

DOI: 10.1002/cphc.201402345

Determination of Solubility Parameters of Ionic Liquids and Ionic Liquid/Solvent Mixtures from Intrinsic Viscosity

Piyarat Weerachanchai,^[a] Yewen Wong,^[a] Kok Hwa Lim,^[a, b] Timothy Thatt Yang Tan,^[a] and Jong-Min Lee^{*[a]}

The total and partial solubility parameters (dispersion, polar and hydrogen-bonding solubility parameters) of ten ionic liquids were determined. Intrinsic viscosity approaches were used that encompassed a one-dimensional method (1D-Method), and two different three-dimensional methods (3D-Method1 and 3D-Method2). The effect of solvent type, the dimethylacetamide (DMA) fraction in the ionic liquid, and dissolution temperature on solubility parameters were also investigated. For all types of effect, both the 1D-Method and 3D-Method2 pres-

ent the same trend in the total solubility parameter. The partial solubility parameters are influenced by the cation and anion of the ionic liquid. Considering the effect on partial solubility parameters of the solvent type in the ionic liquid, it was observed that in both 3D methods, the dispersion and polar parameters of a 1-ethyl-3-methylimidazolium acetate/solvent (60:40 vol%) mixture tend to increase as the total solubility parameter of the solvent increases.

1. Introduction

In recent years, there has been intense interest in ionic liquids and their wide range of applications. Ionic liquids are a new class of molten salts, having numerous unique properties such as negligible vapor pressures, low melting points, good thermal stabilities, and tunability.^[1,2] In view of these outstanding properties, they can be used in applications such as electrochemical sensors, analytical chemistry, plasticizers and catalysis.^[3–6] Ionic liquids have been increasingly considered as alternative, environmentally friendly solvents that can be used to improve existing processes such as biomass pretreatment, food analysis, gas absorption, and drug delivery.^[7–10] Thus, it is important to understand solvation properties of ionic liquids for designing or selecting an appropriate solvent for a particular application. Several approaches including Abraham solvation model, Kamlet–Taft parameters, and Hildebrand and Hansen solubility parameters have been used to describe the solvation power of solvents.^[11] In particular, solubility parameters have been widely used in many practical applications as a basis for the choice of solvent or solvent blends for a solute, in which a solute is soluble in solvents that have close solubility parameters.^[12,13] Namely, solubility parameters can be applied to the coatings/paint processing industries, pharmaceuti-

cal industries, and cleaning operations in the electronics industries.^[12,14,15]

The solubility parameter concept was first put forward by Hildebrand. The total or Hildebrand solubility parameter (δ_T) is defined as the square root of cohesive energy density (CED), the energy required to break the interactions between molecules [Eq. (1)]:^[11,16,17]

$$\delta_T = CED^{1/2} = \left(\frac{\Delta U}{V}\right)^{1/2} = \left[\frac{\Delta H^{vap} - RT}{V}\right]^{1/2} \quad (1)$$

where V is the molar volume, ΔU is the molar internal energy, which is equal to the difference of ΔH^{vap} , the enthalpy of vaporization, R is the ideal gas constant and T is temperature. The Hildebrand solubility parameter is one of the oldest measures of solvent polarity. Generally, a higher value of solubility parameter indicates greater solvent polarity.^[18] The Hildebrand solubility parameter was extended to a three-dimensional solubility parameter system by Hansen, who proposed that the cohesive energy density arises from atomic dispersive interactions, molecular permanent dipole–permanent dipole interactions, and molecular hydrogen-bonding interactions. Overall, the Hildebrand solubility parameter can be expressed in terms of partial or Hansen solubility parameters by Equation (2):^[11,17,19]

$$\delta_T = (\delta_D^2 + \delta_P^2 + \delta_H^2)^{1/2} \quad (2)$$

where δ_D , δ_P and δ_H are the partial solubility parameters of Hansen representing contributions from dispersion, polar and hydrogen-bonding interactions, respectively. These partial solubility parameters can be visualized as coordinates in a three-di-

[a] Dr. P. Weerachanchai, Y. Wong, Prof. K. H. Lim, Prof. T. T. Y. Tan, Prof. J.-M. Lee
School of Chemical and Biomedical Engineering
Nanyang Technological University
62 Nanyang Drive
Singapore 637459 (Singapore)
Tel.: (+65) 6513-8129
E-mail: jmlee@ntu.edu.sg

[b] Prof. K. H. Lim
Singapore Institute of Technology
10 Dover Drive
Singapore 138683 (Singapore)

mensional diagram, which allows an excellent illustration of the miscibility of different materials. In this three-dimensional space, two substances with a shorter distance between their coordinates have greater affinity for each other.^[20]

Solubility parameters can be evaluated by a diverse range of methods, including heat vaporization (ΔH^{vap})–temperature data, group contribution, intrinsic viscosity, swelling, solubility measurements, turbidimetric titration, and inverse gas chromatography.^[13,16,21] The solubility parameters of a wide range of materials have been determined by various methods. In the determination of partial solubility parameters of biodegradable polymers such as poly(ϵ -caprolactone) and poly(D,L-lactide-co-glycolide), the group contribution, turbidimetric titration and swelling methods have been employed.^[21,22] The inverse gas chromatography method has been used to examine the solubility parameters of assorted substances such as soybean oil, polyethylene glycol surfactant, and pharmaceutical excipients (Cetiol B (di-*n*-butyladipat), Labrasol, and Tween 80).^[23–25] The solubility measurement method has been used to obtain the partial solubility parameters of nonpolymeric excipients such as lactose, mannitol, and saccharose as well as drugs such as aceclofenac.^[26,27] For compounds with either low or no volatility, the determination of solubility parameters from ΔH^{vap} is not possible. A widespread approach towards measuring the extremely low vapor pressure of such compounds is intrinsic viscosity.^[16,28]

The Hildebrand solubility parameter obtained from the intrinsic viscosity method (1D Method) involves the measurement of intrinsic viscosity of solute in a series of solvents. The Hildebrand solubility parameter of the solute is equivalent to the Hildebrand solubility parameter of the solvent, which gives the highest value of the intrinsic viscosity of the solute.^[16,29,30] Hence, maximum intrinsic viscosity indicates maximum mutual compatibility between solute and solvent. This 1D Method has been used to derive the Hildebrand solubility parameters of various materials such as ionic liquids and (bio)polymers.^[16,30,31] This method is superior because it is straightforward and because accurate values can be obtained from intrinsic viscosity measurements in a short period of time.^[29]

With the introduction of Hansen's concept, the measurements of intrinsic viscosity have also been applied to determine the partial solubility parameters of Hansen. The determination of Hansen solubility parameters using the intrinsic viscosity method has been associated with two main methodologies. The first three-dimensional (3D) method has been proposed to calculate the different contributions of the solubility parameter of a solute from intrinsic viscosity values. The partial solubility parameters are defined as the summation of the series of partial solubility parameters of solvent multiplying with normalized intrinsic viscosity of solute in solvent per summation of the normalized intrinsic viscosities of solute derived from different solvents. This is represented in Equations (6)–(8) of the Experimental Section. This method was initially used to obtain the Hansen solubility parameters of the polyesteramide polymer.^[32] In addition, it has been applied to obtain the solubility parameters of various materials, for instance, aliphatic polyesters such as poly(lactic acid) and poly(glycolic acid) and

rubbers such as styrene-butadiene-styrene triblock copolymer.^[33,34] The second 3D method is an extended regression model involving Hansen solubility parameters.^[20] This model is based upon a regression between the natural logarithm of intrinsic viscosity measurements and the partial solubility parameters of a series of solvents, as represented in Equation (9) in the Experimental Section. This model has been applied to evaluate the partial solubility parameters of several polymers such as hydroxypropyl methylcellulose, epoxy resin and alkyd resin.^[35,36] It was adapted from the model used to obtain the solubility parameters of drugs, where the natural logarithm of solubility mole fraction of solute is regressed against the partial solubility parameters of solvent.^[35] To test the reliability and validity of the latter model, determination of partial solubility parameters have been performed across different types of drugs such as sodium salts of acidic drugs containing a single hydrogen-bonding group (ibuprofen, sodium ibuprofen, benzoic acid, and sodium benzoate) and nonsteroidal anti-inflammatory drugs, Lewis base (piroxicam) and Lewis acid (niflumic acid).^[37,38] This model has been noted as an approach to overcome the difficulty in the determination of ΔH^{vap} because most drug compounds are found to decompose before evaporation.^[38] Moreover, it has been tested to obtain the partial solubility parameters of nonpolymeric pharmaceutical excipients such as lactose, mannitol, and saccharose.^[26]

