Calorimetric Study of Ionic Liquids Based on 4-Vinylbenzyl Triethylammonium with Chloride and Tetrafluoroborate Anion

M E Atlaskina, A N Markov, O V Kazarina

1 Nizhny Novgorod State Technical University n.a. R.E. Alekseev, Laboratory of Membrane and Catalytic Processes, 24 Minin str., 603950 Nizhny Novgorod, Russia

E-mail: atlaskina.m.e@gmail.com, markov.art.nik@gmail.com, olga_kazarina@list.ru

Abstract. In the present research, the temperature dependence of heat capacity of two ionic liquids VBTEA-Cl (1) and VBTEA-BF₄ (2) were studied. 4-Vinylbenzyl triethylammonium chloride was synthesized by original methodic. 4-Vinylbenzyl triethylammonium tetrafluoroborate was obtained via anion exchange reaction. Compounds was characterized by FTIR and NMR spectroscopies, their purity was proven. Compounds 1 and 2 were studied by different scanning calorimetry over the temperature range from 300 to 600 K. The melting point were determined for both substances, but 4-vinylbenzyl pyridine triethylammonium tetrafluoroborate wasn’t stable after melting in contrast with 4-vinylbenzyl pyridine chloride. The experimental data were used to calculate the enthalpy of phase transition (melting) for compound 1.

1. Introduction

Monomeric ionic liquids (ILs) due to their bifunctionality – the presence of a bulk anionic or cationic group and double bond able to polymerize, have an increasing interest for obtaining the new polymer materials with unique properties. The structure of anion or cation significantly affects on the physical and chemical properties as for monomeric ionic liquids themselves (viscosity, melting point, glass transition, solubility, reactivity) as well as polymers based on them [1]. Such polyelectrolytes can be used to create gas separation membranes, hydrophobic surfaces, antistatic and antibacterial coatings [2,3]. Membrane gas separation technologies are widely used due to their advantages: high selectivity, low energy consumption, and the ability to be used at low temperatures and moderate pressure [4,5]. Polymer ionic liquids with ammonium, imidazolium, and pyridinium cations are of particular interest, since membranes based on them represent an alternative to the traditional amine method of sorption and selective isolation of acid gases from gas mixtures [3,6]. In addition, polymer ionic liquids can be used as a selective membrane layer for separating metal ions [7] and in pervaporation [8]. This paper describes the synthesis of monomeric ionic liquids based on 4-vinylbenzyl chloride containing ammonium cation and chloride and tetrafluoroborate anions – as the potential candidates for creating polymeric membranes – and their physical properties measured by DSC.
2. Experimental

2.1. General remarks

The samples of compound were synthesized as described further. Air sensitive experiments were carried out under vacuum using standard Schlenk line techniques. Acetone, diethyl ether were dried using standard methodic, then distilled under reduced pressure and stored for at least 48 h over activated molecular sieves (4 Å) prior to use. Deionized water (DI) was used from Millipore Direct-Q3 water purification system with resistivity 28.7 MΩ•cm to NiCl2 solution, separated by centrifugation from solution and filtered with paper filter MACHEREY-NAGEL 1670 (density 85 g/m2).

NMR Spectroscopy. 1H NMR and 13C NMR spectra were recorded on an Agilent DD2 400 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) for the solution of compounds in D2O, DMSO-d6, with the residual peak of the solvent as an internal reference. J values are in hertz.

IR Spectroscopy. Samples were characterized by FTIR spectroscopy (IRrafinity-1 (Shimadzu, Kioto, Japan)) at ambient temperature and inert atmosphere of argon (99.9995 %) using the KBr pellet method. A 6 minimum of 30 scans was signal-averaged with a resolution of 4 cm⁻¹ at the 4000-400 cm⁻¹ range. All other parameters were not controlled and corresponded to the testing characteristics established by the manufacturer. Samples were milled in an agate mortar to a consistency providing minimal scattering effect in a potassium bromide matrix. In each case, the ratio of mixable components was chosen in such a way that a pellet absorbing in the corresponding spectral range with the minimum background absorption could be recorded. Samples for FTIR were prepared by cooperative pressing of resins and dehydrated. KBr powder at pressure 90 MPa under vacuum at 295 K.

2.2. Calorimetric measurements

A differential scanning calorimeter DSC 204 F1 Phoenix (Netzsch, Geraetebau, Germany) was used to investigate 1, 2, and solid solutions in the range of 300−600 K. The design of the DSC 204 F1 calorimeter and the measurement procedure were described previously [9]. The reliability of the calorimeter was checked by standard calibration experiments to measure the thermodynamic characteristics for the melting of cyclohexane, mercury, indium, tin, lead, bismuth, and zinc. Temperature and enthalpy of transitions were estimated according to Netzsch Software Proteus.18 The shape of DSC curves inside the temperature interval of transition depends on the composition of samples. The inaccuracy of temperature definition changes from ±1 K the inaccuracy of enthalpy definition 3%. The entropy of transition was not evaluated because of evident uncertainty of its determination. Measurements of thermophysical characteristics were conducted at an average rate of heating of a crucible containing the substance at 10 K/min in an argon flow of 20 mL/min. Most of the parameters were kept identical during all measurements: argon flow, initial temperature, heating rate, weight of the crucible and its cover, and the position of the crucible on the sensor.

