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Schiff base ligands and their transition metal complexes in the mixtures of ionic liquid + organic solvent: thermodynamic study

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Abstract

Schiff bases and their metal complexes in the mixtures of ionic liquid (IL) + organic solvent have presented great potential in attractive oxidation catalytic processes. The efficiency of such process is strongly dependent on the various molecular interactions existing between components. Thermodynamic properties of these systems can provide valuable information about structural interactions. Therefore, in this work, the interactions of the IL 1-hexyl-3-methylimidazolium chloride ([HMIm]Cl) with Schiff bases and organic solvents were studied through the measurements of density, viscosity, and electrical conductivity. The effect of solvent structure on the interactions was examined by the solutions of IL + BPIC Schiff base + solvent ($C_2H_6O/C_3H_8O/C_4H_{10}O$). Moreover, the influence of structure of Schiff base ligands and Schiff base complexes was probed by the solutions of IL + DMA + ligand (salcn/salpr/salen) and IL + DMA + complex (VO(3-OMe-salen)/VO(salophen)/VO(salen)), respectively. Using the experimental data, some important thermodynamic properties, such as standard partial molar volume ($V_{\phi,IL}^0$), experimental slope (S_v), viscosity B-coefficient, solvation number ($B/V_{\phi,IL}^0$), and limiting molar conductivity (Λ_0) were calculated and discussed in terms of solute-solvent (IL-DMF/alcohol) and solute-cosolute (IL-Schiff base) interactions.

Keywords: Ionic liquid, Schiff base, Density, Viscosity, Conductivity, Ion-solvent interaction.

1. Introduction

Schiff bases are extensively used as analytical reactants since they allow simple and inexpensive determination of several organic and inorganic substances.[1] They also form stable complexes with metals that perform important role in biological systems. Due to their interest in analytical and bioinorganic chemistry, complexes of tetra-coordinated Schiff bases and transition metals are widely studied. Such complexes present many applications in catalysis and oxygen storage devices[2] and also present antitumoral, antiviral, and antibacterial activity[3] and are used as mimetic systems for enzyme models.[4] Several Schiff bases have recently been investigated as corrosion inhibitors for various metals and alloys in acid media.[5–9] The existing data show that these inhibitors act by adsorption on the metal/solution interface.[10]

One of the major drawbacks of the homogeneous catalysts is the difficulty in separating catalysts from the reaction mixture at the end of the process. The possible contamination of catalyst in the product also restricts their use in industry. Recently, ionic liquids have shown unique class of reaction media for catalytic processes. The number of catalytic reactions involving ionic liquids is rapidly increasing. These liquids offer promising solutions to the problems associated with conventional organic solvents, and the potential advantages may include enhanced reaction rates and facile separation of products and catalyst recovery.[11–14] Because most transition metal complexes are soluble in ionic liquids, the ionic liquids are particularly suitable for the isolation of catalysts from products. It will be desirable to have a high solubility of the reactants combined with a low solubility of the main products in the ionic liquid phase. In such a system, the removal of the reaction products from the ionic liquid phase can totally lead to high yields. Also ionic liquids referred to *designer solvents* because their properties can be tailored by the variation of the structure and the composition of the cations and

anions. This advantage permits to design ionic liquids with the possibility to alter the solubility of organic reactants in the ionic liquids.

Moreover, the addition of co-solvents has been found to strongly affect various physico-chemical properties of ionic liquids. The mixed organic solvents and ionic liquids can be used advantageously to achieve homogeneous systems in which the reactants and catalysts have the best solubility. Therefore, various thermophysical properties of the systems composed of Schiff base, ionic liquid, and molecular solvents can provide useful information about ion-ion and ion-solvent interactions that probably characterize their solution thermodynamics and structure in solution phase and such information would permit developing a suitable experimental procedure for a convenient biphasic reusable catalytic system.

In this article, we synthesized several Schiff base ligands and their oxovanadium complexes and reported some of their thermodynamic properties in the mixtures of ionic liquid ([HMIm]Cl) with different organic solvents (C_2H_6O, C_3H_8O, $C_4H_{10}O$, and DMF). The results were discussed in terms of IL-solvent and IL-Schiff base interactions. In addition, the influence of the solvent structure, temperature, and the structure of Schiff base ligands and their complexes were examined on the interactions.

2. Experimental section

2.1 Materials

The solvents used in this work are C_2H_6O (>99.5%, Merck), C_3H_8O (>99%, Merck), $C_4H_{10}O$ (>99%, Merck), and DMF (99.9%, Merck), and the chemicals used to synthesize and purify the ionic liquid ([HMIm]Cl) are *N*-methylimidazole (>99%, Merck), 1-chlorohexane (>99%, Merck), and ethyl acetate (99.8%, Merck). The materials for synthesis of Schiff bases and their complexes are pyridine-2-aldehyde (>99%, Merck) and 1,2-cyclohexanediamine (>99%, Merck) for BPIC,

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salicylaldehyde (2-hydroxybenzaldehyde) (99%, Fluka) and ethylenediamine (99.9%, Merck) for salen, 1,3-diaminopropane (>99%, Merck) and salicylaldehyde for salpr, 1,2-diaminocyclohexane (>99%, Merck) and salicylaldehyde for salcn, vanadyl acetylacetonate, which was added to salen, for VO(salen), 3-OMe-salen and vanadyl acetylacetonate for VO(3-OMe-salen), and salophen and vanadyl acetylacetonate for the synthesis of VO(salophen).

2.2 General method for preparation of the Schiff base ligands

The bis-salicyldimine Schiff base ligands: salen [*N,N′*-bis(salicylidene)-ethylenediamine], salpr [*N,N′*-bis(salicylaldehyde)-1,3-diaminopropane], and salcn [*N,N′*-1,2-cyclohexyl-bis(salicyldiamine)] were prepared as follows:[15,16]

A solution of salicyladehyde was added drop wise onto a solution of the amine in 50ml ethanol in molar ratio of 1:1 or 1:2 for a period of 1h. The reaction mixture was refluxed for 1h with continuous stirring. The reaction was left to cool where coloured compounds were filtrated off and washed several times with water and ethanol and dried in vacuum desiccator.

The Schiff base BPIC [*N,N′*-bis(2-pyridylmethylidene)-trans-1,2-diiminocyclohexane] was also prepared as follows:

The pyridine-2-aldehyde was added slowly to 1,2-cyclohexanediamine in ethanol solution. After stirring the mixture gently for 1 h and the removal of the ethanol by rotary evaporation, an orange-yellow residual liquid product was obtained. The product was extracted with hot hexane several times. After cooling, an orange product was obtained and recrystallized from diethyl ether. The schematic reactions of the ligands preparation are given as follows:
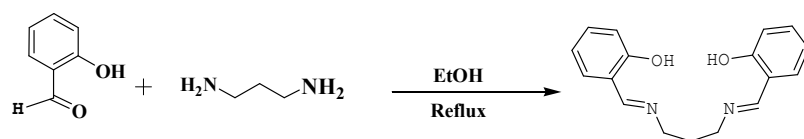
BPIC: elemental analysis. Calc. for $C_{18}N_4H_{20}$: C, 73.93; H, 6.91; N, 19.16. Found: C, 73.95; H, 6.92; N, 19.32.
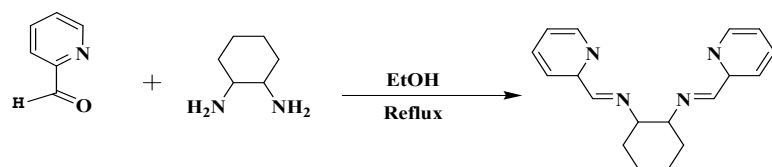
Salen: elemental analysis. Calc. for $C_{16}N_2O_2H_{16}$: C, 71.61; H, 6.02; N, 10.44. Found: C, 71.40; H, 6.20; N, 10.30.
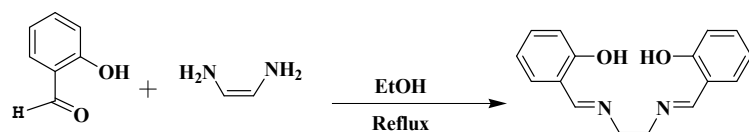
Salpr: elemental analysis. Calc. for $C_{17}N_2O_2H_{18}$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.11; H, 6.24; N, 9.78.

