The Hildebrand Solubility Parameters of Ionic Liquids—Part 2

Andrzej Marciniak

Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland; E-Mail: a.marciniak@ch.pw.edu.pl; Tel.: +48-222-345-816; Fax: +48-226-282-741

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Abstract: The Hildebrand solubility parameters have been calculated for eight ionic liquids. Retention data from the inverse gas chromatography measurements of the activity coefficients at infinite dilution were used for the calculation. From the solubility parameters, the enthalpies of vaporization of ionic liquids were estimated. Results are compared with solubility parameters estimated by different methods.

Keywords: ionic liquid; Hildebrand solubility parameter; enthalpy of vaporization

1. Introduction

Ionic liquids (ILs) are a relatively new class of salts with a melting temperature below 373.15 K. In general, ILs are composed of organic cations with either inorganic or organic anions. Ionic liquids have unique properties, namely, a wide liquid range, stability at high temperatures and negligible vapor pressure. Because of the last mentioned property, the inverse gas chromatography (IGC) is a suitable method for measuring thermodynamic properties of pure substances and their mixtures [1]. From the IGC measurements, the activity coefficients at infinite dilution, Flory-Huggins interaction parameters as well as the Hildebrand solubility parameters can be determined. By this method the solubility parameters were determined previously for different ionic liquids [2–6].

The Hildebrand solubility parameters have numerous applications including gas-liquid solubility, solvent extraction and many others as described in detail in the literature [7,8]. The solubility parameter is the square root of the cohesive energy density, which is defined as the ratio of the energy of vaporization, $\Delta_{vap} U$, to the molar volume, $\nu$:
\[ \delta = \sqrt{\frac{\Delta_{vap}^H}{\nu}} = \sqrt{\frac{\Delta_{vap}U - RT}{\nu}} \]  

(1)

Because ILs have negligible vapor pressure, experimental measurements of their energy of vaporization are difficult. For this reason, experimental data of \( \Delta_{vap}U \) are unavailable. Alternative methods have been considered for estimation of the solubility parameters of ionic liquids: From melting temperatures of ILs [9], from intrinsic viscosity measurements [10], from the activation energy of viscosity [11,12], from surface tension measurements [13], from Kamlet-Taft equation [14], using non random hydrogen bonding (NRHB) and PC-SAFT models [15], from lattice energy density [16].

This paper provides information on the Hildebrand solubility parameters determined for eight ionic liquids as a function of temperature and the enthalpies of vaporization calculated from the values of the solubility parameters. The solubility parameters were calculated using the experimental data from the activity coefficients at infinite dilution measurements. The list of investigated ionic liquids is shown in Table 1. The values of the activity coefficients at infinite dilution for the investigated ionic liquids were published earlier [17–24].

**Table 1.** Abbreviations, names, sources, purities and structures of investigated ionic liquids.

| Abbreviation, Name, Source, Purity | Structure | Reference |
|-----------------------------------|-----------|-----------|
| abbreviation: [N-C<sub>3</sub>OHPY][FAP]  
name: 1-(3-hydroxypropyl)pyridinium trifluorotris(perfluoroethyl)phosphate  
source: MERCK  
purity > 0.999 mass fraction  
water content < 100 ppm  
halide content < 100 ppm | ![Structure](image1.png) | [17] |
| abbreviation: [N-C<sub>3</sub>OHPY][NTf<sub>2</sub>]  
name: 1-(3-hydroxypropyl)pyridinium bis(trifluoromethylsulfonyl)-amide  
source: MERCK  
purity > 0.999 mass fraction  
water content < 100 ppm  
halide content < 100 ppm | ![Structure](image2.png) | [18] |
| abbreviation: [emim][TCB]  
name: 1-ethyl-3-methylimidazolium tetracyanoborate  
source: MERCK  
purity > 0.99 mass fraction  
water content < 200 ppm  
halide content < 100 ppm | ![Structure](image3.png) | [19] |
### Table 1. Cont.

| Abbreviation, Name, Source, Purity | Structure | Reference |
|-----------------------------------|-----------|-----------|
| abbreviation: [dmim][TCB] <br>name: 1-decyl-3-methylimidazolium tetracyanoborate <br>source: MERCK <br>purity > 0.9996 mass fraction <br>water content: < 100 ppm <br>halide content < 100 ppm | ![Structure](image1) | [20] |
| abbreviation: [bmPIP][SCN] <br>name: 1-butyl-1-methylpiperidinium thiocyanate <br>source: IoLiTec <br>purity > 0.98 mass fraction <br>water content: < 100 ppm <br>halide content < 100 ppm | ![Structure](image2) | [21] |
| abbreviation: [pmPIP][NTf₂] <br>name: 1-propyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)-amide <br>source: IoLiTec <br>purity > 0.99 mass fraction <br>water content: < 100 ppm <br>halide content < 100 ppm | ![Structure](image3) | [22] |
| abbreviation: [bmPIP][NTf₂] <br>name: 1-butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)-amide <br>source: IoLiTec <br>purity > 0.99 mass fraction <br>water content: < 250 ppm <br>halide content < 100 ppm | ![Structure](image4) | [23] |
| abbreviation: [OiQuin][NTf₂] <br>name: N-octyl-isoquinolinium bis(trifluoromethylsulfonyl)-amide <br>source: synthesized <br>purity > 0.99 mass fraction <br>water content: < 180 ppm <br>halide content < 100 ppm | ![Structure](image5) | [24] |

### 2. Results and Discussion

The Hildebrand solubility parameters were calculated for the ionic liquids presented (with abbreviations and structures) in Table 1. The results are presented in Table 2.
on [FAP]$^-$ and [NTf$_2$]$^-$ anions with the same cation, [N-C$_3$OHPY]$^+$, the solubility parameter is higher for IL with [NTf$_2$]$^-$ anion. Estimated enthalpy of vaporization is higher for [N-C$_3$OHPY][FAP] than for [N-C$_3$OHPY][NTf$_2$], the higher molar mass and more complex structure of [FAP]$^-$ anion causes higher enthalpy of vaporization. For ionic liquids [bmPIP][SCN] and [bmPIP][NTf$_2$] the solubility parameter as well as the enthalpy of vaporization is higher for ionic liquid with [SCN]$^-$ anion. In this case the structure of [SCN]$^-$ anion is much simpler than for [NTf$_2$]$^-$ and the molar mass is lower, but very strong interaction of thiocyanate group increases the enthalpy of vaporization. With an increase of the alkyl chain in the cation structure of an ionic liquid the solubility parameter decreases. Due to increase of molar mass and alkyl chain length the enthalpy of vaporization also increases. This is typical behavior observed with increasing of alkyl chain length for example in linear alkanes or alkylbenzenes. This effect is visible in two pairs of ionic liquids, namely [emim][TCB]–[dmim][TCB] and [pmPIP][NTf$_2$]–[bmPIP][NTf$_2$].

Table 2. Hildebrand solubility parameters, $\delta_2$ and standard enthalpies of vaporization for the investigated ionic liquids.

| Ionic Liquid          | $T/K$  | $\delta_2$/MPa$^{0.5}$ | $\Delta_{\text{vap}} H$/kJ·mol$^{-1}$ |
|-----------------------|--------|------------------------|---------------------------------------|
| [N-C$_3$OHPY][FAP]    | 298.15 | 25.0 $^a$              | 212.3                                 |
|                       | 308.15 | 24.7                   | 209.6                                 |
|                       | 318.15 | 24.5                   | 206.6                                 |
|                       | 328.15 | 24.2                   | 203.3                                 |
|                       | 338.15 | 23.9                   | 199.6                                 |
|                       | 348.15 | 23.6                   | 196.2                                 |
|                       | 358.15 | 23.3                   | 192.1                                 |
| [N-C$_3$OHPY][NTf$_2$]| 298.15 | 26.0 $^a$              | 186.1                                 |
|                       | 318.15 | 25.6                   | 182.0                                 |
|                       | 328.15 | 25.3                   | 179.5                                 |
|                       | 338.15 | 25.1                   | 176.9                                 |
|                       | 348.15 | 24.8                   | 174.2                                 |
|                       | 358.15 | 24.5                   | 171.2                                 |
| [emim][TCB]           | 298.15 | 25.9                   | 149.5                                 |
|                       | 308.15 | 25.7                   | 149.0                                 |
|                       | 318.15 | 25.5                   | 147.9                                 |
|                       | 328.15 | 25.3                   | 146.8                                 |
|                       | 338.15 | 25.1                   | 145.6                                 |
|                       | 348.15 | 24.9                   | 144.4                                 |
|                       | 358.15 | 24.6                   | 142.6                                 |
| [dmim][TCB]           | 298.15 | 24.0 $^a$              | 205.6                                 |
|                       | 328.15 | 23.6                   | 201.9                                 |
|                       | 338.15 | 23.3                   | 199.4                                 |
|                       | 348.15 | 23.1                   | 197.1                                 |
|                       | 358.15 | 22.8                   | 194.2                                 |
|                       | 368.15 | 22.5                   | 190.5                                 |
Table 2. Cont.

