Thermodynamic Properties of Ternary Systems Containing (LiCl and LiBr) + Propylene Carbonate + Ionic Liquid (1-Alkyl-3-methylimidazolium Thiocyanate)

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ABSTRACT: The development of the Li-ion battery Industry in a green way is crucial for human beings’ future. Ionic liquids (ILs) are green cosolvents that could be applied in Li-ion battery electrolytes. A thermodynamic study has been carried out for a Li-ion electrolyte (propylene carbonate (PC) + LiCl and LiBr) in the presence of IL 1-alkyl-3-methylimidazolium thiocyanate [RMIM][SCN] (R = butyl, hexyl, and octyl). The studied thermodynamic properties were density, speed of sound, apparent molar volume, and compressibility. The effect of ILs in propylene carbonate (PC) has been investigated under atmospheric pressure at T = (288.15−318.15) K. Also, a microscopic approach using scaled particle theory has been implemented. The solvation effect of lithium halides, LiX (X = Cl, Br−), on the volumetric and compressibility properties of the ILs has been studied at 298.15 K. The results show that [OMIM][SCN] has the strongest interactions with PC in the studied ILs and these interactions are more weakened with the addition of LiBr than LiCl. According to the partial molar compressibility results, the systems containing [OMIM][SCN] could be used under pressure more beneficially than other systems from the thermodynamic aspect of view.

INTRODUCTION

Rechargeable world is the aim of recent research studies to reduce excessive energy resource consumption. Lithium capacitors are one of the most important rechargeable energy-storage devices. The lithium capacitors’ industry development led to an increased demand for lithium sources than ever. The investigations about extraction, separation, and purification around the systems containing lithium species have been increased.† Also, there is some promising investigation that suggests optimization of the capacitors for a long life span instead of expensive separation methods that may cause environmental damages. Achieving environmentally friendly lithium power sources is the subject of the literature.*

Ionic liquids as environmentally friendly and biodegradable chemicals have advantages for industrial uses such as high thermal stability, etc. Imidazole-based ionic liquids with fluorinated anions have been used effectively to enhance the properties of the lithium batteries. However, it found that using fluorinated anion-based ILs may cause environmental damages in long term. To overcome this problem, cyanobased anions have been suggested recently. One of the best options for replacing fluorinated anions is thiocyanate. The imidazolium-based ILs with a thiocyanate anion are used effectively in various applications. Based on the literature, the use of these ILs, as well as fluorinated ILs, is promising.

An electrolyte is an important part of a battery that affects ion mobility and consequently generated energy. Also, the electrolyte is the part that would be eliminated after cycles of usage. Accordingly, the electrolyte is related to the life span of the battery rather than other parts. One of the main and convenient species of a lithium capacitor electrolyte is propylene carbonate (PC) that has the best benefits for the developed technologies of Li capacitors. However, there are limited thermodynamic investigations around these systems.

In the present work, in the continuation of our previous experiences, a modeled lithium capacitor electrolyte has been designed to be investigated with a thermodynamic approach. The ILs with a thiocyanate anion, [RMIM][SCN] (R = butyl, hexyl, and octyl), have been studied. The density and speed of sound of binary and ternary systems containing (PC + ILs) and (PC + ILs + LiX (X = Cl, Br−)), respectively, have been measured. Based on the measured properties, the apparent molar volume and apparent molar isentropic compressibility of the ILs have been evaluated and the standard partial molar isentropic compressibility have been calculated. Scaled particle theory was used to obtain the different properties.
contributions of the standard partial molar volume. The results are used to interpret the interactions between the species.

## RESULTS AND DISCUSSION

### Volumetric Properties.

The density data of propylene carbonate are compared in Figure 1 with the literature and good agreement has been achieved. The error bars have been used in a 0.5% range for our data to compare with literature data, which show less difference than this value. However, in the previous work, the density and speed of sound data for propylene carbonate were different due to different sources of the supplier.

The density of solutions containing ([RMIM][SCN] + PC) is measured under atmospheric pressure (P = 0.086 MPa) at temperature ranges T = (288.15–318.15) K. These data are given in Table 1, which shows the density data decrease with the addition of IL content. The apparent molar volumes, $V_\phi$ of the ILs in the PC solutions were evaluated using the following equation

$$V_\phi = \frac{M}{d} - \left[ \frac{(d - d_0)}{mdd_0} \right]$$  

where $M$ is the molar mass of the IL, $m$ is the molality of the IL, and $d_0$ and $d$ are the densities of the solvent (PC) and the solution, respectively. The $V_\phi$ values for the studied ILs in binary solutions are given in Table 1, and Figure 2 shows the plot of the $V_\phi$ values versus molality of ILs with different cation sizes where the $V_\phi$ values increased from butyl to octyl.

Also, the increasing $V_\phi$ values with temperature and molality are shown in Figure 3. The standard partial molar volumes, $V_\phi^0$, have been calculated with the Redlich–Mayer equation

$$V_\phi = V_\phi^0 + S_\phi m^{1/2} + B_\phi m$$

where $V_\phi^0$, $S_\phi$, and $B_\phi$ are given in Table 2, for the binary solutions. The $V_\phi^0$ values are criteria of solute–solvent interaction, while the $S_\phi$ values are criteria of solute–solvent interactions, and $B_\phi$ is an adjustable parameter. The $V_\phi^0$ values of the studied ILs are increased by the alkyl chain length and increasing temperature in the binary solutions.

Scaled particle theory (SPT), as a microscopic viewpoint, was used to determine different contributions of the partial molar volume, namely, the cavity volume ($V_{cav}$), the interactional volume ($V_{int}$), and the state transition volume ($\kappa_TRT$) changes due to components' isothermal transition from a vapor to liquid phase, and $\kappa_T$ is isothermal compressibility of the solvent. The corresponding equation is

$$V_\phi^0 = V_{cav} + V_{int} + \kappa_TRT$$

where $R$ is the universal gas constant and $T$ is the absolute temperature. The cavity volume was calculated using equations

$$V_{cav} = \kappa_TRT \left( \frac{y}{1-y} + \frac{3yz(1+z)}{(1-y)^3} + \frac{9y^2z^2}{(1-y)^4} \right)$$

$$y = \frac{\pi N_A \sigma^3}{6 V}$$

$$z = \frac{\sigma_s}{\sigma_l}$$

In eqs 4–6, $N_A$ is the Avogadro constant, $V$ is the molar volume of the solvent, and $\sigma_s$ and $\sigma_l$ are the diameters of the solvent (PC) and solute (IL), respectively, which are obtained by a procedure defined by Abraham using the Bondi method for atomic Van der Waals volumes. The symbol z is the ratio of the solute to solvent diameters. The $\kappa_T$ values for PC were calculated by the following equation

$$\kappa_T = \kappa_s + \frac{\alpha^2 TV}{C_p}$$

The $V_\phi^0$ values of temperature dependence are fitted with a second-degree polynomial equation

$$V_\phi^0 = A + BT + CT^2$$

where $A$, $B$, and $C$ are the empirical parameters of the equation. The standard apparent molar expansibility at constant pressure $E_\phi^0$ was calculated using the following equation

$$E_\phi = \left. \left( \frac{\partial V_\phi}{\partial T} \right) \right|_p$$

The $E_\phi$ values are given in Table 2. These values are positive and increased with increasing IL cation size. Also, this variable decreased with increasing temperature. The isobaric thermal expansion was evaluated as a function of $V_\phi^0$ and $E_\phi^0$ by the following equation

$$\alpha = \frac{E_\phi^0}{V_\phi^0}$$
Table 1. Density ($d$), Speed of Sound ($u$), Solvation Number ($S_n$), Apparent Molar Volume ($V_\phi$), and Apparent Molar Isentropic Compressibility ($\kappa_\phi$) Data of ([RMI][SCN] + PC) at $T = (288.15 \text{ to } 318.15 \text{ K})$ under Pressure ($P = 0.086 \text{ MPa}$)