Salcn: elemental analysis. Calc. for $C_{20}N_2O_2H_{22}$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.34; H, 6.57; N, 8.85.
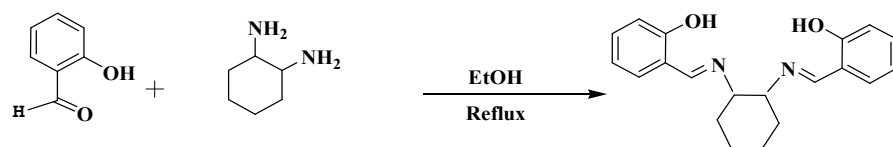
2.3 General method for the preparation of VO complexes

The vanadium complexes of Schiff base were prepared as follows:

The required weights of the inorganic salts were dissolved in methanol (20 ml) for Schiff base and refluxed with the desired weight of the ligand in methanol (20 ml) for Schiff base. The

reaction mixture was refluxed with stirring. The corresponding solid complexes were filtered,

washed several times with methanol and dried in vacuum desiccator. The schematic reactions of
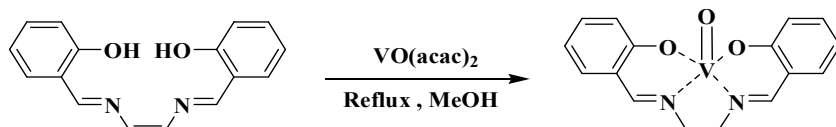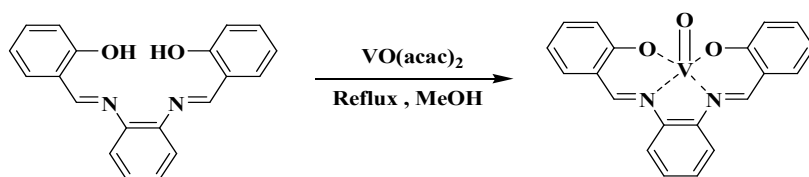
the VO complexes preparation are given as follows:

VO(salen): elemental analysis. Calc.for $C_{20}N_2O_2H_{22}$: C, 57.67; H, 4.23; N, 8.41. Found: C, 57.50;

H, 4.10; N, 8.50. IR (KBr, cm^{-1}): υ 989 (V=O), υ 1623 (C=N).

VO(salophen): elemental analysis. Calc. for $C_{20}N_2O_3VH_{14}$: C, 58.13; H, 3.41; N, 6.78; V, 12.33.

Found: C, 58.00; H, 3.32; N, 6.89; V, 12.28. IR (KBr, cm^{-1}): υ 980 (V=O), υ 1630 (C=N).

VO(3-OMe-salen): elemental analysis. Calc. for $C_{18}N_2O_5VH_{18}$: C, 54.96; H, 4.62; N, 7.12; V,

12.95. Found: C, 54.85; H, 4.70; N, 7.00; V, 12.89.
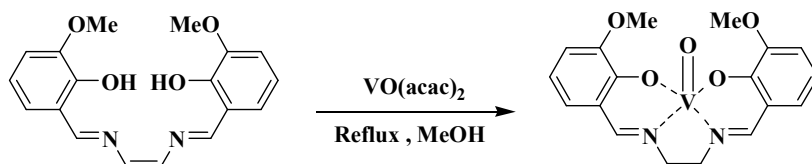
2.4 Synthesis of the ionic liquid

1-Hexyl-3-methylimidazolium chloride was prepared by the reaction of *N*-methylimidazole with

an excess amount of 1-chlorohexane in a round bottom flask mixed by a magnetic stirrer under a

nitrogen atmosphere. The reaction mixture was stirred for one week, and finally, the crude

product was separated from reagents and then washed three times with fresh ethylacetate. The removal of residual volatile compounds from the ionic liquid was done in high vacuum at 60 ^{0}C using a rotary evaporator for at least 4 h at reduced pressure. The obtained ionic liquid had purity greater than 98% verified by ^{1}H NMR spectroscopy. The ionic liquid was used after vacuum desiccated for at least 48 h to remove trace amount of moisture. Water content found by Karl Fischer method in the ionic liquid was less than 0.2%. The schematic reaction of the ionic liquid preparation is given as follows:

^{1}HNMR (300 MHZ, CDCl$_3$) (ppm): 10.21 (s, 3H), 7.52 (d, 1H, J= 1.5 HZ), 7.28 (d, 1H, J= 1.5 HZ), 4.02 (t, 2H, J= 12.9 HZ), 3.83 (s, 1H), 1.59 (m, 2H), 0.99 (t, 3H, J= 6.6).
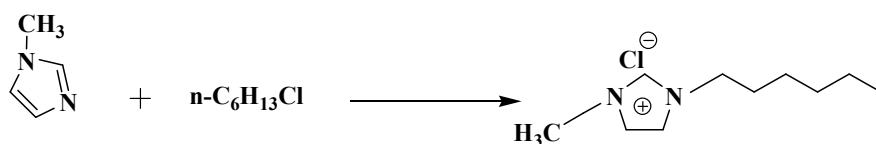
2.5 Instruments and methods

Densities were measured with a vibrating-tube densimeter (Anton Paar, DMA 4500 M), calibrated at the experimental temperatures with doubly distilled water at atmospheric pressure. The temperature was automatically kept constant with an accuracy of $\pm 1 \times 10^{-2}$ K using the built-in Peltier technique. The stated repeatability and uncertainty of the densities were $\pm 1 \times 10^{-5}$ g cm^{-3} and $\pm 5 \times 10^{-5}$ g cm^{-3}, respectively. However, the estimated uncertainty of the measured densities tested by the solutions with known densities was found to be less than $\pm 3 \times 10^{-5}$ g cm^{-3} for most of the solutions.

Viscosities were measured using an Ubbelohde-type viscometer, calibrated at the experimental temperatures with doubly distilled water. The clean, dried viscometer was filled with experimental liquid and placed vertically in a glass sided thermostat maintained constant to ± 0.01 K. After attainment of thermal equilibrium, the efflux times of flow of liquids were

recorded with a digital stopwatch correct to ±0.01 s. The maximum uncertainty of the solutions

viscosities was estimated to be ±0.006 mPa s.

Specific conductivities were measured using a conductivity meter (Metrohm model 712,

Switzerland) with accuracy of ±0.5%. The cell constant was calculated by repeated

measurements of KCl solution in 0.01 mol kg^{-1}. About 50 ml of solvent (Schiff base

ligand/complex + organic solvent) was filled into the conductivity cell and the cell was closed.

Weighting was performed by an analytical balance (Sartrious, AG TE214S) with precision

±1×10^{-4} g. After the measurement of the solvent conductivity, a weighed amount of pure ionic

liquid ([HMIm]Cl) was added with a syringe to the cell containing solvent and the measurement

was repeated. To minimize the risk of the presence of concentration gradients in the cell, the

solution was continuously stirred with a magnetic stirrer. The water from a thermostatically

regulated bath was circled around the cell with double wall to maintain the temperature with an

uncertainty ±0.02 K.

3. Data processing

3.1 Density

The measured densities of the solutions (Table 1) were used to calculate the apparent molar

volumes ($V_{\phi,IL}$) of the ionic liquid ([HMIm]Cl) at T = 298.15, 303.15, 308.15, and 313.15 K

using the following equation:

$$V_{\phi,IL} = \frac{M_{IL}}{d} - \frac{1000(d - d_0)}{m_{IL}dd_0},\tag{1}$$

where M_{IL} and m_{IL} are the molar mass and the molality of the IL, and d and d_0 are the densities of

ternary solutions (IL + Schiff base + solvent) and binary mixtures (Schiff base + solvent),

respectively. The obtained values for apparent molar volume are shown in Table 1. The standard

partial molar volumes ($V_{\phi,IL}^0$) of the IL were calculated by the extrapolation of $V_{\phi,IL}$ against m_{IL} to zero concentration using the following equation:

$$V_{\phi,IL} = V_{\phi,IL}^0 + S_v m_{IL},\tag{2}$$

where S_v is experimental slope and represents solute-cosolute and ion-ion interactions. We know that the use of purely empirical Masson equation to extrapolate the apparent molar volume at infinite dilution is at best a crude approximation. The proper method is to use the Redlich-Mayer and Pitzer equations. However, these equations make use of the theoretical slope, and this approach requires accurate data of the pressure derivative of the dielectric constant of the solvent. These data for organic solvents are not available or available at 298.15 K only. Since the value of the pressure derivative of the relative permittivity of the solvent seems to be very sensitive to temperature and our data cover the temperature range from 298.15 to 313.15 K, we decided to fit our data to the simplest equation.

The temperature variation of $V_{\phi,IL}$ values is expressed as follows:

$$V_{\phi,IL}^0 = a_0 + a_1 T + a_2 T^2,\tag{3}$$

where a_0, a_1, and a_2 are regression coefficients. Differentiation of Eq. (3) with respect to temperature at constant pressure gives the partial molar expansivities of the IL ($E_{\phi,IL}^0$) by the following relation:

$$E_{\phi,IL}^0 = \left(\frac{\partial V_{\phi,IL}^0}{\partial T}\right)_P = a_1 + 2a_2 T.\tag{4}$$

The sign of second derivatives of $V_{\phi,IL}^0$ with respect to temperature at constant pressure is used to discuss the structure-breaking or -making tendency of the ionic liquid in the solutions. This equation is given as:

$$\left(\frac{\partial C_P^0}{\partial P}\right)_T = -T\left(\frac{\partial^2 V_{\phi,IL}^0}{\partial T^2}\right)_P, \tag{5}$$

where C_P^0 is the heat capacity of the ionic liquid at infinite dilution.