| Ionic Liquid | T/K  | \(\delta/\text{MPa}^{0.5}\) | \(\Delta_{\text{vap}}H/\text{kJ}\cdot\text{mol}^{-1}\) |
|--------------|------|-----------------------------|---------------------------------------------|
| [bmPIP][SCN] | 298.15 | 30.7 \(^a\) | 198.9 |
|              | 318.15 | 30.1 | 193.4 |
|              | 328.15 | 29.8 | 190.4 |
|              | 338.15 | 29.5 | 187.2 |
|              | 348.15 | 29.1 | 183.9 |
|              | 358.15 | 28.8 | 180.5 |
| [pmPIP][NTf\(_2\)] | 298.15 | 23.8 \(^b\) | 172.4 |
|              | 308.15 | 23.6 | 170.9 |
|              | 318.15 | 23.3 | 167.9 |
|              | 328.15 | 23.2 | 166.5 |
|              | 338.15 | 22.9 | 164.2 |
|              | 348.15 | 22.7 | 162.6 |
|              | 358.15 | 22.5 | 160.7 |
| [bmPIP][NTf\(_2\)] | 298.15 | 23.4 \(^b\) | 175.1 |
|              | 308.15 | 23.2 | 173.4 |
|              | 318.15 | 23.0 | 171.7 |
|              | 328.15 | 22.8 | 169.7 |
|              | 338.15 | 22.6 | 168.0 |
|              | 348.15 | 22.4 | 166.4 |
|              | 358.15 | 22.2 | 164.6 |
| [OiQuin][NTf\(_2\)] | 298.15 | 22.5 \(^b\) | 201.3 |
|              | 328.15 | 21.9 | 195.5 |
|              | 338.15 | 21.7 | 193.2 |
|              | 348.15 | 21.6 | 192.1 |
|              | 358.15 | 21.4 | 189.7 |
|              | 368.15 | 21.2 | 187.6 |

\(^a\) Extrapolated values calculated using polynomial regression; \(^b\) Extrapolated values calculated using linear regression.

Table 3 presents comparison of the Hildebrand solubility parameters determined by different methods for selected ionic liquids based on [NTf\(_2\)]\(^-\) anion. Camper et al. presents different values of \(\delta\) for ionic liquid [emim][NTf\(_2\)] estimated from the IL melting point [9] and from lattice energy density [16]. These values differ about 2.4 times and are inconsistent with \(\delta\) obtained by other methods. Solubility parameters determined from enthalpy of vaporization are in good agreement with values of \(\delta\) obtained by IGC for [emim][NTf\(_2\)] and [hmim][NTf\(_2\)] and with values of \(\delta\) estimated from surface tension for [bmim][NTf\(_2\)] and [bmPYR][NTf\(_2\)]. Kilaru et al. estimated solubility parameters from activation energy of viscosity using the equation presented below [11]:

\[ \delta = \left[ \frac{K_v RT}{\nu} \ln \left( \frac{10^{-9} \mu \nu}{hN_A} \right) \right]^{0.5} \]  

(2)

where: \(\mu\) is the dynamic viscosity of IL (in units of mPa-s), \(\nu\) is the molar volume (in units of cm\(^3\)·mol\(^{-1}\)), \(h\) is Planck constant (in units of J·s), \(N_A\) is Avogadro constant (in units of mol\(^{-1}\)), and \(K_v\) is a proportionality constant. They calculated \(K_v\) value of 7.8 for ILs based on [NTf\(_2\)]\(^-\) anion from
solubility parameters determined from intrinsic viscosity [10]. Consequently the solubility parameters estimated from Equation 2 are consistent with those estimated from intrinsic viscosity. In this work $K_v$ value of 5.23 was obtained from the solubility parameters determined from experimental enthalpy of vaporization (the procedure is described in Supporting Information). Based on this value the solubility parameters were determined for [N-C$_3$OHPY][NTf$_2$], [pmPIP][NTf$_2$] and [bmPIP][NTf$_2$] ionic liquids for which the molar volumes and viscosities were determined (see Table 3S). Results are presented in Table 4. The differences in results are in the range from 3 to 10%.

**Table 3.** Hildebrand solubility parameters, $\delta$ determined by different methods for selected ionic liquids based on [NTf$_2$]$^-$ anion at $T=298.15$ K.

| Ionic Liquid | $\delta/\text{MPa}^{0.5}$ | Method, Reference |
|--------------|-----------------------------|--------------------|
| [emim][NTf$_2$] | 16.2 | melting temperature [9] |
| | 19.3 | activation energy of viscosity [12] |
| | 21.3$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 120.6$) [25] |
| | 22.3 | IGC [4] |
| | 22.6$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 134$) [26] |
| | 22.7$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 136$) [27] |
| | 27.5$^a$ | activation energy of viscosity [11] |
| | 27.6 | intrinsic viscosity [10] |
| | 38.4 | lattice energy density [16] |
| [bmim][NTf$_2$] | 19.8$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 118.5$) [25] |
| | 20.9 | activation energy of viscosity [12] |
| | 21.2$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 134$) [26] |
| | 21.3 | surface tension [13] |
| | 22.9$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 155$) [27] |
| | 25.5 | Kamlet-Taft Equation [14] |
| | 26.5$^a$ | activation energy of viscosity [11] |
| | 26.7 | intrinsic viscosity [10] |
| [hmim][NTf$_2$] | 19.0$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 124.1$) [25] |
| | 19.5 | activation energy of viscosity [12] |
| | 20.3 | IGC [2] |
| | 20.5$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 139$) [26] |
| | 22.9$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 173$) [27] |
| | 25.2$^a$ | activation energy of viscosity [11] |
| | 25.6 | intrinsic viscosity [10] |
| [omim][NTf$_2$] | 18.9$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 132.3$) [25] |
| | 20.2$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 149$) [28] |
| | 20.2$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 149$) [26] |
| | 23.0$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 192$) [27] |
| | 25.0 | intrinsic viscosity [10] |
| [bmPY][NTf$_2$] | 20.6 | IGC [2] |
| | 21.2 | activation energy of viscosity [12] |
| [bmPYR][NTf$_2$] | 21.1 | from surface tension [13] |
| | 22.2$^b$ | enthalpy of vaporization ($\Delta_{\text{vap}}H_{298.15}/\text{kJ}\cdot\text{mol}^{-1} = 152$) [29] |
Table 3. Cont.

| Ionic Liquid | $\delta_2$/MPa$^{0.5}$ | Method, Reference |
|--------------|------------------------|-------------------|
| [N-C$_3$OHPY][NTf$_2$] | 25.6 $^c$ | IGC [this work] |
| | 23.0 $^c$ | activation energy of viscosity [this work] |
| [pmPIP][NTf$_2$] | 23.6 $^c$ | IGC [this work] |
| | 23.5 $^c$ | NRHB [15] |
| | 23.4 $^c$ | PC-SAFT [15] |
| | 22.2 $^c$ | activation energy of viscosity [this work] |
| [bmPIP][NTf$_2$] | 23.2 $^c$ | IGC [this work] |
| | 21.8 $^c$ | activation energy of viscosity [this work] |

$^a$ at $T = 303.15$ K; $^b$ calculated from experimental value of $\Delta_{vap}H_{298.15}$; $^c$ at $T = 308.15$ K.

Table 4. Hildebrand solubility parameters, $\delta_2$ determined by different methods for [N-C$_3$OHPY][NTf$_2$], [pmPIP][NTf$_2$] and [bmPIP][NTf$_2$] ionic liquids.

| Ionic Liquid | $T$/K | IGC | Activation Energy of Viscosity |
|--------------|-------|-----|--------------------------------|
| [N-C$_3$OHPY][NTf$_2$] | 308.15 | 25.6 | 23.0 |
| | 318.15 | 25.3 | 22.8 |
| | 328.15 | 25.1 | 22.7 |
| | 338.15 | 24.8 | 22.6 |
| | 348.15 | 24.5 | 22.6 |
| [pmPIP][NTf$_2$] | 308.15 | 23.6 | 22.2 |
| | 318.15 | 23.3 | 22.0 |
| | 328.15 | 23.2 | 21.9 |
| | 338.15 | 22.9 | 21.8 |
| | 348.15 | 22.7 | 21.8 |
| [bmPIP][NTf$_2$] | 308.15 | 23.2 | 21.8 |
| | 318.15 | 23.0 | 21.6 |
| | 328.15 | 22.8 | 21.5 |
| | 338.15 | 22.6 | 21.4 |
| | 348.15 | 22.4 | 21.3 |

3. Calculation of Solubility Parameters

3.1. Experimental Procedure

On the basis of the experimental data from the activity coefficients at infinite dilution measurements, the Hildebrand solubility parameters have been calculated using the equations presented below. The activity coefficients at infinite dilution for all investigated ionic liquids were measured using inverse gas chromatography. Detailed descriptions of materials, apparatus and methods used in each experiment are presented in the relevant papers [17–24].
3.2. Theoretical Basis