The solvation properties of ionic liquids have been investigated by using approaches such as Kamlet–Taft parameters and Hildebrand solubility parameter.^[39] However, there are certain restrictions in the use of Kamlet–Taft parameters for some materials because it is strictly applied to pure components. For mixed components such as mixtures of ionic liquid and solvent, it is possible that there is the effect of preferential solvation due to the difference in the composition of molecule-ions surrounding the dye probe compared with that of pure solute.^[40] However, the Hildebrand solubility parameter is applicable for liquid mixing and for solutions where the Hildebrand value of a mixture can be determined by averaging the Hildebrand values of the individual components by volume.^[41] This could be used for the reliable characterization of solvation properties of mixtures of ionic liquid and solvent. The Hildebrand solubility parameter of ionic liquids can be determined from numerous methods such as solvent dependence on bimolecular rate constant of Diels–Alder reactions, computation-based techniques, intrinsic viscosity measurements, inverse gas chromatography, melting temperature, activation energy of viscosity, and surface tension.^[30,42,43] The total Hildebrand solubility parameter of ionic liquids obtained from intrinsic viscosity has been marked as an accurate method that showed good agreement with different methodologies such as the solvent-dependence on bimolecular rate constant of Diels–Alder reactions, computational-based techniques, and activation energy of viscosity.^[16,42] However, the single parameter of the Hildebrand solubility parameter only determines the dispersion forces between molecules and it is more applicable for nonpolar compounds.^[36] Splitting of the Hildebrand solubility parameter into the three Hansen solubility parameters, accounting for dispersion, polar, and hydrogen-bonding interactions, could

provide a more profound description of the molecular interactions of samples. Moreover, it is a more accurate approach towards the prediction of solubility properties.^[11] Nevertheless, the Hansen solubility parameters of ionic liquids have not been widely published. Thus, an investigation of Hansen solubility parameters of ionic liquids with the simple method of intrinsic viscosity was attempted to provide more information on the physicochemical properties of ionic liquids.

In this work, the intrinsic viscosity method, which is an easy, rapid, and reliable method, was used to determine the Hildebrand and Hansen solubility parameters of several types of ionic liquids. The Hildebrand solubility parameter determined from the 1D method was compared with the Hildebrand solubility parameter determined from Kay's mixing rule^[44] as well as with the Hildebrand solubility parameter derived from the other two mentioned 3D methods. The partial solubility parameters of Hansen were compared across the two 3D methods as well as with the partial solubility parameters determined from the mixing rule. In addition, the Hildebrand and Hansen solubility parameters of mixtures of ionic liquid and organic solvent (60:40 vol%), different DMA fractions in ionic liquid as well as different dissolution temperature of ionic liquid and mixtures of ionic liquid and DMA (60:40 vol%) were studied.

Experimental

Chemicals

Numerous ionic liquids including 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄, ≥ 98.0%), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆, ≥ 98.0%), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (MBPYRRO-Tf₂N, ≥ 98.0%), 1-butyl-1-methylpyrrolidinium dicyanamide (MBPYRR-O-N(CN)₂, ≥ 98.0%), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM-Tf₂N, ≥ 98.0%), and 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HOEMIM-Tf₂N, ≥ 98.0%) were purchased from Merck. 1,3-Dimethylimidazolium methylsulfate (MMIM-MeSO₄, ≥ 97.0%), 1-ethyl-3-methylimidazolium acetate (EMIM-AC, ≥ 96.5%), 1-butyl-3-methylimidazolium chloride (BMIM-Cl, ≥ 98.0%), and 1-ethyl-3-methylimidazolium diethyl phosphate (EMIM-DEPO₄, ≥ 98.0%) were purchased from Sigma-Aldrich. Analytical grade of solvents that were used possessed different Hildebrand solubility parameters including 2-butanol (22.2 MPa^{1/2}), 1-butanol (23.1 MPa^{1/2}), 2-propanol (23.5 MPa^{1/2}), 1-propanol (24.5 MPa^{1/2}), *N,N*-dimethylformamide (DMF; 24.8 MPa^{1/2}), nitromethane (25.1 MPa^{1/2}), allyl alcohol (25.7 MPa^{1/2}), ethanol (26.5 MPa^{1/2}), dimethyl sulfoxide (DMSO; 26.7 MPa^{1/2}), propylene carbonate (27.3 MPa^{1/2}), 2-pyrrolidone (28.4 MPa^{1/2}), methanol (29.6 MPa^{1/2}), diethylene glycol (29.9 MPa^{1/2}), ethanolamine (31.3 MPa^{1/2}), and water (47.9 MPa^{1/2}) were obtained from Sigma-Aldrich.

Determination of Intrinsic Viscosity

The intrinsic viscosities of ionic liquids and several mixtures of ionic liquid and organic solvent at different dissolution temperatures (25, 40, and 60 °C) were measured with an Ubbelohde viscometer. The solutions of solute (ionic liquid or the mixtures of ionic liquid and solvent) in different solvents were prepared for five concentrations (0.5–5 vol%). The viscosities of solutions were measured at controlled temperatures. The efflux times were mea-

sured at least five times (variation of efflux time being within 0.1 s). The intrinsic viscosity (η ; dLg⁻¹) was determined from the common intercept of Huggins and Kraemer relationships as shown in Equations (3) and (4), respectively, by fitting of specific viscosity

($\eta_{sp} = \frac{t_{\text{solution}} - t_{\text{solvent}}}{t_{\text{solvent}}}$) per concentration and natural logarithm of relative viscosity ($\ln \eta_r = \frac{t_{\text{solution}}}{t_{\text{solvent}}}$) per concentration as a function of concentration (C ; g/dL). t_{solution} and t_{solvent} are the efflux times of solution and solvent, respectively. k_H and k_K are Huggins, and Kraemer constants, respectively.

$$\frac{\eta_{sp}}{C} = \eta + k_H \eta^2 C \quad (3)$$

$$\frac{\ln \eta_r}{C} = \eta + k_K \eta^2 C \quad (4)$$

Determination of Solubility Parameters

Total or Hildebrand solubility Parameter: One-Dimensional Method (1D Method)

The intrinsic viscosities against the Hildebrand solubility parameters (δ_H) of different solvents were plotted and fitted by the Mangaraj equation [Eq. (5)] to determine the Hildebrand solubility parameters of ionic liquids and mixtures of ionic liquid and solvent at different dissolution temperatures:

$$\eta = \eta_{\text{max}} \exp[-A(\delta_{\text{solvent}} - \delta_{\text{sample}})^2] \quad (5)$$

where η_{max} is the maximum intrinsic viscosity, A is a constant, δ_{solvent} and δ_{sample} are the Hildebrand solubility parameters of the solvent and the ionic liquid or the mixture of ionic liquid and solvent, respectively. δ_{sample} , A , and η_{max} were obtained from curve fitting with OriginPro 8 program.

Partial or Hansen Solubility Parameters: Three-Dimensional Method1 (3D-Method1)

The 3D-Method1 using the values of intrinsic viscosity had first been proposed to predict the partial solubility parameters of polymers. This method is based on the principle that the use of different solvents to dissolve the sample results in the formation of a solubility range. The solubility region for a sample can be visualized as lying within a sphere, in a 3D coordinate system with the axes δ_D , δ_P and δ_H , the center coordinates of which corresponds to the partial solubility parameters of the sample. To determine the Hansen solubility parameters of a sample by this method, the intrinsic viscosities of sample in different solvents are measured. Intrinsic viscosity is being used as a factor, in conjunction with the partial solubility parameters of solvent, to account for solute-solvent interactions. High intrinsic viscosity values reflect better interactions between the sample and the solvent. Hence, solvents that demonstrate greater solubility of sample are closer to the center coordinates of the sphere, and vice versa.^[32]

For this work, the equations of the center coordinates of the sphere were adapted to the determination of partial solubility parameters of ionic liquids or mixtures of ionic liquid and solvent. The partial or Hansen solubility parameters of a sample are shown in accordance to Equations (6)–(8). The equations encompassed the combination of the Hansen solubility parameters of the solvents ($\delta_{D,D}$, $\delta_{P,D}$, $\delta_{H,D}$)^[45] and intrinsic viscosities of solute in different

solvents, normalized by the maximum value of intrinsic viscosity:^[32,34]

$$\delta_{D,\text{sample}} = \frac{\sum \delta_{D,i}[\eta]_i}{\sum [\eta]_i} \quad (6)$$

$$\delta_{P,\text{sample}} = \frac{\sum \delta_{P,i}[\eta]_i}{\sum [\eta]_i} \quad (7)$$

$$\delta_{H,\text{sample}} = \frac{\sum \delta_{H,i}[\eta]_i}{\sum [\eta]_i} \quad (8)$$

where the subscripts D, P, and H refers to dispersion, polar and hydrogen-bonding contributions, respectively. The subscript sample refers to ionic liquid or mixture of ionic liquid and solvent and $[\eta]_i$ is the normalized intrinsic viscosity of ionic liquid or the mixture in solvent *i*.