The isobaric thermal expansion coefficients of the IL at infinite dilution (α_{IL}) were also determined as follows:

$$\alpha_{IL} = \frac{1}{V_{\phi,IL}^0}\left(\frac{\partial V_{\phi,IL}^0}{\partial T}\right)_P = \frac{E_{\phi,IL}^0}{V_{\phi,IL}^0}. \tag{6}$$

3.2 Viscosity

Viscosity of the solutions (η) is given by the following equation:

$$\frac{\eta}{d} = Lt - \frac{K}{t}, \tag{7}$$

where d is density, t is the efflux time of solutions, and L and K are viscometer constants. The values of L and K were obtained, respectively, as 3.9648×10^{-6} mPa cm^3 g^{-1} and 2.1995×10^{-3} mPa s^2 cm^3 g^{-1} using the known viscosity values of double distilled water.[17] The viscosity data (Table 3) were analysed using the Jones–Dole viscosity equation:

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc + Dc^2, \tag{8}$$

where η and η_0 are the viscosities of ternary solutions (IL + Schiff base + solvent) and binary mixtures (Schiff base + solvent), respectively. c is the molarity of the IL, and A, B, and D are empirical constants known as the viscosity A-, B-, and D-coefficients. According to conventional technique of the viscosity coefficient determination, the B- and D-coefficients can be estimated from the experimental viscosity data by extrapolating the following function:

$$B + Dc = \frac{\eta/\eta_0 - 1 - Ac^{1/2}}{c} \tag{9}$$

to zero concentration using the value of A, which can be obtained theoretically or as the intercept

of the dependence $[(\eta/\eta_0)-1]/c^{1/2}$ on $c^{1/2}$ as follows:

$$\frac{\eta/\eta_0-1}{c^{1/2}} = A + Bc^{1/2}. \tag{10}$$

The A value can be calculated theoretically as follows:[18]

$$A = A^*\eta_0^{-1}(\varepsilon_0 T)^{-1/2} f \tag{11}$$

$$A^* = Fe^2 N_A^{1/2}(1+\sqrt{2})(12\pi)^{-1}(\varepsilon k)^{-1/2} \tag{12}$$

$$f = \frac{z_+ z_-(\lambda_+^\infty + \lambda_-^\infty)}{4(2+\sqrt{2})(\lambda_+^\infty \lambda_-^\infty)}[1 - \frac{4(\lambda_+^\infty - \lambda_-^\infty)^2}{(1+\sqrt{2})^2(\lambda_+^\infty + \lambda_-^\infty)^2}], \tag{13}$$

where A^*=1.113×10^{-5} C^2 m$^{1/2}$ K$^{1/2}$ mol$^{-3/2}$, f is the function of the equivalent conductivities ($\lambda_\pm^\infty$) at

infinite dilution of the ions and the ion charges ($z_\pm$), ε_0 is dielectric constant, k is Boltzmann

constant, and ε is vacuum permittivity.

In this article, the A-coefficients were obtained by the intercept of Eq (10) and used to

calculate the B- and D-coefficients by Eq (9).

3.3 Conductivity

The molar conductivities of [HMIm]Cl in the mixtures of Schiff base + solvent were calculated

by the following equation:

$$\Lambda = \frac{1000\kappa}{c}, \tag{14}$$

where κ is the specific conductivity of the ionic liquid solutions. The obtained Λ values are

included in Table 5. Limiting molar conductivities (Λ_0) and ion association constants (K_A) of the

IL were obtained by least-squares fitting the experimental molar conductivities to a well-known

conductivity equation, named as low concentration Chemical Model (lcCM).[19] Three adjustable

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parameters: limiting molar conductivity (Λ_0), ion association constant (K_A), and distance

parameter (R) are defined from the analysis of conductivity data based on this model as the

following set of equations:

$$\Lambda = \alpha[\Lambda_0 - S(c\alpha)^{1/2} + Ec\alpha \ln(c\alpha) + J_1 c\alpha + J_2(c\alpha)^{3/2}]$$ (15)

$$K_A = \frac{1-\alpha}{\alpha^2 c \gamma_\pm^2}$$ (16)

$$\ln \gamma_\pm = -\frac{\kappa q}{1+\kappa R}$$ (17)

$$\kappa^2 = \frac{16 \times 10^3 N_A z^2 e^2 \alpha c}{\varepsilon_0 \varepsilon k_B T}$$ (18)

$$q = \frac{z^2 e^2}{8\pi \varepsilon_0 \varepsilon k_B T},$$ (19)

where Λ and Λ_0 are the molar conductivities at molarity c and at infinite dilution, $1-\alpha$ is the

fraction of oppositely charged ions acting as ion pairs, K_A, R, and $\gamma_\pm$ are the ion association

constant of ionic liquid, distance parameter, and the corresponding mean activity coefficient of

the free ions, respectively. In Eq (15), S is the coefficient of the Debye-Hückel-Onsager, and E

depends only on the properties of the solvent and the charge of the ions. J_1 and J_2 depend on the

same parameters as E does as well as the distance parameter. The E, J_1, and J_2 values required for

calculations were taken from literature.[19] The rest quantities have the usual meaning. Three-

parameter fits of molar conductivity data yield the ion-association constant (K_A), the limiting

molar conductivity (Λ_0), and the distance parameter (R) by non-linear least-squares iteration

procedure. The starting Λ_0 value were obtained from Debye-Hückel-Onsager extrapolation of the

data. The calculation was made by finding the Λ_0, K_A, and R values that minimized the standard deviation $\sigma(\Lambda)$ as follows:

$$\sigma(\Lambda) = \left(\sum [\Lambda_{\exp} - \Lambda_{calc}]^2 / (n-p) \right)^{1/2}, \tag{20}$$

where n and p show the number of experimental data and the obtained parameters, respectively.

4. Results and discussion

4.1 Volumetric properties

Volumetric properties of ternary solutions give important information about structural changes and different kinds of interactions happening in the solution. These interactions can be affected by many elements, such as the solvent, the solute, the solution concentration, and the temperature.

4.1.1 Effect of solvent on the volumetric properties

To examine the effect of solvent structure on the interactions of the studied ternary systems, we obtained the values of experimental slopes (S_v) and standard partial molar volumes ($V_{\phi,IL}^0$) of the ionic liquid ([HMIm]Cl) in the mixtures of BPIC Schiff base ligand (0.05 mol kg^{-1}) + C_2H_6O/C_3H_8O/$C_4H_{10}O$ at temperatures ranging from 298.15 K to 313.15 K. The obtained values have been reported in Table 2, and the solvent effect on the $V_{\phi,IL}^0$ values is graphically presented by Fig. 1. In the studied systems, the S_v values show the solute-cosolute interactions between the IL and the ligand and also the solute-solute or the ion-ion interactions between the ions of the IL. Moreover, the $V_{\phi,IL}^0$ values display the solute-solvent interactions mainly between the IL and the alcohol. These interactions can be classified into three major kinds including (i) nonpolar-

nonpolar interactions between the alkyl chain of the IL cation and the alkyl chain of alcohol, (ii) hydrogen bond between the H atom of alcohol and the Cl⁻ anion of the IL, and (iii)[20] interactions between the O atom of alcohol and the cationic ring π-electrons. Table 2 shows that the $V^0_{\phi,IL}$ values increase with the elongation of the alcohol chain and also increase with the increase of temperature. This observation indicates that the solute-solvent interactions are favoured at higher temperatures and when the alcohol has longer alkyl chain. According to the classified IL-alcohol interactions, it seems that the elongation of alcohol alkyl chain has two opposite effects on the solute-solvent interactions. On the one hand, the alcohols under investigation exhibit dipole moments in the sequence $C_2H_6O > C_3H_8O > C_4H_{10}O$ reflecting their individual abilities to form hydrogen bonds. Therefore, the (ii)-type interactions are weakened when the alcohol chain is lengthened, which results in the lower $V^0_{\phi,IL}$ values. On the other hand, butanol with a long alkyl chain feels less electron deficit on its O-H bond and as a sequence shows stronger O−π-electrons interactions. Moreover, the nonpolar-nonpolar interactions between the alkyl chains of the IL and the alcohol are intensified by the increase of alcohol chain length resulting in the higher $V^0_{\phi,IL}$ values. The increasing trend found in the $V^0_{\phi,IL}$ values implies that the (i)- and (iii)-type interactions predominate over (ii)-type interactions in the studied systems. It is also clear from Table 2 that the $V^0_{\phi,IL}$ values increase with temperature. It seems that the anion-alcohol interaction has a significant portion in the increasing $V^0_{\phi,IL}$ values with temperature due to the smaller molecular weight of the anion. At high temperatures, the hydrogen-bonding formation between the alcohol and the Cl⁻ anion may be favoured due to the faster molecular movement of the anion and the alcohol that would lead to a higher number of molecules with energy to overcome the energy barrier for hydrogen-bonding formation. The increase of temperature makes

the small anions get into the interstices within hydrogen bonded clusters of alcohol molecules and interact with them.

Table 2 also indicates that the S_v values are positive and decrease with the elongation of alcohol alkyl chain but increase as temperature increases. The positive S_v values show that there exist interactions between the ligand and the IL, but these interactions are weakened as the alcohol chain is lengthened. We previously discussed[21] that the interactions between the Schiff base and ionic liquid can be categorized as follows: (i) the polar–ionic interactions between the polar N-groups of the Schiff base and the ions of IL, (ii) polar–polar interactions between the polar groups of the Schiff base and the imidazolium ring of IL, (iii) polar–nonpolar interactions between the N-group of the Schiff base and the nonpolar alkyl chain of IL, and (iv) nonpolar–nonpolar interactions between the nonpolar groups of the Schiff base and the alkyl chain of IL. Of these interactions, those of types (i) and (ii) make a reduction in the electrostriction effect and, as a sequence, lead to positive transfer volumes, while the interactions of types (iii) and (iv) lead to negative transfer volumes. The negative values of transfer volumes obtained in our earlier paper[21] indicate that the polar–nonpolar group and nonpolar–nonpolar group interactions predominate over the polar–ionic group and polar–polar group interactions between the Schiff base and ionic liquid. The fact that the experimental slopes increase with the decrease of alcohol chain length could be related to the reduced nonpolar–nonpolar interactions of the cation and the short-chain alcohol that results in an enhancement in the IL-Schiff base interactions.