| $m_{IL}$ (mol kg$^{-1}$) | $d$ (kg m$^{-3}$) | $u$ (m s$^{-1}$) | $S_n$ | $10^6 V_\phi$ (m$^3$ mol$^{-1}$) | $10^{14} \kappa_\phi$ (m$^3$ mol$^{-1}$ Pa$^{-1}$) |
|--------------------------|-------------------|-----------------|-------|-------------------------------|-----------------------------|
| [BMIM][SCN] $T = 288.15$ K |
| 0.0000 | 1209.663 | 1478.33 | 76.49 | 177.13 | 4.25 |
| 0.0129 | 1209.398 | 1479.24 | 76.19 | 177.16 | 4.26 |
| 0.0165 | 1209.324 | 1479.49 | 76.27 | 177.19 | 4.26 |
| 0.0192 | 1209.268 | 1479.68 | 76.24 | 177.22 | 4.26 |
| 0.0218 | 1209.214 | 1479.86 | 76.06 | 177.23 | 4.28 |
| 0.0235 | 1209.179 | 1479.97 | 75.59 | 177.24 | 4.29 |
| 0.0272 | 1209.103 | 1480.22 | 75.29 | 177.26 | 4.29 |
| 0.0289 | 1209.066 | 1480.34 | 75.24 | 177.30 | 4.29 |
| 0.0331 | 1208.978 | 1480.62 | 74.80 | 177.36 | 4.30 |
| [HMIM][SCN] $T = 288.15$ K |
| 0.0000 | 1199.037 | 1442.90 | 97.46 | 178.82 | 3.83 |
| 0.0129 | 1198.772 | 1443.99 | 97.19 | 178.90 | 3.84 |
| 0.0165 | 1198.697 | 1444.29 | 96.61 | 178.92 | 3.86 |
| 0.0192 | 1198.587 | 1444.72 | 96.12 | 178.95 | 3.87 |
| 0.0235 | 1198.551 | 1444.86 | 96.03 | 178.99 | 3.88 |
| 0.0272 | 1198.475 | 1445.16 | 95.74 | 179.01 | 3.89 |
| 0.0289 | 1198.437 | 1445.30 | 95.50 | 179.07 | 3.90 |
| 0.0331 | 1198.349 | 1445.64 | 95.20 | 179.12 | 3.91 |
| [HMIM][SCN] $T = 298.15$ K |
| 0.0000 | 1209.663 | 1478.33 | 76.49 | 177.13 | 4.25 |
| 0.0129 | 1209.398 | 1479.24 | 76.19 | 177.16 | 4.26 |
| 0.0165 | 1209.324 | 1479.49 | 76.27 | 177.19 | 4.26 |
| 0.0192 | 1209.268 | 1479.68 | 76.24 | 177.22 | 4.26 |
| 0.0218 | 1209.214 | 1479.86 | 76.06 | 177.23 | 4.28 |
| 0.0235 | 1209.179 | 1479.97 | 75.59 | 177.24 | 4.29 |
| 0.0272 | 1209.103 | 1480.22 | 75.29 | 177.26 | 4.29 |
| 0.0289 | 1209.066 | 1480.34 | 75.24 | 177.30 | 4.29 |
| 0.0331 | 1208.978 | 1480.62 | 74.80 | 177.36 | 4.30 |
| [HMIM][SCN] $T = 308.15$ K |
| 0.0000 | 1188.430 | 1407.38 | 97.46 | 178.82 | 3.83 |
| 0.0129 | 1188.172 | 1408.61 | 97.19 | 178.90 | 3.84 |
| 0.0165 | 1188.100 | 1408.95 | 96.61 | 178.92 | 3.86 |
| 0.0192 | 1188.045 | 1409.20 | 96.12 | 178.95 | 3.87 |
| 0.0235 | 1187.957 | 1409.59 | 96.03 | 178.99 | 3.88 |
| 0.0272 | 1187.883 | 1409.93 | 95.74 | 179.01 | 3.89 |
| 0.0289 | 1187.847 | 1410.08 | 95.50 | 179.07 | 3.90 |
| 0.0331 | 1187.761 | 1410.48 | 95.20 | 179.12 | 3.91 |
| [HMIM][SCN] $T = 318.15$ K |
| 0.0000 | 1177.840 | 1372.65 | 97.46 | 178.82 | 3.83 |
| 0.0129 | 1177.595 | 1373.99 | 97.19 | 178.90 | 3.84 |
| 0.0165 | 1177.527 | 1374.36 | 96.61 | 178.92 | 3.86 |
| 0.0192 | 1177.475 | 1374.64 | 96.12 | 178.95 | 3.87 |
| 0.0235 | 1177.425 | 1374.90 | 96.03 | 178.99 | 3.88 |
| 0.0272 | 1177.392 | 1375.07 | 95.74 | 179.01 | 3.89 |
| 0.0289 | 1177.322 | 1375.44 | 95.50 | 179.07 | 3.90 |
| 0.0331 | 1177.207 | 1376.02 | 95.20 | 179.12 | 3.91 |

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| $m_L$ (mol kg$^{-1}$) | $d$ (kg m$^{-3}$) | $u$ (m s$^{-1}$) | $S_n$ | $10^6 V_\phi$ (m$^3$ mol$^{-1}$) | $10^{14} \kappa_\phi$ (m$^3$ mol$^{-1}$ Pa$^{-1}$) | $T$ (K) |
|---------------------|-----------------|----------------|-------|------------------|------------------|-------|
| 0.0265              | 1198.066        | 1445.25        | 90.11 | 213.56           | 5.46             | 298.15 |
| 0.0299              | 1197.941        | 1445.54        | 89.80 | 213.67           | 5.47             | 308.15 |
| 0.0000              | 1188.430        | 1407.38        |       |                  |                  | 318.15 |
| 0.0119              | 1187.999        | 1408.62        | 114.74| 215.27           | 4.95             |       |
| 0.0147              | 1187.898        | 1408.90        | 114.12| 215.38           | 4.97             |       |
| 0.0174              | 1187.796        | 1409.18        | 113.48| 215.47           | 4.99             |       |
| 0.0205              | 1187.683        | 1409.49        | 112.93| 215.54           | 5.01             |       |
| 0.0215              | 1187.644        | 1409.59        | 112.70| 215.65           | 5.03             |       |
| 0.0241              | 1187.545        | 1409.85        | 111.97| 215.75           | 5.05             |       |
| 0.0265              | 1187.453        | 1410.09        | 111.47| 215.86           | 5.07             |       |
| 0.0299              | 1187.327        | 1410.43        | 111.37| 215.97           | 5.08             | 288.15 |
| 0.0000              | 1199.037        | 1442.91        |       |                  |                  | 298.15 |
| 0.0088              | 1198.601        | 1443.94        | 118.19| 246.86           | 5.81             |       |
| 0.0115              | 1198.465        | 1444.23        | 115.34| 246.14           | 5.91             |       |
| 0.0133              | 1198.370        | 1444.43        | 113.87| 246.31           | 5.97             |       |
| 0.0161              | 1198.223        | 1444.70        | 109.26| 246.62           | 6.13             |       |
| 0.0183              | 1198.108        | 1444.90        | 105.85| 246.81           | 6.26             |       |
| 0.0206              | 1197.985        | 1445.11        | 102.91| 247.03           | 6.36             |       |
| 0.0229              | 1197.864        | 1445.29        | 99.18 | 247.27           | 6.50             |       |
| 0.0252              | 1197.734        | 1445.49        | 96.31 | 247.50           | 6.61             | 308.15 |
| 0.0000              | 1188.430        | 1407.45        |       |                  |                  | 318.15 |
| 0.0088              | 1188.007        | 1408.60        | 141.96| 247.31           | 5.31             |       |
| 0.0115              | 1187.875        | 1408.93        | 139.49| 247.60           | 5.41             |       |
| 0.0133              | 1187.782        | 1409.15        | 137.33| 247.81           | 5.50             |       |
| 0.0161              | 1187.641        | 1409.48        | 134.60| 248.03           | 5.60             |       |
| 0.0183              | 1187.526        | 1409.71        | 130.75| 248.36           | 5.75             |       |
| 0.0206              | 1187.406        | 1409.95        | 127.45| 248.59           | 5.88             |       |
| 0.0229              | 1187.290        | 1410.18        | 124.76| 248.77           | 5.98             |       |
| 0.0252              | 1187.161        | 1410.41        | 121.37| 249.08           | 6.12             |       |
| 0.0000              | 1177.840        | 1372.72        |       |                  |                  | 318.15 |
| 0.0088              | 1177.427        | 1373.98        | 164.92| 249.03           | 4.76             |       |
| 0.0115              | 1177.297        | 1374.34        | 161.89| 249.38           | 4.89             |       |
| 0.0133              | 1177.208        | 1374.59        | 160.61| 249.49           | 4.94             |       |
| 0.0161              | 1177.069        | 1374.95        | 157.21| 249.77           | 5.09             |       |
| 0.0183              | 1176.961        | 1375.23        | 155.23| 249.92           | 5.17             |       |
Table 1. continued

| m (mol kg\(^{-1}\)) | d (kg m\(^{-3}\)) | \(\phi\) (m3 mol\(^{-1}\)) | \(10^6 V_\phi\) (m\(^3\) mol\(^{-1}\)) | \(10^4 k_\phi\) (m\(^3\) mol\(^{-1}\) Pa\(^{-1}\)) |
|-------------------|-------------------|-----------------|-------------------|-------------------|
|                   |                   |                 |                   |                   |
| 0.0206            | 1176.845          | 1375.49         | 151.09            | 250.13            | 5.33              |
| 0.0229            | 1176.732          | 1375.75         | 148.37            | 250.32            | 5.45              |
| 0.0252            | 1176.606          | 1376.02         | 145.36            | 250.63            | 5.57              |

“Standard uncertainties for molality, temperature, and pressure were \(u (m) = 0.002 \text{ mol kg}^{-1}\), \(u (T) = 0.02 \text{ K}\), and \(u (P) = 10 \text{ hPa}\), respectively, with a 0.68 level of confidence, and the combined standard uncertainties for density and speed of sound were \(u (\rho) = 0.07 \text{ kg m}^{-3}\) and \(u (u) = 1.3 \text{ m s}^{-1}\) with a 0.68 level of confidence. The standard uncertainties for the apparent molar volume and apparent molar isentropic compressibility were \(u_\phi (V_\phi) = 5.10 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}\) (level of confidence of 0.68) and \(u_\phi (k_\phi) = 3.10 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} \text{ Pa}^{-1}\) (level of confidence of 0.68), respectively.