Three-Dimensional Method2 (3D-Method2)

An extended Hansen solubility approach was developed to calculate the partial solubility parameters of solid materials.^[46] In the determination of the partial solubility parameters of drugs, the extended regression model is based upon a regression between $\ln \alpha/U$ and the partial solubility parameters of solvent, where α is the activity coefficient of the drug and U is a function of the molar volume of the drug and the volume fraction of the solvent.^[37] This regression model has been simplified to directly relate the logarithm of the solubility mole fraction of the drug ($\ln X$) to the partial solubility parameters of the solvent.^[37,38] Furthermore, to determine the partial solubility parameters of the polymer, the term X was replaced by η , the intrinsic viscosity of polymer in a solvent, in the regression model.^[35] In this work, the simplified model using intrinsic viscosity was applied, as expressed in Equation (9). For the determination of the Hansen solubility parameters of a sample, the natural logarithm of the intrinsic viscosities of solute in different solvents were regressed against the Hansen solubility parameters of a series of solvents:

$$\ln[\eta] = C_0 + C_1\delta_{D,i} + C_2\delta_{D,i}^2 + C_3\delta_{P,i} + C_4\delta_{P,i}^2 + C_5\delta_{H,i} + C_6\delta_{H,i}^2 \quad (9)$$

where $\delta_{D,i}$, $\delta_{P,i}$ and $\delta_{H,i}$ are the partial solubility parameters of solvent representing contributions from the dispersion, polar and hydrogen-bonding interactions, respectively, and the terms C_0 – C_6 are constant coefficients. The coefficients were obtained from multiple regression analysis by using OriginPro 8 program. From the value of the regression coefficients of Equation (9), the partial solubility parameters of the ionic liquids or mixtures of ionic liquid and solvent were calculated according to Equations (10)–(12):

$$\delta_{D,\text{sample}} = -\left(\frac{C_1}{2C_2}\right) \quad (10)$$

$$\delta_{P,\text{sample}} = -\left(\frac{C_3}{2C_4}\right) \quad (11)$$

$$\delta_{H,\text{sample}} = -\left(\frac{C_5}{2C_6}\right) \quad (12)$$

Kay's Mixing Rule of Hildebrand and Hansen Solubility Parameters

The total and partial solubility parameters of the mixtures of ionic liquid and solvent were calculated from the solubility parameters

of the pure component and the volume fraction of the component in the mixture according to Equation (13):

$$\delta_m = \sum \phi_i \delta_i \quad (13)$$

where ϕ_i and δ_i refer to the volume fraction and solubility parameter of the mixture's component *i*, respectively, and δ_m is the solubility parameter of the mixture of interest.

Estimation of Solubility Parameters at Different Temperatures

The Hansen solubility parameters of solvents at different temperatures (40 and 60 °C) are estimated from their reported values at 25 °C by using the correlations available for their variation with temperature according to Equations (14)–(16):^[19]

$$\frac{d\delta_D}{dT} = -1.25 \alpha \delta_D \quad (14)$$

$$\frac{d\delta_P}{dT} = -0.5 \alpha \delta_P \quad (15)$$

$$\frac{d\delta_H}{dT} = -\delta_H(1.22 \times 10^{-3} + 0.5 \alpha) \quad (16)$$

where α is the coefficient of thermal expansion for the solvents estimated using Aspen HYSYS V7.2 program.

2. Results and Discussion

2.1. Solubility Parameters of Ionic Liquid Type

The total and partial solubility parameters of ten ionic liquids determined from 1D-Method, 3D-Method1, and 3D-Method2 are shown in Table 1. As reported in our previous work,^[30] in the 1D-Method, for ionic liquids containing BMIM cations, the highest total solubility parameter was given by BMIM-PF₆, whereas the lowest value was obtained from BMIM-Cl. The values of ionic liquids containing BMIM cations are in the following order: [PF₆] > [Tf₂N] > [Cl]. This trend is evident across both 3D-Method1 and 3D-Method2. For ionic liquids containing EMIM cations, the values according to 1D-Method are in the following order: [BF₄] > [DEPO₄] > [AC]. This sequence of values is noted to be the same in 3D-Method2 but different in 3D-Method1, in which it is of the following order: [BF₄] > [AC] > [DEPO₄]. In the case of ionic liquids containing [Tf₂N] anions, HOEMIM-Tf₂N presents the highest total solubility value, whereas BMIM-Tf₂N gives the lowest value in the 1D-Method. The values of ionic liquids containing [Tf₂N] anions are in the following order: HOEMIM > MBPYRRO > BMIM. This order is apparent in both 3D-Method1 and 3D-Method2.

It can be observed from Table 1 that the solubility parameter values obtained for the same ionic liquids differ across the different methods. Generally, the total solubility parameter of ionic liquids obtained from 3D-Method1 is greater than that of 1D-Method by the range of 0.02–0.59, except for the ionic liquids, BMIM-PF₆, HOEMIM-Tf₂N, and MMIM-MeSO₄. The values derived from 3D-Method2 are smaller than that of 1D-Method by a more pronounced range of 0.46–1.43. Comparing the total solubility parameter of ionic liquids calculated from 3D-

Table 1. Solubility parameters of ionic liquids.^[a]

No.	Chemical	Solubility parameters [MPa ^{1/2}]	1D ^[a]	3D-1	3D-2	Difference between methods		
						1D/3D-1	1D/3D-2	3D-1/3D-2
Ionic liquids containing BMIM cations								
1	BMIM-PF ₆	δ_D	–	17.13	16.32	–	–	0.81
		δ_P	–	13.38	12.48	–	–	0.90
		δ_H	–	15.49	17.45	–	–	–1.96
		δ_T	28.09	26.69	26.95	1.40	1.14	–0.26
2	BMIM-Tf ₂ N	δ_D	–	18.07	14.82	–	–	3.25
		δ_P	–	14.84	9.19	–	–	5.65
		δ_H	–	10.70	17.50	–	–	–6.80
		δ_T	25.69	25.71	24.71	–0.02	0.98	1.01
3	BMIM-Cl	δ_D	–	16.81	15.10	–	–	1.71
		δ_P	–	10.53	8.47	–	–	2.06
		δ_H	–	13.92	14.70	–	–	–0.78
		δ_T	24.14	24.23	22.71	–0.09	1.43	1.53
Ionic liquids containing EMIM cations								
4	EMIM-BF ₄	δ_D	–	17.87	16.27	–	–	1.60
		δ_P	–	14.81	10.74	–	–	4.07
		δ_H	–	12.18	15.82	–	–	–3.64
		δ_T	26.11	26.21	25.11	–0.10	1.00	1.10
5	EMIM-DEPO ₄	δ_D	–	17.65	14.67	–	–	2.99
		δ_P	–	13.39	9.12	–	–	4.27
		δ_H	–	12.67	17.04	–	–	–4.37
		δ_T	25.41	25.52	24.26	–0.11	1.15	1.26
6	EMIM-AC	δ_D	–	17.52	14.25	–	–	3.27
		δ_P	–	12.70	8.83	–	–	3.87
		δ_H	–	13.97	16.96	–	–	–2.99
		δ_T	25.16	25.75	23.85	–0.59	1.31	1.91
Ionic liquids containing [Tf ₂ N] anions								
7	HOEMIM-Tf ₂ N	δ_D	–	18.23	14.70	–	–	3.53
		δ_P	–	15.17	9.86	–	–	5.31
		δ_H	–	11.04	19.08	–	–	–8.04
		δ_T	26.49	26.16	26.03	0.33	0.46	0.13
8	MBPYRRO-Tf ₂ N	δ_D	–	18.01	13.89	–	–	4.12
		δ_P	–	15.21	8.96	–	–	6.25
		δ_H	–	10.64	18.85	–	–	–8.21
		δ_T	25.81	25.86	25.07	–0.05	0.74	0.79
2	BMIM-Tf ₂ N	δ_D	–	18.07	14.82	–	–	3.25
		δ_P	–	14.84	9.19	–	–	5.65
		δ_H	–	10.70	17.50	–	–	–6.80
		δ_T	25.69	25.71	24.71	–0.02	0.98	1.01
Other ionic liquid types								
9	MMIM-MeSO ₄	δ_D	–	17.89	14.58	–	–	3.32
		δ_P	–	14.62	9.68	–	–	4.95
		δ_H	–	11.23	19.06	–	–	–7.83
		δ_T	26.36	25.69	25.88	0.67	0.48	–0.18
10	MBPYRRO-N(CN) ₂	δ_D	–	17.96	15.85	–	–	2.10
		δ_P	–	14.71	9.84	–	–	4.87
		δ_H	–	11.57	15.81	–	–	–4.25
		δ_T	25.54	25.94	24.46	–0.40	1.08	1.48

[a] Mixing rule (Mix), 1D Method (1D), 3D-Method 1 (3D-1), 3D-Method 2 (3D-2).

Method1 and 3D-Method2, the former approach gives a higher value than the latter, in the range of 0.13–1.91, except for the ionic liquids BMIM-PF₆ and MMIM-MeSO₄.

The total solubility parameter of ionic liquids is divided into partial solubility parameters to acquire further information on molecular interactions of samples. In the case of partial solubility parameters of ionic liquids containing BMIM cations, the dispersion parameters are in the following order: [Tf₂N] > [PF₆] > [Cl] and [PF₆] > [Cl] > [Tf₂N], in accordance with values attained from 3D-Method1 and 3D-Method2, respectively. As for the polar solubility parameters, they are of the following

order: [Tf₂N] > [PF₆] > [Cl] and [PF₆] > [Tf₂N] > [Cl], according to values given by 3D-Method1 and 3D-Method2, respectively. Probably, 3D-Method2 could show a more appropriate trend of the polar parameters when the values are compared with the $E_{T(30)}$ scale or equivalent normalized E_T^N scale. The $E_{T(30)}$ scale or equivalent normalized E_T^N scale, which is normalized by using results with water and tetramethylsilane, is a widely used empirical scale of solvent polarity.^[47] Pursuant to this scale, BMIM-PF₆ ($E_T^N = 0.675$)^[48] is more polar than BMIM-Tf₂N ($E_T^N = 0.645$)^[48] as reflected in 3D-Method2. Thus, it appears that the trend of the polar parameters derived from 3D-Method2 is in agreement with the E_T^N scale.