The partial molar expansibilities ($E^0_{\phi,IL}$) measure the variation of the volume of the ionic liquid with temperature. These values are included in Table 2. Clearly, the $E^0_{\phi,IL}$ values for each alcohol are positive and decrease with temperature rising from 298.15 K to 313.15 K. The

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positive $E^0_{\phi,IL}$ values suggest that at high temperatures, alcohol molecules are loosely held around the IL and thus there is an increase in the standard partial molar volumes.

The sign of second derivatives of $V^0_{\phi,IL}$ with respect to temperature at constant pressure is a better parameter to discuss the structure-breaking or -making tendency of the IL in the solutions. For a structure-breaking solute, the left side of Eq (5) should be positive and $(\partial^2 V^0_{\phi,IL}/\partial T^2)_P$ consequently should be negative for structure-breaking and positive for structure-making solutes. The values of $(\partial^2 V^0_{\phi,IL}/\partial T^2)_P$ for the IL (Table 2) were found to be negative, which means that the IL acts as a structure-breaker in the alcohol mixtures.

Cabani et al.[22] have shown that the coefficient of thermal expansion (α) can be used for understanding the solute-solvent interactions. From Table 2, it is observed that the α_{IL} values of the ionic liquid in C_3H_8O mixtures at all temperatures except for $T = 313.15$ K are greater than those in C_2H_6O and $C_4H_{10}O$ mixtures. This is consistent with the results of the temperature variation of the $V^0_{\phi,IL}$ values.

4.1.2 Effect of Schiff base ligand structure on the volumetric properties

To study the effect of ligand structure on the volumetric properties, we measured densities of the solutions composed of [HMIm]Cl + salcn/salpr/salen (0.05 mol kg^{-1}) + DMF at $T = 298.15$ to 313.15 K. Using Eqs (2) and (3), the values of experimental slopes and standard partial molar volumes of the ionic liquid were obtained and reported in Table 2. It is obvious that the $V^0_{\phi,IL}$ values in pure DMF are greater than those in the mixed solvent and decrease in the order salcn > salpr > salen (see Fig. 2). The most likely reason for the observed trend may be attributed to molecular volume of the studied ligands. This volume follows the above order. It seems that the large volume does not allow the ligand to approach the ions, especially the cation, and

interact with them. This steric strain increases in the case of salcn due to the presence of a hexyl cycle on its structure. As a result, the weaker interaction of the IL with salcn leads to an enhancement in the ion-solvent interactions evident by the higher $V^0_{\phi,IL}$ values in salcn mixtures.

Table 2 shows that the S_v values decrease as the sequence salen > salpr > salcn, which is the inverse of the order observed for the $V^0_{\phi,IL}$ values. This means that an increase in the solute-solvent interactions is normally accompanied by a reduction in the solute-cosolute interactions. It is also clear that the experimental slopes increase with temperature. It seems that at high temperatures, some loosely bound DMF molecules are released from the secondary solvation shells of the ions, and hence the IL-ligand interactions can become stronger with the increase of temperature.

The values of partial molar expansibilities ($E^0_{\phi,IL}$) of the IL in ligand + DMF mixtures are given in Table 2. Clearly, the $E^0_{\phi,IL}$ values at all temperatures are negative that means the standard partial molar volumes decrease with the increase of temperature (see Fig. 2). At high temperatures, some of DMF molecules may be hydrolyzed back into formic acid and dimethylamine, which causes to release a portion of the solvent molecules from the solvation sphere of the IL.

The $(\partial^2 V^0_{\phi,IL}/\partial T^2)_P$ values of the IL in ligand + DMF mixtures are shown in Table 2. These values are all negative showing that the IL acts as a structure-breaker in the mixtures.

The coefficient of thermal expansion (α_{IL}) are also given in Table 2. It is clear that the α_{IL} values are all negative and become more negative for salcn and salen but less negative for salpr at higher temperatures. The fact that the coefficients of thermal expansion have a different

order of magnitude for the ligand mixtures suggests a thermal behaviour practically dependent of the ligand nature.

4.1.3 Effect of Schiff base complex structure on the volumetric properties

The standard partial molar volumes of the IL in the binary mixtures of DMF + vanadium Schiff base complex (VO(3-OMe-salen), VO(salophen), and VO(salen)) at different temperatures are given in Table 2. Surprisingly, it was observed that the $V^0_{\phi,IL}$ values increase with increasing temperature (see Fig. 3), which this tendency is opposite the trend we previously observed in the case of $V^0_{\phi,IL}$ values in the Schiff base ligand mixtures. It is also clear that the $V^0_{\phi,IL}$ values in the complex mixtures follow the order VO(3-OMe-salen) > VO(salophen) > VO(salen), showing that the standard partial molar volumes have greater values in the presence of larger VO complex.

The comparison of the experimental slopes of the complex solutions with those of the ligand solutions, especially the salen ligand and its corresponding vanadium complex, reveals their different thermal behavior in the studied mixtures. Table 2 shows that the S_v values of the complex mixtures decrease with the increase of temperature, while these values for the ligand mixtures increase with temperature. It seems that the coordination of vanadium to the Schiff base ligand changes the thermal behavior of the obtained complex.

The values of partial molar expansibilities ($E^0_{\phi,IL}$) of the IL in DMF + complex mixtures are given in Table 2. It is obvious that the $E^0_{\phi,IL}$ values at all temperatures are positive that means the standard partial molar volumes increase at higher temperatures. The $(\partial^2 V^0_{\phi,IL} / \partial T^2)_P$ values are also given in Table 2. These values are negative showing that the IL behaves as a structure-breaker in DMF + complex mixtures.

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The coefficient of thermal expansion (α_{IL}) were also calculated and reported in Table 2. It is clear that the α_{IL} values are all positive and decrease for VO(3-OMe-salen) and VO(salen) but increase for VO(salophen) at higher temperatures. Moreover, the greatest values of thermal coefficient were obtained for VO(3-OMe-salen) at lower temperatures and for VO(salophen) at higher temperatures.

4.2 Viscosity *B*-coefficients

Viscosity is one of the key transport properties of electrolyte solutions. The accurate viscosity data (viscosity *A*- and *B*-coefficients) is known to give valuable information regarding ion–solvent and ion–ion interactions. The *A*-coefficient depends on the Coulombic interactions between the ions (ion– ion interactions) and can be theoretically calculated from Eq (11), and the viscosity *B*-coefficient reflects the variations of the solvation properties of ions in the solutions. The viscosity *D*-coefficient includes all solute–solvent and solute–solute structural interactions that were not accounted by the *A*- and *B*-coefficients at high concentrations, such as high terms of the Coulombic forces, high term hydrodynamic effect, and interactions arising from changes in solute–solvent interactions with concentration.[23] According to Donald and Jenkins[24], for most solutes, the *D*-coefficient is unimportant at $c < 0.5$ mol dm^{-3}, and the *A*-coefficient can be obtained if highly accurate data at sufficiently low concentrations ($c < 0.05$ mol dm^{-3}) are available. The concentration range studied here overlaps the range where only the *B*-coefficient is essential. Therefore, in this work, the *A*-, *B*-, and *D*-viscosity coefficients were calculated and reported in Table 4, but only the viscosity *B*-coefficient was discussed.

4.2.1 Effect of solvent structure on the viscosity *B*-coefficient

The values of viscosity B-coefficient of [HMIm]Cl in binary mixtures of BPIC + $C_2H_6O/C_3H_8O/C_4H_{10}O$ at 298.15 K are reported in Table 4. Obviously, the B values are positive and increase with increasing the alkyl chain length of alcohol, which is consistent with the observed trend in the $V^0_{\phi,IL}$ values. The viscosity B-coefficient provides information about ion-solvent interactions and their effect on the solvent structure in the vicinity of the ions. The obtained positive B values demonstrate the presence of ion-solvent interactions, and these interactions are stronger for $C_4H_{10}O$ relative to C_3H_8O and C_2H_6O. This trend is probably attributed to the increased nonpolar-nonpolar interactions of the IL with the longer butyl chain of the $C_4H_{10}O$ alcohol.

The solvation number of the IL is a better tool to study its solvation behavior. When the IL [HMIm]Cl dissolves in alcohol, the alcohol molecules cluster around the separated ions. This process is called solvation. Alcohol frequently attaches to the cation ions by co-ordinate bonds (a shared pair of electrons in which both electrons come from the same atom) and attaches to the Cl^- anions using hydrogen bonds. The values of solvation number are given in Table 4. It is clear from this table that the solvation numbers of the IL in the presence of alcohols has the sequence $C_4H_{10}O > C_3H_8O > C_2H_6O$. Although the solvation number of the IL does not show the exact number of solvent molecules attached to the IL (because the solvation sphere of the ions in the studied ternary mixtures may not include alcohol molecules only), the resulted order for the solvation numbers indicates that the number of $C_4H_{10}O$ molecules solvate each ion is more than that of the other two alcohols. Due to the larger volume of $C_4H_{10}O$ molecule and its greater number in the solvation sell of the IL, the radius of the solvation sphere of the ions must be larger in the $C_4H_{10}O$ mixtures, which is demonstrated by the greater $V^0_{\phi,IL}$ values of the IL in the presence of $C_4H_{10}O$.