Retention data were used for the calculation of Hildebrand solubility parameters, $\delta_2$. According to the Flory-Huggins theory the interaction parameter at infinite dilution can be determined using the following expression:

$$
\chi_{12}^\infty = \ln \left( \frac{273.15 R}{P_1^* V_s^* M_1} \right) - \frac{P_1^* (B_{11} - V_1^*)}{RT} + \ln \left( \frac{\rho_1}{\rho_2} \right) - \left( 1 - \frac{V_1^*}{V_2^*} \right)
$$

(3)

where $R$ denotes the gas constant, $T$ the temperature, $P_1^*$ the saturated vapor pressure of the solute at temperature $T$, $B_{11}$ the second virial coefficient of pure solute, $V_1^*$ and $V_2^*$ the molar volume of the solute and solvent respectively, $M_1$ the molar mass of solute, $\rho_1$ and $\rho_2$ density of solute and solvent respectively, $V_s$ specific retention volume which is given by:

$$
V_s = \frac{273.15 V_N}{T m_2}
$$

(4)

where $m_2$ denotes the mass of the solvent on the column packing and $V_N$ the net retention volume of the solute given by:

$$
V_N = J_2^2 U_o (t_R - t_G)
$$

(5)

where $t_R$ and $t_G$ are the retention times for the solute and an unretained gas, respectively, $U_o$ is the column outlet flow rate, $J_2^2$ the pressure correction term given by:

$$
J_2^2 = \frac{2 \left( \frac{P_i}{P_o} \right)^2 - 1}{3 \left( \frac{P_i}{P_o} \right)^2 - 1}
$$

(6)

where $P_i$ and $P_o$ denote the inlet and the outlet pressure, respectively.

The column outlet flow rate corrected for the vapor pressure of water $U_o$ is given by:

$$
U_o = U \left( 1 - \frac{P_w}{P_o} \right) \frac{T}{T_f}
$$

(7)

where $T_f$ is the temperature at the column outlet, $P_w$ is the vapor pressure of water at $T_f$ and $U$ is the flow rate measured with the flow meter.

The interaction parameter $\chi_{12}^\infty$ may be expressed as a function of $\delta_1$ and $\delta_2$ which denote the solubility parameters of the solute and of the solvent, respectively, by:

$$
\chi_{12}^\infty = \frac{V_1^* (\delta_1 - \delta_2)^2}{RT}
$$

(8)

Equation 8 can be rewritten as:

$$
\left( \frac{\delta_1^2}{RT^2} - \frac{\chi_{12}^\infty}{V_1^*} \right) = \left( \frac{2\delta_1}{RT} \right) \delta_1 - \frac{\delta_2^2}{RT}
$$

(9)

The solubility parameters $\delta_1$ of the solutes were calculated using following equation:

$$
\delta_1^2 = \frac{\Delta v_{29} H - RT}{\nu}
$$

(10)
where \( \Delta vap H \) denotes enthalpy of vaporization and \( \nu \) the molar volume. The thermophysical properties required in calculations were calculated using equations and constants taken from the literature [30].

Values of \( \chi_{12}^\infty \) were determined from Equation 2 and are presented in Table 1S. If the left side of Equation 9 is plotted against \( \delta_1 \), a straight line having a slope of \( 2\delta_2 / RT \) and an intercept of \( -\delta_2^2 / RT \) is obtained. The solubility parameter of the solvent \( \delta_2 \) (ionic liquid) can be calculated from the slope. Example of calculations is presented in the Supporting Information. Hildebrand solubility parameters of the investigated ionic liquids and the estimated enthalpies of vaporization calculated using Equation 10 are listed in Table 2.

4. Conclusions

The Hildebrand solubility parameters estimated by different methods are divergent. The most reliable results are from the experiment especially from the enthalpies of vaporization. As presented in Table 3, solubility parameters calculated from enthalpies of vaporization and determined by IGC are in good consistency for \([\text{emim}][\text{NTf}_2]\) and \([\text{hmim}][\text{NTf}_2]\) ionic liquids. Therefore, the inverse gas chromatography is an appropriate method to determine Hildebrand solubility parameters of ionic liquids. While the ionic liquids have negligible vapor pressure, experimental measurements of their enthalpy of vaporization are difficult; therefore, this property can be estimated from the solubility parameters.

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Appendix

Electronic Supporting Information

Table S1, interaction parameters, \( \chi_{12}^{\infty} \). Example of calculation of the solubility parameter. Calculation of the \( K_v \) constant from Equation 2; Table S2, data used in calculation of \( K_v \) constant; Table S3, densities and viscosities for \([N\text{-C}_3\text{OHPY}][\text{NTf}_2]\), \([\text{pmPIP}][\text{NTf}_2]\) and \([\text{bmPIP}][\text{NTf}_2]\) ionic liquids.

| Table S1. Interaction parameters, \( \chi_{12}^{\infty} \). |
| --- |
| \( T/K \) | \( n\text{-pentane} \) | \( n\text{-hexane} \) | \( n\text{-heptane} \) | \( n\text{-octane} \) | \( n\text{-nonane} \) | \( n\text{-decane} \) |
| 308.15 | 3.62 | 3.96 | 4.32 | 4.68 | 5.04 | 5.42 |
| 318.15 | 3.50 | 3.83 | 4.17 | 4.52 | 4.86 | 5.24 |
| 328.15 | 3.39 | 3.71 | 4.04 | 4.38 | 4.72 | 5.08 |
| 338.15 | 3.27 | 3.58 | 3.91 | 4.24 | 4.57 | 4.93 |
| 348.15 | 3.18 | 3.48 | 3.78 | 4.11 | 4.44 | 4.78 |
| 358.15 | 3.09 | 3.37 | 3.67 | 3.99 | 4.30 | 4.64 |
Table S1. Cont.

| $T/K$ | cyclopentane | cyclohexane | cycloheptane | cyclooctane | 1-pentene | 1-hexene | 1-heptene | 1-octene | 1-hexyne | 1-heptyne | 1-octyne | benzene | toluene | ethylbenzene | o-xylene | m-xylene | p-xylene | methanol | ethanol | 1-propanol | 1-butanol | water | thiophene | tetrahydrofuran | 2-pentanone | 3-pentanone | acetone |
|-------|--------------|-------------|--------------|-------------|-----------|---------|----------|----------|----------|-----------|---------|--------|---------|-------------|---------|----------|---------|----------|---------|-----------|-----------|-------|----------|----------------|-----------|-------------|--------|
| 308.15 | 3.19         | 3.55        | 3.81         | 4.08        | 2.75      | 3.07    | 3.40     | 3.79     | 2.01     | 2.33      | 2.69    | 0.482  | 0.732   | 1.12       | 0.944   | 1.01     | 1.06     | 1.01     | 0.873   | 1.01       | 1.20      | 2.95   | 0.557    | −0.967       | −1.66    | −1.56      | −1.47   |
| 318.15 | 3.08         | 3.42        | 3.67         | 3.93        | 2.66      | 2.97    | 3.31     | 3.68     | 1.96     | 2.28      | 2.63    | 0.495  | 0.743   | 1.12       | 0.950   | 1.02     | 1.07     | 0.979    | 0.832   | 0.965      | 1.14      | 2.85   | 0.564    | −0.859       | −1.56    | −1.47      | −1.38   |
| 328.15 | 2.97         | 3.29        | 3.54         | 3.80        | 2.58      | 2.88    | 3.22     | 3.58     | 1.92     | 2.23      | 2.57    | 0.505  | 0.751   | 1.12       | 0.955   | 1.03     | 1.07     | 0.944    | 0.761   | 0.916      | 1.08      | 2.77   | 0.572    | −0.776       | −1.47    | −1.38      | −1.30   |
| 338.15 | 2.75         | 3.05        | 3.30         | 3.55        | 2.43      | 2.72    | 3.14     | 3.48     | 1.87     | 2.18      | 2.51    | 0.519  | 0.769   | 1.12       | 0.966   | 1.04     | 1.08     | 0.913    | 0.777   | 0.878      | 1.03      | 2.69   | 0.578    | −0.683       | −1.38    | −1.30      | −1.23   |
| 348.15 | 2.67         | 2.94        | 3.19         | 3.43        | 2.36      | 2.64    | 2.97     | 3.29     | 1.79     | 2.08      | 2.40    | 0.537  | 0.699   | 0.803      | 0.926   | 2.54     | 0.591    | 0.882    | 0.835   | 0.903      | 1.11      | 2.54   | 0.585    | −0.601       | −1.38    | −1.23      | −1.23   |
| 358.15 | 2.50         | 2.36        | 2.38         | 2.54        | 2.26      | 2.46    | 2.75     | 3.05     | 1.69     | 2.19      | 2.40    | 0.510  | 0.414   | 0.504      | 1.45    | 2.16     | 0.792    | 0.694    | 0.817   | 0.903      | 1.11      | 2.16   | 0.557    | −0.759       | −1.38    | −1.23      | −1.23   |