![Figure 2. Apparent molar volumes \(V_\phi\) of [RMM][SCN] in PC solution versus its molality \(m\) at \(T = 298.15 \text{ K}\).](image1)

![Figure 3. Apparent molar volumes \(V_\phi\) of [BMIM][SCN] in PC versus its molality \(m\) at different temperatures.](image2)

![Figure 4. Apparent molar volumes \(V_\phi\) of [HMIM][SCN] against its molality \(m\) in a (PC + LiBr) solution at \(T = 298.15 \text{ K}\) at different concentrations of LiBr.](image3)

![Figure 5. Apparent molar volumes \(V_\phi\) of [HMIM][SCN] in PC versus its molality \(m\) in the presence of about 0.01 mol kg\(^{-1}\) of LiX salts at \(T = 298.15 \text{ K}\).](image4)

The calculated values of \(\alpha\) for ([RMM][SCN] + PC) are given in Table 2. The \(\alpha\) value is increased with increasing cation size and decreases with increasing temperature. The value of \(\alpha\) is a criterion for the response of the volume of a system to increasing temperature. The large value of this factor gets more sensitive in the system volume with temperature change. The observed trend for \(\alpha\) and \(E_\phi^0\) is similar to the cavity volume. The pressure would also break the solvent structure and the same reason suggests that the heat capacity decreases. Hepler et al.s\(^{19}\) determined relation for structure making or breaking behavior of a solute in a solution is given by the following equations

\[
\frac{\partial C_p}{\partial P} = -T \left( \frac{\partial^2 V_\phi^0}{\partial T^2} \right)_P \tag{11}
\]

\[
-T \left( \frac{\partial^2 V_\phi^0}{\partial T^2} \right)_P = -2CT \tag{12}
\]

where \(\left( \frac{\partial^2 V_\phi^0}{\partial T^2} \right)\) is the constant for the ILs, as given in Table 2. As can be seen, this parameter decreases with increasing cation size. Negative values of this parameter mean the ILs have structure-breaking behavior in PC, and this behavior intensity order is octyl > hexyl > butyl. The measured density data of ternary solutions containing solute [RMM][SCN], in the solvent consisting of (PC + LiCl or LiBr), and the corresponding \(V_\phi\) values that have been calculated with eq 1 are given in Table 4.

The effect of LiX (\(X = \text{Cl}, \text{Br}\)) on the \(V_\phi\) values of the [HMIM][SCN] is shown in Figure 4. This figure demonstrates that the addition of the LiBr content increases the \(V_\phi\) values of [HMIM][SCN].

In Figure 5, the effect of anion size (Cl\(^-\) and Br\(^-\)) on the \(V_\phi\) values of [HMIM][SCN] has been shown. It is clear that a Br\(^-\) anion has a stronger effect rather than a Cl\(^-\) anion.

The standard partial molar volumes \(V_\phi^0\) of the ILs in (LiX + PC) solutions at different concentrations of LiX are given in Table 5. Results show that a Br\(^-\) anion has a stronger effect than a Cl\(^-\) anion on the \(V_\phi\) values. The partial molar volumes of transfer \(\Delta_\phi V_\phi^0\) of the ionic liquids have been obtained for [RMM][SCN] from PC to (LiX + PC) solutions.
Table 3. Isothermal Compressibility ($\kappa_T$), Isothermal Volume Transition Contribution ($\kappa_T \Delta \nu RT$), and Interactional and Cavity Volumes of the Standard Partial Molar Volume of [RMIM][SCN] in Propylene Carbonate with SPT at $T = 288.15$–318.15 K under Pressure ($P = 0.086$ MPa)$^{a}$

| $T$ (K) | $10^6 \kappa_T$ (Pa$^{-1}$) | $10^6 \kappa_T \Delta \nu RT$ (m$^3$ mol$^{-1}$) | $10^6 \nu_{cav}$ | $10^6 \nu_{ext}$ |
|---------|----------------------------|---------------------------------|-----------------|-----------------|
|         | [RMIM][SCN]                | [HMIM][SCN]                    | [OMIM][SCN]     | [OMIM][SCN]     |
| 288.15  | 5.22                       | 1.25                            | 1563.23         | -1391.64        |
| 298.15  | 5.08                       | 1.26                            | 1465.88         | -1292.68        |
| 308.15  | 5.00                       | 1.28                            | 1376.51         | -1201.98        |
| 318.15  | 4.99                       | 1.32                            | 1294.33         | -1118.69        |
| 288.15  | 5.60                       | 1.34                            | 1760.58         | -1567.32        |
| 298.15  | 5.17                       | 1.28                            | 1651.17         | -1456.08        |
| 308.15  | 4.90                       | 1.26                            | 1550.73         | -1353.96        |
| 318.15  | 4.79                       | 1.24                            | 1458.38         | -1260.68        |
| 288.15  | 5.99                       | 1.44                            | 2015.52         | -1778.93        |
| 298.15  | 5.43                       | 1.35                            | 1890.17         | -1650.69        |
| 308.15  | 5.05                       | 1.30                            | 1775.11         | -1534.00        |
| 318.15  | 4.86                       | 1.28                            | 1669.32         | -1426.50        |

$^a$Standard uncertainties for temperature and pressure were $u(T) = 0.02$K and $u(P) = 10$ kPa, respectively, with a 0.68 level of confidence.

The $\Delta_{\nu} V_{\nu}^0$ values are reported in Table 5. These values are positive and increase with increasing LiX concentration. The $\Delta_{\nu} V_{\nu}^0$ value is a measure of interaction between solute1 (IL) and solute2 (LiX). The possible interactions for the studied solutions due to the different functional groups of the components are polar–ionic, polar–polar, polar–nonpolar, and nonpolar–nonpolar interactions.$^{24,41}$ According to the cosphere overlap model, the positive $\Delta_{\nu} V_{\nu}^0$ value indicates strong ion–ion and ion–polar interactions between [RMIM][SCN] and LiX.$^{24,26}$ On the other hand, LiBr has stronger interactions than LiCl with ionic liquids, as shown in Table 5.

Compressibility Properties. The measured speeds of sound ($u$) data for the binary (IL + PC) and ternary (IL + PC + LiX) solutions are given in Tables 1 and 4, respectively. These data were used to calculate the isentropic compressibility, $\kappa_s$, with help of Laplace–Newton’s relation.$^{24,26}$

$$\Delta_{\nu} V_{\nu}^0 = V_{\nu}^0 (\text{in PC + LiX(X = Cl, Br)}) - V_{\nu}^0 (\text{in PC})$$

$$\kappa_s = \frac{1}{du^2}$$

This quantity can be considered as the bulk modulus behavior of the solution. The solvation numbers were calculated from the $\kappa_s$ values by the Pasynski equation.$^{24}$

$$S_n = \frac{n_1}{n_2} \left( 1 - \frac{\kappa_s}{\kappa_{so}} \right)$$

where $n_1$ and $n_2$ are numbers of moles of the solvent and the solute, respectively, and $\kappa_s$ and $\kappa_{so}$ are isentropic compressibility of the solution and the solvent [PC or (PC + LiX)], respectively. The calculated values of $S_n$ are given in Tables 1 and 4 for the investigated binary and ternary solutions. The $S_n$ values were increased with increasing temperature. These values were decreased with the addition of the LiX salt. This may be related to the coordination of PC molecules to Li$^+$, as confirmed by the Raman spectroscopy study of the lithium salts in PC.
Table 4. Density ($d$), Speed of Sound ($u$), Solvation Number ($S_n$), Apparent Molar Volume ($V_{\phi}$), and Apparent Molar Compressibility ($\kappa_{\phi}$) Data of [RMIM][SCN] in (PC + LiX (X = Cl$^-$ and Br$^-$)) Solutions at $T = 298.15$ K under Pressure ($P = 0.086$ MPa)$^a$

