CONDUCTIVITY AND VISCOSITY OF TETRAMETHYLAMMONIUM BIS(SALICYLATO)BORATE IN SOLUTIONS OF APROTIC DIPOLAR SOLVENTS

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Our studies of quaternary ammonium bis(chelato)borate Me_4NBSB in DMFA and DMAA showed that depending on the solvent obtained electrolytes may exhibit different properties. For the design of an electrolyte with desired properties the structural and chemical properties of salt and solvent and the possibility of chemical interaction leading to the formation of solvatocomplex compounds should be taken into account.

Supercapacitors are permanently under research and design, being practically ideal electric energy accumulators. Electrolytes in such systems play an important role associated with the expansion of the potential range in which the electrochemical system is stable and can increase its specific energy due to the formation of sandwich structures [1]. The main requirements to modern electrolytes used in such systems are high ionic conductivity and high ion transport numbers in a wide temperature interval, resistance to mechanical, thermal, and electrochemical actions, and compatibility with the electrodes [2–5].

As an example, a solution of Et_4NBF_4 in acetonitrile meets these requirements to the best extent [1–3]. It exhibits high electrochemical stability (~2.8 V on carbon) [1] and high thermal stability in a wide temperature range (up to 320°C) [2]. However, it has a number of drawbacks: high cost, toxicity, and corrosion activity with respect to electrode materials [2]. Bis(chelato)borates of quaternary ammonium cations [3] were suggested as an attempt to eliminate the above drawbacks. These compounds exhibit sufficiently high thermal stability [up to ~220°C in the case of $Et_4NB(C_2O_4)_2$], but are inferior to Et_4NBF_4 in electrochemical properties. Methods were suggested for decreasing the toxicity of these electrolytes by introducing such complex anions as chelatoborates.

So, up-to-date electrolytes for supercapacitors based on bis(chelato)borates of quaternary ammonium cations are extensively studied [1-10]. Their electrochemical activity only slightly depends on the kind of the cation and is limited by low solubility of the salts in organic solvents [3]. Recently, it has been shown that the solubility of such salts could be enhanced with the application of microwave method of synthesis [7]. The latter, according to [8], are recommended as a protective additive in electrolytes for lithium-ion batteries for enhancing the anticorrosion action, protection of aluminum slip rings and other metal parts of battery.

The aim of current study was to determine the dependence of electrical conductivity of tetraalkilamonium bis(chelato)borates on temperature and viscosity in solvents of different structure for implementation of electrode design.

Research methodology

The synthesis of tetraalkilamonium bis(chelato)borate (Me$_4$NBSB) was performed by heating aqueous solution of tetramethyl hydroxide, boric and salicylic acid. The resulting compound was dried in a vacuum at a temperature of 110 ± 10 ^{0} C, recrystallized from isopropyl alcohol and then was again dried in a vacuum under the same conditions. Solvents were dried by standard methods and distilled in high vacuum.

The conductivity was determined by electrochemical impedance spectra (EIS) analysis on their active input. The EIS spectra were recorded in the two electrode cell with 1 cm^2 platinum electrodes spaced by 1 cm using the Autolab - 30 electrochemical module (PGSTAT301N Metrohm Autolab) equipped with FRA (Frequency Response Analyzer) unit within the range of $10^{-2} \div 10^6$ Hz. The module was controlled by Autolab 4.9 software according to the standard procedure with further data processing in Zview 2.0.

Kinematic viscosity was measured in the capillary viscometer DAW - 1 and DAW - 4 on leakage time in a thermostatted conditions (temperature control accuracy of ± 1^{0}C). Solutions were prepared in sealed box at a relative humidity of 8 ÷ 10% at 10 ^{0}C. While measuring the protection against excessive humidity was supported by CaCl$_2$ tube.

Based on the relevance of studies, a sample of synthesized salt was dissolved in a standard set of solvents and transport properties of obtained electrolytes were studied.

Obtained results show (Fig. 1) that at equal concentrations of Me$_4$NBSB the solutions viscosity correlates with the viscosity of solvents - DMAA and DMFA. The viscosity of the Me$_4$NBSB solution in propylene carbonate and acetonitrile are sharply different from the viscosity of pure

solvents which have practically the same viscosity, close in chemical nature and similar in size.
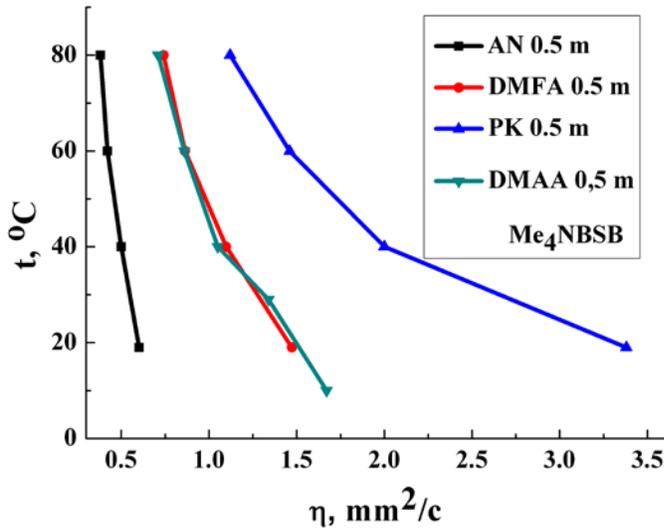
Fig. 1. The dependence of Me4NBSB solution viscosity in various aprotic dipolar solvents on temperature

Taking into account the Navier-Stokes equations, electrolyte density dependences on temperature and empirical temperature correlation of the density and viscosity (eq. 1, [11]) some differences of interaction between salt and solvents were found.

$$\eta = \eta_0 \exp(-\frac{E}{k(T+T_0)}, \tag{1}$$

where η is the viscosity of electrolyte at temperature T; η_0 is the viscosity of electrolyte at reference temperature T_0; k is the Boltzmann constant.