$T$, temperature; $K$, kelvin; $cyclohexane$, cyclohexane; $cycloheptane$, cycloheptane; $cyclooctane$, cyclooctane; $1-pentene$, 1-pentene; $1-hexene$, 1-hexene; $1-heptene$, 1-heptene; $1-octene$, 1-octene; $1-hexyne$, 1-hexyne; $1-heptyne$, 1-heptyne; $1-octyne$, 1-octyne; benzene, benzene; toluene, toluene; ethylbenzene, ethylbenzene; o-xylene, o-xylene; m-xylene, m-xylene; p-xylene, p-xylene; methanol, methanol; ethanol, ethanol; 1-propanol, 1-propanol; 1-butanol, 1-butanol; water, water; thiophene, thiophene; tetrahydrofuran, tetrahydrofuran; 2-pentanone, 2-pentanone; 3-pentanone, 3-pentanone; acetone, acetone.
Table S1. Cont.

| $T$/K | $n$-pentane | $n$-hexane | 3-methylpentane | 2,2-dimethylbutane | $n$-heptane | $n$-octane | $2,2,4$-trimethylpentane | $n$-nonane | $n$-decane | cyclopentane | cyclohexane | methylcyclohexane |
|-------|-------------|-------------|------------------|-------------------|-------------|-------------|-----------------------------|-------------|-------------|----------------|-------------|-------------------|
| 318.15 | 3.67        | 4.04        | 3.90             | 3.81              | 4.45        | 4.86        |                             |              |             |                |             |                   |
| 328.15 | 3.59        | 3.94        | 3.80             | 3.71              | 4.34        | 4.73        |                             |              |             |                |             |                   |
| 338.15 | 3.50        | 3.84        | 3.70             | 3.61              | 4.22        | 4.61        |                             |              |             |                |             |                   |
| 348.15 | 3.43        | 3.76        | 3.62             | 3.53              | 4.13        | 4.50        |                             |              |             |                |             |                   |
| 358.15 | 3.35        | 3.67        | 3.54             | 3.44              | 4.03        | 4.40        |                             |              |             |                |             |                   |
|        |             |             |                  |                   |             |             | $T$/K                        |              |             |                |             |                   |
| 318.15 | 4.40        | 5.27        | 5.70             | 3.08              | 3.45        | 3.78        |                             |              |             |                |             |                   |
| 328.15 | 4.30        | 5.13        | 5.54             | 2.99              | 3.35        | 3.68        |                             |              |             |                |             |                   |
| 338.15 | 4.20        | 5.00        | 5.41             | 2.91              | 3.26        | 3.58        |                             |              |             |                |             |                   |
| 348.15 | 4.11        | 4.89        | 5.29             | 2.84              | 3.18        | 3.49        |                             |              |             |                |             |                   |
| 358.15 | 4.03        | 4.77        | 5.16             | 2.78              | 3.10        | 3.41        |                             |              |             |                |             |                   |
|        |             |             |                  |                   |             |             | $T$/K                        |              |             |                |             |                   |
| 318.15 | 3.73        | 4.03        | 2.89             | 3.28              | 2.75        | 3.67        |                             |              |             |                |             |                   |
| 328.15 | 3.63        | 3.92        | 2.83             | 3.20              | 2.68        | 3.59        |                             |              |             |                |             |                   |
| 338.15 | 3.53        | 3.81        | 2.76             | 3.12              | 2.62        | 3.51        |                             |              |             |                |             |                   |
| 348.15 | 3.44        | 3.71        | 2.71             | 3.06              | 2.57        | 3.44        |                             |              |             |                |             |                   |
| 358.15 | 3.36        | 3.63        | 2.65             | 3.00              | 2.52        | 3.38        |                             |              |             |                |             |                   |
|        |             |             |                  |                   |             |             | $T$/K                        |              |             |                |             |                   |
| 318.15 | 4.09        | 4.91        | 2.10             | 2.48              | 2.89        | 0.886       |                             |              |             |                |             |                   |
| 328.15 | 4.00        | 4.80        | 2.08             | 2.45              | 2.84        | 0.887       |                             |              |             |                |             |                   |
| 338.15 | 3.91        | 4.70        | 2.05             | 2.41              | 2.79        | 0.888       |                             |              |             |                |             |                   |
| 348.15 | 3.83        | 4.61        | 2.03             | 2.39              | 2.76        | 0.888       |                             |              |             |                |             |                   |
| 358.15 | 3.75        | 4.51        | 2.01             | 2.35              | 2.71        | 0.888       |                             |              |             |                |             |                   |
|        |             |             |                  |                   |             |             | $T$/K                        |              |             |                |             |                   |
| 318.15 | 1.18        | 1.62        | 1.38             | 1.51              | 1.51        | 0.896       |                             |              |             |                |             |                   |
| 328.15 | 1.18        | 1.61        | 1.38             | 1.51              | 1.51        | 0.850       |                             |              |             |                |             |                   |
| 338.15 | 1.18        | 1.60        | 1.38             | 1.51              | 1.51        | 0.805       |                             |              |             |                |             |                   |
| 348.15 | 1.18        | 1.58        | 1.38             | 1.51              | 1.51        | 0.761       |                             |              |             |                |             |                   |
| 358.15 | 1.18        | 1.58        | 1.38             | 1.51              | 1.51        | 0.719       |                             |              |             |                |             |                   |
|        |             |             |                  |                   |             |             | $T$/K                        |              |             |                |             |                   |
| 318.15 | 0.885       | 1.02        | 1.23             | 2.21              | −0.614      | 0.754       |                             |              |             |                |             |                   |
| 328.15 | 0.836       | 0.968       | 1.17             | 2.13              | −0.534      | 0.756       |                             |              |             |                |             |                   |
| 338.15 | 0.788       | 0.918       | 1.11             | 2.06              | −0.464      | 0.756       |                             |              |             |                |             |                   |
| 348.15 | 0.745       | 0.868       | 1.05             | 1.99              | −0.397      | 0.757       |                             |              |             |                |             |                   |
| 358.15 | 0.698       | 0.822       | 0.995            | 1.94              | −0.334      | 0.756       |                             |              |             |                |             |                   |
|        |             |             |                  |                   |             |             | $T$/K                        |              |             |                |             |                   |
| 318.15 | 0.125       | −0.205      | 1.26             | 1.69              | 1.34        | 2.43        |                             |              |             |                |             |                   |
| 328.15 | 0.166       | −0.157      | 1.29             | 1.70              | 1.35        | 2.40        |                             |              |             |                |             |                   |
| 338.15 | 0.201       | −0.112      | 1.31             | 1.71              | 1.36        | 2.38        |                             |              |             |                |             |                   |
| 348.15 | 0.230       | −0.070      | 1.33             | 1.73              | 1.37        | 2.36        |                             |              |             |                |             |                   |
| 358.15 | 0.260       | −0.032      | 1.35             | 1.74              | 1.38        | 2.35        |                             |              |             |                |             |                   |
### Table S1. Cont.

| $T$/K | di-$n$-butyl ether | acetone | 2-pentanone | 3-pentanone |
|-------|---------------------|---------|-------------|-------------|
| 318.15 | 3.30                | −0.351  | 0.193       | 0.253       |
| 328.15 | 3.25                | −0.314  | 0.217       | 0.277       |
| 338.15 | 3.20                | −0.284  | 0.242       | 0.301       |
| 348.15 | 3.16                | −0.255  | 0.261       | 0.322       |
| 358.15 | 3.12                | −0.229  | 0.281       | 0.341       |

| $T$/K | $n$-pentane | $n$-hexane | $n$-heptane | $n$-octane | 2,2,4-trimethylpentane | $n$-nonane |
|-------|------------|------------|-------------|------------|------------------------|-----------|
| 298.15 | 3.26       | 3.63       | 4.05        | 4.46       | 4.14                   | 4.90      |
| 308.15 | 3.16       | 3.54       | 3.94        | 4.34       | 4.03                   | 4.76      |
| 318.15 | 3.11       | 3.47       | 3.86        | 4.25       | 3.96                   | 4.65      |
| 328.15 | 3.02       | 3.38       | 3.75        | 4.14       | 3.87                   | 4.52      |
| 338.15 | 2.96       | 3.30       | 3.67        | 4.04       | 3.78                   | 4.41      |
| 348.15 | 2.90       | 3.24       | 3.60        | 3.95       | 3.71                   | 4.31      |
| 358.15 | 2.84       | 3.18       | 3.52        | 3.86       | 3.63                   | 4.21      |