| $m_{li}$ (mol kg$^{-1}$) | $d$ (kg m$^{-3}$) | $u$ (m s$^{-1}$) | $S_n$ | $10^6 V_{\phi}$ (m$^3$ mol$^{-1}$) | $10^{14} \kappa_{\phi}$ (m$^3$ mol$^{-1}$ Pa$^{-1}$) |
|-------------------------|------------------|-----------------|-------|-------------------------------|----------------------------------|
| [BMIm]SCN + PC + LiBr | $m_{li} = 0.0035$ mol kg$^{-1}$ |
| 0.0000 | 1199.180 | 1442.83 | | | |
| 0.0141 | 1198.884 | 1443.78 | 74.26 | 179.16 | 4.64 |
| 0.0177 | 1198.808 | 1444.04 | 75.53 | 179.19 | 4.59 |
| 0.0206 | 1198.748 | 1444.25 | 76.50 | 179.20 | 4.56 |
| 0.0250 | 1198.656 | 1444.59 | 78.46 | 179.20 | 4.49 |
| 0.0281 | 1198.591 | 1444.83 | 79.53 | 179.22 | 4.45 |
| 0.0317 | 1198.515 | 1445.11 | 80.39 | 179.22 | 4.42 |
| 0.0340 | 1198.467 | 1445.29 | 81.02 | 179.23 | 4.40 |
| 0.0383 | 1198.375 | 1445.62 | 81.54 | 179.26 | 4.38 |
| [BMIm]SCN + PC + LiBr | $m_{li} = 0.0062$ mol kg$^{-1}$ |
| 0.0000 | 1199.383 | 1442.70 | | | |
| 0.0142 | 1199.040 | 1443.60 | 66.34 | 181.34 | 5.00 |
| 0.0167 | 1198.979 | 1443.77 | 67.27 | 181.38 | 4.97 |
| 0.0197 | 1198.905 | 1443.98 | 68.28 | 181.41 | 4.93 |
| 0.0235 | 1198.813 | 1444.24 | 69.18 | 181.46 | 4.90 |
| 0.0290 | 1198.679 | 1444.63 | 70.50 | 181.49 | 4.85 |
| 0.0326 | 1198.590 | 1444.90 | 71.66 | 181.53 | 4.81 |
| 0.0334 | 1198.571 | 1444.98 | 72.82 | 181.54 | 4.77 |
| 0.0385 | 1198.444 | 1445.35 | 73.40 | 181.59 | 4.75 |
| [BMIm]SCN + PC + LiBr | $m_{li} = 0.0097$ mol kg$^{-1}$ |
| 0.0000 | 1199.688 | 1442.63 | | | |
| 0.0131 | 1199.333 | 1443.40 | 57.91 | 183.40 | 5.37 |
| 0.0172 | 1199.220 | 1443.66 | 59.10 | 183.42 | 5.33 |
| 0.0189 | 1199.174 | 1443.77 | 59.83 | 183.46 | 5.30 |
| 0.0242 | 1199.028 | 1444.10 | 60.14 | 183.48 | 5.29 |
| 0.0282 | 1198.920 | 1444.36 | 61.04 | 183.49 | 5.26 |
| 0.0325 | 1198.802 | 1444.65 | 62.07 | 183.52 | 5.22 |
| 0.0358 | 1198.712 | 1444.89 | 63.43 | 183.55 | 5.18 |
| 0.0392 | 1198.618 | 1445.15 | 64.93 | 183.58 | 5.12 |
| [BMIm]SCN + PC + LiCl | $m_{li} = 0.0031$ mol kg$^{-1}$ |
| 0.0000 | 1199.109 | 1442.84 | | | |
| 0.0138 | 1198.829 | 1443.85 | 83.11 | 178.70 | 4.33 |
| 0.0171 | 1198.761 | 1444.10 | 83.46 | 178.71 | 4.31 |
| 0.0211 | 1198.681 | 1444.40 | 84.12 | 178.72 | 4.29 |
| 0.0241 | 1198.619 | 1444.63 | 84.39 | 178.74 | 4.28 |
| 0.0295 | 1198.510 | 1445.04 | 84.97 | 178.77 | 4.26 |
| 0.0332 | 1198.434 | 1445.32 | 85.00 | 178.78 | 4.25 |
| 0.0359 | 1198.377 | 1445.53 | 85.14 | 178.82 | 4.25 |
| 0.0395 | 1198.302 | 1445.80 | 85.13 | 178.86 | 4.25 |
| [BMIm]SCN + PC + LiCl | $m_{li} = 0.0059$ mol kg$^{-1}$ |
| 0.0000 | 1199.241 | 1442.73 | | | |
| 0.0130 | 1198.960 | 1443.63 | 77.12 | 179.63 | 4.58 |
| 0.0174 | 1198.864 | 1443.94 | 77.31 | 179.65 | 4.57 |
| 0.0204 | 1198.798 | 1444.16 | 77.88 | 179.67 | 4.55 |
| 0.0240 | 1198.721 | 1444.41 | 77.96 | 179.68 | 4.55 |
| 0.0290 | 1198.611 | 1444.77 | 78.22 | 179.71 | 4.54 |
| 0.0331 | 1198.523 | 1445.07 | 78.75 | 179.71 | 4.52 |
| 0.0356 | 1198.467 | 1445.26 | 79.09 | 179.73 | 4.50 |
| 0.0400 | 1198.372 | 1445.58 | 79.41 | 179.75 | 4.49 |
| [BMIm]SCN + PC + LiCl | $m_{li} = 0.0100$ mol kg$^{-1}$ |
| 0.0000 | 1199.447 | 1442.65 | | | |
| 0.0131 | 1199.142 | 1443.47 | 66.79 | 180.70 | 4.99 |
| 0.0174 | 1199.042 | 1443.74 | 66.94 | 180.74 | 4.98 |
| 0.0198 | 1198.987 | 1443.89 | 67.04 | 180.74 | 4.98 |
| 0.0234 | 1198.901 | 1444.13 | 67.56 | 180.77 | 4.96 |
| 0.0280 | 1198.796 | 1444.42 | 67.78 | 180.78 | 4.95 |
Table 4. continued

| $m_{li}$ (mol kg$^{-1}$) | $d$ (kg m$^{-3}$) | $u$ (m s$^{-1}$) | $S_{i}$ | $10^6 V_{p}$ (m$^3$ mol$^{-1}$) | $10^4 k_{p}$ (m$^3$ mol$^{-1}$ Pa$^{-1}$) |
|-------------------------|------------------|-----------------|--------|-------------------------------|---------------------------------------|
| 0.0318                  | 1198.706         | 1444.66         | 67.68  | 180.82                        | 4.95                                  |
| 0.0355                  | 1198.620         | 1444.91         | 68.29  | 180.83                        | 4.93                                  |
| 0.0388                  | 1198.543         | 1445.12         | 68.27  | 180.84                        | 4.93                                  |

$[\text{HMIm}]\text{SCN} + \text{PC} + \text{LiBr}$

$[\text{HMIm}]\text{SCN} + \text{PC} + \text{LiBr}$

$\mu_{liCl} = 0.0100$ mol kg$^{-1}$

| $m_{liBr}$ = 0.0035 mol kg$^{-1}$ | $m_{liBr}$ = 0.00005 mol kg$^{-1}$ | $m_{liBr}$ = 0.00095 mol kg$^{-1}$ | $m_{liCl} = 0.0033$ mol kg$^{-1}$ | $m_{liCl} = 0.0061$ mol kg$^{-1}$ | $m_{liCl} = 0.0104$ mol kg$^{-1}$ |
|------------------------------------------|-------------------------------------------|----------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 0.0111                                  | 1198.787                                   | 1443.58                                | 56.07                           | 214.47                          | 6.67                            |
| 0.0143                                  | 1198.662                                   | 1443.80                                | 56.94                           | 214.49                          | 6.64                            |
| 0.0197                                  | 1198.458                                   | 1444.15                                | 57.06                           | 214.51                          | 6.64                            |
| 0.0236                                  | 1198.311                                   | 1444.41                                | 57.58                           | 214.55                          | 6.62                            |
| 0.0278                                  | 1198.149                                   | 1444.70                                | 58.11                           | 214.56                          | 6.60                            |
| 0.0358                                  | 1197.847                                   | 1445.25                                | 59.09                           | 214.59                          | 6.56                            |
| 0.0390                                  | 1197.726                                   | 1445.46                                | 59.05                           | 214.63                          | 6.56                            |
| 0.0447                                  | 1197.508                                   | 1445.85                                | 59.31                           | 214.67                          | 6.55                            |

$[\text{HMIm}]\text{SCN} + \text{PC} + \text{LiBr}$

$[\text{HMIm}]\text{SCN} + \text{PC} + \text{LiBr}$

$\mu_{liCl} = 0.0008$ mol kg$^{-1}$

| $m_{liBr}$ = 0.0058 mol kg$^{-1}$ | $m_{liBr}$ = 0.0035 mol kg$^{-1}$ | $m_{liBr}$ = 0.00005 mol kg$^{-1}$ | $m_{liBr}$ = 0.00095 mol kg$^{-1}$ | $m_{liBr}$ = 0.0035 mol kg$^{-1}$ | $m_{liBr}$ = 0.00005 mol kg$^{-1}$ |
|------------------------------------------|-------------------------------------------|----------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 0.0103                                  | 1199.479                                   | 1443.38                                | 48.23                           | 216.27                          | 7.02                            |
| 0.0159                                  | 1198.948                                   | 1443.72                                | 48.56                           | 216.31                          | 7.00                            |
| 0.0203                                  | 1198.672                                   | 1443.99                                | 49.16                           | 216.32                          | 6.98                            |
| 0.0251                                  | 1198.477                                   | 1444.29                                | 49.62                           | 216.34                          | 6.96                            |
| 0.0282                                  | 1198.348                                   | 1444.49                                | 49.89                           | 216.35                          | 6.95                            |
| 0.0336                                  | 1198.130                                   | 1444.82                                | 49.90                           | 216.36                          | 6.95                            |
| 0.0387                                  | 1197.926                                   | 1445.13                                | 49.97                           | 216.40                          | 6.95                            |
| 0.0426                                  | 1197.767                                   | 1445.38                                | 50.28                           | 216.43                          | 6.94                            |