Considering the hydrogen-bonding parameters of ionic liquids containing BMIM cations, they are of the following order: [PF₆] > [Cl] > [Tf₂N] and [Tf₂N] ≈ [PF₆] > [Cl], in accordance with values derived from 3D-Method1 and 3D-Method2, respectively. To discern which of the 3D methods could most appropriately reflect the effect of the anion on hydrogen-bonding parameters, it could be plausible to survey Kamlet–Taft parameters comprised of hydrogen-bonding acidity (α) and hydrogen-bonding basicity (β). These parameters are usually used to evaluate the hydrogen-bonding properties of ionic liquids.^[49] It appears that BMIM-Tf₂N and BMIM-PF₆ tend to exhibit similar hydrogen-bonding capacity in accordance

to the close α and β values of BMIM-Tf₂N ($\alpha = 0.635$ and $\beta = 0.248$)^[48] and BMIM-PF₆ ($\alpha = 0.654$ and $\beta = 0.246$)^[48]. Probably, 3D-Method2 could provide a more reasonable trend of hydrogen-bonding parameters when the values are compared with the values of α and β .

When comparing the partial solubility parameters of ionic liquids containing EMIM cations, the dispersion and polar parameters from both 3D methods are in the following order: [BF₄] > [DEPO₄] > [AC]. In both 3D methods, it is noted that the polar parameter of EMIM-BF₄ is greater than that of EMIM-AC. This agrees with the $E_{T(30)}$ scale, in which EMIM-BF₄ ($E_{T(30)} =$

53.7)^[50] is more polar than EMIM-AC ($E_{T(30)}=49.8$).^[50] The hydrogen-bonding parameters are of the following order: [AC] > [DEPO₄] > [BF₄] and [DEPO₄] ≈ [AC] > [BF₄], according to values determined from 3D-Method1 and 3D-Method2, respectively. In accordance with the Kamlet–Taft parameters, EMIM-DEPO₄ seems to have the highest capacity for hydrogen-bonding interactions, with high values of $\alpha=0.51$ and $\beta=1.00$,^[51] and with lower values of EMIM-AC ($\alpha=0.40$ and $\beta=0.95$)^[50] and EMIM-BF₄ ($\alpha=0.70$ and $\beta=0.26$),^[50] respectively. Therefore, it could be more probable for the hydrogen-bonding parameter to be in the order shown in 3D-Method2 when compared with the values of α and β .

In the case of partial solubility parameters of ionic liquids containing [Tf₂N] anions, the dispersion parameters are in the following order: HOEMIM > BMIM ≈ MBPYRRO and BMIM > HOEMIM > MBPYRRO, in accordance with the values attained from 3D-Method1 and 3D-Method2, respectively. In both 3D methods, MBPYRRO cation provides the lowest dispersion parameter. The polar parameters are in the following order: MBPYRRO ≈ HOEMIM > BMIM

and HOEMIM > BMIM > MBPYRRO,

according to values determined from 3D-Method1 and 3D-Method2, respectively. In both 3D methods, it is recognized that the polar parameter of HOEMIM cation is more than that of BMIM cation, as expected. With both HOEMIM-Tf₂N and BMIM-Tf₂N being imidazolium-based, the hydroxyl group at the C-1 position on the imidazole

ring of HOEMIM-Tf₂N confers a more polar character on the ionic liquid than the butyl group at the same position on the imidazole ring of BMIM-Tf₂N. 3D-Method2 could probably show a more rational trend of polar parameters that is consistent with the $E_{T(30)}$ scale. According to this scale, BMIM-Tf₂N ($E_{T(30)}=52.4$)^[52] is expected to be more polar than MBPYRRO-Tf₂N ($E_{T(30)}=49.6$),^[52] as reflected in 3D-Method2.

The hydrogen-bonding parameters of ionic liquids containing [Tf₂N] anions are in the order: HOEMIM > BMIM ≈ MBPYRRO and HOEMIM > MBPYRRO > BMIM, which is consistent with values derived from 3D-Method1 and 3D-Method2, respectively. It is observed that HOEMIM-Tf₂N presents the highest hydrogen-bonding parameter in both 3D methods and it is greater than that of BMIM-Tf₂N, as expected. This is due to the presence of a hydroxyl group at the C-1 position on the imidazole ring of HOEMIM-Tf₂N, as mentioned earlier. Consequently, HOEMIM-Tf₂N has higher hydrogen-bonding capacity than BMIM-Tf₂N. When considering α and β values, the β values of MBPYRRO-Tf₂N and BMIM-Tf₂N are similar, at 0.23 and 0.24, respectively, whereas the α value of MBPYRRO-Tf₂N (0.57) is less than that of BMIM-Tf₂N (0.72).^[52] It thus appears that MBPYRRO-Tf₂N could have a lower hydrogen-bonding capacity than BMIM-Tf₂N. In either of the 3D methods, it seems that the order does not correspond to those for the Kamlet–Taft parameters.

Comparing the partial solubility parameters of ionic liquids obtained from 3D-Method1 and 3D-Method2, the former approach presents higher dispersion and polar parameters than that of the latter by the range of 0.81–4.12 and 0.90–6.25, respectively. Conversely, the hydrogen-bonding parameter attained from 3D-Method1 is less than that of 3D-Method2, ranging between 0.78–8.21.

2.2. Solubility Parameters of Mixtures of Ionic Liquid and Solvent (60:40 vol %)

Samples with the same fraction of different solvents in EMIM-AC were prepared to study the effect of solvent type on solubility parameter. Table 2 shows the total solubility parameters obtained from the mixing rule [where δ_i in Eq. (13) is obtained from 1D-Method], 1D-Method, 3D-Method1, and 3D-Method2. It is observed that the total solubility parameter of the mixtures of ionic liquid and solvent (60:40 vol %) calculated from 1D-Method and 3D-Method2 demonstrate the same order as

Table 2. Total solubility parameters (δ_T ; MPa ^{1/2}) of the mixtures of ionic liquid and different solvent (60:40 vol %). ^[a]									
No.	Chemical	Mix	1D	3D-1	3D-2	Difference between methods			
						Mix/1D	1D/3D-1	1D/3D-2	3D-1/3D-2
1	EMIM-AC/DMA	24.18	25.07	24.76	23.54	0.89	0.31	1.53	1.22
2	EMIM-AC/DMF	25.02	25.48	24.26	24.52	0.46	1.22	0.96	−0.26
3	EMIM-AC/DMSO	25.78	26.10	25.10	25.40	0.32	1.00	0.70	−0.30
4	EMIM-AC/ethanolamine	27.62	26.95	25.31	26.15	−0.67	1.64	0.80	−0.85

[a] Mixing rule (Mix), 1D Method (1D), 3D-Method 1 (3D-1), 3D-Method 2 (3D-2).

follows: EMIM-AC/ethanolamine > EMIM-AC/DMSO > EMIM-AC/DMF > EMIM-AC/DMA. In contrast, the values attained from 3D-Method1 are in the following order: EMIM-AC/ethanolamine > EMIM-AC/DMSO > EMIM-AC/DMA > EMIM-AC/DMF. According to the mixing rule, the total solubility parameter of the mixtures of ionic liquid and solvent increases as the total solubility parameter of the solvents (Table 3) increases from 22.7 (DMA) to 31.3 (ethanolamine). Hence, it could be stated that both 1D-Method and 3D-Method2 show trends that are consistent with the theoretical trend or mixing rule.

In addition, from Table 2, it is observed that the total solubility parameter of mixtures of ionic liquid and solvent (60:40 vol %) obtained from the 1D-Method is greater than that of the mixing rule by 0.32–0.89, except for the mixture of EMIM-

Table 3. Solubility parameters of studied solvents at 25 °C.				
Chemical	Partial solubility parameters [MPa ^{1/2}]			Total solubility parameter [δ_T , MPa ^{1/2}]
	δ_D	δ_P	δ_H	
DMA	16.8	11.5	10.2	22.7
DMF	17.4	13.7	11.3	24.8
DMSO	18.4	16.4	10.2	26.7
ethanolamine	17.2	15.5	21.3	31.3

AC/ethanolamine. Comparing the total solubility parameter of the mixtures of ionic liquid and solvent determined by the 1D-Method with those given by both 3D methods, the 1D-Method presents higher values than both 3D-Method1 and 3D-Method2, by the range of 0.31–1.64 and 0.70–1.53, respectively. When comparing the total solubility parameter of mixtures of ionic liquid and solvent obtained from 3D-Method1 and 3D-Method2, the latter approach gives a larger value than the former by 0.26–0.85, except for the mixture of EMIM-AC/DMA. From these comparisons, it is noted that the values of the total solubility parameter given by the mixing rule and by the

1D-Method are closer to each other and the values of the total solubility parameter determined by 3D-Method1 and 3D-Method2 are closer to each other.