| $T$/K | $n$-decane | cyclopentane | cyclohexane | methylcyclohexane | cycloheptane | cyclooctane |
|-------|------------|--------------|-------------|-------------------|--------------|-------------|
| 298.15 | 5.32       | 2.64         | 3.01        | 3.35              | 3.23         | 3.49        |
| 308.15 | 5.18       | 2.57         | 2.92        | 3.24              | 3.13         | 3.38        |
| 318.15 | 5.06       | 2.52         | 2.86        | 3.17              | 3.07         | 3.31        |
| 328.15 | 4.92       | 2.44         | 2.77        | 3.08              | 2.98         | 3.21        |
| 338.15 | 4.81       | 2.39         | 2.70        | 3.00              | 2.90         | 3.14        |
| 348.15 | 4.69       | 2.34         | 2.64        | 2.94              | 2.83         | 3.06        |
| 358.15 | 4.58       | 2.28         | 2.57        | 2.88              | 2.77         | 2.98        |

| $T$/K | 1-pentene | 1-hexene | cyclohexene | 1-heptene | 1-octene | 1-hexyne |
|-------|-----------|----------|-------------|-----------|----------|----------|
| 298.15 | 2.42      | 2.80     | 2.21        | 3.18      | 3.61     | 1.50     |
| 308.15 | 2.37      | 2.73     | 2.16        | 3.10      | 3.52     | 1.49     |
| 318.15 | 2.34      | 2.69     | 2.14        | 3.06      | 3.46     | 1.49     |
| 328.15 | 2.29      | 2.62     | 2.09        | 2.99      | 3.37     | 1.48     |
| 338.15 | 2.25      | 2.57     | 2.04        | 2.92      | 3.30     | 1.48     |
| 348.15 | 2.22      | 2.53     | 2.01        | 2.89      | 3.24     | 1.47     |
| 358.15 | 2.15      | 2.48     | 1.98        | 2.83      | 3.18     | 1.47     |

| $T$/K | 1-heptyne | 1-octyne | benzene | toluene | ethylbenzene | $o$-xylene |
|-------|-----------|----------|---------|---------|--------------|-----------|
| 298.15 | 1.86      | 2.23     | 0.433   | 0.710   | 1.10         | 0.922     |
| 308.15 | 1.84      | 2.21     | 0.443   | 0.721   | 1.10         | 0.927     |
| 318.15 | 1.83      | 2.18     | 0.455   | 0.730   | 1.10         | 0.933     |
| 328.15 | 1.81      | 2.16     | 0.462   | 0.739   | 1.10         | 0.937     |
| 338.15 | 1.80      | 2.14     | 0.471   | 0.747   | 1.10         | 0.943     |
| 348.15 | 1.78      | 2.12     | 0.477   | 0.757   | 1.09         | 0.949     |
| 358.15 | 1.77      | 2.11     | 0.483   | 0.762   | 1.09         | 0.950     |

| $T$/K | $m$-xylene | $p$-xylene | methanol | ethanol | 1-propanol | 1-butanol |
|-------|------------|------------|----------|---------|------------|-----------|
| 298.15 | 1.08       | 1.02       | 0.968    | 1.04    | 1.11       | 1.29      |
| 308.15 | 1.08       | 1.03       | 0.886    | 0.944   | 1.01       | 1.17      |
| 318.15 | 1.09       | 1.03       | 0.812    | 0.856   | 0.909      | 1.06      |
| 328.15 | 1.09       | 1.04       | 0.739    | 0.770   | 0.816      | 0.953     |
Table S1. Cont.

| T/K | water | thiophene | tetrahydrofuran | methyl tert-butyl ether | methyl tert-pentyl ether | diethyl ether |
|-----|-------|-----------|-----------------|------------------------|-------------------------|-------------|
| 298.15 | 2.39 | 0.316 | −0.0164 | 1.19 | 1.53 | 1.21 |
| 308.15 | 2.27 | 0.325 | 0.0104 | 1.20 | 1.54 | 1.21 |
| 318.15 | 2.19 | 0.331 | 0.0335 | 1.21 | 1.54 | 1.21 |
| 328.15 | 2.10 | 0.337 | 0.0458 | 1.22 | 1.55 | 1.21 |
| 338.15 | 2.01 | 0.345 | 0.0626 | 1.23 | 1.55 | 1.21 |
| 348.15 | 1.92 | 0.348 | 0.0878 | 1.24 | 1.56 | 1.21 |
| 358.15 | 1.85 | 0.355 | 0.101 | 1.24 | 1.56 | 1.20 |

| T/K | di-n-propyl ether | di-n-butyl ether | acetone | 2-pentanone | 3-pentanone | 2-hexanone |
|-----|-------------------|------------------|---------|-------------|-------------|------------|
| 298.15 | 2.24 | 3.06 | −0.445 | −0.0425 | −0.0790 | 0.210 |
| 308.15 | 2.21 | 2.99 | −0.421 | −0.0239 | −0.0528 | 0.225 |
| 318.15 | 2.18 | 2.94 | −0.398 | −0.0018 | −0.0208 | 0.238 |
| 328.15 | 2.14 | 2.87 | −0.379 | 0.0155 | 0.0047 | 0.247 |
| 338.15 | 2.12 | 2.83 | −0.358 | 0.0298 | 0.0266 | 0.261 |
| 348.15 | 2.09 | 2.78 | −0.344 | 0.0427 | 0.0464 | 0.272 |
| 358.15 | 2.06 | 2.73 | −0.325 | 0.0601 | 0.0678 | 0.283 |

| T/K | n-pentane | n-hexane | n-heptane | n-octane | 2,2,4-trimethylpentane | n-nonane |
|-----|-----------|----------|-----------|----------|------------------------|----------|
| 328.15 | 1.98 | 2.11 | 2.27 | 2.44 | 2.35 | 2.62 |
| 338.15 | 1.94 | 2.07 | 2.23 | 2.39 | 2.30 | 2.57 |
| 348.15 | 1.90 | 2.03 | 2.18 | 2.34 | 2.25 | 2.52 |
| 358.15 | 1.85 | 1.99 | 2.13 | 2.30 | 2.21 | 2.47 |
| 368.15 | 1.81 | 1.94 | 2.09 | 2.25 | 2.17 | 2.42 |

| T/K | n-decane | cyclopentane | cyclohexane | methylcyclohexane | cycloheptane | cyclooctane |
|-----|----------|--------------|-------------|-------------------|-------------|-------------|
| 328.15 | 2.82 | 1.58 | 1.73 | 1.84 | 1.78 | 1.88 |
| 338.15 | 2.76 | 1.54 | 1.68 | 1.79 | 1.73 | 1.83 |
| 348.15 | 2.71 | 1.50 | 1.63 | 1.75 | 1.69 | 1.79 |
| 358.15 | 2.65 | 1.46 | 1.59 | 1.71 | 1.65 | 1.74 |
| 368.15 | 2.60 | 1.42 | 1.54 | 1.67 | 1.61 | 1.70 |
| $T/K$ | 1-pentene | 1-hexene | cyclohexene | 1-heptene | 1-octene | 1-hexyne |
|-------|-----------|-----------|-------------|-----------|----------|----------|
| 328.15 | 1.49      | 1.63      | 1.28        | 1.78      | 1.96     | 0.853    |
| 338.15 | 1.47      | 1.59      | 1.25        | 1.75      | 1.93     | 0.857    |
| 348.15 | 1.45      | 1.56      | 1.23        | 1.73      | 1.90     | 0.860    |
| 358.15 | 1.42      | 1.53      | 1.21        | 1.70      | 1.87     | 0.859    |
| 368.15 | 1.40      | 1.51      | 1.18        | 1.68      | 1.84     | 0.861    |

| $T/K$ | 1-heptene | 1-octyne | benzene | toluene | ethylbenzene | $o$-xylene |
|-------|-----------|----------|---------|---------|--------------|------------|
| 328.15 | 0.983     | 1.14     | 0.0698  | 0.182   | 0.382        | 0.266      |
| 338.15 | 0.987     | 1.14     | 0.0826  | 0.201   | 0.396        | 0.283      |
| 348.15 | 0.990     | 1.14     | 0.0957  | 0.218   | 0.409        | 0.302      |
| 358.15 | 0.991     | 1.14     | 0.105   | 0.233   | 0.421        | 0.318      |
| 368.15 | 0.992     | 1.14     | 0.114   | 0.247   | 0.429        | 0.330      |

| $T/K$ | methyl $m$-xylene | $p$-xylene | methanol | ethanol | 1-propanol | 1-butanol |
|-------|--------------------|------------|----------|---------|------------|-----------|
| 328.15 | 0.361              | 0.343      | 0.997    | 0.835   | 0.682      | 0.635     |
| 338.15 | 0.381              | 0.366      | 0.929    | 0.759   | 0.613      | 0.565     |
| 348.15 | 0.402              | 0.386      | 0.870    | 0.693   | 0.555      | 0.507     |
| 358.15 | 0.416              | 0.401      | 0.803    | 0.625   | 0.497      | 0.452     |
| 368.15 | 0.437              | 0.422      | 0.752    | 0.566   | 0.441      | 0.392     |