$[\text{HMIm}]\text{SCN} + \text{PC} + \text{LiCl}$

$[\text{HMIm}]\text{SCN} + \text{PC} + \text{LiCl}$

$\mu_{liCl} = 0.0003$ mol kg$^{-1}$

| $m_{liBr}$ = 0.0061 mol kg$^{-1}$ | $m_{liBr}$ = 0.0035 mol kg$^{-1}$ | $m_{liBr}$ = 0.00005 mol kg$^{-1}$ | $m_{liBr}$ = 0.00095 mol kg$^{-1}$ | $m_{liBr}$ = 0.0035 mol kg$^{-1}$ | $m_{liBr}$ = 0.00005 mol kg$^{-1}$ |
|------------------------------------------|-------------------------------------------|----------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 0.0114                                  | 1199.225                                   | 1443.63                                | 62.35                           | 214.41                          | 6.47                            |
| 0.0142                                  | 1198.793                                   | 1443.83                                | 62.96                           | 214.42                          | 6.44                            |
| 0.0191                                  | 1198.686                                   | 1443.83                                | 62.96                           | 214.42                          | 6.44                            |
| 0.0248                                  | 1198.501                                   | 1444.17                                | 63.16                           | 214.43                          | 6.44                            |
| 0.0299                                  | 1198.285                                   | 1444.57                                | 63.42                           | 214.45                          | 6.42                            |
| 0.0328                                  | 1198.093                                   | 1444.92                                | 63.32                           | 214.48                          | 6.43                            |
| 0.0381                                  | 1197.800                                   | 1445.13                                | 63.45                           | 214.50                          | 6.42                            |
| 0.0401                                  | 1197.705                                   | 1445.51                                | 63.93                           | 214.52                          | 6.40                            |

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| $m_{\text{li}}$ (mol kg$^{-1}$) | $d$ (kg m$^{-3}$) | $u$ (m s$^{-1}$) | $S_n$ | $10^6 V_p$ (m$^3$ mol$^{-1}$) | $10^4 K_p$ (m$^3$ mol$^{-1}$ Pa$^{-1}$) |
|-----------------------------|-----------------|----------------|-------|----------------|-----------------|
| 0.0236 | 1198.503 | 1443.95 | 43.80 | 216.48 | 7.19 |
| 0.0278 | 1198.329 | 1444.19 | 43.76 | 216.50 | 7.19 |
| 0.0358 | 1198.005 | 1444.65 | 44.18 | 216.52 | 7.18 |
| 0.0390 | 1197.876 | 1444.84 | 44.55 | 216.54 | 7.16 |
| 0.0447 | 1197.644 | 1445.17 | 44.68 | 216.56 | 7.16 |
| $[\text{OMIm}][\text{SCN} + \text{PC} + \text{LiBr}]$ | $m_{\text{li}} = 0.0104$ mol kg$^{-1}$ | | | | |
| 0.0000 | 1199.227 | 1442.80 | | | |
| 0.0096 | 1198.733 | 1443.41 | 44.26 | 247.20 | 8.39 |
| 0.0133 | 1198.543 | 1443.66 | 45.84 | 247.26 | 8.34 |
| 0.0155 | 1198.428 | 1443.81 | 46.29 | 247.27 | 8.32 |
| 0.0184 | 1198.280 | 1444.01 | 47.22 | 247.30 | 8.29 |
| 0.0237 | 1198.010 | 1444.37 | 48.03 | 247.33 | 8.26 |
| 0.0266 | 1197.856 | 1444.58 | 48.60 | 247.37 | 8.24 |
| 0.0300 | 1197.686 | 1444.81 | 48.97 | 247.37 | 8.23 |
| 0.0322 | 1197.570 | 1444.98 | 49.74 | 247.39 | 8.20 |
| $m_{\text{li}} = 0.0038$ mol kg$^{-1}$ | | | | | |
| 0.0000 | 1199.422 | 1442.68 | | | |
| 0.0099 | 1198.897 | 1443.28 | 39.14 | 248.38 | 8.61 |
| 0.0127 | 1198.743 | 1443.47 | 40.65 | 248.44 | 8.56 |
| 0.0162 | 1198.562 | 1443.69 | 41.38 | 248.43 | 8.54 |
| 0.0194 | 1198.389 | 1443.90 | 41.82 | 248.44 | 8.52 |
| 0.0227 | 1198.217 | 1444.11 | 42.20 | 248.47 | 8.51 |
| 0.0263 | 1198.027 | 1444.34 | 42.41 | 248.49 | 8.50 |
| 0.0299 | 1197.832 | 1444.58 | 42.76 | 248.53 | 8.49 |
| 0.0322 | 1197.709 | 1444.74 | 43.32 | 248.58 | 8.47 |
| $m_{\text{li}} = 0.0098$ mol kg$^{-1}$ | | | | | |
| 0.0000 | 1199.584 | 1442.52 | | | |
| 0.0097 | 1199.043 | 1443.09 | 34.22 | 250.03 | 8.85 |
| 0.0132 | 1198.850 | 1443.31 | 35.92 | 250.07 | 8.79 |
| 0.0168 | 1198.648 | 1443.54 | 36.95 | 250.13 | 8.76 |
| 0.0194 | 1198.504 | 1443.70 | 37.13 | 250.14 | 8.75 |
| 0.0244 | 1198.230 | 1444.02 | 38.23 | 250.16 | 8.71 |
| 0.0267 | 1198.100 | 1444.18 | 39.03 | 250.19 | 8.68 |
| 0.0302 | 1197.904 | 1444.40 | 39.04 | 250.22 | 8.68 |
| 0.0330 | 1197.749 | 1444.59 | 39.71 | 250.25 | 8.66 |
| $[\text{OMIm}][\text{SCN} + \text{PC} + \text{LiCl}]$ | $m_{\text{li}} = 0.0032$ mol kg$^{-1}$ | | | | |
| 0.0000 | 1199.177 | 1442.90 | | | |
| 0.0110 | 1198.620 | 1443.65 | 51.88 | 246.98 | 8.13 |
| 0.0140 | 1198.445 | 1443.89 | 52.32 | 247.04 | 8.11 |
| 0.0180 | 1198.237 | 1444.18 | 52.92 | 247.07 | 8.09 |
| 0.0200 | 1198.161 | 1444.29 | 53.41 | 247.12 | 8.07 |
| 0.0240 | 1197.926 | 1444.62 | 53.81 | 247.13 | 8.06 |
| 0.0290 | 1197.715 | 1444.91 | 53.77 | 247.17 | 8.06 |
| 0.0300 | 1197.646 | 1445.01 | 54.00 | 247.18 | 8.05 |
| 0.0340 | 1197.459 | 1445.29 | 54.86 | 247.21 | 8.02 |
| $m_{\text{li}} = 0.0064$ mol kg$^{-1}$ | | | | | |
| 0.0000 | 1199.276 | 1442.74 | | | |
| 0.0100 | 1198.724 | 1443.41 | 44.61 | 248.42 | 8.44 |
| 0.0150 | 1198.479 | 1443.72 | 45.77 | 248.49 | 8.40 |
| 0.0170 | 1198.394 | 1443.83 | 46.22 | 248.51 | 8.39 |
| 0.0200 | 1198.233 | 1444.04 | 46.99 | 248.55 | 8.36 |
| 0.0220 | 1198.124 | 1444.18 | 47.24 | 248.58 | 8.35 |
| 0.0260 | 1197.869 | 1444.51 | 47.76 | 248.60 | 8.33 |
| 0.0300 | 1197.669 | 1444.77 | 48.10 | 248.62 | 8.32 |
| 0.0320 | 1197.556 | 1444.92 | 48.38 | 248.63 | 8.31 |
| $m_{\text{li}} = 0.0100$ mol kg$^{-1}$ | | | | | |
| 0.0000 | 1199.413 | 1442.63 | | | |
| 0.0095 | 1198.887 | 1443.17 | 32.51 | 250.01 | 8.92 |
Table 4. continued

| mIL (mol kg⁻¹) | d (kg m⁻³) | u (m s⁻¹) | S_i | 10⁶ Vₚ (m⁴ mol⁻¹) | 10⁸ κφ (m⁴ mol⁻¹ Pa⁻¹) |
|----------------|-----------|-----------|------|-----------------|-------------------------|
| 0.0133         | 1198.675  | 1443.40   | 33.78 | 250.05          | 8.88                    |
| 0.0155         | 1198.551  | 1443.54   | 34.70 | 250.07          | 8.85                    |
| 0.0184         | 1198.391  | 1443.72   | 35.53 | 250.11          | 8.82                    |
| 0.0237         | 1198.100  | 1444.04   | 36.04 | 250.13          | 8.80                    |
| 0.0266         | 1197.934  | 1444.23   | 36.63 | 250.16          | 8.78                    |
| 0.0300         | 1197.750  | 1444.45   | 37.56 | 250.19          | 8.75                    |
| 0.0322         | 1197.625  | 1444.60   | 38.11 | 250.21          | 8.73                    |

“Standard uncertainties for molality, temperature, and pressure were u (m) = 0.002 mol kg⁻¹, u (T) = 0.02 K, and u (P) = 10 hPa, respectively, with a 0.68 level of confidence, and the combined standard uncertainties for density and speed of sound were u(ρ) = 0.07 kg m⁻³ and u(υ) = 1.3 m s⁻¹ with a 0.68 level of confidence. The standard uncertainties of the apparent molar volume and apparent molar isentropic compressibility were υκ (Vₚ) = 5.10⁻³ m³ mol⁻¹ (level of confidence of 0.68) and υκ κφ (κφ) = 3.10⁻³ m⁴ mol⁻¹ Pa⁻¹ (level of confidence of 0.68), respectively.”

