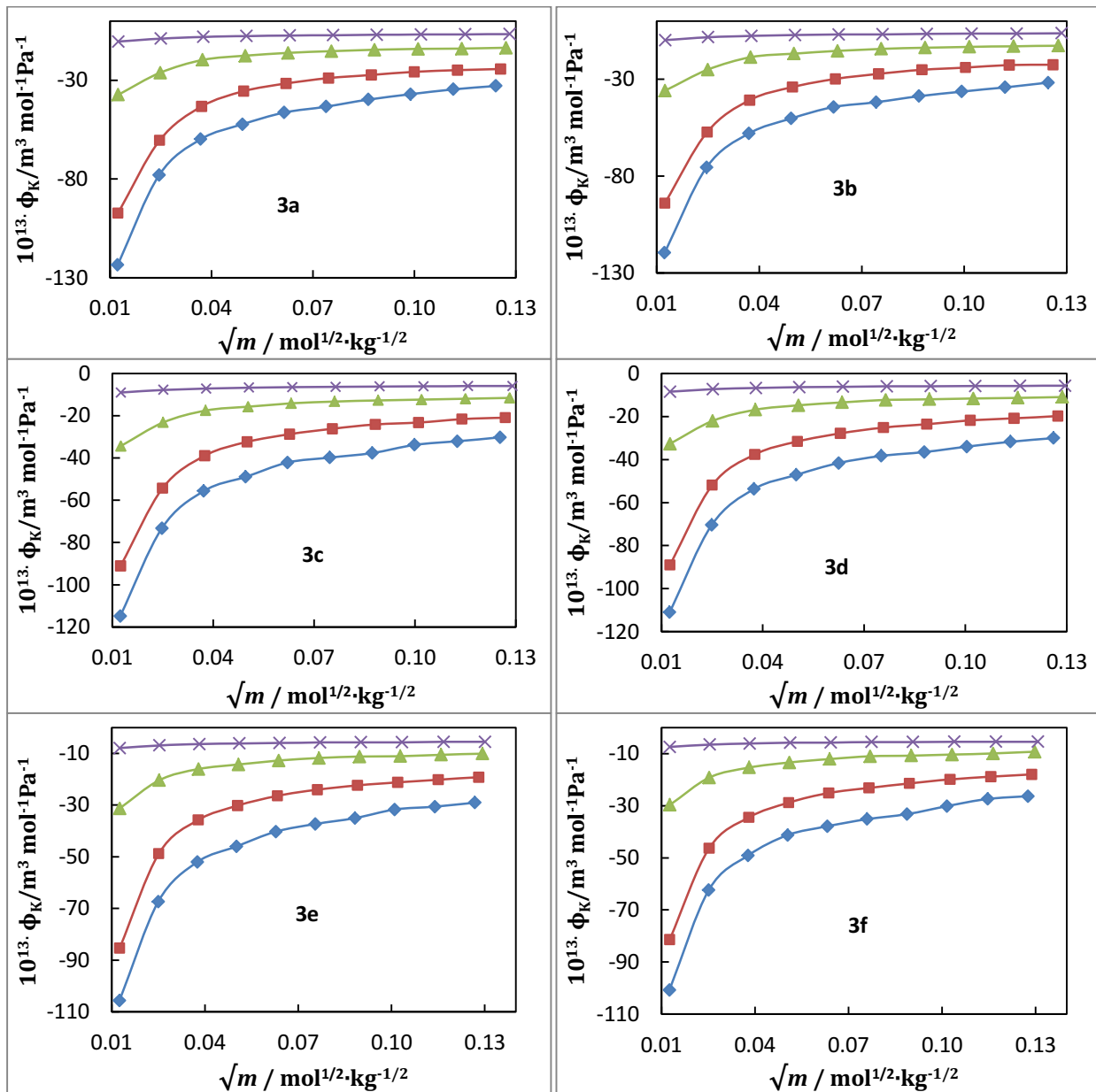
■ **Figure VI.1.** A plot of apparent molar volume (ϕ_V) of ionic liquid (1-ethyl-3-methylimidazolium chloride-aluminum chloride) with a corresponding concentration in methanol (1a), ethanol (1b), 1-propanol (1c), and 1-butanol (1d), at $T=293.15\text{K}$ - 318.15K and atmospheric pressure