4.2.2 Effect of the structures of ligand and complex on the viscosity *B*-coefficient

The values of the viscosity *B*-coefficient of [HMIm]Cl in the binary mixtures of DMA + ligand (salcn/salpr/salen) and DMA + complex (VO(3-OMe-salen)/VO(salophen)/VO(salen)) at 298.15 K are reported in Table 4. This table shows that the *B* values of the IL in the ligand mixtures follow the order salcn > salpr > salen, which verifies the obtained volumetric results. Table 4 also indicates that the viscosity *B*-coefficients of the IL in the complex mixtures increase with the size of complex as the order VO(3-OMe-salen) > VO(salophen) > VO(salen), which again confirms the volumetric results. It is also clear that the viscosity *B*-coefficient in pure DMF is greater than that in the mixed solvents. This shows that the solvation of the ions decreases in the presence of the Schiff base ligand or complex.

4.3 Conductivity

The conductance studies of electrolytes in solutions are of great importance for obtaining information about the intermolecular interactions existing in the solutions.

4.3.1 Effect of solvent on the limiting molar conductivities

The values of limiting molar conductivity (Λ_0) of [HMIm]Cl in the binary mixtures of BPIC + C_2H_6O/C_3H_8O/$C_4H_{10}O$ and also in the pure alcohols at 298.15 K are given in Table 6. This table shows that the limiting molar conductivities of the studied IL in pure alcohols are generally greater than those in the mixed solutions. This behavior is due to the fact that the viscosity of medium increases as BPIC is added to the solution. Moreover, the solvated radii of the ions get larger due to the interactions with the Schiff base. Both of theses reasons make the ionic mobility decrease, and consequently the molar conductivity of the IL reduces in the presence of the Schiff base. It is also obvious that the Λ_0 values of the IL decrease as the alcohol chain length increases

in the order $C_2H_6O > C_3H_8O > C_4H_{10}O$. This observation is because of the fact that the nonpolar-nonpolar interactions between the alkyl chain of the IL and the chain of alcohol are strengthened as the chain length of alcohol increases. This results in the more association of the ions and the alcohol, which reduces the ions mobility leading to the lower Λ_0 values.

4.3.2 Effect of the structures of ligand and complex on the limiting molar conductivities

The values of limiting molar conductivity of [HMIm]Cl in the binary mixtures of DMF + ligand (salcn/salpr/salen) and DMA + complex (VO(3-OMe-salen)/VO(salophen)/VO(salen)) at 298.15 K are reported in Table 6. Clearly, the Λ_0 values of the IL decrease with increasing the size of ligand and complex. This behavior may be due to the higher viscosity of the mixture containing the larger complex or ligand, which results in a reduction in the ionic mobility. Moreover, it can be related to the fact that the ionic mobility decreases as the size of ligand or complex existing in the solvation sphere of the ions increases, which results in lower limiting molar conductivities.

5. Conclusions

The study of solvent effect on the ion-solvent interactions indicated that the IL-alcohol interactions are strengthened as the alcohol chain length increases. It was also revealed that the nonpolar-nonpolar interactions between the alkyl chain of the IL cation and the chain of alcohol predominates over other types of IL-alcohol interactions. The effect of Schiff base ligand structure on the IL-ligand interactions was also examined, and the results showed that theses interactions for the ligands are in the order salcn < salpr < salen, indicating that the IL-ligand interactions are weakened with the increase of the ligand size. This behavior was attributed to the higher steric strain of the larger ligand that does not allow getting close enough to the IL and interacting with it. The same trend was observed for the IL-complex interactions and this type of

interaction decreases as the size of complex gets larger. Surprisingly, it was found that the thermal behavior of the studied Schiff base ligands and their complexes are different. The IL-ligand interactions are strengthened with the increase of temperature, while the IL-complex interactions are weakened at higher temperatures. It seems that the coordination of transition metal to the Schiff base ligand changes the thermal behavior of the obtained complex.

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Figure Captions

Fig. 1 Standard partial molar volumes ($V_{\phi,IL}^0$) of the IL [HMIm]Cl in the mixtures of BPIC Schiff base ligand + alcohol (●C_2H_6O, ■C_3H_8O, and ▲$C_4H_{10}O$) at T = 298.15-313.15 K.

Fig. 2 Standard partial molar volumes ($V_{\phi,IL}^0$) of the IL [HMIm]Cl in the mixtures of DMA + Schiff base ligand (●salen, ■salpr, and ▲salcn) at T = 298.15-313.15 K.

Fig. 3 Standard partial molar volumes ($V_{\phi,IL}^0$) of the IL [HMIm]Cl in the mixtures of DMA + Schiff base complex (●VO(salen), ■VO(salophen), and ▲VO(3-OMe-salen)) at T = 298.15-313.15 K.

Table 1 Densities (d) and apparent molar volumes ($V_{\phi,IL}$) of the IL [HMIm]Cl in binary mixtures of Schiff base (0.05 mol kg^{-1}) + organic solvent at T = 298.15-313.15 K

m_{IL} mol kg^{-1}	T = 298.15 K		T = 303.15 K		T = 308.15 K		T = 313.15 K	
	d g cm^{-3}	$V_{\phi,IL}$ cm^3 mol^{-1}	d g cm^{-3}	$V_{\phi,IL}$ cm^3 mol^{-1}	d g cm^{-3}	$V_{\phi,IL}$ cm^3 mol^{-1}	d g cm^{-3}	$V_{\phi,IL}$ cm^3 mol^{-1}
[HMIm]Cl + BPIC + C$_2$H$_6$O								
0.0000	0.79130		0.78799		0.78467		0.78135	
0.0242	0.79302	142.32	0.78970	143.11	0.78638	143.23	0.78305	144.02
0.0419	0.79425	143.12	0.79093	143.63	0.78760	144.15	0.78427	144.66
0.0599	0.79550	143.53	0.79217	144.20	0.78884	144.60	0.78551	145.00
0.0823	0.79703	143.90	0.79370	144.43	0.79036	144.96	0.78702	145.50
0.1019	0.79834	144.60	0.79501	145.05	0.79168	145.35	0.78833	145.98
0.1218	0.79965	145.18	0.79631	145.72	0.79298	146.00	0.78964	146.42
0.1449	0.80114	145.91	0.79780	146.40	0.79447	146.66	0.79112	147.16
0.1629	0.80229	146.44	0.79896	146.80	0.79562	147.16	0.79227	147.62
0.1772	0.80319	146.82	0.79986	147.17	0.79652	147.51	0.79317	147.95
0.2061	0.80499	147.56	0.80165	147.97	0.79831	148.30	0.79496	148.70
[HMIm]Cl + BPIC + C$_3$H$_8$O								
0.0000	0.80034		0.79711		0.79387		0.79064	
0.0242	0.80201	145.21	0.79877	146.01	0.79552	146.82	0.79229	146.98
0.0419	0.80321	145.75	0.79997	146.28	0.79672	146.81	0.79348	147.35
0.0599	0.80443	146.03	0.80118	146.71	0.79793	147.14	0.79469	147.56
0.0824	0.80592	146.59	0.80266	147.32	0.79941	147.68	0.79617	148.04
0.0986	0.80699	146.82	0.80373	147.47	0.80047	147.96	0.79723	148.29
0.1193	0.80832	147.44	0.80507	147.87	0.80181	148.31	0.79856	148.75
0.1416	0.80972	148.15	0.80648	148.44	0.80323	148.73	0.79998	149.13
0.1605	0.81090	148.61	0.80766	148.89	0.80441	149.17	0.80117	149.45
0.1797	0.81209	149.01	0.80883	149.46	0.80560	149.56	0.80237	149.74
0.2069	0.81374	149.70	0.81050	149.97	0.80727	150.08	0.80403	150.35
[HMIm]Cl + BPIC + C$_4$H$_{10}$O								
0.0000	0.81125		0.80801		0.80477		0.80153	
0.0217	0.81270	148.07	0.80945	148.96	0.80621	149.15	0.80297	149.34
0.0415	0.81400	148.77	0.81075	149.33	0.80751	149.52	0.80427	149.71
0.0622	0.81534	149.26	0.81210	149.46	0.80886	149.65	0.80562	149.84
0.0820	0.81663	149.21	0.81338	149.59	0.81014	149.79	0.80691	149.79
0.1013	0.81783	149.94	0.81460	149.99	0.81137	150.04	0.80815	149.93
0.1203	0.81905	149.90	0.81580	150.23	0.81258	150.18	0.80936	150.12
0.1415	0.82035	150.45	0.81713	150.44	0.81391	150.43	0.81071	150.19
0.1601	0.82148	150.89	0.81828	150.72	0.81507	150.63	0.81188	150.34
0.1820	0.82282	151.14	0.81963	150.93	0.81643	150.79	0.81325	150.48
0.2014	0.82400	151.31	0.82080	151.22	0.81761	151.05	0.81445	150.63
[HMIm]Cl + salen + DMF								
0.0000	0.94528		0.94051		0.93576		0.93084	
0.0204	0.94591	179.73	0.94117	178.80	0.93644	178.39	0.93156	177.48
0.0448	0.94663	180.46	0.94192	179.67	0.93722	179.12	0.93238	178.39
0.0630	0.94715	180.89	0.94246	180.19	0.93778	179.64	0.93297	178.95
0.0880	0.94783	181.54	0.94316	181.00	0.93851	180.43	0.93374	179.76
0.1014	0.94818	181.90	0.94354	181.19	0.93888	180.91	0.93415	180.04
0.1270	0.94883	182.50	0.94419	182.08	0.93958	181.55	0.93488	180.83
0.1367	0.94906	182.79	0.94444	182.29	0.93984	181.77	0.93514	181.19
0.1604	0.94960	183.48	0.94504	182.74	0.94045	182.33	0.93578	181.79
0.1795	0.95000	184.12	0.94544	183.54	0.94088	183.07	0.93626	182.39
0.2061	0.95055	184.81	0.94602	184.24	0.94148	183.82	0.93688	183.26
[HMIm]Cl + salpr + DMF								
0.0000	0.94622		0.94145		0.93669		0.93183	
0.0203	0.94682	181.14	0.94208	180.21	0.93735	179.26	0.93251	178.86
0.0448	0.94752	181.58	0.94281	180.81	0.93811	180.02	0.93330	179.48