 Consequently, IL solvation numbers were decreased. It means that the coordination of PC to Li⁺ is more favorable rather than the IL solution. The apparent molar isentropic compressibility, κφ of the ILs has been determined in the solution with the following relation.

$$\kappa = \frac{\kappa_m \cdot d - \kappa_s}{md \cdot d} \tag{16}$$

The κφ values of the ILs in the studied solutions are given in Tables 1 and 4 for the corresponding binary and ternary solutions, respectively. These values increase by the addition of the IL in the studied binary solutions (IL + PC). The κφ values are higher for a longer alkyl chain length of the ILs [OMIM][SCN], as shown in Figure 6.

The results indicate that the κφ values of the ILs, [OMIM][SCN], increase at a higher concentration of LiBr (Figure 7).

Also, it found that the LiBr solution κφ values are larger than LiCl solutions, as shown in Table 4. The influence of temperature on the κφ values of [BMIM][SCN] at (288.15–318.15) K is plotted in Figure 8, which represents a decreasing trend at a higher temperature.

The obtained κφ values of the studied ILs of binary (IL + PC) and ternary (IL + LiX + PC) solutions were fitted to the following equation.

$$\kappa = \kappa_{0} + S_{b}m^{1/2} + B_{k}m \tag{17}$$

where κ₀ is the partial molar isentropic compressibility and S₀ and B₀ are the empirical parameters of the equation. The obtained parameters for the investigated solutions are listed in Tables 6 and 7 for the studied solutions. The κφ values increase with the alkyl chain length of the ILs.

The κ₀ values for the ILs in PC and in the presence of LiX salts are positive, which increase with increasing LiX content, and also, it is found that the value κ₀ of in the presence of LiBr is higher than LiCl. This trend shows that bulk propylene carbonate is more compressible rather than electrostrictive PC molecules (solvated PC molecules); upon addition of LiX, electrostriction interactions between IL and PC become weaker due to PC molecules’ coordination on Li⁺, as previously mentioned. On the other hand, according to the SPT results, it is seen that interactional and cavity volumes are increased for a longer alkyl chain length of the ILs. The highly available cavity volume is the main reason for the high compressibility value of [OMIM][SCN] in the PC solution. The intermolecular interaction between the cation of the IL and PC is the dominant factor of this phenomenon but there is intramolecular negative ion interaction, which is another factor that is negligible in the dilute region.

**CONCLUSIONS**

This study is a thermodynamic approach to a model of Li-ion battery electrolytes. The volumetric and compressibility properties of the ILs [RMIM][SCN], in PC in the presence of LiCl and LiBr have been investigated to understand the existing interactions in these systems. The ILs’ interaction with PC increased with the alkyl chain length of the imidazolium cation from butyl to octyl. However, these interactions were weakened at a higher temperature. The studied ILs, [RMIM][SCN], show structure-breaking behavior in propylene carbonate with the following trend: [OMIM][SCN] > [HMIM][SCN] > [BMIM][SCN]. Although ILs with larger cations are more compressible, this feature decreases with increasing temperature. The ion–polar interactions are dominant rather than other interactions in the ternary systems. Also, interactions between LiX and ILs increase with the lithium halide content, and LiBr has a stronger...
Table 5. Standard Partial Molar Volume (\(V_\varphi^0\)), Empirical Parameters of eq 2, \(S_\varphi\) and \(B_\varphi\), the Partial Molar Volume of Transfer (\(\Delta_v\), \(V_\varphi^0\)), and the Standard Deviation of the Partial Molar Volume \((\sigma(V_\varphi^0))\) for the Ternary Solutions Containing (IL + LiX + PC) at Different Concentrations of LiX at \(T = 298.15\) K Under Pressure (\(P = 0.086\) MPa)\(^a\)

| \(m_{\text{LiX}}\) (mol kg\(^{-1}\)) | \(10^6 V_\varphi^0\) (m\(^3\) mol\(^{-1}\)) | \(10^6 S_\varphi\) (m\(^3\) mol\(^{-1}\) kg\(^{-1}\) \(1^{1/2}\)) | \(10^6 B_\varphi\) (m\(^3\) mol\(^{-1}\) kg\(^{-1}\) \(1^{1/2}\)) | \(10^6 \Delta_v\), \(V_\varphi^0\) (m\(^3\) mol\(^{-1}\)) | \(10^6 \sigma(V_\varphi^0)\) |
|---|---|---|---|---|---|
| 0.0000 | 178.31 ± 0.32 | 4.67 ± 0.04 | −1.71 ± 0.15 | 0.015 |
| 0.0035 | 178.96 ± 0.13 | 2.02 ± 0.02 | −2.96 ± 0.05 | 0.65 | 0.008 |
| 0.0056 | 180.93 ± 0.16 | 3.81 ± 0.02 | −2.44 ± 0.06 | 2.62 | 0.008 |
| 0.0095 | 183.10 ± 0.17 | 2.89 ± 0.02 | −2.74 ± 0.07 | 4.79 | 0.011 |
| 0.0000 | 178.31 ± 0.32 | 4.67 ± 0.04 | −1.71 ± 0.15 | 0.015 |
| 0.0028 | 178.98 ± 0.12 | −4.92 ± 0.02 | 21.37 ± 0.05 | 0.67 | 0.007 |
| 0.0057 | 179.40 ± 0.08 | 2.3 ± 0.01 | −2.88 ± 0.03 | 1.09 | 0.006 |
| 0.0100 | 180.45 ± 0.12 | 2.55 ± 0.02 | −2.79 ± 0.05 | 2.13 | 0.008 |
| 0.0000 | 213.52 ± 0.60 | −13.97 ± 0.09 | 86.42 ± 0.31 | 0.026 |
| 0.0036 | 214.46 ± 0.08 | −0.66 ± 0.01 | 7.79 ± 0.3 | 0.94 | 0.007 |
| 0.0064 | 216.29 ± 0.07 | −0.84 ± 0.01 | 7.08 ± 0.03 | 2.77 | 0.007 |
| 0.0099 | 218.46 ± 0.08 | 0.57 ± 0.01 | 3.20 ± 0.02 | 4.94 | 0.005 |
| 0.0000 | 213.52 ± 0.60 | −13.97 ± 0.09 | 86.42 ± 0.31 | 0.026 |
| 0.0036 | 214.53 ± 0.07 | −2.46 ± 0.01 | 12.52 ± 0.03 | 1.01 | 0.005 |
| 0.0065 | 215.47 ± 0.02 | 0.20 ± 0.00 | 4.97 ± 0.01 | 1.95 | 0.002 |
| 0.0104 | 216.39 ± 0.07 | −0.07 ± 0.01 | 4.18 ± 0.03 | 2.87 | 0.006 |
| 0.0000 | 244.84 ± 0.24 | 2.44 ± 0.04 | 90.02 ± 0.15 | 0.009 |
| 0.0038 | 246.94 ± 0.07 | 3.09 ± 0.01 | −3.07 ± 0.04 | 2.10 | 0.005 |
| 0.0060 | 248.58 ± 0.22 | −3.86 ± 0.03 | 21.02 ± 0.12 | 3.74 | 0.016 |
| 0.0092 | 249.73 ± 0.14 | 3.37 ± 0.02 | −3.09 ± 0.07 | 4.89 | 0.010 |
| 0.0000 | 244.84 ± 0.24 | 2.44 ± 0.04 | 90.02 ± 0.15 | 0.009 |
| 0.0032 | 246.64 ± 0.16 | 3.67 ± 0.02 | −3.20 ± 0.08 | 1.80 | 0.010 |
| 0.0060 | 248.10 ± 0.16 | 3.60 ± 0.02 | −3.16 ± 0.08 | 3.26 | 0.010 |
| 0.0100 | 249.73 ± 0.08 | 3.18 ± 0.01 | −3.07 ± 0.04 | 4.89 | 0.006 |

\(^a\)Standard uncertainties for molality, temperature, and pressure were \((m) = 0.002\) mol kg\(^{-1}\), \((T) = 0.02\) K, and \((P) = 10\) hPa, respectively, with a 0.68 level of confidence.

Figure 8. Apparent molar isentropic compressibility \(\kappa_\varphi\), values of [BMIM][SCN] in PC versus its molality \(m\) at different temperatures. (●) \(T = 288.15\) K, (■) \(T = 298.15\) K, (♦) \(T = 308.15\) K, and (▲) \(T = 318.15\) K, and solid lines represent the Redlich–Mayer model.

**EXPERIMENTAL SECTION**

**Chemicals.** All of the reagents used in this work are listed in Table 8. Also, the purification methods, supplier company names, and CAS numbers are given. The water content of all components was determined with Karl-Fisher titration (Titirino GPD 751, electrode: Metrohm Pt—6.0338.100).

**Ionic Liquids [BMIM][SCN] and their Properties.** The ionic liquid synthesis procedure is given in our previous publications with the corresponding density and speed of sound data at different temperatures.\(^a\) Also, brief information about the synthesized ionic liquids is given in Table 8.

