



Ionic molar volumes in methanol mixtures with acetonitrile, N,N-dimethylformamide and propylene carbonate at $T = 298.15$ K



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ABSTRACT

The densities of dilute solutions of three electrolytes (NaI, NaBPh₄ and Ph₄PI) in methanol mixtures with propylene carbonate (PC), N,N-dimethylformamide (DMF) and acetonitrile (AN) have been measured by Anton Paar 5000 densimeter at $T = 298.15$ K. Apparent molar volumes, V_{ϕ} have been determined at an electrolyte concentration of $0.06 \text{ mol} \cdot \text{kg}^{-1}$ over the entire mixed solvent composition range. Single ionic apparent molar volumes of transfer, $\Delta_r V_{\phi}(\text{ion})$ were calculated using the tetraphenylphosphonium tetraphenylborate (TPTB) assumption. The results are discussed in terms of ionic preferential solvation.

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1. Introduction

Volumetric functions as the derivatives of chemical potential in relation to pressure play important role in the understanding of interactions in investigated system. For this reason the analysis of the discussed functions concerning liquid mixtures provides valuable information about the interactions between the molecules of mixture components. In the case of electrolyte solutions, the examination of volumetric functions makes possible to analyze the influence of solvent properties on the interactions between ions in solutions and between ions and molecules of the binary solvent.

Systematic studies of thermodynamic properties of electrolyte solutions in binary organic solvents have been carried out in our laboratory for many years [1]. We investigated widely the dissolution enthalpies of electrolytes in organic mixtures containing N,N-dimethylformamide (aprotic, proton-acceptor, non-hydrogen bonded solvent) or acetonitrile, which molecules, in contrast to the mentioned above solvent, are not able to form H-bonds in “classical” sense neither as a proton-donor nor as proton-acceptor. In order to get more complete picture of these systems the calorimetric data were supplemented by the results of volumetric investigations, e.g. [2]. The results were discussed from the point of view of the effect of the mixed solvent properties on observed behavior

of the solutions. The organic mixtures containing methanol (protic, hydrogen bonded solvent) are another group of binary solvents we were interested in. Earlier we examined the heat capacities and volumetric properties of mixtures of methanol with organic solvents [3,4], as well as we and our colleagues from laboratory measured the dissolution enthalpy of electrolytes in some of these mixtures [4–6]. In the present work the volumetric properties of NaI solutions in the mixtures of methanol with propylene carbonate, N,N-dimethylformamide and acetonitrile are reported. The analysis of interactions between the solvent molecules and single ions requires the examined thermodynamic functions to be divided into the ionic contributions. To this goal the method based on the assumption about equality of thermodynamic functions of solvation of tetraphenyl-phosphonium (Ph_4P^+) cation and tetraphenylborate anion (BPh_4^-) (so called TPTB method) [7,8] was applied. However, due to the weak solubility of tetraphenylphosphonium tetraphenylborate the apparent molar volumes of NaBPh₄, Ph₄PI and NaI were used for these calculations.

As we were interested mainly in the course of dependence of volumetric functions of ions vs. the mixed solvent composition, following the work of Atkins and coworkers [9] as well as our earlier work [10] we decided to examine the apparent molar volumes at one defined low concentration of electrolyte rather than the partial molar functions which are more difficult for precise determination. We chose molality of $m = 0.06 \text{ mol} \cdot \text{kg}^{-1}$ which corresponds to the recommended in the mentioned papers value in molar concentration $c = 0.05 \text{ mol} \cdot \text{dm}^{-3}$.

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2. Experimental

The chemicals used in this work, their source and purity are collected in [table 1](#).

Methanol, acetonitrile, propylene carbonate and N,N-dimethylformamide were dried prior to distillation, using freshly activated molecular sieves 3A type. All solvents were stored in a glove box in a dry atmosphere and were degassed before use.

Sodium iodide was dried and stored at $T = 333.15$ K. Sodium tetraphenylborate and tetraphenylphosphonium iodide were dried for several days over phosphorus pentoxide under vacuum at the acetone boiling point. The salts were protected against light.

The mixtures and the solutions of electrolytes were prepared by mass with an accuracy of $\pm 2 \cdot 10^{-8}$ kg using a Sartorius RC 210D balance. All operations before weigh were performed in dry atmosphere in the glove box.

Densities d were measured using the Anton Paar 5000 densimeter with an accuracy of $\pm 5 \cdot 10^{-3}$ kg · m⁻³ and a reproducibility $\pm 1 \cdot 10^{-2}$ kg · m⁻³ (as given by the manufacturer). Prior to each measurement series the densimeter was calibrated by measuring the density of triply distilled water ($d_{298.15} = 997.043$ kg · m⁻³, $p = 1$ bar) and dry air ($d_{298.15} = 1.169$ kg · m⁻³, $p = 1$ bar). The density measurements of electrolyte solutions were carried out within the whole composition range of mixed solvent at $T = (298.15 \pm 0.01)$ K. The temperature stability, according to producer information was $T = \pm 0.001$ K.

The densities of the examined electrolyte solutions, with concentration 0.06 mol · kg⁻¹ (within the precision $\pm 10^{-4}$ mol · kg⁻¹), were determined for (8 to 11) independent measurements. Each time these densities were measured in relation to the density of a mixture with a specified molar composition used as a solvent for electrolyte.