Particulary, when DMFA is used as a solvent, the electrolyte conductivity is formed by the solvent (Fig. 2), and in the case of dimethylacetamide (DMAA) the behavior of the system does not depend on temperature. It has a linear dependence, not like an exponent (Fig. 3). So, according to the deviations from the Walden – Pisarzhevsky rule

$$\lambda_{0i}\eta = \frac{Ze_0F}{6\pi r_i} = const \tag{2}$$

λ_{0i} is the equivalent conductivity, η is the viscosity of electrolyte, Z is the charge, F is the Faraday constant, r_i is the ion radius.

The formation of large quasi - spherical particles is confirmed and for such particles the ratio of Stokes fits much better [12]. In the system Me4NBSB - 0.5 M DMAA the high probability exists for the formation of some complex with charge transfer (with increasing temperature viscosity decreases

evenly). In the solution of Me₄NBSB in DMAA the viscosity increases with increasing concentration (Fig. 4) what supposes no complex compounds.
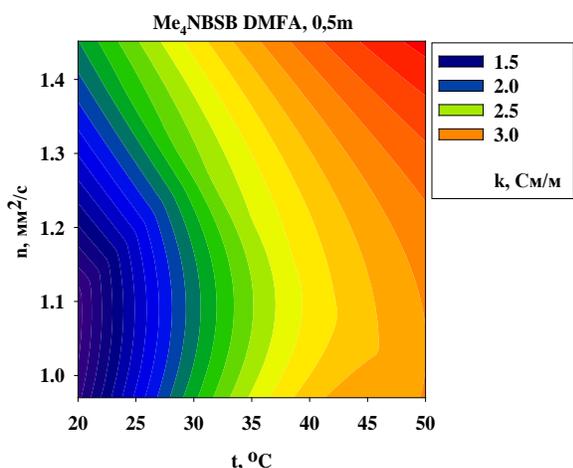
Fig. 2. Energy chart temperature - viscosity - conductivity for Me₄NBSB in 0.5 M DMFA
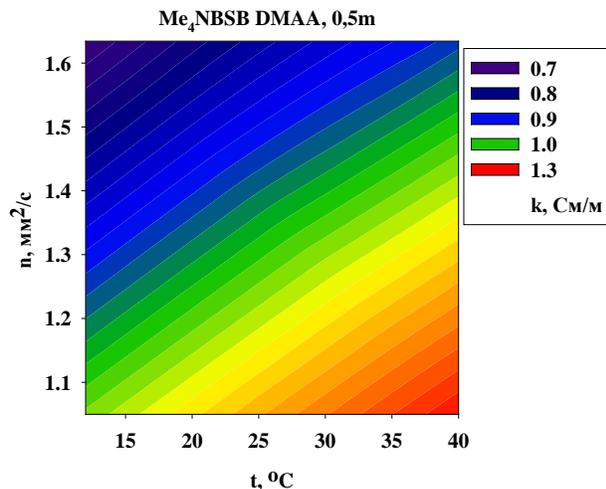
Fig. 3. Energy chart temperature - viscosity - conductivity for Me₄NBSB in 0.5 M DMAA
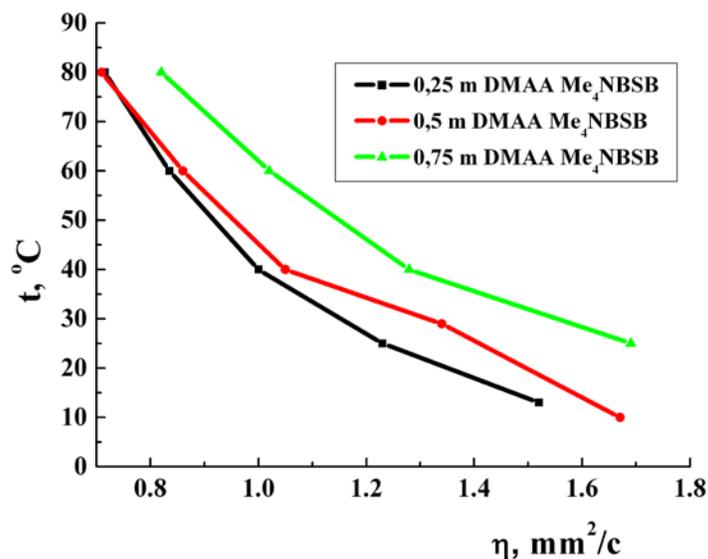
Fig. 4. Dependencies of viscosity on temperature in the solution of Me₄NBSB of different concentrations in DMAA

Conclusions

Thus, depending on the solvent nature, the salt Me₄NBSB may exhibit different properties in the solution. So, for the electrolyte with desired properties the structural and chemical properties of salt and solvent and the possibility of chemical interaction leading to the formation of solvatocomplex compounds should be taken into account.

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