**Apparatus and Procedure.** The solutions were prepared using an analytical balance (Shimadzu AWS-220) with a precision of \(\pm 1 \times 10^{-4}\) g in a molal-based concentration. The density and speed of sound were measured with a digital densitometer (Anton Paar DSA5000). The instrument was calibrated with air pressure and distilled water. The frequency for the speed of sound measurement was 3 MHz.

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**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03517.
Table 6. Partial Molar Isentropic Compressibility $\kappa^0_{\phi}$, Empirical Parameters of eq 17, $S_0$ and $B_0$ and Standard Deviation of Apparent Molar Isentropic Compressibility $\sigma(\kappa^0_{\phi})$ of [RMIM][SCN] in PC $T = (288.15–318.15)$ K under Pressure ($P = 0.086$ MPa)$^a$

| $T$ (K) | $10^4 \kappa^0_{\phi}$ (m$^3$ mol$^{-1}$ Pa$^{-1}$) | $10^4 S_0$ (m$^3$ mol$^{-1/2}$ kg$^{1/2}$ Pa$^{-1}$) | $10^4 B_0$ (m$^3$ mol$^{-2}$ kg Pa$^{-1}$) | $10^4 \sigma(\kappa^0_{\phi})$ |
|---------|----------------------------------|---------------------------------|-----------------|-----------------|
| 288.15  | 4.17 ± 0.07                       | 0.56 ± 0.01                     | 0.81 ± 0.03     | 0.004           |
| 298.15  | 3.72 ± 0.07                       | 0.89 ± 0.01                     | 0.91 ± 0.03     | 0.004           |
| 308.15  | 3.27 ± 0.22                       | 1.14 ± 0.03                     | 0.99 ± 0.10     | 0.01            |
| 318.15  | 2.84 ± 0.09                       | 1.15 ± 0.01                     | 1.02 ± 0.04     | 0.009           |

*Table 6. Partial Molar Isentropic Compressibility $\kappa^0_{\phi}$, Empirical Parameters of eq 17, $S_0$ and $B_0$ and Standard Deviation of Apparent Molar Isentropic Compressibility $\sigma(\kappa^0_{\phi})$ of [RMIM][SCN] in PC $T = (288.15–318.15)$ K under Pressure ($P = 0.086$ MPa)*

$^a$Standard uncertainties for temperature and pressure were $u(T) = 0.02$ K and $u(P) = 10$ hPa, respectively, with a 0.68 level of confidence.

Table 7. Partial Molar Isentropic Compressibility $\kappa^0_{\phi}$, Empirical Parameters of eq 17, $S_0$ and $B_0$ and Standard Deviation of Apparent Molar Isentropic Compressibility $\sigma(\kappa^0_{\phi})$ of [RMIM][SCN] in (PC + LiX) at Different Concentrations of LiX at $T = 298.15$ K under Pressure ($P = 0.086$ MPa)$^a$

| $m_{\text{LiX}}$ (mol kg$^{-1}$) | $10^4 \kappa^0_{\phi}$ (m$^3$ mol$^{-1}$ Pa$^{-1}$) | $10^4 S_0$ (m$^3$ mol$^{-1/2}$ kg$^{1/2}$ Pa$^{-1}$) | $10^4 B_0$ (m$^3$ mol$^{-2}$ kg Pa$^{-1}$) | $10^4 \sigma(\kappa^0_{\phi})$ |
|-----------------------------|----------------------------------|---------------------------------|-----------------|-----------------|
| 0.0000         | 3.72 ± 0.07                       | 0.89 ± 0.01                     | 0.91 ± 0.03     | 0.004           |
| 0.0035         | 5.05 ± 0.15                       | −3.44 ± 0.02                    | −0.49 ± 0.06     | 0.009           |
| 0.0056         | 5.37 ± 0.22                       | −3.09 ± 0.03                    | −0.40 ± 0.09     | 0.011           |
| 0.0095         | 5.76 ± 0.39                       | −3.03 ± 0.05                    | −0.38 ± 0.16     | 0.023           |

*Table 7. Partial Molar Isentropic Compressibility $\kappa^0_{\phi}$, Empirical Parameters of eq 17, $S_0$ and $B_0$ and Standard Deviation of Apparent Molar Isentropic Compressibility $\sigma(\kappa^0_{\phi})$ of [RMIM][SCN] in (PC + LiX) at Different Concentrations of LiX at $T = 298.15$ K under Pressure ($P = 0.086$ MPa)*

$^a$Standard uncertainties for molality, temperature, and pressure were $u(m) = 0.002$ mol kg$^{-1}$, $u(T) = 0.02$ K, and $u(P) = 10$ hPa, respectively, with a 0.68 level of confidence.
Table 8. Summary of the Chemicals and their Characteristics That Were Used in This Work

| Chemical name          | CAS number | abbreviation | structure | Supplier | Initial mass fraction purity | Purification method | Water content (ppm) | Final mass fraction purity | Analysis method |
|------------------------|------------|--------------|-----------|----------|-----------------------------|--------------------|----------------------|--------------------------|------------------------|
| Lithium bromide        | 7596-      |              | Li⁺ Br⁻   | Merck    | >0.99                        | Dried at 398.15 K  | 16                   |                          | KF                     |
| Lithium chloride       | 7447-      |              | Li⁺ Cl⁻   | Merck    | >0.99                        | Dried at 393.15 K  | 12                   |                          | KF                     |
| Propylene carbonate    | 108-32-7   |              |           | Samchun  | >0.995                       | None               | anhydrous            |                          | KF                     |
| 1-butyl-3-methylimidazolium thiocyanate | 344796-87-0 | [BMM][SCN] | Synthesized | Extraction / filtration / rotary evaporation / vacuum | 120 | >0.93 | H²NMR / FT-IR / KF |
| 1-octyl-3-methylimidazolium thiocyanate | 847499-72-3 | [OMIM][SCN] | Synthesized | Extraction / filtration / rotary evaporation / vacuum | 115 | >0.97 | H²NMR / FT-IR / KF |
| 1-hexyl-3-methylimidazolium thiocyanate | 847499-74-5 | [HMIM][SCN] | Synthesized | Extraction / filtration / rotary evaporation / vacuum | 95 | >0.97 | H²NMR / FT-IR / KF |

REFERENCES

(1) Holtstiege, F.; Wilken, A.; Winter, M.; Placke, T. Running out of Lithium? A Route to Differentiate between Capacity Losses and Active Lithium Losses in Lithium-Ion Batteries. Phys. Chem. Chem. Phys. 2017, 19, 25905–25918.

(2) Guo, Z. Y.; Ji, Z. Y.; Chen, H. Y.; Liu, J.; Zhao, Y. Y.; Li, F.; Yuan, J. S. Effect of Impurity Ions in the Electrosorption Lithium Extraction Process: Generation and Restriction of "Selective Concentration Polarization. ACS Sustainable Chem. Eng. 2020, 8, 11834–11844.

(3) Kazemzadeh, H.; Karimi-Sabet, J.; Towfigh Darian, J.; Adhami, A. Evaluation of Polymer Inclusion Membrane Efficiency in Selective Separation of Lithium Ion from Aqueous Solution. Sep. Purif. Technol. 2020, 251, No. 117298.

(4) Lee, Y.; Cha, J. H.; Jung, D. Y. Lithium Separation by Growth of Lithium Aluminum Layered Double Hydroxides on Aluminum Metal Substrates. Solid State Sci. 2020, 110, No. 106488.

(5) Linneen, N.; Bhave, R.; Woerner, D. Purification of Industrial Grade Lithium Chloride for the Recovery of High Purity Battery Grade Lithium Carbonate. Sep. Purif. Technol. 2019, 214, 168–173.

(6) Lu, H.; Chen, Z.; Yuan, Y.; Du, H.; Wang, J.; Liu, X.; Hou, Z.; Zhang, K.; Fang, J.; Qu, Y. A Rational Balance Design of Hybrid Electrolyte Based on Ionic Liquid and Fluorinated Ether in Lithium Sulfur Batteries. J. Electrochem. Soc. 2019, 166, A2453–A2458.

(7) Wang, X.; Salari, M.; Jiang, D.; et al. Electrode Material–Ionic Liquid Coupling for Electrochemical Energy Storage. Nature 2020, 5, 787–808.

(8) Andrea Calderón, C.; Vizintin, A.; Bobnar, J.; Barraco, D. E.; Leiva, E. P. M.; Fantini, S.; Fischer, F.; Dominko, R. Lithium Metal Protection by a Cross-Linked Polymer Ionic Liquid and Its Application in Lithium Battery. ACS Appl. Energy Mater. 2020, 3, 2020–2027.

(9) Yang, W.; Wang, S.; Zhang, X.; Zhang, Q.; Ma, W.; Yu, S.; Sun, G. Substituent Effect of Imidazolium Ionic Liquid: A Potential Strategy for High Coulombic Efficiency Al Battery. J. Phys. Chem. C 2019, 123, 11522–11528.

(10) Molinari, N.; Mailoa, J. P.; Koziinsky, B. General Trend of a Negative Li Effective Charge in Ionic Liquid Electrolytes. J. Phys. Chem. Lett. 2019, 10, 2313–2319.

