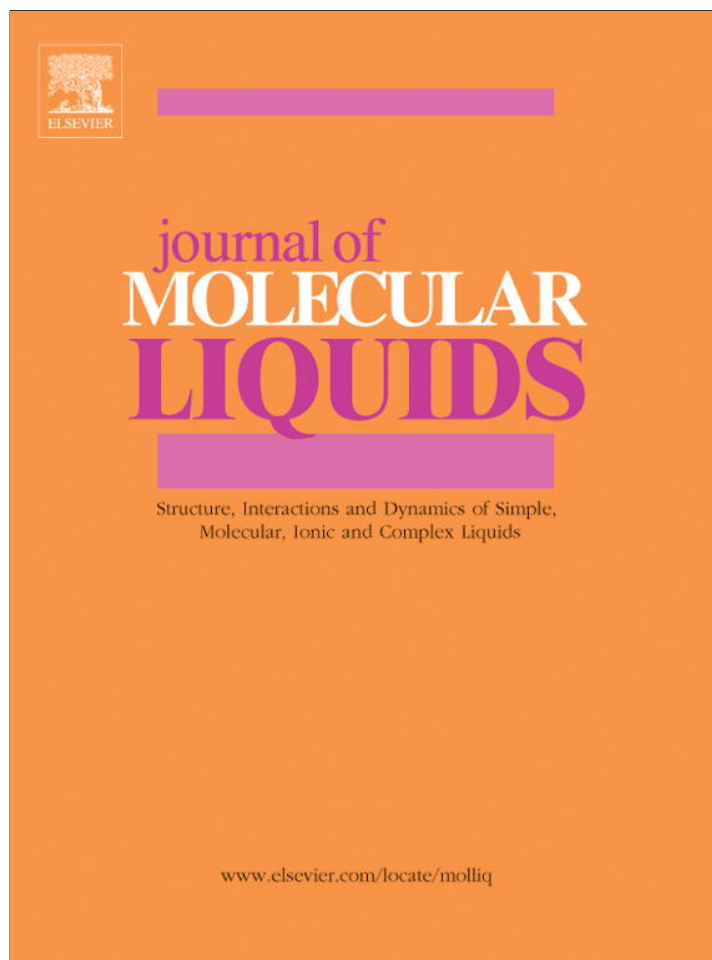


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## Some physico-chemical properties of ethanolamine ionic liquids: Behavior in different solvents

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### ABSTRACT

The series of ethanolamine derived ionic liquids (ILs) **1–9**, was synthesized, characterized by IR and  $^1\text{H}$  NMR spectroscopy and investigated by DFT study, to explore their properties in solvents with different dielectric constants. The investigation of the anion–cation and ion–solvent interactions of ILs in solvents with different polarity was performed. The obtained results showed that solvation has significant influence on anion–cation interaction. The binding energies of the anion–cation interaction obtained in different solvents showed that in polar solvents ILs exist as separated solvated ions, while in solvents with lower polarity as the contacted ion pair. Density functional studies showed that solvation energies decrease with the increase of solvent polarity.

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### 1. Introduction

Ethanolamines (monoethanolamine – MEA, diethanolamine – DEA, and triethanolamine – TEA) and their derivatives are bifunctional natural and synthetic organic compounds. As structural parts of cephalin and lecithin, phospholipids of eukaryotic membranes, they are ubiquitous in the biosphere [1–5]. Owing to amine and alcoholic groups these compounds show relevant biological and pharmacological activities, making them useful in a broad variety of industrial applications, such as pharmaceutical, agricultural, chemical, and petrochemical [6–12].

Taking into account considerable participation of ethanolamines in different industrial products, which are finally found and stored in the environment, some authors tested their antimicrobial activity [13,14]. Studies of few different ethanolamines showed their antimicrobial effect to be enhanced at high pH (12, 13). The antimicrobial activity of some ionic liquids derived from ethanolamines has been also studied [15,16].

Ionic liquids (ILs) are a class of novel compounds composed exclusively of organic cations and inorganic or organic anions [17–20]. Room temperature ionic liquid (RTIL), molten salt, liquid organic salt, and fused salt – all these terms have been used to describe this class of chemicals accepted from the chemical industry and academia [21]. Most of ILs are liquid up to 200 °C. In recent years, the number of possible cation and anion combinations has increased significantly. Their

careful choice provides designing and developing ILs with desirable properties [22–26].