2.3. Synthesis of VBTEA-Cl

The compound was synthetized by original solvent-free methodic as followed. 4-Vinylbenzyl chloride 10 mL (10.83 g, 0.064 mol) and 10 mL (7.26 g, 0.072 mol) of triethylamine were added into a 100 mL round bottom flask and bubbled with nitrogen during 30 min. The reaction was run at 60 °C with reflux for 1 h. Then, the heat was turned off and the solution was stirring overnight at room temperature under N2 protection. The resulting light-yellow solid was formed filtered, then washed with an excess of acetone to remove the traces of initial compounds and impurities and dried to the constant weight on vacuum. A white powder was obtained m =15.4 g (yield 95%).

1H NMR (400 MHz, D2O, δ in ppm): 7.63 − 7.60 (m, 2H, ArH), 7.52 − 7.49 (m, 2H, ArH), 6.85 (dd, J = 17.7, 11.0 Hz, 1H, CH=CH), 5.95 (dd, J = 17.7, 0.8 Hz, 1H, CH2=CH cis), 5.43 (dd, J = 11.0,
0.8 Hz, 1H, CH=CH trans), 4.40 (s, 2H, C₆H₅-CH₂-N), 3.24 (q, J = 7.3 Hz, 6H, N-CH₂-CH₃), 1.40 (t, J = 7.3 Hz, 9H, N-CH₃-CH₂). ¹³C NMR (101 MHz, δ in ppm): 139.49 (1C, 4°-C, C₆H₅), 135.60 (CH=CH₂), 132.62 (2C, CH, C₆H₅), 126.64 (2C, CH, C₆H₅), 126.37 (1C, 4°-C, C₆H₅), 116.12 (CH=CH₂), 59.43 (C₆H₅-CH₂-N), 52.06 (N-CH₂-CH₃), 6.91 (N-CH₂-CH₃). FT-IR (KBr), δ (cm⁻¹): 3428 (H₂O), 3073, 2996, 2975, 2943 (CH₂, CH), 1514, twin: 1631, 1606, 1482, 1464, 1411, 1398 (C = C).

**Synthesis of VBTEA-BF₄.** VBTEA-Cl (5.0 g, 0.020 mol) was solved into DI water (30 mL) in a 100 mL round-bottom flask with magnetic stirrer and bubbled with nitrogen during 30 min. At this time a solution of NaBF₄ (2.42 g, 0.022 mol) in deionized water (10 mL) was added drop wise to the aqueous phase, and the white solid is formed immediately. The reaction mixture was stirred under N₂ protection for 3 h. The solid was washed with DI H₂O (3x100 mL) and dissolved into dry acetone. The organic phase was dried over anhydrous MgSO₄, and the filtrate reduced by rotary evaporation. The remaining solvent was removed under vacuum lines to the constant weight. The resulting product was obtained as white solid, m = 5.58 g (yield 85 %).

¹H NMR (400 MHz, DMSO-d₆, δ in ppm): δ 7.64 – 7.55 (m, 2H, ArH), 7.53 – 7.43 (m, 2H, ArH), 6.80 (dd, J = 17.7, 11.0 Hz, 1H, CH=CH), 5.95 (dd, J = 10.9, 0.9 Hz, 1H, CH=CH cis), 4.45 (s, 2H, C₆H₅-CH₂-N), 3.15 (q, J = 7.2 Hz, 6H, NCH₂CH₃), 1.30 (t, J = 7.2 Hz, 9H, N-CH₂-CH₂). ¹³C NMR (101 MHz, DMSO-d₆, δ in ppm) 138.85 (1C, 4°-C, C₆H₅), 135.76 (CH=CH₂), 132.85 (2C, CH, C₆H₅), 127.20 (1C, 4°-C, C₆H₅), 126.64 (2C, CH, C₆H₅), 116.30 (CH=CH₂), 59.18 (C₆H₅-CH₂-N), 51.98 (N-CH₂-CH₃), 7.49 (N-CH₂-CH₃). FT-IR (KBr), δ (cm⁻¹): 3428 (H₂O), 3099, 3004, 2992, 2956 (CH₂, CH), 1519, twin: 1631, 1610, 1477, 1459, 1408, 1400 (C = C), 1062 (BF₄⁻).

3. **Results and discussion**

The syntheses of VBTEA-Cl (compound 1) was performed by Menshutkin reactions from tertiary amines and alkyl halogenides to quaternary ammonium salts via an SN₂ mechanism (Scheme 1). Reaction easily proceeds without solvent with a high yield of desired product.