(11) Falcone, R. D.; Correa, N. M.; Silber, J. J. Amphiphilic Ionic Liquids as Sustainable Components to Formulate Promising Vesicles to Be Used in Nanomedicine. In Current Opinion in Green and Sustainable Chemistry; Elsevier B.V., 2020; p 100382.

(12) Barbosa, L. C.; Nascimento, M. V. da C.; Araújo, O. de Q. F.; de Medeiros, J. L. A Cleaner and More Sustainable Decarbonation Process via Ionic-Liquid Absorption for Natural Gas with High Carbon Dioxide Content. J. Clean. Prod. 2020, 242, No. 118421.

(13) Francis, C. F. J.; Kyratzis, I. L.; Best, A. S. Lithium-Ion Battery Separators for Ionic-Liquid Electrolytes: A Review. Adv. Mater. 2020, 32, No. 1904205.

(14) Liu, X.; Zhang, S.; Wang, J.; Wang, J.; Shao, Y.; Zhu, L. Biochemical Responses and DNA Damage in Earthworms (Eisenia fetida).
Fetid) Induced by Ionic Liquid [Omic]PF6. Environ. Sci. Pollut. Res. 2016, 23, 6836–6844.

(15) Deng, X. Y.; Li, D.; Wang, L.; Hu, X. L.; Cheng, J.; Gao, K. Potential Toxicity of Ionic Liquid ([C12mim][BF4]) on the Growth and Biochemical Characteristics of a Marine Diatom Phaeodactylum Tricornutum. Sci. Total Environ. 2017, 586, 675–684.

(16) Li, W.; Zhu, L.; Du, Z.; Li, B.; Wang, J.; Wang, J.; Zhang, C.; Zhu, L. Acute Toxicity, Oxidative Stress and DNA Damage of Three Task-Specific Ionic Liquids ([C2NH2MIm][BF4], [MOEMIm][BF4], and [HOEMIm][BF4]) to Zebraﬁsh (Danio Rerio). Chemosphere 2020, 249, No. 126119.

(17) Rout, A.; Binnemans, K. Efﬁcient Separation of Transition Metals from Rare Earths by an Undiluted Phosphonium Thiocyanate Ionic Liquid. Phys. Chem. Chem. Phys. 2016, 18, 16039–16045.

(18) Gupta, K. M.; Chen, Y.; Hu, Z.; Jiang, J. Metal-Organic Framework Supported Ionic Liquid Membranes for CO2 Capture: Anion Efﬁcacy. Phys. Chem. Chem. Phys. 2012, 14, 5785–5794.

(19) Nam, J. E.; Jo, H. J.; Kang, J. K.; Woo, S.; Hwang, D. K. Optimization of Electrolyte Components on the Performance of Organic-Dye-Sensitized Solar Cells. J. Nanosci. Nanotechnol. 2017, 17, 8100–8104.

(20) Rosol, Z. P.; German, N. J.; Gross, S. M. Solubility, Ionic Conductivity and Viscosity of Lithium Salts in Room Temperature Ionic Liquids. Green Chem. 2009, 11, 1453–1457.

(21) Vogl, T.; Menne, S.; Balducci, A. Mixture of Protic Ionic Liquids and Propylene Carbonate as Advanced Electrolytes for Lithium-Ion Batteries. Phys. Chem. Chem. Phys. 2014, 16, 25014–25023.

(22) Levy, N. R.; Lifshits, S.; Yohanan, E.; Ein-Eli, Y. Hybrid Ionic Liquid Propylene Carbonyl-Based Electrolytes for Aluminum-Air Batteries. ACS Appl. Energy Mater. 2020, 3, 2585–2592.

(23) Karuppasamy, K.; Vikraman, D.; Hwang, I. T.; Kim, H. J.; Nicholson, A.; Bose, R.; Kim, H. S. Nonaqueous Liquid Electrolytes Based on Novel 1-Ethyl-3-Methylimidazolium Bis(Nonafluorobutane-1-Sulfonyl Imidate) Ionic Liquid for Energy Storage Devices. J. Mater. Res. Technol. 2020, 9, 1251–1260.

(24) Shekaari, H.; Zafarani-Moattar, M. T.; Golmohammadi, B. Solvation Properties of 1-Alkyl-3-Methylimidazolium Thiocyanate Ionic Liquids in the Presence of Lithium Halide Salts in N-Methyl-2-Pyrrolidone. J. Mol. Liq. 2019, 280, 191–204.

(25) Zafarani-Moattar, M. T.; Shekaari, H.; Sadmousavi Dizaj, A. Investigation of Solute-Solute Interactions in Binary and Quaternary Solutions Containing Lithium Perchlorate, Propylene Carbonate, and the Deep Eutectic Solvent (Choline Chloride/Ethylene Glycol) at T=(288.15 to 318.15) K. J. Mol. Liq. 2020, 319, No. 114090.

(26) Shekaari, H.; Tagh Zafarani-Moattar, M.; Golmohammadi, B. Thermodynamic and Transport Properties of Ionic Liquids, 1-Alkyl-3-Methylimidazolium Thiocyanate in the Aqueous Lithium Halides Solutions. J. Chem. Thermodyn. 2020, 141, No. 105953.

(27) Vranes, M.; Zec, N.; Tot, A.; Papović, S.; Dožić, S.; Gadjžurić, S. Density, Electrical Conductivity, Viscosity and Excess Properties of 1-Butyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl)Imide + Propylene Carbonate Binary Mixtures. J. Chem. Thermodyn. 2014, 68, 98–108.

(28) Tuynina, E.; Afanasev, V.; Chekunova, M. Viscosity and Density of Solutions of Tetraethylammonium Tetraﬂuoroborate in Propylene Carbonate at Different Temperatures. J. Solution Chem. 2012, 41, 307–317.

(29) Moumouzias, G.; Ritzioulis, G. Relative Permeativities and Refractive Indices of Propylene Carbonate + Toluene Mixtures from 283.15 K to 313.15 K. J. Chem. Eng. Data 1997, 42, 710–713.

(30) Zhao, Y.; Wang, J.; Xuan, X.; Lu, J. Effect of Temperature on Excess Molar Volumes and Viscosities for Propylene Carbonate + N,N-Dimethylformamide Mixtures. J. Chem. Eng. Data 2000, 45, 440–444.

(31) Marrieta-Guevara, F.; Trejo Rodríguez, A. Liquid Density as a Function of Temperature of Five Organic Solvents. J. Chem. Eng. Data 1984, 29, 204–206.

(32) Wang, H.; Hu, L.; Wu, Y. Excess Volumes and Partial Molar Volumes of Binary Mixtures of 1,2-Propanediol Carbonate with Xylene in the Temperature Range of (293.15 to 353.15) K. J. Chem. Thermodyn. 2005, 37, 1119–1129.

(33) Pires, J.; Timperman, L.; Jacquemin, J.; Balducci, A.; Anouti, M. Density, Conductivity, Viscosity, and Excess Properties of (Pyrrolidinium Nitrate-Based Protonic Ionic Liquid + Propylene Carbonate) Binary Mixture. J. Chem. Thermodyn. 2013, 59, 10–19.

(34) Barthel, J.; Neudeer, R.; Rock, H. Density, Relative Permeativity, and Viscosity of Propylene Carbonate+dimethoxymethane Mixtures from 25 °C to 125 °C. J. Chem. Eng. Data 2000, 45, 1007–1011.

(35) Zhao, Y. H.; Abraham, M. H.; Zissimos, A. M. Fast Calculation of van der Waals Volume as a Sum of Atomic and Bond Contributions and Its Application to Drug Compounds. J. Org. Chem. 2003, 68, 7368–7373.

(36) Bondi, A. Van Der Waals Volumes and Radii. J. Phys. Chem. A. 1964, 68, 441–451.

(37) Chernyak, Y.; Clements, J. H. Vapor Pressure and Liquid Heat Capacity of Alkylene Carbonates. J. Chem. Eng. Data 2004, 49, 1180–1184.

(38) Piekarski, H.; Kubalczyk, K.; Wasia, M. Volumes, Heat Capacities, and Compressibilities of the Mixtures of Acetonitrile with N,N-Dimethylacetamide and Propylene Carbonate. J. Chem. Eng. Data 2010, 55, 5435–5440.

(39) Hepler, L. G. Thermal Expansion and Structure in Water and Aqueous Solutions. Can. J. Chem. 1969, 47, 4613–4617.

(40) Gorobets, M. I.; Ataev, M. B.; Gafurov, M. M.; Kirillov, S. A. Speciation in Solutions of Lithium Salts in Dimethyl Sulfoxide, Propylene Carbonate, and Dimethyl Carbonate from Raman Data: A Mini-Review. J. Spectrosc. 2016, 2016, No. 6978560.

(41) Angenendt, K.; Johansson, P. Ionic Liquid Based Lithium Battery Electrolytes: Charge Carriers and Interactions Derived by Density Functional Theory Calculations. J. Phys. Chem. B 2011, 115, 7808–7813.

(42) Hinton, J. F.; Amis, E. S. Solvation Numbers of Ions. Chem. Rev. 1971, 71, 627–674.