| $T/K$ | water | acetic acid | butyric acid | thiophene | tetrahydrofuran | methyl tert-butyl ether |
|-------|-------|-------------|--------------|-----------|-----------------|-------------------------|
| 328.15 | 2.78  | −0.332      | 0.118        | 0.0626    | −0.338          | 0.547                   |
| 338.15 | 2.68  | −0.284      | 0.116        | 0.0761    | −0.307          | 0.565                   |
| 348.15 | 2.57  | −0.238      | 0.114        | 0.0845    | −0.279          | 0.585                   |
| 358.15 | 2.49  | −0.198      | 0.111        | 0.0968    | −0.255          | 0.605                   |
| 368.15 | 2.42  | −0.164      | 0.109        | 0.107     | −0.230          | 0.619                   |

| $T/K$ | methyl tert-pentyl ether | diethyl ether | di- $n$-propyl ether | di-$n$-butyl ether | acetone | 2-pentanone |
|-------|--------------------------|---------------|----------------------|---------------------|---------|-------------|
| 328.15 | 0.711                    | 0.626         | 1.15                 | 1.49                | −0.450  | −0.462      |
| 338.15 | 0.728                    | 0.635         | 1.14                 | 1.48                | −0.428  | −0.431      |
| 348.15 | 0.746                    | 0.641         | 1.13                 | 1.47                | −0.409  | −0.404      |
| 358.15 | 0.760                    | 0.646         | 1.13                 | 1.46                | −0.394  | −0.380      |
| 368.15 | 0.772                    | 0.649         | 1.12                 | 1.45                | −0.378  | −0.353      |

| 3-pentanone |
|-------------|
| 328.15      | −0.497       |
| 338.15      | −0.460       |
| 348.15      | −0.426       |
| 358.15      | −0.395       |
| 368.15      | −0.364       |

| $T/K$ | $n$-hexane | $n$-heptane | $n$-octane | $n$-nonane | $n$-decane | cyclopentane |
|-------|------------|-------------|------------|------------|------------|--------------|
| 318.15 | 4.90       | 5.19        | 5.49       | 5.82       | 6.19       | 3.55         |
| 328.15 | 4.73       | 5.00        | 5.36       | 5.69       | 6.07       | 3.42         |
| 338.15 | 4.57       | 4.89        | 5.24       | 5.60       | 5.97       | 3.32         |
| 348.15 | 4.44       | 4.75        | 5.11       | 5.46       | 5.84       | 3.21         |
| 358.15 | 4.30       | 4.67        | 5.03       | 5.37       | 5.74       | 3.15         |
### Table S1. Cont.

| T/K  | cyclohexane | cycloheptane | cyclooctane | 1-hexene | 1-heptene | 1-octene |
|------|-------------|--------------|-------------|----------|-----------|----------|
| 318.15 | 3.85        | 3.91         | 4.17        | 3.82     | 4.16      | 4.54     |
| 328.15 | 3.74        | 3.84         | 4.07        | 3.71     | 4.08      | 4.46     |
| 338.15 | 3.64        | 3.74         | 3.97        | 3.64     | 4.00      | 4.38     |
| 348.15 | 3.54        | 3.65         | 3.88        | 3.56     | 3.92      | 4.30     |
| 358.15 | 3.46        | 3.60         | 3.81        | 3.49     | 3.87      | 4.24     |

| T/K  | 1-hexyne | 1-heptyne | 1-octyne | benzene | toluene | ethylbenzene |
|------|----------|-----------|----------|---------|---------|--------------|
| 318.15 | 1.94     | 2.30      | 2.66     | 0.907   | 1.32    | 1.76         |
| 328.15 | 1.94     | 2.30      | 2.66     | 0.916   | 1.33    | 1.76         |
| 338.15 | 1.95     | 2.30      | 2.66     | 0.924   | 1.33    | 1.75         |
| 348.15 | 1.95     | 2.30      | 2.66     | 0.930   | 1.33    | 1.75         |
| 358.15 | 1.95     | 2.30      | 2.66     | 0.938   | 1.34    | 1.74         |

| T/K  | o-xylene | m-xylene | p-xylene | methanol | ethanol | water |
|------|----------|----------|----------|----------|---------|-------|
| 318.15 | 1.54     | 1.77     | 1.72     | -0.187   | 0.103   | 0.413 |
| 328.15 | 1.55     | 1.77     | 1.73     | -0.190   | 0.0822  | 0.429 |
| 338.15 | 1.55     | 1.77     | 1.73     | -0.191   | 0.0600  | 0.445 |
| 348.15 | 1.56     | 1.77     | 1.73     | -0.196   | 0.0405  | 0.460 |
| 358.15 | 1.56     | 1.77     | 1.74     | -0.198   | 0.0241  | 0.476 |

| T/K  | thiophene | tetrahydrofuran | methyl tert-butyl ether | diethyl ether | di-n-propyl ether | di-n-butyl ether |
|------|-----------|-----------------|-------------------------|--------------|------------------|-----------------|
| 318.15 | 0.434     | 1.14            | 2.70                     | 2.67         | 3.63             | 4.39            |
| 328.15 | 0.459     | 1.15            | 2.66                     | 2.62         | 3.56             | 4.31            |
| 338.15 | 0.486     | 1.16            | 2.63                     | 2.57         | 3.50             | 4.24            |
| 348.15 | 0.504     | 1.16            | 2.59                     | 2.54         | 3.44             | 4.17            |
| 358.15 | 0.525     | 1.17            | 2.57                     | 2.50         | 3.39             | 4.12            |

| T/K  | acetone | 2-pentanone | 3-pentanone |
|------|---------|-------------|-------------|
| 318.15 | 0.795   | 1.29        | 1.30        |
| 328.15 | 0.794   | 1.29        | 1.30        |
| 338.15 | 0.792   | 1.29        | 1.30        |
| 348.15 | 0.790   | 1.29        | 1.30        |
| 358.15 | 0.789   | 1.29        | 1.30        |

| T/K  | n-pentane | n-hexane | n-heptane | n-octane | n-nonane | n-decane |
|------|-----------|----------|-----------|----------|----------|----------|
| 308.15 | 3.31      | 3.40     | 3.58      | 3.81     | 4.08     | 4.38     |
| 318.15 | 3.02      | 3.21     | 3.44      | 3.70     | 3.98     | 4.30     |
| 328.15 | 2.98      | 3.14     | 3.35      | 3.60     | 3.88     | 4.18     |
| 338.15 | 2.85      | 3.06     | 3.29      | 3.53     | 3.80     | 4.09     |
| 348.15 | 2.75      | 2.95     | 3.19      | 3.43     | 3.70     | 3.99     |
| 358.15 | 2.72      | 2.93     | 3.14      | 3.37     | 3.63     | 3.91     |

| T/K  | cyclopentane | cyclohexane | cycloheptane | cyclooctane | 1-pentene | 1-hexene |
|------|--------------|-------------|--------------|-------------|-----------|----------|
| 308.15 | 2.72        | 2.93        | 3.05         | 3.23        | 2.48      | 2.64     |
| 318.15 | 2.52        | 2.77        | 2.94         | 3.15        | 2.30      | 2.52     |
| 328.15 | 2.47        | 2.71        | 2.86         | 3.04        | 2.27      | 2.48     |
| 338.15 | 2.38        | 2.62        | 2.78         | 2.98        | 2.32      | 2.41     |
| 348.15 | 2.29        | 2.51        | 2.70         | 2.89        | 2.13      | 2.34     |
| 358.15 | 2.26        | 2.48        | 2.64         | 2.82        | 2.13      | 2.31     |
Table S1. Cont.