Figure 1a–c illustrate the effect of solvent type of the mixture of EMIM-AC/solvent (60:40 vol%) on the dispersion, polar and hydrogen-bonding solubility parameters attained from 3D-Method1, 3D-Method2, Mixing Rule1 [where δ_i in Eq. (13) is obtained from 3D-Method1], and Mixing Rule2 (where δ_i in Eq. (13) is obtained from 3D-Method2). In both 3D methods, it is observed that the dispersion and polar parameters tend to increase as the total solubility parameter of the solvents in-

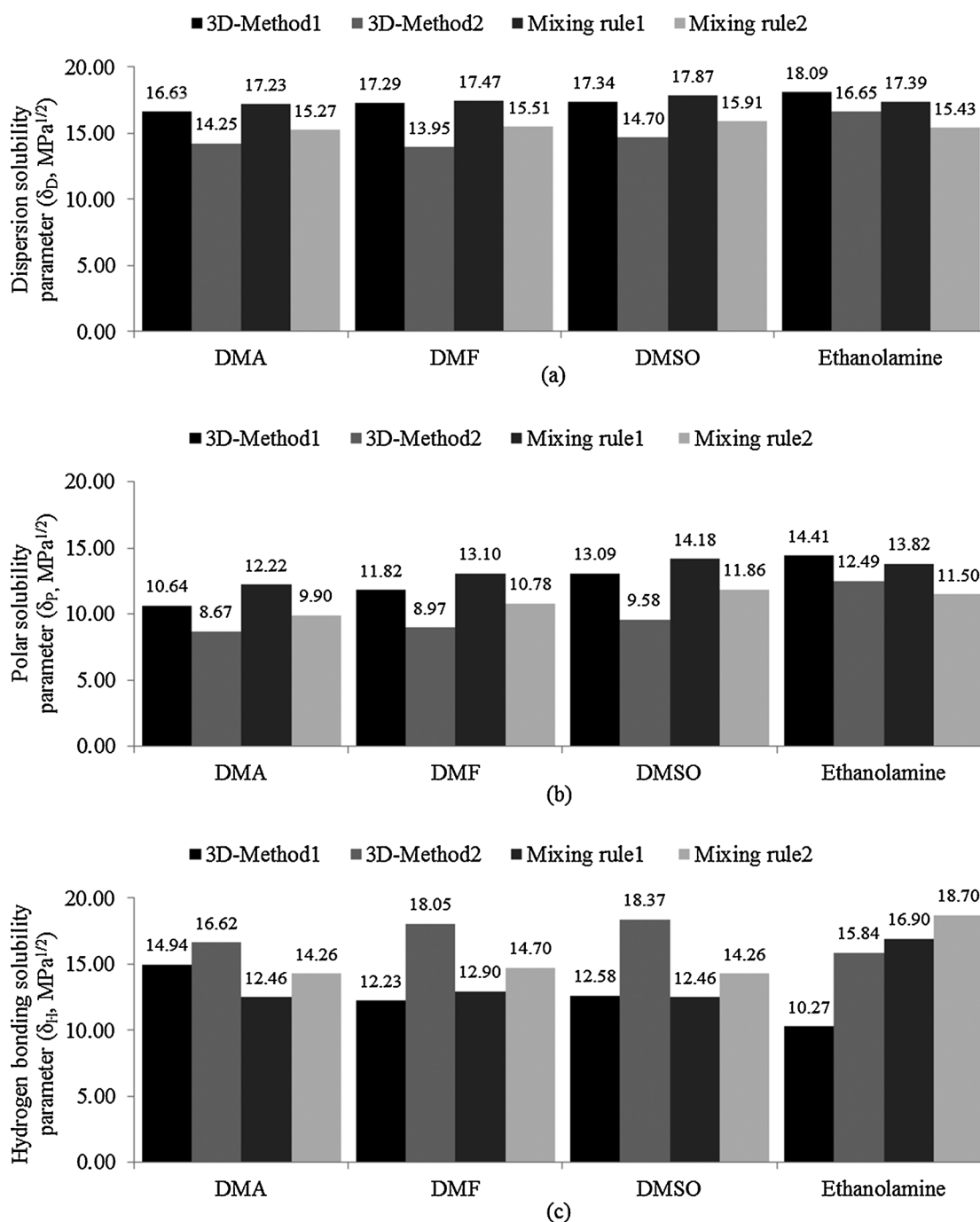


Figure 1. The effect of solvent type of EMIM-AC/solvent mixture (60:40 vol%) on a) dispersion, b) polar, and c) hydrogen-bonding solubility parameters attained from 3D-Method1, 3D-Method2, Mixing Rule1, and Mixing Rule2.

creases from 22.7 (DMA) to 31.3 (ethanolamine). The order is as follows: EMIM-AC/ethanolamine > EMIM-AC/DMSO > EMIM-AC/DMF > EMIM-AC/DMA. In both 3D methods, it is found that EMIM-AC/ethanolamine presents the highest polar parameter, implying that it is the most polar. Furthermore, it is noted that ethanolamine is a protic solvent, whereas DMA, DMF, and DMSO are aprotic solvents with polarity in the following order: DMSO > DMF > DMA.^[53] It could be deduced that the polar parameter of the mixtures of EMIM-AC/aprotic solvent increases with the polarity of aprotic solvents.

The trend of hydrogen-bonding parameters is notably different across both 3D methods. In 3D-Method1, the hydrogen-bonding parameter tends to decrease with increasing total solubility parameter of the solvents from 22.7 (DMA) to 31.3 (ethanolamine), whereas in 3D-Method2, the hydrogen-bonding parameter increases as the total solubility parameter of the solvents increases from 22.7 (DMA) to 26.7 (DMSO) and a minimum value was observed for the mixture of EMIM-AC/ethanolamine.

The values of partial solubility parameters determined from both 3D methods and their respective mixing rule, correspond to the trends of dispersion and polar parameters derived from these methods. Both dispersion and polar parameters tend to increase with the total solubility parameter of the solvent. The hydrogen-bonding parameter derived from 3D-Method1 tends to decrease as the total solubility parameter of the solvent increases. This is in contrast with the trend derived from Mixing Rule1. As for 3D-Method2, the hydrogen-bonding parameter increases with the total solubility parameter of solvent, followed by a decreased value for the mixture of EMIM-AC/ethanolamine, as mentioned earlier. Conversely, the hydrogen-bonding parameter attained from Mixing Rule2 shows no significant change with increasing total solubility parameter of solvent but provide a prominent increase for the mixture of EMIM-AC/ethanolamine.

Comparing the partial solubility parameters of the mixtures of ionic liquid and solvent obtained between both 3D methods with their respective mixing rules, both 3D methods present smaller dispersion and polar parameter values than their respective mixing rules, except for the mixture of EMIM-AC/ethanolamine. In contrast, the hydrogen-bonding parameter attained from both 3D methods is generally greater than their respective mixing rule, except for the mixture of EMIM-AC/ethanolamine.

2.3. Solubility Parameters of Mixtures of Ionic Liquids with Different DMA Fractions

Table 4 shows the total solubility parameters of mixtures of BMIM-Cl with different DMA fraction, derived from mixing rule, 1D Method, 3D-Method1, and 3D-Method2. As noted in our

Table 4. Total solubility parameters (δ_T ; MPa^{1/2}) of ionic liquids and the mixtures of ionic liquid and DMA solvent.^[a]

No.	Chemical (ratio vol%)	Mix	1D	3D-1	3D-2	Difference between methods			
						Mix/1D	1D/3D-1	1D/3D-2	3D-1/3D-2
1	BMIM-Cl	–	24.14	24.23	22.71	–	–0.09	1.43	1.52
2	BMIM-Cl/DMA (60:40)	23.56	24.35	23.61	22.18	0.79	0.74	2.17	1.44
3	BMIM-Cl/DMA (40:60)	23.28	24.78	24.41	23.28	1.50	0.37	1.50	1.13
4	BMIM-Cl/DMA (10:90)	22.84	24.57	24.42	22.73	1.73	0.15	1.84	1.69

[a] Mixing rule (Mix), 1D Method (1D), 3D-Method 1 (3D-1), 3D-Method 2 (3D-2).

previous work, in the 1D Method, increasing the amount of DMA from 0 to 60 vol% in BMIM-Cl increases the total solubility parameter marginally. Upon addition of 90 vol% of DMA into BMIM-Cl, the total solubility parameter decreases. This trend is observed notably in 3D-Method2. In contrast, in 3D-Method1, the total solubility parameter tends to remain relatively constant when 90 vol% of DMA is further added into BMIM-Cl.

When comparing the total solubility parameter of the mixtures of BMIM-Cl with different DMA fraction attained from the 1D-Method and the mixing rule, a higher value is derived from the former than from the latter, by 0.79–1.73 (Table 4). In addition, the total solubility parameter of the mixtures given by the 1D-Method is greater than that obtained by 3D-Method1 and 3D-Method2 by a range of 0.15–0.74 and, more prominently, by range of 1.50–2.17, respectively. 3D-Method1 presents higher total solubility parameter values than that of 3D-Method2 by a range of 1.13–1.69.