Ionic liquids are non-flammable and less toxic than conventional solvents due to their low vapor pressure. Moreover, the low volatility of ILs results in an increase in process safety. They have the potential to increase chemical reactivity and thus lead to more efficient processes [27–29]. ILs attract much interest in the context of green chemistry as environment-friendly media as highly biodegradable and exceptionally harmless materials [30]. Due to these facts, ILs related research has become one of the most exciting topics nowadays.

In recent years, the methods for investigation of IL properties have been developed to a great extent. The anion–cation and ion–solvent interactions of ILs have been examined by experimental methods (such as X-ray [31], neutron diffraction [32], NMR [33], infrared or Raman spectroscopy [34,35], dielectric spectroscopy [36], and theoretical methods such as molecular dynamics simulations [37,38] and quantum chemical calculations) [39–42]. Computational methods are particularly useful in the investigations of ILs, due to their ability to provide electronic structure, anion–cation binding energy and orbital properties.

Considering the fact that ILs are often used in the presence of different molecular solvents, it is necessary to understand their microstructure and anion–cation interactions in solution. Recent detailed study of ILs has shown that the interactions between cations and anions depend on the type of solvent, particularly on its polarity [43,44]. Namely, ILs behave as contacted ion pair in the solvents of low polarity, and as solvated ion pairs in the solvents of high polarity.

Recently, we investigated the antimicrobial activity of some green ethanolamine ILs and their Pd(II) complexes [16]. In the present study, a series of nine ethanolamine ILs was synthesized, and characterized

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by IR and  $^1\text{H}$  NMR spectroscopy. To explore their properties in solvents with different dielectric constants density functional theory (DFT) was employed. It is worth pointing out that this type of data for the investigated ILs cannot be found in literature.

## 2. Experimental

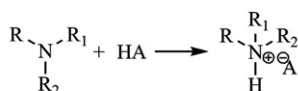
The compounds lactic, acetic, chloroacetic, and hydrochloric acids were obtained from Aldrich Chemical Co. All common chemicals were of reagent grade. DEA, TEA, and N,N diethylethanolamine (DEAE) were purchased from Fluka. The IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using the thin film technique. The  $^1\text{H}$  NMR spectra were run in  $\text{CDCl}_3$  on a Varian Gemini 200 MHz spectrometer.

### 2.1. Preparation of ionic liquids

All investigated ILs (**1–9** in Scheme 1) were prepared by dropping the stoichiometric amount of corresponding carboxylic acid (acetic, lactic or chloroacetic acid) or hydrochloric acid to the dichloromethane-ethanol solution of corresponding amino alcohol (DEA, DEAE or TEA). The reaction mixture was stirred during 2 h at room temperature. After completion of the reaction, the resulting solution was washed with ethyl acetate ( $2 \times 5 \text{ cm}^3$ ) and ethyl ether ( $2 \times 5 \text{ cm}^3$ ). The organic solvents were evaporated under the reduced pressure. The residue was dried *in vacuo* at  $50^\circ\text{C}$  for 4 h to generate the corresponding product. The prepared ILs are colorless viscous liquids. Spectral characterizations of ILs are presented in Table 1.

### 2.2. Computational details

The geometrical parameters of all stationary points were optimized with Gaussian 09 [45]. The structures of all ILs, as well as of the corresponding separated ions, were optimized using the M06 functional [46] and 6-311+G(d,p) basis set. This triple split valence basis set adds p functions to hydrogen atoms in addition to the d and diffuse functions on heavy atoms. The calculations were performed for vacuum and condensed phase, using the CPCM model. This Conductor-like Polarized Continuum Model defines the cavity as the union of a series of joint atomic spheres, whereas solvent is represented as a continuum of a given dielectric constant. The gas phase geometry for each IL was used as the starting structure for optimizations in different solvents. The optimizations were performed without any constraints, except for the cases of **1**, **2**, **5**, **6**, and **8**. For these molecules, the N–H bond length was set to the fixed value. This restriction was applied to better simulate ionic nature of these compounds, and thus, agreement between the experimental and calculated spectra. Nine different solvents were used: water ( $\epsilon = 80.1$ ), dimethyl sulfoxide ( $\epsilon = 46.7$ ), acetonitrile ( $\epsilon = 37.5$ ), methanol ( $\epsilon = 32.7$ ), ethanol ( $\epsilon = 24.5$ ), tetrahydrofuran ( $\epsilon = 7.58$ ), chloroform ( $\epsilon = 4.81$ ), diethyl ether ( $\epsilon = 4.33$ ), and carbon tetrachloride ( $\epsilon = 2.44$ ). All calculated structures, in both phases, were