| T/K   | 1-heptene | 1-octene | 1-hexyne | 1-heptyne | 1-octyne | benzene | toluene | ethylbenzene | o-xylene | m-xylene | p-xylene | methanol | ethanol | 1-propanol | 1-butanol | water | thiophene | tetrahydrofuran |
|-------|-----------|----------|----------|-----------|----------|---------|---------|-------------|----------|----------|----------|----------|---------|-----------|-----------|-------|-----------|-----------------|
| 308.15| 2.84      | 3.11     | 1.47     | 1.71      | 1.98     | 0.418   | 0.615   | 0.913       | 0.752    | 0.822    | 0.812    | 1.62     | 1.54    | 0.377      | 0.363     | 0.370 | 0.386     | 0.384           |
| 318.15| 2.76      | 3.04     | 1.46     | 1.70      | 1.98     | 0.427   | 0.619   | 0.915       | 0.772    | 0.851    | 0.845    | 1.54     | 1.44    | 0.392      | 0.392     | 0.389 | 0.401     | 0.385           |
| 328.15| 2.71      | 2.96     | 1.45     | 1.68      | 1.95     | 0.433   | 0.635   | 0.932       | 0.775    | 0.849    | 0.849    | 1.44     | 1.36    | 0.395      | 0.395     | 0.390 | 0.401     | 0.384           |
| 338.15| 2.65      | 2.92     | 1.46     | 1.69      | 1.94     | 0.436   | 0.642   | 0.930       | 0.787    | 0.865    | 0.864    | 1.36     | 1.28    | 0.404      | 0.404     | 0.398 | 0.416     | 0.398           |
| 348.15| 2.59      | 2.85     | 1.44     | 1.67      | 1.95     | 0.444   | 0.655   | 0.936       | 0.795    | 0.875    | 0.876    | 1.28     | 1.20    | 0.416      | 0.416     | 0.404 | 0.425     | 0.404           |
| 358.15| 2.55      | 2.81     | 1.44     | 1.67      | 1.91     | 0.456   | 0.668   | 0.942       | 0.811    | 0.892    | 0.894    | 1.20     |         |           |           |       |           |                 |
| T/K   | methyl tert-butyl ether | diethyl ether | di-n-propyl ether | di-n-butyl ether | acetone | 2-pentanone |
|-------|--------------------------|--------------|-------------------|--------------|---------|-------------|
| 308.15| 1.38                     | 1.47          | 2.16              | 2.78         | −0.0329 | 0.181       |
| 318.15| 1.37                     | 1.41          | 2.12              | 2.72         | −0.0217 | 0.200       |
| 328.15| 1.36                     | 1.41          | 2.10              | 2.68         | −0.0151 | 0.209       |
| 338.15| 1.35                     | 1.39          | 2.07              | 2.63         | 0.0007  | 0.225       |
| 348.15| 1.34                     | 1.36          | 2.02              | 2.57         | −0.0029 | 0.229       |
| 358.15| 1.33                     | 1.36          | 2.01              | 2.53         | 0.0071  | 0.244       |
| T/K   | 3-pentanone |
|-------|-------------|
| 308.15| 0.161       |
| 318.15| 0.178       |
| 328.15| 0.208       |
| 338.15| 0.225       |
| 348.15| 0.235       |
| 358.15| 0.256       |

[bmPIP][NTf₂]
Table S1. Cont.

| $T/K$ | 2,2,4-trimethylpentane | $n$-nonane | $n$-decane | cyclopentane | cyclohexane | methylcyclohexane |
|-------|-------------------------|------------|------------|--------------|-------------|------------------|
| 308.15 | 3.03                    | 3.71       | 4.01       | 2.22         | 2.48        | 2.67             |
| 318.15 | 2.92                    | 3.55       | 3.84       | 2.11         | 2.36        | 2.54             |
| 328.15 | 2.81                    | 3.42       | 3.71       | 2.02         | 2.26        | 2.44             |
| 338.15 | 2.74                    | 3.35       | 3.63       | 1.96         | 2.20        | 2.38             |
| 348.15 | 2.69                    | 3.28       | 3.54       | 1.90         | 2.12        | 2.31             |
| 358.15 | 2.63                    | 3.20       | 3.47       | 1.87         | 2.09        | 2.27             |
|       | cycloheptane            | cyclooctane| 1-pentene  | 1-hexene     | cyclohexene | 1-heptene        |
| 308.15 | 2.70                    | 2.91       | 2.00       | 2.26         | 1.95        | 2.51             |
| 318.15 | 2.57                    | 2.78       | 1.91       | 2.16         | 1.87        | 2.41             |
| 328.15 | 2.47                    | 2.67       | 1.83       | 2.08         | 1.79        | 2.33             |
| 338.15 | 2.40                    | 2.60       | 1.81       | 2.03         | 1.75        | 2.29             |
| 348.15 | 2.32                    | 2.51       | 1.76       | 1.97         | 1.70        | 2.23             |
| 358.15 | 2.28                    | 2.47       | 1.73       | 1.94         | 1.64        | 2.21             |
|       | 1-octene                | 1-hexyne   | 1-heptyne  | 1-octyne     | benzene     | toluene          |
| 308.15 | 2.80                    | 1.28       | 1.52       | 1.79         | 0.30        | 0.486            |
| 318.15 | 2.70                    | 1.24       | 1.47       | 1.72         | 0.31        | 0.498            |
| 328.15 | 2.60                    | 1.20       | 1.43       | 1.67         | 0.31        | 0.508            |
| 338.15 | 2.55                    | 1.20       | 1.42       | 1.66         | 0.32        | 0.518            |
| 348.15 | 2.49                    | 1.18       | 1.40       | 1.65         | 0.33        | 0.534            |
| 358.15 | 2.46                    | 1.20       | 1.40       | 1.63         | 0.35        | 0.550            |
|       | ethylbenzene            | o-xylene   | m-xylene   | p-xylene     | methanol    | ethanol          |
| 308.15 | 0.793                   | 0.632      | 0.702      | 0.698        | 1.60        | 1.49             |
| 318.15 | 0.800                   | 0.646      | 0.723      | 0.716        | 1.52        | 1.40             |
| 328.15 | 0.795                   | 0.644      | 0.718      | 0.719        | 1.42        | 1.31             |
| 338.15 | 0.797                   | 0.650      | 0.729      | 0.733        | 1.34        | 1.21             |
| 348.15 | 0.807                   | 0.667      | 0.748      | 0.747        | 1.25        | 1.12             |
| 358.15 | 0.816                   | 0.671      | 0.759      | 0.758        | 1.16        | 1.04             |
|       | 1-propanol              | 1-butanol  | water      | thiophene    | tetrahydrofuran | methyl tert-butyl ether |
| 308.15 | 1.47                    | 1.54       | 3.49       | 0.299        | 0.206       | 1.06             |
| 318.15 | 1.38                    | 1.42       | 3.34       | 0.302        | 0.215       | 1.06             |
| 328.15 | 1.28                    | 1.33       | 3.21       | 0.301        | 0.205       | 1.05             |
| 338.15 | 1.18                    | 1.22       | 3.07       | 0.306        | 0.207       | 1.04             |
| 348.15 | 1.09                    | 1.12       | 2.94       | 0.308        | 0.207       | 1.04             |
| 358.15 | 1.01                    | 1.04       | 2.81       | 0.323        | 0.219       | 1.04             |
|       | diethyl ether           | di-$n$-propyl ether | di-$n$-butyl ether | acetone | 2-pentanone | 3-pentanone |
| 308.15 | 1.19                    | 1.86       | 2.46       | $-0.0841$    | 0.0558      | 0.0284           |
| 318.15 | 1.18                    | 1.85       | 2.43       | $-0.0782$    | 0.0667      | 0.0492           |
| 328.15 | 1.11                    | 1.75       | 2.33       | $-0.0764$    | 0.0885      | 0.0770           |
| 338.15 | 1.12                    | 1.75       | 2.29       | $-0.0739$    | 0.0943      | 0.0842           |
| 348.15 | 1.11                    | 1.73       | 2.25       | $-0.0732$    | 0.106       | 0.114            |
| 358.15 | 1.10                    | 1.70       | 2.21       | $-0.0706$    | 0.115       | 0.124            |
Table S1. Cont.

| $T/K$ | $n$-pentane | $n$-hexane | $n$-heptane | $n$-octane | $n$-nonane | $n$-decane |
|-------|-------------|------------|-------------|------------|------------|------------|
| 328.15 | 1.90 | 2.00 | 2.17 | 2.30 | 2.46 | 2.65 |
| 338.15 | 1.86 | 1.97 | 2.12 | 2.26 | 2.42 | 2.60 |
| 348.15 | 1.82 | 1.93 | 2.07 | 2.21 | 2.37 | 2.54 |
| 358.15 | 1.79 | 1.90 | 2.03 | 2.18 | 2.33 | 2.50 |
| 368.15 | 1.75 | 1.87 | 1.99 | 2.14 | 2.29 | 2.45 |

| $T/K$ | cyclopentane | cyclohexane | cycloheptane | cyclooctane | 1-pentene | 1-hexene |
|-------|-------------|------------|-------------|------------|----------|----------|
| 328.15 | 1.57 | 1.70 | 1.76 | 1.85 | 1.50 | 1.60 |
| 338.15 | 1.54 | 1.66 | 1.72 | 1.81 | 1.48 | 1.58 |
| 348.15 | 1.50 | 1.61 | 1.68 | 1.76 | 1.46 | 1.55 |
| 358.15 | 1.47 | 1.58 | 1.64 | 1.72 | 1.43 | 1.53 |
| 368.15 | 1.43 | 1.54 | 1.61 | 1.68 | 1.41 | 1.51 |

| $T/K$ | 1-heptene | 1-octene | 1-hexyne | 1-heptyne | 1-octyne | benzene |
|-------|----------|---------|--------|---------|---------|--------|
| 328.15 | 1.74 | 1.89 | 0.977 | 1.09 | 1.22 | 0.188 |
| 338.15 | 1.72 | 1.87 | 0.982 | 1.09 | 1.22 | 0.194 |
| 348.15 | 1.70 | 1.84 | 0.981 | 1.09 | 1.21 | 0.206 |
| 358.15 | 1.68 | 1.82 | 0.983 | 1.09 | 1.22 | 0.216 |
| 368.15 | 1.66 | 1.80 | 0.987 | 1.08 | 1.22 | 0.224 |