Figure 2a–c illustrate the effect of DMA (vol%) dissolved in BMIM-Cl on the dispersion, polar and hydrogen-bonding solubility parameters determined from 3D-Method1, 3D-Method2, mixing rule1, and mixing rule2. In both 3D methods, the dispersion parameter is found to remain relatively constant as the amount of DMA in BMIM-Cl is increased from 0 to 90 vol%. The trend of the dispersion parameter determined from 3D-Method1 is similar to that of mixing rule1 whereas in mixing rule2, the dispersion parameter increases slightly with the addition of DMA from 40 to 90 vol% into BMIM-Cl. For polar parameters, in 3D-Method1, when 40 vol% DMA is added into BMIM-Cl, the polar parameter decreases to a minimum and then increases with further addition of DMA of up to 90 vol% into the ionic liquid. According to mixing rule1, the polar parameter tends to remain relatively constant as DMA fraction in BMIM-Cl increases from 40 to 90 vol%. In 3D-Method2, no significant effect on the polar parameter is observed when the

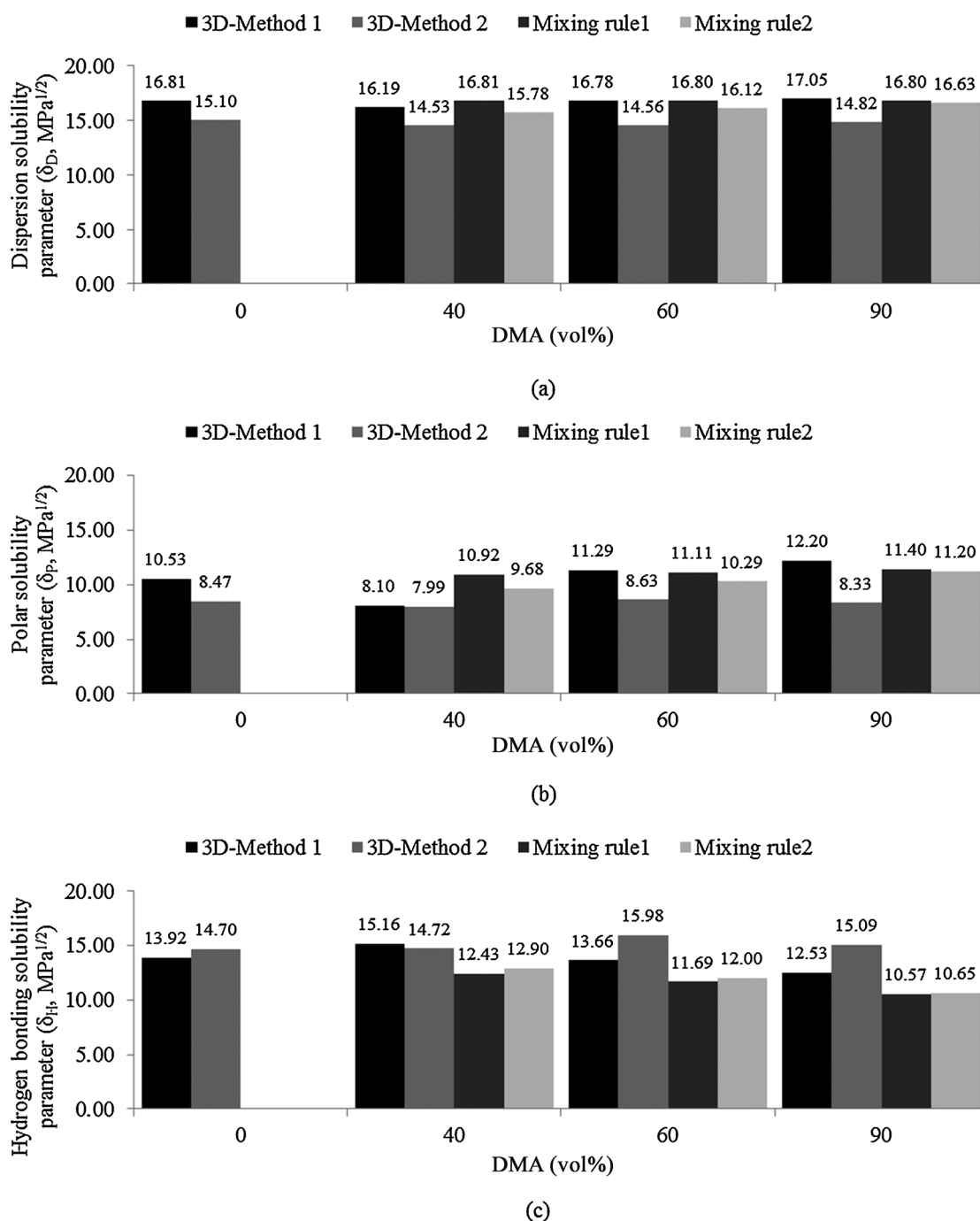


Figure 2. The effect of the amount of DMA (vol%) dissolved in BMIM-Cl on a) dispersion, b) polar, and c) hydrogen-bonding solubility parameters attained from 3D-Method1, 3D-Method2, Mixing Rule1, and Mixing Rule2.

amount of DMA in BMIM-Cl is increased from 0 to 90 vol% but in mixing rule2, the polar parameter increases somewhat as the DMA fraction in BMIM-Cl increases from 40 to 90 vol%. When considering hydrogen-bonding parameters, 3D-Method1 and 3D-Method2 show a maximum value at the addition of 40 and 60 vol% of DMA into BMIM-Cl, respectively, and a change of approximately 1.2 is noted. On the other hand, in both Mixing Rule1 and Mixing Rule2, the hydrogen-bonding parameter decreases with the addition of DMA from 40 to 90 vol% into BMIM-Cl.

Given all of the above, it is observed that the effect of DMA fraction on the partial parameters of ionic liquids varies across different methods. Nevertheless, the partial parameters of the mixtures tend to be closer to that of BMIM-Cl than to DMA. This is consistent with the findings of previous work in which the total solubility parameter of mixtures tends to be closer to those of ionic liquid than to DMA.^[30]

When comparing the partial parameters of BMIM-Cl/DMA mixtures, both 3D methods give lower dispersion parameters than their respective mixing rule, ranging from 0.02 to 1.81,

except for the mixture of BMIM-Cl/DMA (10:90 vol%). Likewise, both 3D methods present lower polar parameter than their respective mixing rule, ranging from 1.66 to 2.82, except for the mixture of BMIM-Cl/DMA (40:60 vol%) and BMIM-Cl/DMA (10:90 vol%). In contrast, the hydrogen-bonding parameter obtained from both 3D methods is greater than their respective mixing rule by 1.82 to 4.44.

2.4. Solubility Parameters of Ionic Liquids and Mixtures of Ionic Liquids and Solvents at Different Dissolution Temperatures

The total solubility parameter of EMIM-AC and the mixtures of EMIM-AC/DMA (60:40 vol%) was investigated in the dissolution temperature range of 25 to 60 °C, as shown in Table 5. The effect of temperature on the total solubility parameter of ionic liquids and mixtures of ionic liquid and solvent is the same across mixing rule, 1D-Method, and both 3D methods. As dissolution temperature increases from 25 to 60 °C, the total solubility parameter of EMIM-AC and mixture of EMIM-AC/DMA (60:40 vol%) decreases. The 1D-Method presents greater total solubility parameter value than mixing rule, 3D-Method2, and 3D-Method1, except for EMIM-AC at 25 and 60 °C. It is found that the range of difference between 1D-Method and 3D-Method2 (0.70–1.35) is more pronounced than that of 1D-Method and 3D-Method1 (0.05–0.74). In addition, 3D-Method1 provides a greater value than 3D-Method2, except for the mixture of EMIM-AC/DMA (60:40 vol%) at 40 °C.