- 1: R=H,  $\text{R}_1=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{R}_2=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{A}=\text{CH}_3\text{COO}^-$
- 2: R=H,  $\text{R}_1=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{R}_2=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{A}=\text{CH}_3\text{CH}(\text{OH})\text{COO}^-$
- 3: R=H,  $\text{R}_1=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{R}_2=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{A}=\text{ClCH}_2\text{COO}^-$
- 4: R=H,  $\text{R}_1=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{R}_2=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{A}=\text{Cl}^-$
- 5: R= $\text{CH}_2\text{CH}_3$ ,  $\text{R}_1=\text{CH}_2\text{CH}_3$ ,  $\text{R}_2=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{A}=\text{CH}_3\text{COO}^-$
- 6: R= $\text{CH}_2\text{CH}_3$ ,  $\text{R}_1=\text{CH}_2\text{CH}_3$ ,  $\text{R}_2=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{A}=\text{CH}_3\text{CH}(\text{OH})\text{COO}^-$
- 7: R= $\text{CH}_2\text{CH}_3$ ,  $\text{R}_1=\text{CH}_2\text{CH}_3$ ,  $\text{R}_2=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{A}=\text{Cl}^-$
- 8: R= $\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{R}_1=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{R}_2=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{A}=\text{CH}_3\text{COO}^-$
- 9: R= $\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{R}_1=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{R}_2=\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{A}=\text{ClCH}_2\text{COO}^-$

Scheme 1. Synthesis of investigated ILs.

confirmed to be minima on the potential energy surface (all real vibrational frequencies) by frequency calculations. The experimental and simulated IR spectra of the investigated compounds were compared. As expected, the computed vibrational frequencies were overestimated. Due to the lack of the scaling factor for the applied theoretical model, the calculated frequencies were decreased by 5%, and agreement with the experimental values was achieved. The natural bond orbital analysis (Gaussian NBO version) was performed for all structures.

The solvation energies were calculated using the equation:

$$\Delta G_{\text{solv}} = G_{\text{solv}} - G_{\text{gas}} \quad (1)$$

Table 1  
Spectral characterization of the ionic liquids.

IL	IR $\text{cm}^{-1}$	Experimental Calculated	$^1\text{H}$ NMR
1	3415 (–NH, –OH st), 2525 (–NH $_2^+$ st), 1637 (–COO $^-$ as), 1619 (–NH $_2^+$ def), 1411 (COO $^-$ s), 1070 (–C–O– st) 651 (–NH def) 3234, 2290, 1612, 1556, 1360, 1063, 712	$\delta_{\text{H}}$ 1.96 (3H, CH $_3$ –CO, s), 3.10 (4H, –CH $_2$ –NH $_2$ , t), 3.87 (4H, –CH $_2$ –OH, t)	
2	3290 (–NH, –OH st), 2450 (–NH $_2^+$ st), 1582 (–COO $^-$ as), 1582 (–NH $_2^+$ def), 1450 (–NH def), 1411 (COO $^-$ s), 1040 (–C–N– st), 853 (–C–O– st) 3274, 2222, 1605, 1556, 1457, 1414, 1051, 1069	$\delta_{\text{H}}$ 1.25 (3H, CH $_3$ –, s), 2.92 (4H, –CH $_2$ –NH $_2$ , t), 3.67 (1H, –CH, q), 3.79 (4H, –CH $_2$ –OH, t)	
3	3242 (–NH, –OH st), 2545 (–NH $_2^+$ st), 1594 (–COO $^-$ as), 1594 (–NH $_2^+$ def), 1448 (–NH def), 1385 (COO $^-$ s), 1248 (–C–N– st), 1066 (–C–O– st) 3241, 2461, 1639, 1566, 1384, 1344, 1139, 1064	$\delta_{\text{H}}$ 3.22 (4H, –CH $_2$ –NH $_2$ , t), 3.87 (4H, –CH $_2$ –OH, t), 4.12 (2H, Cl–CH $_2$ –, s)	
4	3344 (–NH, –OH st), 2250 (–NH $_2^+$ st), 1622 (–NH $_2^+$ def), 1448 (–NH def), 1063 (–C–N– st), 939 (–C–O– st) 3344, 2116, 1622, 1448, 1063, 939	$\delta_{\text{H}}$ 3.27 (4H, –CH $_2$ –NH $_2$ , t), 3.89 (4H, –CH $_2$ –OH, t)	
5	3243 (–OH st), 2126 (–NH $^+$ st), 1570 (–COO $^-$ as), 1395 (COO $^-$ s), 1264 (–C–N– st), 1050 (–C–O– st) 3727, 1957, 1611, 1357, 1113, 1051	$\delta_{\text{H}}$ 1.28 (6H, CH $_3$ –CH $_2$ –, t), 1.99 (3H, CH $_3$ –CO, s), 3.03 (4H, –CH $_2$ –NH, q), 3.11 (2H, –NH–CH $_2$ , t), 3.87 (2H, –CH $_2$ –OH, t)	
6	3307 (–OH st), 2490 (–NH $^+$ st), 1594 (–COO $^-$ as), 1398 (COO $^-$ s), 1084 (–C–N– st), 924 (–C–O– st) 3728, 2385, 1633, 1365, 1038, 952	$\delta_{\text{H}}$ 1.23 (3H, CH $_3$ –, s), 1.34 (6H, CH $_3$ –CH $_2$ –, t), 3.09 (4H, –CH $_2$ –NH, q), 3.16 (2H, –NH–CH $_2$ , t), 3.65 (1H, –CH, q), 3.88 (2H, –CH $_2$ –OH, t)	

