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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}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.

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 ^1H 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 ^1H NMR spectra were run in $CDCl_3$ on a Varian Gemini 200 MHz spectrometer.

2.1. Preparation of ionic liquids

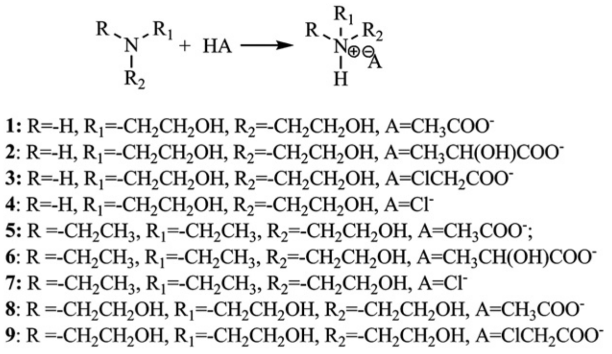
All investigated ILs (**1**–**9** in Scheme 1) were prepared by dropping the stoichiometric amount of corresponding carboxylic acid (acetic, lactic or chloroacetic acid) or hydrochloric acid to the dichlorometane-ethanole solution of corresponding amino alcohol (DEA, DEAE or TEA). The reaction mixture was stirred during 2 h at room temperature. After completion of the reaction, the resulting solution was washed with ethyl acetate (2×5 cm^3) and ethyl ether (2×5 cm^3). The organic solvents were evaporated under the reduced pressure. The residue was dried *in vacuo* at 50 °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 constrains, 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 ($\varepsilon=80.1$), dimethyl sulfoxide ($\varepsilon=46.7$), acetonitryle ($\varepsilon=37.5$), methanol ($\varepsilon=32.7$), ethanol ($\varepsilon=24.5$), tetrahydrofuran ($\varepsilon=7.58$), chloroform ($\varepsilon=4.81$), diethyl ether ($\varepsilon=4.33$), and carbon tetrachloride ($\varepsilon=2.44$). All calculated structures, in both phases, were 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:

$$\Delta G_{solv} = G_{solv} - G_{gas}. \tag{1}$$


1: R=-H, R_1=-CH_2CH_2OH, R_2=-CH_2CH_2OH, A=CH_3COO^-
2: R=-H, R_1=-CH_2CH_2OH, R_2=-CH_2CH_2OH, A=$CH_3CH(OH)COO^-$
3: R=-H, R_1=-CH_2CH_2OH, R_2=-CH_2CH_2OH, A=$ClCH_2COO^-$
4: R=-H, R_1=-CH_2CH_2OH, R_2=-CH_2CH_2OH, A=Cl^-
5: R =-CH_2CH_3, R_1=-CH_2CH_3, R_2=-CH_2CH_2OH, A=CH_3COO^-;
6: R =-CH_2CH_3, R_1=-CH_2CH_3, R_2=-CH_2CH_2OH, A=$CH_3CH(OH)COO^-$
7: R =-CH_2CH_3, R_1=-CH_2CH_3, R_2=-CH_2CH_2OH, A=Cl^-
8: R =-CH_2CH_2OH, R_1=-CH_2CH_2OH, R_2=-CH_2CH_2OH, A=CH_3COO^-
9: R =-CH_2CH_2OH, R_1=-CH_2CH_2OH, R_2=-CH_2CH_2OH, A=$ClCH_2COO^-$

Scheme 1. Synthesis of investigated ILs.

Table 1
Spectral characterization of the ionic liquids.

IL	IR cm^{-1} Experimental Calculated	^1H 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	δ_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	δ_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	δ_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	δ_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	δ_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	δ_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)