Table 1 (*continued*)

m_{IL} mol kg^{-1}	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K		$T = 313.15$ K	
	d g cm^{-3}	$V_{\phi,IL}$ cm^3 mol^{-1}	d g cm^{-3}	$V_{\phi,IL}$ cm^3 mol^{-1}	d g cm^{-3}	$V_{\phi,IL}$ cm^3 mol^{-1}	d g cm^{-3}	$V_{\phi,IL}$ cm^3 mol^{-1}
0.0643	0.94806	181.93	0.94336	181.44	0.93869	180.58	0.93391	178.87
0.0809	0.94850	182.35	0.94383	181.70	0.93917	181.03	0.93441	179.48
0.1003	0.94900	182.74	0.94433	182.37	0.93970	181.63	0.93498	179.89
0.1212	0.94949	183.48	0.94488	182.74	0.94025	182.26	0.93556	180.35
0.1453	0.95008	183.83	0.94547	183.34	0.94089	182.67	0.93618	180.76
0.1578	0.95037	184.07	0.94577	183.60	0.94120	182.97	0.93650	181.39
0.1792	0.95085	184.49	0.94625	184.17	0.94171	183.52	0.93701	182.23
0.1925	0.95114	184.75	0.94655	184.45	0.94202	183.83	0.93733	182.56
[HMIm]Cl + salcn + DMF								
0.0000	0.94658		0.94190		0.93718		0.93244	
0.0206	0.94715	183.21	0.94249	182.87	0.93780	181.97	0.93308	181.60
0.0470	0.94786	183.56	0.94323	183.11	0.93857	182.41	0.93388	181.93
0.0607	0.94822	183.70	0.94361	183.15	0.93896	182.58	0.93428	182.19
0.0823	0.94879	183.78	0.94419	183.43	0.93956	182.93	0.93491	182.42
0.0970	0.94916	183.99	0.94459	183.46	0.93996	183.15	0.93532	182.71
0.1251	0.94987	184.18	0.94532	183.76	0.94071	183.51	0.93609	183.15
0.1452	0.95036	184.37	0.94582	184.03	0.94124	183.68	0.93664	183.31
0.1602	0.95073	184.45	0.94620	184.14	0.94163	183.82	0.93703	183.57
0.1803	0.95120	184.67	0.94669	184.35	0.94213	184.09	0.93754	183.88
0.2054	0.95178	184.89	0.94728	184.65	0.94274	184.40	0.93817	184.19
[HMIm]Cl + VO(salen) + DMF								
0.0000	0.96023		0.95545		0.95071		0.94581	
0.0202	0.96084	178.22	0.95606	178.95	0.95133	179.12	0.94643	179.87
0.0449	0.96156	178.75	0.95679	179.24	0.95205	179.97	0.94717	180.23
0.0607	0.96200	179.14	0.95724	179.52	0.95251	180.06	0.94763	180.45
0.0856	0.96267	179.74	0.95792	180.09	0.95321	180.43	0.94834	180.80
0.0989	0.96302	180.01	0.95828	180.30	0.95357	180.70	0.94870	181.12
0.1205	0.96357	180.43	0.95883	180.81	0.95413	181.18	0.94928	181.48
0.1415	0.96410	180.72	0.95936	181.16	0.95467	181.51	0.94983	181.80
0.1624	0.96459	181.18	0.95987	181.52	0.95519	181.85	0.95034	182.28
0.1779	0.96495	181.46	0.96023	181.84	0.95556	182.15	0.95073	182.48
0.1973	0.96538	181.84	0.96067	182.20	0.95601	182.50	0.95120	182.76
[HMIm]Cl + VO(salophen) + DMF								
0.0000	0.95087		0.94489		0.94008		0.93491	
0.0203	0.95148	179.85	0.94551	180.22	0.94070	180.97	0.93553	181.78
0.0470	0.95226	180.25	0.94630	180.70	0.94150	181.21	0.93633	182.02
0.0614	0.95267	180.43	0.94672	180.81	0.94191	181.56	0.93675	182.19
0.0845	0.95331	180.79	0.94738	181.06	0.94257	181.82	0.93742	182.36
0.1002	0.95374	180.96	0.94781	181.34	0.94301	181.98	0.93786	182.57
0.1191	0.95424	181.26	0.94833	181.54	0.94353	182.20	0.93838	182.83
0.1446	0.95490	181.60	0.94901	181.84	0.94421	182.52	0.93907	183.10
0.1588	0.95527	181.71	0.94938	182.01	0.94458	182.70	0.93945	183.23
0.1805	0.95581	181.98	0.94993	182.30	0.94513	183.01	0.94002	183.45
0.1997	0.95628	182.20	0.95041	182.52	0.94561	183.24	0.94051	183.66
[HMIm]Cl + VO(3-OMe-salen) + DMF								
0.0000	0.95057		0.94650		0.94109		0.93626	
0.0281	0.95134	182.80	0.94727	183.46	0.94187	183.93	0.93705	184.31
0.0505	0.95194	182.97	0.94787	183.63	0.94248	184.05	0.93766	184.61
0.0674	0.95238	183.18	0.94832	183.67	0.94293	184.22	0.93812	184.66
0.0859	0.95285	183.46	0.94880	183.85	0.94341	184.47	0.93861	184.86
0.1079	0.95340	183.70	0.94935	184.15	0.94398	184.61	0.93919	184.97
0.1233	0.95378	183.84	0.94973	184.32	0.94437	184.74	0.93959	185.06
0.1440	0.95427	184.12	0.95024	184.47	0.94488	184.96	0.94011	185.27
0.1641	0.95474	184.34	0.95072	184.66	0.94537	185.13	0.94061	185.43
0.1807	0.95512	184.52	0.95111	184.81	0.94577	185.26	0.94101	185.60
0.2036	0.95563	184.78	0.95164	185.00	0.94631	185.44	0.94156	185.78

Table 1 (*continued*)

m_{IL}	T = 298.15 K		T = 303.15 K		T = 308.15 K		T = 313.15 K	
mol kg	d g cm^{-3}	$V_{\phi,IL}$ cm^3 mol^{-1}	d g cm^{-3}	$V_{\phi,IL}$ cm^3 mol^{-1}	d g cm^{-3}	$V_{\phi,IL}$ cm^3 mol^{-1}	d g cm^{-3}	$V_{\phi,IL}$ cm^3 mol^{-1}
[HMIm]Cl + DMF								
0.0000	0.94451		0.93977		0.93567		0.93157	
0.0226	0.94513	183.73	0.94042	182.99	0.93636	181.62	0.93230	180.22
0.0468	0.94578	183.95	0.94111	183.01	0.93708	181.95	0.93306	180.61
0.0600	0.94610	184.62	0.94147	183.31	0.93746	182.24	0.93346	180.95
0.0797	0.94661	184.69	0.94200	183.60	0.93801	182.67	0.93404	181.43
0.1002	0.94711	185.04	0.94253	183.99	0.93858	182.92	0.93463	181.83
0.1216	0.94762	185.35	0.94307	184.34	0.93912	183.58	0.93522	182.31
0.1410	0.94807	185.63	0.94354	184.70	0.93963	183.80	0.93572	182.88
0.1621	0.94854	185.97	0.94403	185.12	0.94014	184.29	0.93627	183.28
0.1781	0.94888	186.28	0.94440	185.38	0.94051	184.67	0.93667	183.62
0.2012	0.94934	186.77	0.94490	185.84	0.94104	185.12	0.93722	184.14

Table 2 Standard partial molar volumes ($V_{\phi,IL}^0$), experimental slopes (S_v), partial molar expansibilities ($E_{\phi,IL}^0$), thermal coefficient of expansion (α), and Hepler's constants ($(\partial^2 V_{\phi,IL}^0/\partial T^2)_P$) for the solutions of [HMIm]Cl + Schiff base (0.05 mol kg^{-1}) + organic solvent