The effect of dissolution temperature on the dispersion, polar and hydrogen-bonding solubility parameters of EMIM-AC determined from 3D-Method1 and 3D-Method2 is illustrated in Figure 3 a–c, respectively. Generally, in 3D-Method1, the dispersion, polar and hydrogen-bonding parameters decrease as temperature increases from 25 to 60 °C. In 3D-Method2, there is marginal change of dispersion and polar parameters with temperature but the hydrogen-bonding parameter decreases with temperature. From the correlations of temperature dependence of solubility parameters for liquids [Eqs. (14)–(16)], solubility parameter values are expected to decrease with an increase in temperature. Hydrogen bonding is especially sensitive to temperature change. At higher temperatures, more hydrogen bonds are gradually broken or weakened and the hydrogen-bonding parameters will decrease faster than others. It could be concluded that both 3D methods show correspond-

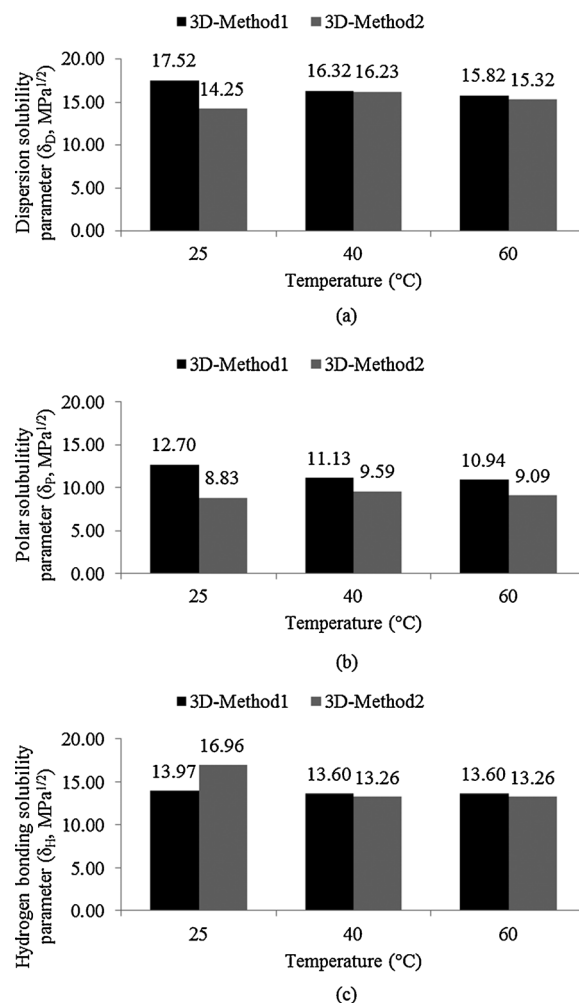


Figure 3. The effect of dissolution temperature on a) dispersion, b) polar, and c) hydrogen-bonding solubility parameters of EMIM-AC attained from 3D-Method1 and 3D-Method2.

ing trends with the correlations. In particular, for 3D-Method2, the significant change of hydrogen-bonding parameter with temperature among other parameters agrees with the sensitivity of hydrogen-bonding towards changes in temperature.

Figure 4 a–c illustrates the effect of dissolution temperature on the dispersion, polar and hydrogen-bonding solubility parameters of EMIM-AC/DMA (60:40 vol%) mixture obtained from 3D-Method1, 3D-Method2, Mixing Rule1, and Mixing Rule2. It is noted that in 3D-Method1, as temperature increases from 25 to 60 °C, the dispersion and polar parameters tend to be constant but the hydrogen-bonding parameter decreases. However, in mixing rule1, the dispersion, polar and hydrogen-bonding parameters show a slight decrease of up to 1.3 in value with temperature. Moreover, in the comparison of the values of partial parameters,

No.	Chemical	Temp. [°C]	Mix	Difference between method						
				1D	3D-1	3D-2	Mix/1D	1D/3D-1	1D/3D-2	3D-1/3D-2
1	EMIM-AC	25	–	25.16	25.75	23.85	–	–0.59	1.31	1.90
2	EMIM-AC	40	–	24.04	23.99	23.05	–	0.05	0.99	0.94
3	EMIM-AC	60	–	23.28	23.56	22.21	–	–0.28	1.07	1.35
4	EMIM-AC/DMA ^[b]	25	24.18	25.07	24.76	23.54	0.89	0.31	1.53	1.22
5	EMIM-AC/DMA ^[b]	40	23.38	24.20	23.46	23.50	0.82	0.74	0.70	–0.04
6	EMIM-AC/DMA ^[b]	60	23.18	23.65	22.96	22.30	0.47	0.69	1.35	0.66

[a] Mixing rule (Mix), 1D Method (1D), 3D-Method 1 (3D-1), 3D-Method 2 (3D-2). [b] Ratio 60:40 vol%.

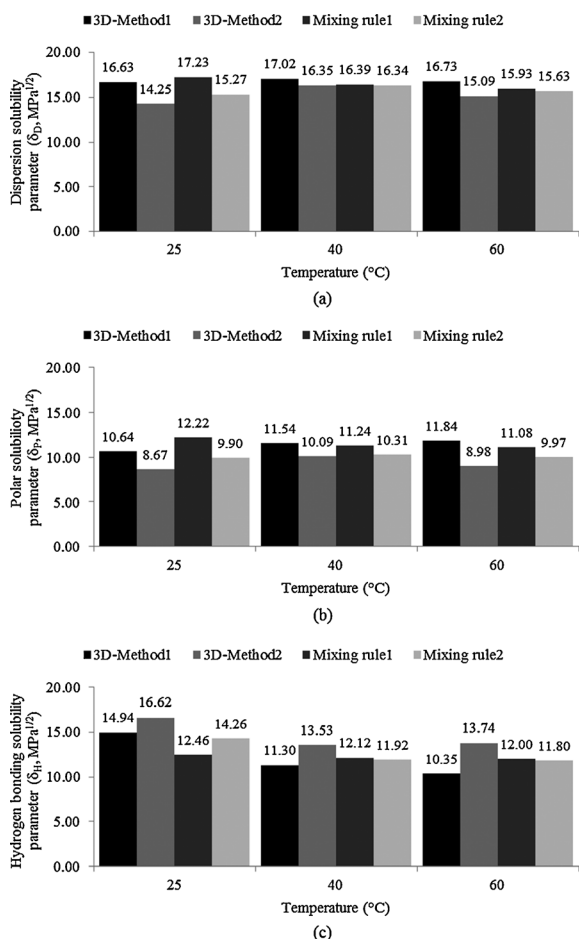


Figure 4. The effect of dissolution temperature on a) dispersion, b) polar, and c) hydrogen-bonding solubility parameters of the mixture of EMIM-AC/DMA (60:40 vol%) attained from 3D-Method1 and 3D-Method2.

3D-Method1 presents greater dispersion and polar parameters as well as lower hydrogen-bonding parameters than that of Mixing Rule1, except for the mixture at 25 °C. When comparing the effect of dissolution temperature attained from 3D-Method2 with that of Mixing Rule2, in both 3D-Method2 and Mixing Rule2, the dispersion and polar parameters tend to increase with temperature with a maximum observed for the mixture at 40 °C, but the hydrogen-bonding parameter tends to decrease with temperature. 3D-Method2 presents lower values of dispersion and polar parameters up to an approximate difference of 1.3 as well as higher hydrogen-bonding parameter than Mixing Rule2 by a range of 1.61–2.36. From this study, it could be noted that, among other parameters, the hydrogen-bonding parameter of the mixture of EMIM-AC/ethanolamine provides a more significant decrease with temperature. This is analogous with the sensitivity of hydrogen-bonding with temperature.

When considering the partial parameters of EMIM-AC and mixture of EMIM-AC/DMA (60:40 vol%) at the same temperature, it is noted that in 3D-Method1, the dispersion and polar parameters of the mixture at 25 °C is lower than those of EMIM-AC at 25 °C whereas the dispersion and polar parameters

of the mixture at 40 and 60 °C is higher than those of EMIM-AC at 40 and 60 °C. This is in contrast to the hydrogen-bonding parameter. In 3D-Method2, it is observed that the dispersion, polar and hydrogen-bonding parameters of the mixture tends to be similar to those of EMIM-AC at 25, 40, and 60 °C.

3. Conclusions

This study provides basic information on the total and partial solubility parameters of ionic liquids, and mixtures of ionic liquids and solvents at different composition and dissolution temperature by using the intrinsic viscosity approach. It was found that the values of the total solubility parameter, derived from 3D-Method1, tend to be closer to that of 1D-Method and a more pronounced range of values between 1D-Method and 3D-Method2 is observed. For all types of effect on the total solubility parameter, the trends are identified to be the same for 1D-Method and 3D-Method2. However, 3D-Method1 does not present the same trend in the total solubility parameter as 1D-Method for the ionic liquid type, in particular, ionic liquids containing [EMIM] cations, and for the solvent type in the ionic liquid as well as the DMA fraction in the ionic liquid. In the study of the effect of ionic liquid type on partial solubility parameters, 3D-Method2 appears to reflect a more appropriate trend than 3D-Method1 when compared with the $E_{T(30)}$ scale or equivalent normalized E_T^N scale, as well as with Kamlet–Taft parameters. It is noted that the anion type significantly affects the partial solubility parameters. According to 3D-Method2, EMIM-BF₄ presents the highest dispersion and polar parameters as well as lowest the hydrogen-bonding parameter, whereas EMIM-AC provides the lowest value of both dispersion and polar parameters. The nature of the cation also influences the partial solubility parameters. Among a range of cations with the same anion, the MBPYRRO cation provides the lowest dispersion and polar parameters, whereas the BMIM cation presents the lowest hydrogen-bonding parameter. The study of the effect of solvent type in the ionic liquid on partial solubility parameters in accordance to both 3D methods, indicates that the dispersion and polar parameters tend to increase with the total solubility parameter of the solvent. The hydrogen-bonding parameter in 3D-Method2 increases as the total solubility parameter of solvents increases, and a minimum is found with the EMIM-AC/ethanolamine (60:40 vol%) mixture. In contrast, the hydrogen-bonding parameter in 3D-Method1 tends to decrease with increasing total solubility parameter of solvent. In the study of the effect of the DMA fraction in the ionic liquid on partial solubility parameters, it was demonstrated from 3D-Method2 that the dispersion and polar parameters tend to remain relatively constant with an increase of DMA fraction from 0 to 90 vol% in BMIM-Cl, whereas a maximum value was found for the hydrogen-bonding parameter for the BMIM-Cl/DMA (40:60 vol%) mixture. On the contrary, values attained from 3D-Method1 are either constant or there is no particular associated trend. Nevertheless, in both 3D methods, it was noted that the partial parameters tend to be closer to that of BMIM-Cl than DMA. In general, an increase in temperature from 25 to 60 °C results in a decrease of the dispersion, polar,

and hydrogen-bonding parameters of EMIM-AC, derived from both 3D methods. Among other parameters of EMIM-AC and the EMIM-AC/ethanolamine (60:40 vol%) mixture, the hydrogen-bonding parameter demonstrates great sensitivity towards changes in temperature.