■ **Figure VI.2.** Plot of molar refraction (R_M) of ionic liquid ([EMIm]Cl/ AlCl_3) vs concentration for (2a) methanol, (2b) ethanol, (2c) 1-propanol, and (2d) 1-butanol, at different temperature and at atmospheric pressure

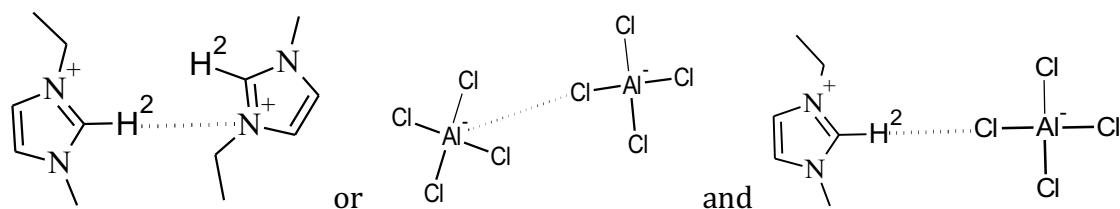


■ **Figure VI.3.** Plot of apparent molar isentropic compressibility (ϕ_κ) of ionic liquid ([EMIm]Cl/AlCl₃) vs concentration for methanol (◆), ethanol (■), 1-propanol (▲), and 1-butanol (×), at 293.15K (3a), 298.15K (3b), 303.15K (3c), 308.15K (3d), 313.15K (3e), 318.15K (3f) and at atmospheric pressure.

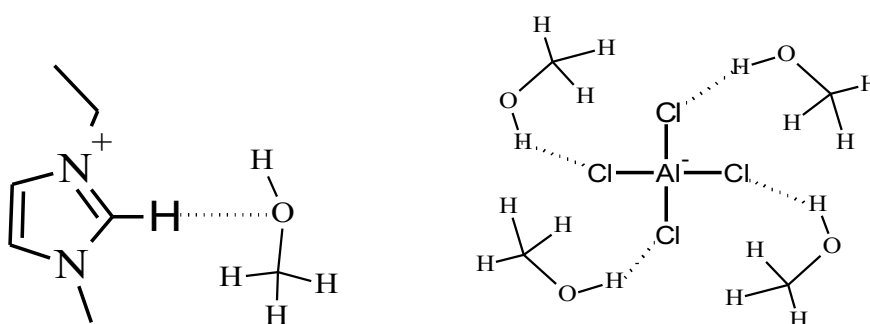


SCHEMES

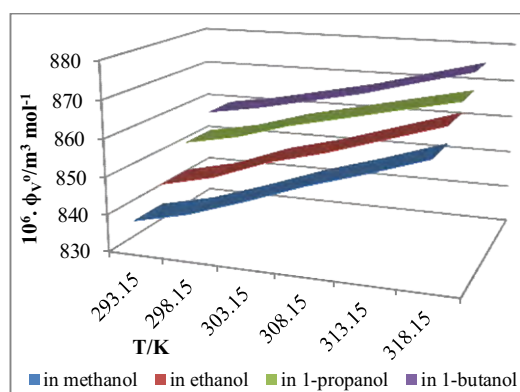
■ **Scheme VI.1.** Plausible inter-ion interaction of ionic liquid ([EMIm]Cl/AlCl₃)



■ **Scheme VI.2.** Plausible form of Hydrogen bonding of ionic liquid [EMIm]Cl/AlCl₃ with methanol [32]