	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K	$(\partial^2 V_{\phi,IL}^0/\partial T^2)_P$ cm^3 mol^{-1} K^{-2}
[HMIm]Cl + BPIC + C$_2$H$_6$O					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	141.74 ± 0.07	142.45 ± 0.07	142.81 ± 0.10	143.46 ± 0.05	-1.401 × 10^{-9}
S_v /cm^3 mol^{-2} kg	28.48 ± 0.60	26.64 ± 0.58	26.51 ± 0.80	25.29 ± 0.42	
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	0.1210	0.1140	0.1070	0.1000	
$10^3 \alpha$ / K^{-1}	0.854	0.800	0.749	0.697	
[HMIm]Cl + BPIC + C$_3$H$_8$O					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	144.58 ± 0.07	145.39 ± 0.07	146.13 ± 0.07	146.53 ± 0.03	-8.112 × 10^{-9}
S_v /cm^3 mol^{-2} kg	24.62 ± 0.53	21.92 ± 0.52	18.82 ± 0.60	18.19 ± 0.25	
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	0.1925	0.1519	0.1113	0.0708	
$10^3 \alpha$ / K^{-1}	1.331	1.045	0.762	0.483	
[HMIm]Cl + BPIC + C$_4$H$_{10}$O					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	147.94 ± 0.13	148.71 ± 0.05	149.01 ± 0.04	149.33 ± 0.06	-8.944 × 10^{-9}
S_v /cm^3 mol^{-2} kg	17.51 ± 1.02	12.34 ± 0.36	10.02 ± 0.28	6.36 ± 0.45	
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	0.1560	0.1113	0.0666	0.0218	
$10^3 \alpha$ / K^{-1}	1.055	0.748	0.447	0.146	
[HMIm]Cl + salen + DMF					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	179.17 ± 0.05	178.34 ± 0.08	177.84 ± 0.05	176.98 ± 0.05	-2.600 × 10^{-3}
S_v /cm^3 mol^{-2} kg	27.09 ± 0.38	28.66 ± 0.61	28.94 ± 0.42	30.37 ± 0.40	
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	-0.1158	-0.1288	-0.1418	-0.1548	
$10^3 \alpha$ / K^{-1}	-0.646	-0.722	-0.797	-0.8747	
[HMIm]Cl + salpr + DMF					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	180.63 ± 0.07	179.77 ± 0.05	178.87 ± 0.08	178.15 ± 0.08	2.820 × 10^{-3}
S_v /cm^3 mol^{-2} kg	21.68 ± 0.55	24.51 ± 0.41	26.21 ± 0.62	27.85 ± 0.64	
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	-0.1880	-0.1739	-0.1598	-0.1457	
$10^3 \alpha$ / K^{-1}	-1.041	-0.967	-0.893	-0.818	
[HMIm]Cl + salcn + DMF					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	183.11 ± 0.03	182.61 ± 0.04	181.81 ± 0.05	181.30 ± 0.03	-3.492 × 10^{-4}
S_v /cm^3 mol^{-2} kg	8.67 ± 0.25	9.61 ± 0.30	12.81 ± 0.38	14.16 ± 0.24	
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	-0.1215	-0.1233	-0.1250	-0.1268	
$10^3 \alpha$ / K^{-1}	-0.663	-0.675	-0.687	-0.699	
[HMIm]Cl + VO(salen) + DMF					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	177.91 ± 0.05	178.45 ± 0.04	178.94 ± 0.07	179.46 ± 0.04	-4.708 × 10^{-10}
S_v /cm^3 mol^{-2} kg	20.20 ± 0.43	18.99 ± 0.35	18.12 ± 0.59	16.83 ± 0.32	
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	0.1064	0.1040	0.1017	0.0993	
$10^3 \alpha$ / K^{-1}	0.598	0.583	0.568	0.553	
[HMIm]Cl + VO(salophen) + DMF					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	179.64 ± 0.03	180.04 ± 0.03	180.70 ± 0.03	181.52 ± 0.02	9.582 × 10^{-9}
S_v /cm^3 mol^{-2} kg	13.13 ± 0.26	12.52 ± 0.23	12.67 ± 0.26	10.70 ± 0.19	

Table 2 (*continued*)

	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K	$(\partial^2 V_{\phi,IL}^0 / \partial T^2)_P$ cm^3 mol^{-1} K^{-2}
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	0.0710	0.1189	0.1668	0.2147	
$10^3 \alpha$ / K^{-1}	0.395	0.660	0.923	1.183	
[HMIm]Cl + VO(3-OMe-salen) + DMF					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	182.43 ± 0.02	183.14 ± 0.04	183.65 ± 0.02	184.13 ± 0.03	-4.494 × 10^{-9}
S_v /cm^3 mol^{-2} kg	11.56 ± 0.17	9.21 ± 0.28	8.89 ± 0.19	8.01 ± 0.25	
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	0.1457	0.1232	0.1008	0.0783	
$10^3 \alpha$ / K^{-1}	0.799	0.673	0.549	0.425	
[HMIm]Cl + C$_2$H$_6$O^a					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	170.36	169.73	168.69	167.73	-6.8 × 10^{-3}
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	-0.1278	-0.1618	-0.1958	-0.2298	
$10^3 \alpha$ / K^{-1}	-0.750	-0.953	-1.161	-1.370	
[HMIm]Cl + C$_3$H$_8$O^a					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	148.05	147.67	146.47	146.63	0.011
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	-0.1902	-0.1362	-0.0822	-0.0282	
$10^3 \alpha$ / K^{-1}	-1.285	-0.922	-0.561	-0.192	
[HMIm]Cl + C$_4$H$_{10}$O^a					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	164.22	165.13	162.87	162.98	-0.016
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	0.0004	-0.0796	-0.1596	-0.2396	
$10^3 \alpha$ / K^{-1}	0.002	-0.482	-0.980	-1.470	
[HMIm]Cl + DMF					
$V_{\phi,IL}^0$ /cm^3 mol^{-1}	183.37 ± 0.08	182.34 ± 0.08	181.06 ± 0.06	179.63 ± 0.04	-8.240 × 10^{-3}
S_v /cm^3 mol^{-2} kg	16.47 ± 0.70	16.90 ± 0.67	19.97 ± 0.45	22.47 ± 0.31	
$E_{\phi,IL}^0$ /cm^3 mol^{-1}K^{-1}	-0.1888	-0.2300	-0.2712	-0.3124	
$10^3 \alpha$ / K^{-1}	-1.029	-1.261	-1.498	-1.739	

^{a} The values of standard partial molar volume of the IL in pure alcohols have been taken from literature.[25]

Table 3 Viscosities (η) of the solutions of [HMIm]Cl + Schiff base (0.05 mol kg^{-1}) + organic solvent at $T = 298.15$ K

c/mol dm^{-3}	η / mPa s	c/mol dm^{-3}	η / mPa s	c/mol dm^{-3}	η / mPa s
[HMIm]Cl + BPIC + C$_2$H$_6$O		[HMIm]Cl + BPIC + C$_3$H$_8$O		[HMIm]Cl + BPIC + C$_4$H$_{10}$O	
0.0000	1.247	0.0000	2.264	0.0000	2.868
0.0192	1.270	0.0194	2.288	0.0176	2.907
0.0332	1.282	0.0336	2.314	0.0338	2.948
0.0477	1.296	0.0482	2.345	0.0507	2.985
0.0656	1.310	0.0664	2.381	0.0670	3.036
0.0814	1.324	0.0796	2.408	0.0828	3.076
0.0974	1.334	0.0965	2.424	0.0985	3.115
0.1161	1.353	0.1147	2.451	0.1160	3.156
0.1307	1.362	0.1301	2.491	0.1315	3.206
0.1423	1.372	0.1459	2.524	0.1497	3.254
0.1659	1.388	0.1684	2.568	0.1659	3.292
[HMIm]Cl + salen + DMF		[HMIm]Cl + salpr + DMF		[HMIm]Cl + salcn + DMF	
0.0000	0.895	0.0000	0.930	0.0000	0.972
0.0189	0.908	0.0192	0.935	0.0195	0.975
0.0426	0.917	0.0424	0.948	0.0445	0.985
0.0597	0.925	0.0610	0.957	0.0576	0.994
0.0834	0.932	0.0767	0.965	0.0781	1.004
0.0958	0.940	0.0952	0.971	0.0921	1.011
0.1205	0.951	0.1151	0.981	0.1188	1.021
0.1300	0.960	0.1380	0.993	0.1380	1.035
0.1519	0.966	0.1500	1.003	0.1523	1.047
0.1710	0.979	0.1704	1.010	0.1715	1.056
0.1958	0.990	0.1831	1.018	0.1955	1.069
[HMIm]Cl + VO(salen) + DMF		[HMIm]Cl + VO(salophen) + DMF		[HMIm]Cl + VO(3-OMe-salen) + DMF	
0.0000	0.927	0.0000	0.946	0.0000	0.970
0.0195	0.931	0.0193	0.955	0.0267	0.979
0.0452	0.947	0.0448	0.974	0.0481	0.994
0.0590	0.961	0.0585	0.984	0.0642	1.008
0.0813	0.972	0.0805	0.995	0.0819	1.024
0.0965	0.982	0.0955	1.013	0.1029	1.042
0.1147	0.997	0.1136	1.028	0.1176	1.048
0.1394	1.014	0.1380	1.045	0.1374	1.065
0.1531	1.023	0.1517	1.057	0.1567	1.081
0.1742	1.038	0.1725	1.073	0.1726	1.097
0.1928	1.052	0.1910	1.087	0.1945	1.115
		[HMIm]Cl + DMF			
		0.0000	0.861		
		0.0217	0.889		
		0.0417	0.913		
		0.0626	0.929		
		0.0778	0.938		
		0.0998	0.948		
		0.1171	0.981		
		0.1363	0.993		
		0.1507	1.005		
		0.1787	1.030		
		0.1961	1.038		