Acknowledgements

This work was supported by Competitive Research Programme (NRF/CRP/5/2009/03) of National Research Foundation, GSK-EDB Trust Fund Project "Large-scale Chromatography with Green Solvents: Fundamentals and Novel-processes", and Academic Research Fund (RGT27/13) of Ministry of Education in Singapore.

Keywords: hydrogen bonds · ionic liquids · ion pairs · noncovalent interactions · solvent effects

- [1] J.-M. Lee, *Fluid Phase Equilib.* **2012**, *319*, 30–36.
[2] J.-M. Lee, *Chem. Eng. J.* **2011**, *172*, 1066–1071.
[3] W. Di, A. Ivaska, *Anal. Chim. Acta* **2008**, *607*, 126–135.
[4] J.-f. Liu, J. Å. Jönsson, G.-b. Jiang, *TrAC Trends Anal. Chem.* **2005**, *24*, 20–27.
[5] M. Rahman, C. S. Brazel, *Polym. Degrad. Stab.* **2006**, *91*, 3371–3382.
[6] D. Zhao, M. Wu, Y. Kou, E. Min, *Catal. Today* **2002**, *74*, 157–189.
[7] P. Weerachanchai, S. S. J. Leong, M. W. Chang, C. B. Ching, J.-M. Lee, *Bioresour. Technol.* **2012**, *111*, 453–459.
[8] A. Martín-Calero, V. Pino, A. M. Afonso, *TrAC Trends Anal. Chem.* **2011**, *30*, 1598–1619.
[9] M. Hasib-ur-Rahman, M. Sijaj, F. Larachi, *Chem. Eng. Process.* **2010**, *49*, 313–322.
[10] H. Mizuuchi, V. Jaitely, S. Murdan, A. T. Florence, *Eur. J. Pharm. Sci.* **2008**, *33*, 326–331.
[11] M. Mora-Pale, L. Meli, T. V. Doherty, R. J. Linhardt, J. S. Dordick, *Biotechnol. Bioeng.* **2011**, *108*, 1229–1245.
[12] C. M. Hansen, *Prog. Org. Coat.* **2004**, *51*, 77–84.
[13] Y. S. Sista, L. Jain, A. Khanna, *Sep. Purif. Technol.* **2012**, *97*, 51–64.
[14] K. Adamska, A. Voelkel, K. Héberger, *J. Chromatogr. A* **2007**, *1171*, 90–97.
[15] S. Stach (Austin American Technology Corp.), **2009**.
[16] S. H. Lee, S. B. Lee, *Chem. Commun.* **2005**, 3469–3471.
[17] X. Chen, C. Yuan, C. K. Y. Wong, G. Zhang, *J. Mol. Model.* **2012**, *18*, 2333–2341.
[18] L. R. Snyder in *Journal of Chromatography Library, Vol. 51A, 5th ed.* (Ed.: E. Heftmann), Elsevier, Amsterdam, **1992**, pp. A1–A68.
[19] C. M. Hansen in *Hansen Solubility Parameters: A User's Handbook, 2nd ed.*, CRC, Boca Raton, **2007**, pp. 1–26.
[20] K. Vay, S. Scheler, W. Friess, *Int. J. Pharm.* **2011**, *416*, 202–209.
[21] C. Bordes, V. Fréville, E. Ruffin, P. Marote, J. Y. Gauvrit, S. Briançon, P. Lan-téri, *Int. J. Pharm.* **2010**, *383*, 236–243.
[22] S. Schenderlein, M. Luck, B. W. Muller, *Int. J. Pharm.* **2004**, *286*, 19–26.
[23] K. Adamska, A. Voelkel, *Int. J. Pharm.* **2005**, *304*, 11–17.
[24] K. Adamska, A. Voelkel, *J. Chromatogr. A* **2006**, *1132*, 260–267.
[25] J. W. King, *LWT-Food Sci. Technol.* **1995**, *28*, 190–195.
[26] M. A. Pena, Y. Daali, J. Barra, P. Bustamante, *Chem. Pharm. Bull.* **2000**, *48*, 179–183.
[27] P. B. Rathi, P. S. Panzade, A. U. Patil, P. S. Salve, *Asian J. Biomed. Pharm. Sci.* **2013**, *3*, 68–71.
[28] W. R. Song, D. W. Brownawell, *Polym. Eng. Sci.* **1970**, *10*, 222–224.
[29] G. Ovejero, P. Perez, M. D. Romero, I. Guzman, E. Diez, *Eur. Polym. J.* **2007**, *43*, 1444–1449.
[30] P. Weerachanchai, Z. Chen, S. S. J. Leong, M. C. Chang, J.-M. Lee, *Chem. Eng. J.* **2012**, *213*, 356–362.
[31] R. Ravindra, K. R. Krovidi, A. A. Khan, *Carbohydr. Polym.* **1998**, *36*, 121–127.
[32] O. Segarceanu, M. Leca, *Prog. Org. Coat.* **1997**, *31*, 307–310.
[33] A. Agrawal, A. D. Saran, S. S. Rath, A. Khanna, *Polymer* **2004**, *45*, 8603–8612.
[34] G. Ovejero, M. D. Romero, E. Diez, I. Diaz, *Eur. Polym. J.* **2010**, *46*, 2261–2268.
[35] P. Bustamante, J. Navarro-Lupion, B. Escalera, *Eur. J. Pharm. Sci.* **2005**, *24*, 229–237.
[36] K. H. Han, G. S. Jeon, I. K. Hong, S. B. Lee, *J. Ind. Eng. Chem.* **2013**, *19*, 1130–1136.
[37] P. Bustamante, M. A. Peña, J. Barra, *Int. J. Pharm.* **2000**, *194*, 117–124.
[38] P. Bustamante, M. A. Peña, J. Barra, *Int. J. Pharm.* **1998**, *174*, 141–150.
[39] P. Mäki-Arvela, I. Anugwom, P. Virtanen, R. Sjöholm, J. P. Mikkola, *Ind. Crops Prod.* **2010**, *32*, 175–201.
[40] A. Brandt, J. Grasvik, J. P. Hallett, T. Welton, *Green Chem.* **2013**, *15*, 550–583.
[41] A. F. M. Barton, *Pure Appl. Chem.* **1985**, *57*, 905–912.
[42] A. Marciniak, *Int. J. Mol. Sci.* **2011**, *12*, 3553–3575.
[43] K. Swiderski, A. McLean, C. M. Gordon, D. H. Vaughan, *Chem. Commun.* **2004**, 2178–2179.
[44] R. Schoo, A. Hoxie, *Fuel* **2012**, *102*, 701–708.
[45] E. A. Grulke in *Polymer Handbook, 4th ed.* (Eds.: J. Brandrup, E. H. Immergut, E. A. Grulke), Wiley, New York, **1999**, pp. 675–714.
[46] D. Reuteler-Faoro, P. Ruelle, H. Nam-Tran, C. de Reyff, M. Buchmann, J. C. Negre, U. W. Kesselring, *J. Phys. Chem.* **1988**, *92*, 6144–6148.
[47] C. F. Poole, S. K. Poole, *J. Chromatogr. A* **2010**, *1217*, 2268–2286.
[48] C. Chiappe, D. Pieraccini, *J. Phys. Chem. A* **2006**, *110*, 4937–4941.
[49] Y. Fukaya, H. Ohno, *Phys. Chem. Chem. Phys.* **2013**, *15*, 4066–4072.
[50] S. Zhang, X. Qi, X. Ma, L. Lu, Q. Zhang, Y. Deng, *J. Phys. Org. Chem.* **2012**, *25*, 248–257.
[51] Y. Fukaya, K. Hayashi, M. Wada, H. Ohno, *Green Chem.* **2008**, *10*, 44–46.
[52] S. Coleman, R. Byrne, S. Minkovska, D. Diamond, *Phys. Chem. Chem. Phys.* **2009**, *11*, 5608–5614.
[53] F. A. Carey, "Chapter 8: Nucleophilic Substitution", found under <http://www.chem.ucalgary.ca/courses/350/Carey5th/Ch08/ch8-0.html>, **2009**.

Received: May 18, 2014

Published online on August 21, 2014