**Table 1** (continued)

IL	IR cm <sup>-1</sup>	Experimental Calculated	<sup>1</sup> H NMR
7	3361 (-OH st), 1950 (-NH <sup>+</sup> st), 1076 (-C-N- st), 928 (-C-O- st), 3728, 1648, 1412, 1052		$\delta_{\text{H}}$ 1.45 (6H, CH <sub>3</sub> -CH <sub>2</sub> -, t), 3.22 (4H, -CH <sub>2</sub> -NH, q), 3.31 (2H, -NH-CH <sub>2</sub> , t), 3.77 (2H, -CH <sub>2</sub> -OH, t)
8	3213 (-OH st), 2350 (-NH <sup>+</sup> st), 1567 (-COO <sup>-</sup> as), 1336 (COO <sup>-</sup> s), 1063 (-C-N- st), 916 (-C-O- st), 3385, 2056, 1603, 1330, 1036, 899		$\delta_{\text{H}}$ 2.03 (3H, CH <sub>3</sub> -CO, s), 2.90 (6H, -CH <sub>2</sub> -NH, t), 3.76 (6H, -CH <sub>2</sub> -OH, t)
9	3272 (-OH st), 2535 (-NH <sup>+</sup> st), 1602 (-COO <sup>-</sup> as), 1384 (COO <sup>-</sup> s), 1240(-C-N- st), 1050(-C-N- st), 3383, 2553, 1641, 1330, 1101, 1058		$\delta_{\text{H}}$ 3.05 (6H, -CH <sub>2</sub> -NH, t), 3.81 (6H, -CH <sub>2</sub> -OH, t), 4.15 (2H, Cl-CH <sub>2</sub> -, s)

The anion-cation interaction binding energies were determined by the formula:

$$\Delta E_{BE} = E_{IL} - E_{cation} - E_{anion} \quad (2)$$

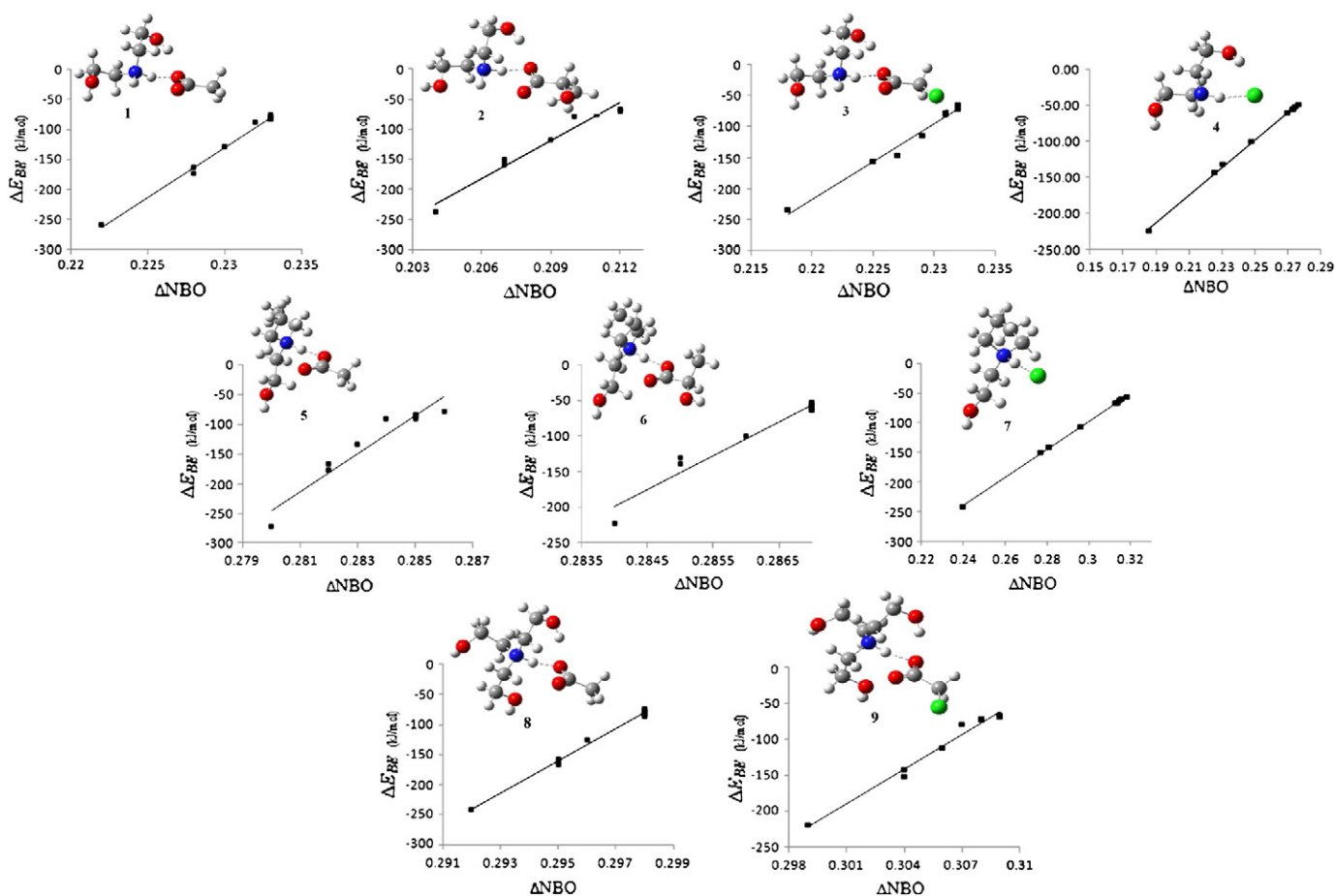
where  $E_{IL}$ ,  $E_{cation}$ , and  $E_{anion}$  represent the calculated enthalpies of the ionic liquid, cation, and anion, respectively, in different solvents.

### 3. Results and discussion

The series of nine ionic liquids: diethanolammonium acetate (**1**), diethanolammonium lactate (**2**), diethanolammonium chloroacetate (**3**), diethanolammonium chloride (**4**), *N,N* diethylethanolammonium acetate (**5**), *N,N* diethylethanolammonium lactate (**6**), *N,N* diethylethanolammonium chloride (**7**), triethanolammonium acetate (**8**), and triethanolammonium chloroacetate (**9**) was synthesized, starting from the corresponding ethanolamine derivative and acid (Scheme 1). Obtained ILs were investigated by IR and <sup>1</sup>H NMR spectroscopy, as well as by density functional theory. We explored the cation-anion interaction enthalpy and the influence of solvents with different dielectric constants on solvation energies.

On the basis of IR spectra it can be observed that stretching vibrations from NH<sub>2</sub><sup>+</sup> (for ILs **1–4** 2500–2250 cm<sup>-1</sup>) to NH<sup>+</sup> (for ILs **5–9** 2535–1950 cm<sup>-1</sup>) lie in the area characteristic for these groups (Table 1). Deformation vibrations from NH<sub>2</sub><sup>+</sup> are in anticipated area (1622–1582 cm<sup>-1</sup>) for this vibration, also. Existence of carboxylate anions in ILs **1–3**, **5**, **6**, **8**, and **9** is confirmed by the presence of the asymmetric stretching vibrations for this type of functional group (1637–1570 cm<sup>-1</sup>), as well as of symmetric vibrations (1411–1336 cm<sup>-1</sup>).

Since all examined ILs contain ethanolamine cation, these compounds are structurally very similar. Bearing in this fact mind, there are two possible binding sites for anions in all cations: hydrogen from N-H or O-H group (Fig. 1). On the basis of the <sup>1</sup>H NMR and



**Fig. 1.** The optimized structures of ILs and dependence of  $\Delta E_{BE}$  from the difference in NBO charges. The squared correlation coefficient in all cases was higher than 0.95.

