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# Application of the Interstice Model to Structure Characterization of 1-Butyl-3-methylimidazolium Acetate

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**Abstract**—The structure of ionic liquid 1-butyl-3-methylimidazolium acetate was characterized by experimental physical parameters and on the basis of the interstice model.

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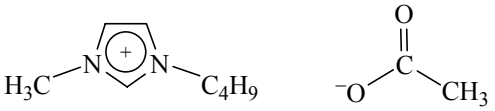
Basic principles of ecologically pure chemistry ("green chemistry") imply exclusion of the use of ecologically hazardous solvents in chemical processes. One of the most extensively developing lines of studies aimed at solving the above problem is synthesis and application of ionic liquids. The latter possess such unique properties as low vapor pressure, wide liquid range, and high specific solvating power [1]. Nevertheless, a number of fundamental parameters characterizing properties and structure of ionic liquids were not determined so far.

The goal of the present work was to determine parameters of structural organization of a low-temperature hydrophilic ionic liquid, 1-butyl-3-methylimidazolium acetate.



*M* 198.27; η = 393.3 (25°C), 22.4 mPa s (80°C); $d$ = 1.0550 (25°C), 1.0192 g/cm$^3$ (80°C); mp < –20°C; electrochemical window –2.3/+0.8 V; Cl 0.34%, $H_2O$ 1.0%.

The most important characteristics of chemical compounds are temperature dependences of such physical parameters as refractive index $n_D$, density $d$, and surface tension σ. We previously showed [2] that the refractive index and the density of 1-butyl-3-methylimidazolium acetate linearly decrease as the temperature rises in the range from 298 to 328 K. Analogous dependence was found for the surface tension. Its temperature dependence is described by Eq. (1):

$$\sigma(T) = a - bT. \quad (1)$$

Here, $b$ characterizes the surface excess entropy ($S_s$) which does not depend on the temperature, and the constant $a$ is related to surface excess energy ($E_s$). The surface excess entropy $S_s$ and energy $E_s$ for 1-butyl-3-methylimidazolium acetate are 0.1036 mJ m$^{-2}$ K$^{-1}$ and 76.6 mJ m$^{-2}$, respectively, and are typical of imidazole derivatives with short-chain alkyl substituents [3]. The thermal expansion coefficient of pure 1-butyl-3-methylimidazolium acetate, $\alpha = 5.2\times10^{-4}$ K$^{-1}$, was determined using Eq. (2):

$$\alpha = (1/V)(dV/dT)_P = -(d\ln d/dT)_P, \quad (2)$$

where $V$ is the molar volume of 1-butyl-3-methylimidazolium acetate. The temperature dependence of its density is given by Eq. (3) (the mean-square deviation $s$ is $8.1\times10^{-5}$):

$$\ln d = 56.2\times10^{-3} - 0.52\times10^{-3}(T - 298). \quad (3)$$

The molecular volume of 1-butyl-3-methylimidazolium acetate was calculated by Eq. (4) from the experimental density $d$ at 298 K:

$$V_m = M N^{-1} d^{-1} = 0.3112 \text{ nm}^3, \quad (4)$$

where $M$ is the molecular weight, and $N$ is the Avogadro number.

Glasser and Jenkins [4] found a linear relation between the standard entropy $S^0$ and molecular volume $V_m$, which is described by Eq. (5); it was successfully applied to ionic liquids [5].

$$S^0 = 1246.5_m + 29.5. \quad (5)$$

The standard entropy for 1-butyl-3-methylimidazolium acetate is $S°$ = 417.4 J mol$^{-1}$ K$^{-1}$.

The structure of 1-butyl-3-methylimidazolium acetate as ionic liquid was characterized in terms of the interstice model [6] on the basis of its physical parameters (see table).

The main provisions of the theoretical models are the following: (1) ions constituting a ionic liquid should have a large size and asymmetric shape, so that their tight packing should be impossible, and a large number of interstices between ions should exist; (2) in the calculation of molar volume, interstices in the structure of ionic liquids are treated as bubbles; (3) $2N$ interstices per mol of a 1 : 1 ionic liquid is assumed ($N$ is the Avogadro number); (4) interstices in ionic liquids are capable of moving like ions or other species; (5) while moving, interstices do not disappear, but may expand or contract (this behavior of interstices is called breathing motion).

To quantify the interstice theory, it is necessary to derive an expression for the calculation of the average interstice volume (ν) [Eq. (6)] and the overall interstice volume (Σν) [Eq. (7)]:

$$\nu = 0.6791(kT/\sigma)^{3/2}, \quad (6)$$

where $k$ is the Boltzmann constant;

$$\Sigma\nu = 2N\nu. \quad (7)$$

The molar volume of 1-butyl-3-methylimidazolium acetate was calculated using Eq. (8), and the average interstice radius, using Eq. (9):

$$V = 3N\nu/\alpha T; \quad (8)$$

$$\alpha = 4\pi r/kT. \quad (9)$$

Thus, on the basis of the theoretical interstice model we determined structural parameters of a ionic liquid, 1-butyl-3-methylimidazolium acetate (see table). Our experimental results are very consistent with those found for most substances characterized by a 10–15% increase in volume upon phase transition from the solid state to liquid, and they demonstrate applicability of the interstice model for structure characterization of 1-butyl-3-methylimidazolium acetate.

## EXPERIMENTAL

The surface tension was measured by the forced bubble (Rebinder) method [7] and was calculated by formula (10):

$$\sigma_x = Kh_x. \quad (10)$$

Here, $h_x$ is the height of the liquid column, corresponding to bubble detachment, and $K$ is a constant intrinsic to the measurement setup; the latter is calculated by formula (11) using a liquid whose surface tension is known:

$$K = \sigma_0/h_0. \quad (11)$$

Here, $\sigma_0$ and $h_0$ are, respectively, the surface tension and the height of column of reference liquid; as the latter we used distilled water.

Physical and structural parameters of 1-butyl-3-methylimidazolium acetate

| Parameter | Value |
|---|---|
| Surface excess entropy $S_s$, mJ m$^{-2}$ K$^{-1}$ | 0.1036 (0.0783)[a] |
| Surface excess energy $E_s$, mJ m$^{-2}$ | 76.60 (69.20)[a] |
| Thermal expansion coefficient $\alpha \times 10^{-4}$, K$^{-1}$ | 5.20 (5.24)[b] |
| Molecular volume $V_m$, nm$^3$ | 0.3112 (0.3190)[b] |
| Standard entropy $S^0$, J mol$^{-1}$ K$^{-1}$ | 417.40 (427.10)[b] |
| Average interstice volume $\nu \times 10^{24}$, cm$^3$ | 18.29 (16.54)[b] |
| Overall interstice volume Σν, cm$^3$ | 22.03 (23.40)[b] |
| Interstice volume fraction $\Sigma\nu/V$ | 0.11 (0.12)[b] |
| Molar volume of ionic liquid $V$, cm$^3$ | 214.40 |
| Average interstice radius $r \times 10^7$, cm | 0.61 |

[a] In parentheses are given the data for 1-butyl-3-methylimidazolium hexafluorophosphate(V) [3]. [b] In parentheses are given the data for 1-ethyl-3-methylimidazolium ethyl sulfate [6].

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