3. Results and discussion

3.1. Apparent molar volume of electrolyte

The measured densities of pure solvents are listed with corresponding literature data in [table 2](#). The agreement between our data and those obtained by other authors is a very good.

The apparent molar volumes of the electrolytes in solution, V_ϕ were calculated from the following formula:

$$V_\phi = M_2/d - (d - d_0)/mdd_0, \quad (1)$$

where: M_2 – the molar mass of the electrolyte (kg · mol⁻¹), m – the molality of the electrolyte (mol · kg⁻¹), d – the density of electrolyte solution (kg · m⁻³) and d_0 – the density of the solvent (kg · m⁻³).

The apparent molar volumes of the examined electrolytes were calculated as above for an electrolyte molality of 0.06 mol · kg⁻¹. The values of apparent molar volumes presented in [table 3](#) are the mean of V_ϕ values calculated for several independent measurements of density of electrolyte solutions.

As we are more interested in the trends of V_ϕ values on the mixed solvent composition than in their absolute values, our

TABLE 1
Sample table.

Chemicals	Source	Purity ^a
Methanol (MeOH)	Chempur	≥0.99
Acetonitrile (AN)	Lab-Scan	≥0.999
Propylene carbonate (PC)	Aldrich	≥0.997
N,N-dimethylformamide (DMF)	Aldrich	≥0.998
Sodium iodide (NaI)	Aldrich	≥0.995
Sodium tetraphenylborate (NaBPh ₄)	Fluka	≥0.995
Tetraphenylphosphonium iodide (Ph ₄ PI)	Fluka	≥0.990

^a Assay in mass fraction.

TABLE 2

Densities of examined pure solvents including literature data at temp. 298.15 K.

Solvent	d_0 /(kg · m ⁻³)	d_0 lit./ (kg · m ⁻³)
MeOH	786.580 ± 0.017	786.475 ^d 786.60 ^b 786.65 ^c 786.707 ^d
AN	776.615 ± 0.013	776.514 ^e 776.614 ^f 776.65 ^g
DMF	943.974 ± 0.011	943.289 ^h 943.840 ⁱ 944.09 ^j
PC	1199.488 ± 0.015	1199.390 ^e 1199.51 ^k 1199.63 ^b

^a Reference [8].

^b Reference [3].

^c Reference [14].

^d Reference [15].

^e Reference [2].

^f Reference [16].

^g Reference [17].

^h Reference [18].

ⁱ Reference [19].

^j Reference [20].

^k Reference [21].

analysis concerns the molar volumes of transfer $\Delta_t V_\phi$ of the electrolyte from methanol to {methanol + cosolvent} mixtures defined as:

$$\Delta_t V_\phi = V_\phi(\text{Mix}) - V_\phi(\text{MeOH}), \quad (2)$$

where $V_\phi(\text{Mix})$ and $V_\phi(\text{MeOH})$ are the electrolyte apparent molar volumes in the mixed solvent and in pure methanol, respectively.

[Figures 1–3](#) show the $\Delta_t V_\phi$ of the electrolytes from methanol to the mixtures examined here as a function of the mixed solvent composition.

In general, the shapes of analyzed function for NaBPh₄ and NaI solutions in the mixtures of methanol with PC and DMF are similar ([figures 1–3](#)). They exhibit a sharp growth of the $\Delta_t V_\phi$ values with increasing co-solvent content up to ca. 0.4 mol fraction. This growth is more pronounced in the case of NaBPh₄ solution. In the further range of the mixed solvent composition the course of the analyzed curves is almost flat. The observed course of the $\Delta_t V_\phi = f(x_2)$ curves for the examined NaI and NaBPh₄ salts suggest that in these mixtures the sodium cation is preferentially solvated by DMF and PC molecules. This suggestion is consistent with the findings from thermochemical investigations carried out in our laboratory [5,6].

The solutions of Ph₄PI in these mixtures behave somewhat differently. In methanol rich region (ca. $x_2 = 0.05$) the small additives of the cosolvent ([figures 1 and 2](#)) does not change the $\Delta_t V_\phi$ (Ph₄PI) values. It seems to be worthy of notice that in the same composition range of the {MeOH + PC} mixture a minimum of excess partial molar volume, V_2^E as well as a maximum of excess partial molar heat capacity, C_{p2}^E of propylene carbonate was observed [3], which was explained as a result of the most ‘compact’ methanol structure by the molecules of added propylene carbonate having the high dipole moment value ($\mu = 4.94$ [11]).

In the {MeOH + AN} system ([figure 3](#)) the values of the $\Delta_t V_\phi$ of examined salts are the smallest in comparison with those observed in two other mixtures under study. Moreover, the values of $\Delta_t V_\phi$ for the organic salts exhibit a growth in the range of small acetonitrile content and almost flat course in further range of the mixed solvent composition, while the values of the $\Delta_t V_\phi$ for NaI are near to zero within the concentration range $x_{AN} = 0$ to 0.70, and then they decrease becoming clearly negative in acetonitrile rich region.

The high positive V_ϕ values of organic salts (NaBPh₄ and Ph₄PI) are the result of their low density of surface charge. This means that their interactions with solvent molecules are weak, and their large intrinsic volume cause significant increase of solution volume. It should be noted that $\Delta_t V_\phi$ values of electrolytes in mixtures containing AN are significantly smaller than those in the mixtures with DMF and PC. It’s worth noting also that the discussed values are the highest in {MeOH + PC} mixtures in the range of high PC content. As no evidence of anion solvation by PC mole-

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