![Scheme 1](image)

**Scheme 1**

VBTEA-BF₄ (compound 2) were easily obtained by anion exchange reaction (Scheme 2). Monomeric ionic liquids with halide anions (in particular, chloride anion) are universal precursors for the production for ILs with other anions due to their solubility in water and facility halide replacing. Anion exchange reactions proceeds in water, and product is usually insoluble in water. It forms precipitate or oily viscous liquid which can be easily separated from reaction mixture.

![Scheme 2](image)
Obtained compounds 1 and 2 were characterized by NMR spectroscopy. Their purity was established as 99% (less than 1% of impurities in NMR spectra, Figures 1 and 2). All compounds have a common fragment of the vinylbenzyl radical, so all proton spectra show signals of identical protons with similar chemical shifts. Thus, in the weak field region, aromatic protons of the benzene ring (doublets or multiplets in the region of 7.40 – 7.60 ppm), geminal (6.6 – 6.8 ppm) and terminal (5 – 6 ppm) protons of the vinyl group are found, splitting on each other and observed in the spectra as a rule in the form of a doublet of doublets in each case. In a weak field, a singlet of the methylene group (4 – 5 ppm) observed. Aliphatic protons of amino groups arise in the strong field.

**Figure 1.** $^1$H NMR spectrum VBTEA-Cl (400 MHz, D$_2$O).

**Figure 2.** $^1$H NMR spectrum VBTEA-BF$_4$ (400 MHz, dmsod$_6$).
Compounds 1 and 2 were characterized by IR spectroscopy. Anion exchange proceeding were proven by IR spectra. Figure 3 presents the FT IR spectra of the obtained compounds having ammonium cation VBTEA+ and Cl− and BF4− counter-anions. Comparing the spectra of produced 2 and initial 1 some shifts arise and new peaks appear. In these spectra, the band corresponding to the 4-vinylbenzyltriethylammonium cation is found between 2900–3100, 1400–1650 cm⁻¹. C-H band vibrations arise as 4 signals in range of 3000 cm⁻¹. Furthermore, the characteristic bands for the C = C stretching vibration from the benzene ring as a single peak at 1515 and twin peaks at 1620, 1470 and 1400 cm⁻¹ arise in both spectra. The anion exchange is observed by the appearance of the new bands – large peak at 1062 cm⁻¹ corresponding to the BF₄⁻ anion [10]. In addition, broad peaks near 3400 cm⁻¹ in some FTIR spectra are from moisture. After repeating several FT IR tests the peaks still exist. Although the IL samples are dried well before tests, they absorb water when exposed in air.

![Figure 3. IR Spectra of compounds 1 and 2.](image)

The phase transition (melting) of compounds 1 and 2 were studied by DSC. The sample information presented in Table 1. The samples were prepared according to the standard methods as described in experimental part.

| Sample         | Source           | State         | Molar Fraction | Analysis methods                  |
|----------------|------------------|---------------|----------------|-----------------------------------|
| [VBTEA]Cl      | Synthesis here   | White solid   | 0.99           | NMR and IR spectroscopy           |
| [VBTEA][BF₄]   | Synthesis here   | White solid   | 0.99           | NMR and IR spectroscopy           |

The DCS curve of 1 shown on Figure 4. In temperature range 300 – 600 K the endothermic peak dedicated to the phase transition (melting) exist. The temperature range is ΔT = 436–491 K. The enthalpy of phase transition is -149.8 kJ/mol. The compound has a significant thermal stability: it is not decomposed up to 600 K.
Figure 4. DCS curve of compound 1.

The DCS curve of 2 shown on Figure 5. The different behavior of compound was observed. In temperature range 300–400 K the endothermic peak dedicated to the phase transition (melting) exist. The melting starts at $T = 391$ K but then decomposition of compound proceeds. Because the sample is decomposed during the melting enthalpy of phase transition could not be calculated.

Figure 5. DCS curve of compound 2.

Thus, the anion plays a critical role and affect on thermal behavior of ionic compounds. More stable compound 1 can be used in wide range of temperatures whereas compound 2 is more sensible to the temperature changing.
4. Summary
In the present research the calorimetric study in temperature range from 300 to 600 K of two synthesized ionic liquids VBTEA-Cl (1) and VBTEA-BF₄ (2) was discussed. 4-Vinylbenzyl triethylammonium chloride was obtained by original solvent free methodic, allows to achieve 95 % yield. 4-Vinylbenzyl triethylammonium tetrafluoroborate was obtained via anion exchange reaction. Characterization and purity detection of compounds were carried out by FTIR and NMR spectroscopies. The melting point were determined for both substances, but 4-vinylbenzyl pyridine triethylammonium tetrafluoroborate wasn’t stable after melting in contrast with 4-vinylbenzyl pyridine chloride. The enthalpy of melting for compound 1 was found: \(-149.8 \text{ kJ/mol}\). The difference of thermal behavior between compounds 1 and 2 is explained by significant anion role in IL.

5. References
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