IR spectra (Table 1), we concluded that the preferred binding pattern in the corresponding ammonium ion is *via* the N–H interaction.

The IR and  $^1\text{H}$  NMR spectra showed that investigated ILs are built of separated cations and anions. This was confirmed by performing density functional theory calculation, followed by comparison of the IR spectra obtained from the frequency calculation to those obtained by experiment. It was observed that, when acetate was employed as an anion (ILs 1, 2, 5, 6 and 8), the optimized structures of these ILs did not correspond to ionic, but neutral molecules consisting of corresponding amine and acetic acid. Namely, when the optimization was performed without any restrictions, the hydrogen atom originally placed between nitrogen of cation and oxygen of acetate anion was attracted by the acetate anion, resulting in neutral molecules. Since in the experimentally obtained IR and  $^1\text{H}$  NMR spectra the signals for the acetic anion and ammonium cation were present, we had to utilize a restriction based on the N–H bond fixation. In this way the ionic structures were achieved, and thus, good agreement between the experimental and calculated IR spectra (Table 1).

### 3.1. Behavior of ILs in different solvents

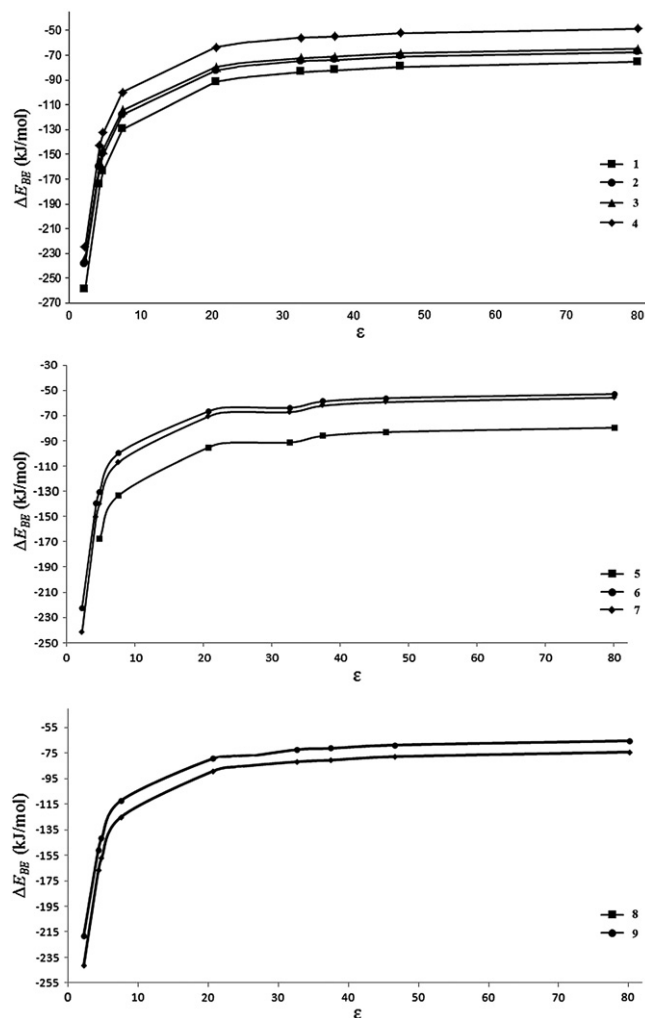
Our DFT calculations showed that distances between ions change with solvent polarity. It can be concluded that this is a consequence of the formation of hydrogen bonds with the molecules of solvents. Namely, as the dielectric constants of solvents increase, the distance between the ions of an investigated ILs also increases (H1–O1 or H1–Cl distances in Tables S1–S9). As a consequence, the N–H1 bond in the cations becomes stronger as solvent polarity increases (except for cases where the bond length is set to the fixed value). It is important to emphasize that in all investigated ILs, hydrogen bonds are present (Tables S1–S9). These hydrogen bonds are created between an anion and alkoxy or alkyl residue of a cation. The intensity of hydrogen bonding is noticeably strong when acetate, chloroacetate, and lactate are used as anions (ILs 1, 2, 3, 5, 6, 8, 9), but they are weaker when it comes to chloride anion (ILs 4, 7). With the employment of solvents, hydrogen bonds between ions become weaker with increase of solvent polarity.