| $T/K$ | toluene | ethylbenzene | $o$-xylene | $m$-xylene | $p$-xylene | methanol |
|-------|--------|-------------|----------|----------|----------|---------|
| 328.15 | 0.247 | 0.471 | 0.255 | 0.386 | 0.399 | 1.62 |
| 338.15 | 0.267 | 0.485 | 0.282 | 0.402 | 0.416 | 1.54 |
| 348.15 | 0.285 | 0.495 | 0.303 | 0.419 | 0.424 | 1.43 |
| 358.15 | 0.302 | 0.505 | 0.322 | 0.430 | 0.437 | 1.35 |
| 368.15 | 0.320 | 0.517 | 0.340 | 0.445 | 0.447 | 1.27 |

| $T/K$ | ethanol | 1-propanol | 1-butanol | 1-pentanol | water | thiophene |
|-------|--------|-----------|---------|-----------|-------|---------|
| 328.15 | 1.43 | 1.29 | 1.24 | 1.15 | 3.53 | 0.215 |
| 338.15 | 1.32 | 1.20 | 1.14 | 1.07 | 3.40 | 0.223 |
| 348.15 | 1.22 | 1.10 | 1.02 | 0.979 | 3.24 | 0.227 |
| 358.15 | 1.14 | 1.02 | 0.943 | 0.896 | 3.12 | 0.231 |
| 368.15 | 1.06 | 0.942 | 0.865 | 0.827 | 2.98 | 0.236 |

| $T/K$ | tetrahydrofuran | methyl tert-butyl ether | diethyl ether | di-$n$-propyl ether | di-$n$-butyl ether | acetone |
|-------|-----------------|------------------------|---------------|---------------------|-------------------|--------|
| 328.15 | 0.0326 | 0.778 | 0.879 | 1.33 | 1.65 | −0.0485 |
| 338.15 | 0.0506 | 0.787 | 0.880 | 1.31 | 1.63 | −0.0465 |
| 348.15 | 0.0653 | 0.793 | 0.881 | 1.30 | 1.60 | −0.0456 |
| 358.15 | 0.0742 | 0.796 | 0.879 | 1.28 | 1.57 | −0.0458 |
| 368.15 | 0.0853 | 0.803 | 0.877 | 1.26 | 1.54 | −0.0465 |

| $T/K$ | 2-pentanone | 3-pentanone |
|-------|-------------|-------------|
| 328.15 | −0.0778 | −0.0596 |
| 338.15 | −0.0694 | −0.0483 |
| 348.15 | −0.0621 | −0.0372 |
| 358.15 | −0.0521 | −0.0285 |
| 368.15 | −0.0461 | −0.0216 |
Example of Calculation of the Solubility Parameter

Experimental data for n-octane + [emim][TCB] system at $T = 298.15$ K:

$T = 298.15$ K
$p_i = 137423$ Pa
$p_o = 97423$ Pa
$T_f = 297.15$ K
$U = 41.2$ mL·min$^{-1}$
$t_R - t_0 = 270.66$ s
$m_2 = 2.1053$ g

$P_w$ (at $T_f$) = 2986.2 Pa (from [30])
$U_o = 6.679 \cdot 10^{-7}$ m$^3$·s$^{-1}$ (from Equation 6)
$J_2^3 = 1.217$ (from Equation 5)
$V_N = 1.485 \cdot 10^{-4}$ m$^3$ (from Equation 4)
$V_g = 6.464 \cdot 10^{-5}$ m$^3$·g$^{-1}$ (from Equation 3)
$P_1^* = 1871.0$ Pa (from [30])
$M_1 = 114.2285$ g·mol$^{-1}$ (from [30])
$B_{11} = -4.496 \cdot 10^{-3}$ m$^3$·mol$^{-1}$ (from [30])
$V_1^* = 1.6256 \cdot 10^{-4}$ m$^3$·mol$^{-1}$ (from [30])
$V_2^* = 2.1818 \cdot 10^{-4}$ m$^3$·mol$^{-1}$ (calculated from density from [19])
$\rho_1 = 0.70268$ g·cm$^{-3}$ (from [30])
$\rho_2 = 1.03627$ g·cm$^{-3}$ (from [19])

$\chi_{12} = 4.463$ (from Equation 2)
$\delta_1 = 15486$ (J·m$^3$)$^{0.5}$ (from [30])

Analogous calculations were made for the rest of solutes. The results are presented in the Table 1S. Based on these values the Equation 7 can be plotted (see Figure S1).
**Figure S1.** An example of the determination of solubility parameter $\delta_2$. Plot of $\frac{\delta_1^2}{RT} - \frac{X_{12}^\infty}{V_1^*}$ versus $\delta_1$ according to the Equation 7 for ionic liquid [emim][TCB] at $T = 298.15$ K. (●) $n$-octane, (●) rest of solutes.

From the slope $(2\delta_2/RT)$ the value of 20.874 is obtained. From this value the $\delta_2$ is calculated giving value 25.9 MPa$^{0.5}$ (see Table 2).

**Calculation of the $K_v$ Constant from Equation 2**

Using data presented in the Table S2 and the $K_v$ value of 7.8 the solubility parameters were determined using Equation 2. Then the $K_v$ value was optimized using the objective function $OF = \sum_{i=1}^{n} \left( \delta_{\text{experimental}}^i - \delta_{\text{calculated}}^i \right)^2$ using MS Excel Solver. Densities and viscosities were taken from the ILThermo database available at http://ilthermo.boulder.nist.gov/ILThermo/. Solubility parameters were calculated from enthalpies of vaporization [25–29].
Table S2. Data used in calculation of $K_v$ constant.

| Ionic Liquid  | $\rho$/g·cm$^{-3}$ | $M$/g·mol$^{-1}$ | $\mu$/mPa·s | $\nu$/cm$^3$·mol$^{-1}$ | $\delta}$/MPa$^{0.5}$ |
|---------------|-------------------|----------------|-------------|----------------|------------------|
| [emim][NTf$_2$] | 1.5192            | 391.32         | 34.29       | 257.6          | 21.3             |
|               | 1.5192            | 391.32         | 34.29       | 257.6          | 22.6             |
|               | 1.5192            | 391.32         | 34.29       | 257.6          | 22.7             |
| [bmim][NTf$_2$] | 1.4366            | 419.37         | 50.70       | 291.9          | 21.2             |
|               | 1.4366            | 419.37         | 50.70       | 291.9          | 19.8             |
|               | 1.4366            | 419.37         | 50.70       | 291.9          | 22.9             |
| [hmim][NTf$_2$] | 1.3706            | 447.42         | 70.96       | 326.5          | 20.5             |
|               | 1.3706            | 447.42         | 70.96       | 326.5          | 19.0             |
|               | 1.3706            | 447.42         | 70.96       | 326.5          | 22.9             |
| [omim][NTf$_2$] | 1.3206            | 475.48         | 92.51       | 360.1          | 20.2             |
|               | 1.3206            | 475.48         | 92.51       | 360.1          | 20.2             |
|               | 1.3206            | 475.48         | 92.51       | 360.1          | 23.0             |
| [dmim][NTf$_2$] | 1.2780            | 499.50         | 108.20      | 390.8          | 17.8             |
| [bmPYR][NTf$_2$] | 1.3940            | 422.41         | 76.92       | 303.0          | 22.2             |

Table S3. Densities and viscosities for [N-C$_3$OHPY][NTf$_2$], [pmPIP][NTf$_2$] and [bmPIP][NTf$_2$] ionic liquids.

| Ionic Liquid    | $T$/K  | $\rho$/g·cm$^{-3}$  | $\mu$/m Pas  |
|-----------------|--------|----------------------|--------------|
| [N-C$_3$OHPY][NTf$_2$] | 308.15 | 1.5451               | 67.03        |
|                  | 318.15 | 1.5357               | 43.85        |
|                  | 328.15 | 1.5266               | 30.56        |
|                  | 338.15 | 1.5175               | 22.21        |
|                  | 348.15 | 1.5085               | 16.90        |
| [pmPIP][NTf$_2$]  | 308.15 | 1.4010               | 86.70        |
|                  | 318.15 | 1.3923               | 55.24        |
|                  | 328.15 | 1.3837               | 37.75        |
|                  | 338.15 | 1.3751               | 27.17        |
|                  | 348.15 | 1.3666               | 20.32        |
| [bmPIP][NTf$_2$]  | 308.15 | 1.3706               | 97.76        |
|                  | 318.15 | 1.3621               | 61.05        |
|                  | 328.15 | 1.3536               | 40.92        |
|                  | 338.15 | 1.3452               | 29.01        |
|                  | 348.15 | 1.3369               | 21.28        |

$^a$ determined using Anton Paar DMA 4500 densitometer; $^b$ determined using Anton Paar AMVn viscometer.

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