Table 4 Viscosity *A*-, *B*-, and *D*-coefficients, standard deviations ($\sigma(\eta)$), and solvation numbers (S_n) of [HMIm]Cl in the mixtures of Schiff base (0.05 mol kg^{-1}) + organic solvent at $T = 298.15$ K

system	A/dm$^{3/2}$ mol$^{-1/2}$	B/dm^3 mol^{-1}	D/dm^6 mol^{-2}	$\sigma(\eta)\times 10^3$	S_n
[HMIm]Cl + BPIC + C$_2$H$_6$O	0.058	0.544	0.013	1.41	3.84
[HMIm]Cl + BPIC + C$_3$H$_8$O	-0.038	0.875	0.065	2.98	6.05
[HMIm]Cl + BPIC + C$_4$H$_{10}$O	-0.027	0.963	-0.012	1.35	6.51
[HMIm]Cl + salen + DMF	0.025	0.486	-0.133	2.73	2.71
[HMIm]Cl + salpr + DMF	-0.032	0.582	0.035	1.85	3.22
[HMIm]Cl + salcn + DMF	-0.071	0.674	-0.028	2.47	3.68
[HMIm]Cl + VO(salen) + DMF	-0.084	0.890	0.054	1.61	5.00
[HMIm]Cl + VO(salophen) + DMF	-0.062	0.926	0.003	2.29	5.15
[HMIm]Cl + VO(3-OMe-salen) + DMF	-0.101	0.993	0.030	2.11	5.44
[HMIm]Cl + DMF	-0.005	0.995	0.023	4.32	5.43

Table 5 Molar conductivities (Λ) of [HMIm]Cl in the mixtures of Schiff base (0.05 mol kg^{-1}) + organic solvent at T = 298.15 K

c_{IL}/mol m^{-3}	Λ/S cm^2 mol^{-1}	c_{IL}/mol m^{-3}	Λ/S cm^2 mol^{-1}	c_{IL}/mol m^{-3}	Λ/S cm^2 mol^{-1}
[HMIm]Cl + BPIC + C$_2$H$_6$O		[HMIm]Cl + BPIC + C$_3$H$_8$O		[HMIm]Cl + BPIC + C$_4$H$_{10}$O	
0.6779	35.61	0.2473	33.12	0.4961	11.34
1.3025	32.43	0.8346	24.12	1.0076	9.35
2.0718	28.67	1.5996	18.87	1.6182	8.08
2.7193	27.89	2.1482	15.79	2.1907	7.31
3.4581	26.45	2.9519	13.77	2.8090	6.57
3.9304	26.09	3.5933	12.65	3.4043	6.17
4.7150	25.52	4.2038	12.12	3.9615	5.87
5.3167	25.23	4.8606	11.53	4.7019	5.46
5.9946	24.50	5.5329	11.05	5.3889	5.21
6.5887	24.29	6.2284	10.59	6.0683	5.00
[HMIm]Cl + salen + DMF		[HMIm]Cl + salpr + DMF		[HMIm]Cl + salcn + DMF	
0.6723	76.43	0.5374	71.40	0.6054	59.02
1.4481	71.40	1.0997	67.83	1.2278	58.45
2.1893	68.78	1.8438	64.92	1.9525	58.04
2.7324	67.30	2.5301	63.44	2.6261	57.58
3.4995	65.69	3.2163	61.90	3.3679	57.34
3.9218	65.32	3.8861	60.65	4.0841	57.03
4.7321	64.47	4.5806	59.82	4.7832	56.85
5.3441	63.62	5.2669	58.90	5.4824	56.77
6.3525	62.71	6.0358	57.76	6.1133	56.75
6.9904	62.37	6.6724	57.12	6.8892	56.71
[HMIm]Cl + VO(salen) + DMF		[HMIm]Cl + VO(salophen) + DMF		[HMIm]Cl + VO(3-OMe-salen) + DMF	
0.8324	69.45	0.3901	65.50	0.2389	58.44
1.6486	65.98	0.9942	61.86	0.8810	56.65
2.3759	63.71	1.6902	58.79	1.5754	55.71
3.1032	62.67	2.3862	57.52	2.3071	54.47
3.4668	61.58	3.1281	55.74	3.0538	53.30
4.0729	60.56	3.8240	54.15	3.7332	52.36
4.8487	59.33	4.4129	53.29	4.3081	51.90
5.5760	58.21	5.0860	52.23	4.9652	51.17
6.4165	57.19	5.5066	51.62	5.3758	50.72
7.2165	55.51	6.0649	50.86	5.9209	50.14
		[HMIm]Cl + DMF			
		0.7025	77.61		
		1.2315	72.77		
		1.9600	69.39		
		2.5497	66.91		
		3.2695	64.96		
		3.9720	63.70		
		4.8046	62.34		
		5.5157	61.17		
		6.2876	60.15		
		6.9987	59.57		

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Table 6 Limiting molar conductivities (Λ_0), association constants (K_A), and standard deviations ($\sigma(\Lambda)$) of [HMIm]Cl in the mixtures of Schiff base (0.05 mol kg^{-1}) + organic solvent at T = 298.15 K

system	Λ_0 / S cm^2 mol^{-1}	K_A/dm^3 mol^{-1}	$\sigma(\Lambda)$
[HMIm]Cl + C$_2$H$_6$O^a	48.38	90	0.10
[HMIm]Cl + C$_3$H$_8$O^a	25.74	352.6	0.47
[HMIm]Cl + C$_4$H$_{10}$O^a	16.77	920	0.21
[HMIm]Cl + BPIC + C$_2$H$_6$O	40.42	206.4	0.84
[HMIm]Cl + BPIC + C$_3$H$_8$O	38.89	1182.0	1.29
[HMIm]Cl + BPIC + C$_4$H$_{10}$O	13.08	498.8	0.38
[HMIm]Cl + DMF	82.08	90.7	0.99
[HMIm]Cl + salen + DMF	78.75	50.8	1.09
[HMIm]Cl + salpr + DMF	73.8	58.3	0.62
[HMIm]Cl + salcn + DMF	60.46	-0.7	0.42
[HMIm]Cl + VO(salen) + DMF	73.95	60.6	0.32
[HMIm]Cl + VO(salophen) + DMF	67.04	71.7	0.58
[HMIm]Cl + VO(3-OMe-salen) + DMF	59.48	30.8	0.12

^{a} The values of Limiting molar conductivity (Λ_0) and association constant (K_A) of the IL in pure alcohol have been taken from literature.[25]
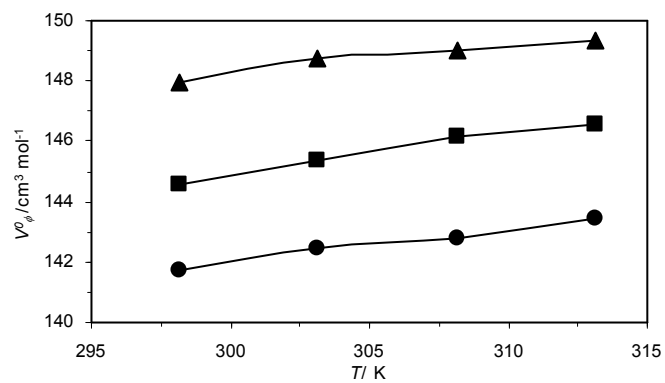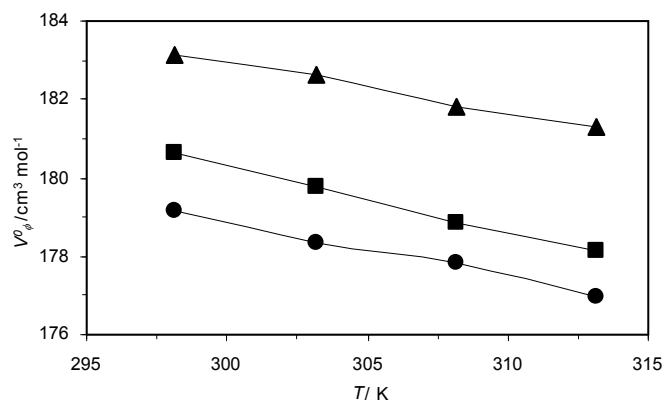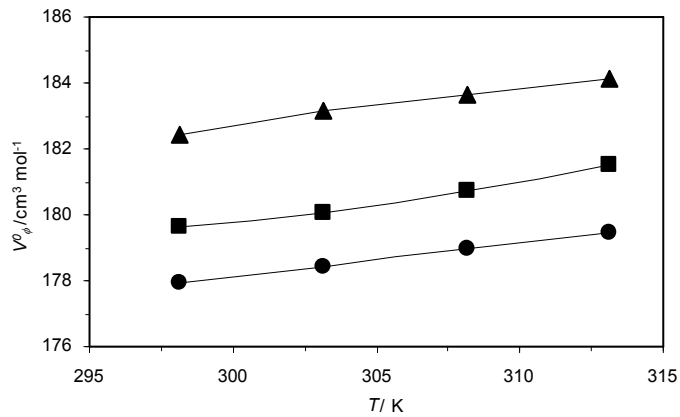
Fig. 1

Fig. 2

Fig. 3