The binding enthalpies ( $\Delta E_{BE}$ ) were calculated for both gas and liquid phases using Eq. (2). The obtained results are presented in Table 2 and Fig. 2. In all investigated cases, the  $\Delta E_{BE}$  values for liquid phases, independently of solvent polarity, are substantially higher than the corresponding  $\Delta E_{BE}$  values calculated for gas. In addition,  $\Delta E_{BE}$  increases with the increasing dielectric constant of applied solvents (Fig. 2). On the basis of these data it can be concluded that behavior of the cation–anion pairs of ILs depends on solvent nature. In cases where lower dielectric constant solvents are used (carbon tetrachloride, diethyl ether, chloroform) cation–anion interaction is kept to contact ion pair. When solvents with higher dielectric constants are employed (water, dimethyl sulfoxide, acetonitrile) the behavior of ILs approaches to that of solvent-separated ion-pair structures. These results are in agreement with the literature data [33].

The solvation energies ( $\Delta G_{solv}$ ) of ILs were calculated using Eq. (1), and are presented in Fig. 3. It can be seen that solvation energies decrease with the increase of solvent polarity. It should be noted that solvation process of investigated species is exothermic. On the basis of this, the ionic pairs of ILs are more stabilized in solvents with higher dielectric constant. This is in accordance with our former statement related to the ionic structure of investigated molecules.

**Table 2**  
Gas phase binding enthalpies for investigated ILs.

IL	$\Delta E_{BE}$ (kJ/mol)	IL	$\Delta E_{BE}$ (kJ/mol)	IL	$\Delta E_{BE}$ (kJ/mol)
1	–495.79	4	–463.91	7	–489.41
2	–458.82	5	–509.81	8	–461.01
3	–455.67	6	–438.43	9	–424.02



**Fig. 2.** The binding energies of ILs in solvents with different dielectric constants.

Also, it should be emphasized that the NBO charges carried by nitrogen of the cationic moiety and oxygen or chlorine of the anionic moiety slightly change with the solvent polarity. Namely, in accord with the behavior of ionic species, the mentioned atoms become more and more negative as the dielectric constant of solvents increases (Fig. S1). This provoked us to investigate possible connections between binding enthalpy of ions, as well as solvation energy, and the difference in NBO charges carried by nitrogen, oxygen, and chlorine. In all cases, both the difference in NBO charges and  $\Delta E_{BE}$  increases with the increase of solvents polarity. In this way, linear dependence between these two quantities is provided (Fig. 1). Dependence of  $\Delta G_{solv}$  on the difference in NBO charges is also linear (Fig. 4). It is worth pointing out that the correlation coefficient for all investigated ILs is higher than 0.99.

## 4. Conclusion

The structure of ethanolamine derived ILs 1–9 has been elucidated on the basis of IR and  $^1\text{H}$  NMR spectroscopy. These ILs were fully optimized using density functional theory in gas phase, as well as in series of solvents with different dielectric constants. Good agreement between the experimental and calculated IR spectra was achieved. It was established, on the basis of the BDE values and strength of hydrogen bonds, that cation–anion interactions in ILs are kept to contact ion pair in solvents with lower dielectric constants, whereas in solvents with higher dielectric constants the behavior of ILs approaches to that of solvent-separated ion-pair structures. Density functional

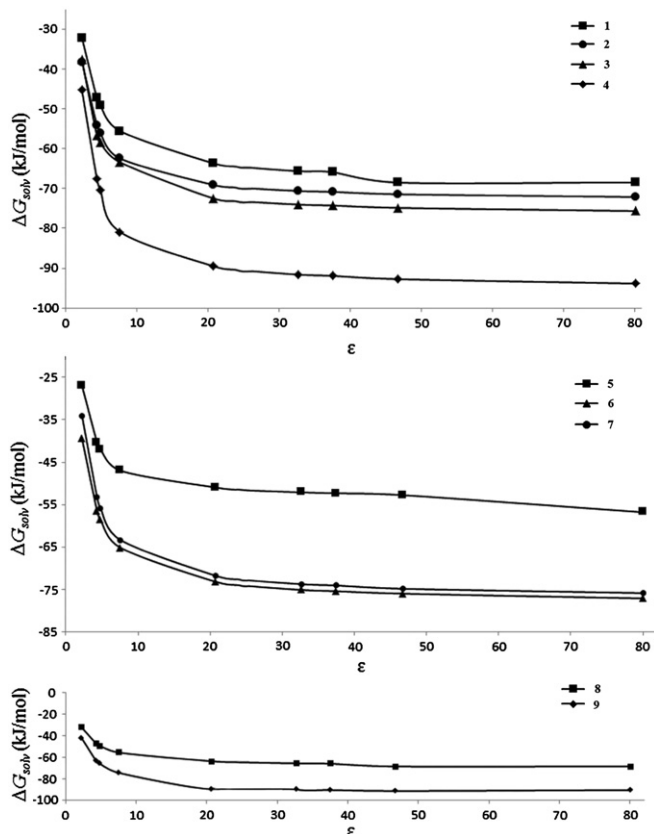


Fig. 3. The solvation energies of ILs in solvents with different dielectric constants.