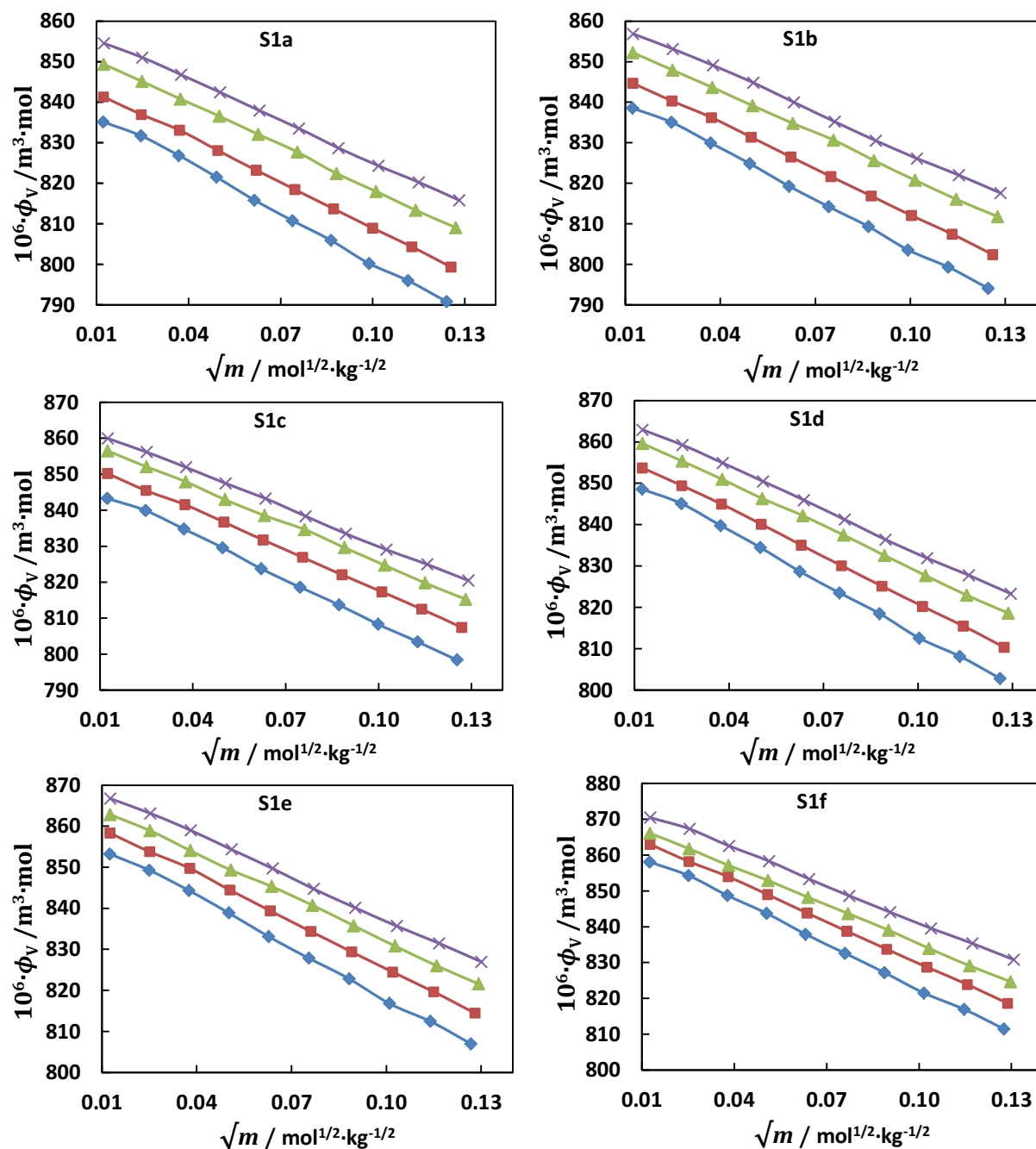


Graphical Abstract

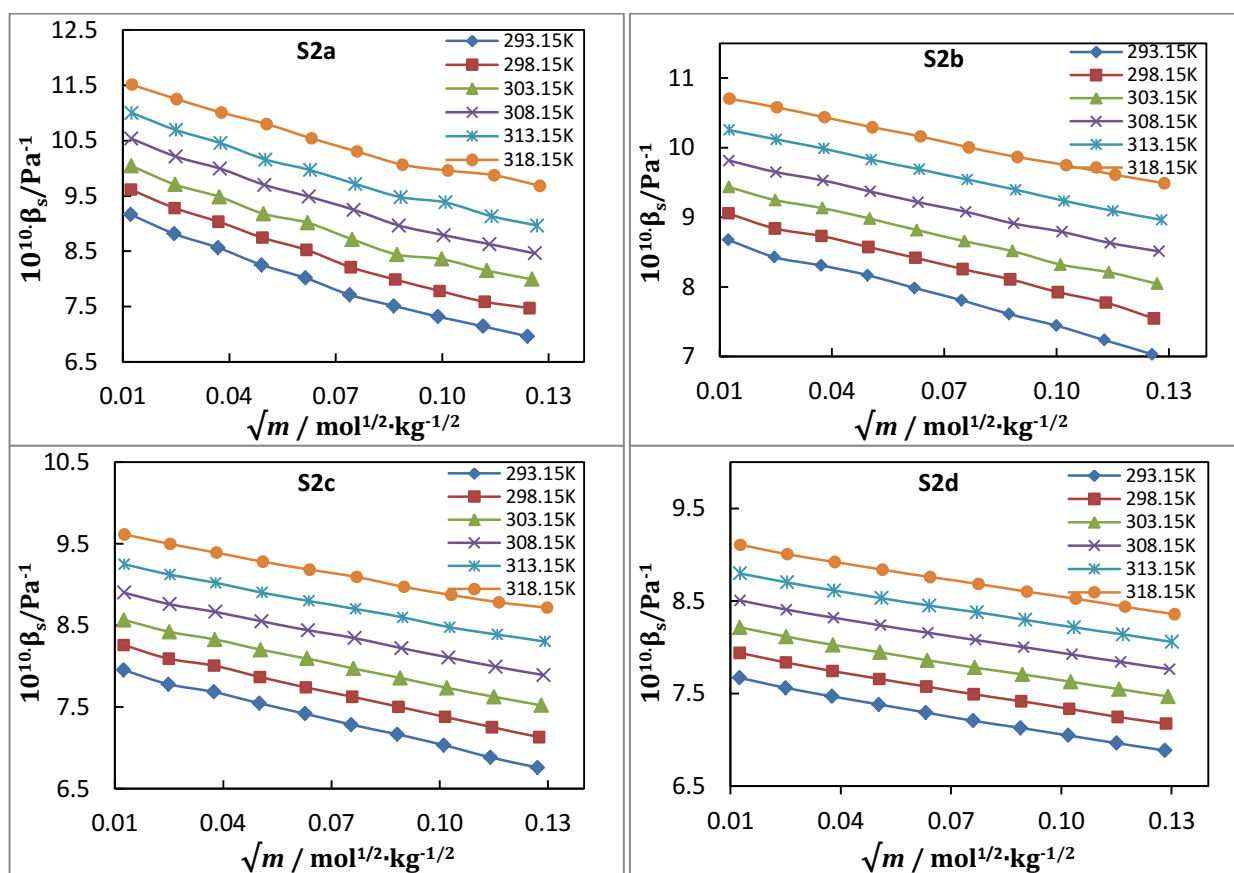


SUPPORTING DATA

■ **Fig S1.** Plot of apparent molar volume (ϕ_V) of ionic liquid ([EMIm]Cl/AlCl₃) vs concentration for methanol (◆), ethanol (■), 1-propanol (▲), and 1-butanol (×), at different temperature and atmospheric pressure



■ **Fig S2.** Plot of isentropic compressibility (β_s) of ionic liquid ([EMIm]Cl/AlCl₃) vs concentration for methanol (S2a), ethanol (S2b), 1-propanol (S2c), and 1-butanol (S2d), at different temperature and atmospheric pressure



■ **Fig S3.** Plot of apparent molar isentropic compressibility (ϕ_κ) of ionic liquid ([EMIm]Cl/AlCl₃) vs concentration for methanol (S3a), ethanol (S3b), 1-propanol (S3c), and 1-butanol (S3d), at different temperature and atmospheric pressure