studies showed that solvation energies decrease with the increase of solvent polarity. Therefore, the ionic pairs of ILs are more stabilized in solvents with higher dielectric constant.

**Acknowledgment**

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.molliq.2012.12.020>.

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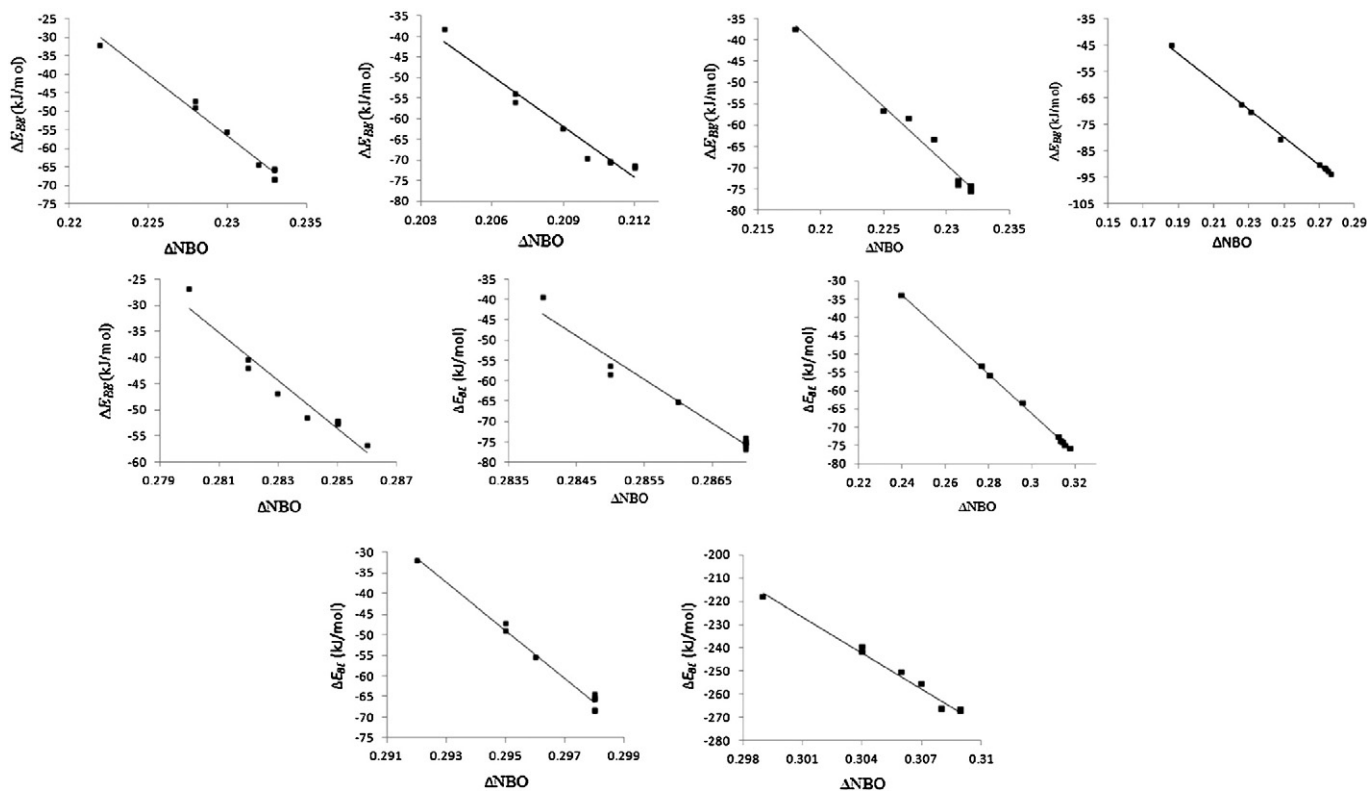


Fig. 4. Dependence of  $\Delta G_{solv}$  from the difference in NBO charges. The correlation coefficient in all cases was higher than 0.99.

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