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The Heat Capacity and Density of Solutions of Barium and Tetrabutylammonium Iodides in N-Methylpyrrolidone at 298.15 K

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Abstract—The heat capacity and density of solutions of barium and tetrabutylammonium iodides in N-methylpyrrolidone (MP) were studied at 298.15 K by calorimetry and densimetry. The standard partial molar heat capacities and volumes ($\overline{C_{p2}^{\circ}}$ and $\overline{V_2^{\circ}}$) of the electrolytes in MP were calculated. The standard heat capacities $\overline{C_{pi}^{\circ}}$ and volumes $\overline{V_i^{\circ}}$ of the Ba^{2+} and $(C_4H_9)_4N^+$ ions in solution in MP at 298.15 K were determined. With the tetrabutylammonium ion, these values were in agreement with those calculated on the basis of the tetraphenylarsonium–tetraphenyl borate and tetraphenylphosphonium–tetraphenyl borate assumptions. The results are discussed in relation to the special features of solvation in solutions of the salts studied.

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INTRODUCTION

This work continues systematic studies of solutions of electrolytes and nonelectrolytes in the aprotic dipolar solvent N-methylpyrrolidone (MP). We studied the heat capacities and volume properties of 1–1 electrolytes in MP in [1–4]. Studies of electrolytes of another valence type and salts containing organic ions, such as tetraalkylammonium ions, which differ from typical inorganic ions by large sizes and small electric charge surface densities, are of certain interest. We selected barium and tetrabutylammonium iodides as objects of study. These salts are fairly well soluble in MP.

EXPERIMENTAL

MP of ch. (pure) grade was dried over molecular sieves 4A and doubly distilled in a vacuum. The content of water in MP determined by titration according to Fischer did not exceed 0.02 wt %. Anhydrous BaI_2 was prepared from barium iodide dehydrate of kh. ch. (chemically pure) grade. It was doubly recrystallized from doubly distilled water and dried at 383–413 K for 24 h. Tetrabutylammonium iodide of ch. d. a. (pure for analysis) grade was doubly recrystallized from acetone and dried at 353–363 K in a vacuum for 10–12 h. Solutions were prepared in a dry box, which completely excluded contact between substances and air moisture.

The heat capacities of solutions (C_p) were measured on a hermetic isothermic-shell calorimeter with a platinum resistance thermometer as a temperature sensor [5]. The errors in C_p measurements were no more than $\pm 1 \times 10^{-3}$ J/(g K). The densities of solutions (ρ) were measured on a precision pycnometric unit [6]. The errors in density measurements were $\pm 2 \times 10^{-5}$ g/cm^3.

RESULTS AND DISCUSSION

The results of C_p and ρ measurements are listed in Table 1. The concentration dependences of C_p and specific volumes V of solutions of BaI_2 and $(C_4H_9)_4NI$ in MP and a 1–1 electrolyte (RbI) in MP (for comparison, according to [1]) are shown in Fig. 1. It follows from these plots that C_p and V decrease as the concentration increases for these electrolytes, as for the majority of inorganic salts. The $C_p(V) = f(m)$ dependences, however, have special features for each type of electrolytes. Compared with solutions of RbI, the properties of solutions of $(C_4H_9)_4NI$ change to a much lesser extent, and those of solutions of BaI_2, to a greater extent as the concentration varies. Two effects influence the properties of solutions. On the one hand, bonds between solvent molecules get broken under the action of the electrostatic field of ions, which increases the heat capacity and volume of solutions. On the other hand, solvent molecules become oriented around ions, and solvation sheaths are formed, which is accompanied by a decrease in heat capacity and volume [7–9] and electrostriction, that is, solvent compression, which also decreases volume [9–11]. The second effect predominates in solutions of BaI_2, because the doubly charged Ba^{2+} ion, first, is in our view capable of forming the sec-

Table 1. Mean heat capacity (C_p, J/(g K)) and density (ρ, g/cm^3) values for solutions of barium and tetrabutylammonium iodides in MP at 298.15 K and various concentrations (m, mol/kg MP)

m	C_p	m	ρ
	BaI_2		
0.0000	1.753	0.0000	1.02802
0.0998	1.708	0.1019	1.06206
0.2000	1.667	0.2000	1.09406
0.2999	1.630	0.2999	1.12584
0.4999	1.561	0.5004	1.18758
0.7001	1.504	0.7508	1.26109
0.8502	1.465	0.9011	1.30330
1.0004	1.429	1.0002	1.33046
	$(C_4H_9)_4NI$		
0.0000	1.753	0.0000	1.02802
0.0997	1.745	0.0999	1.03280
0.1502	1.742	0.1502	1.03565
0.2000	1.740	0.1999	1.03754
0.2500	1.736	0.2505	1.04021
0.3000	1.735	0.3001	1.04193
0.4002	1.729	0.4008	1.04645
0.5001	1.724	0.4996	1.04973
0.5501	1.721	0.5501	1.05204
0.7501	1.712	0.7504	1.05823
0.8107	1.709	0.8100	1.06048
1.0004	1.699	1.0004	1.06562

ond solvation shell, and, secondly, causes stronger solvent electrostriction. Calculations of the standard entropies of the barium and rubidium ions in MP at 298.15 K ($S^\circ_{i(\mathrm{MP})}$) from the thermodynamic functions of transfer $\Delta_{\mathrm{tr}}G^\circ_i$ and $\Delta_{\mathrm{tr}}H^\circ_i$ [12] and the standard entropies of the ions in aqueous solution ($S^\circ_{i(\mathrm{H_2O})}$) [13] give $S^\circ_{\mathrm{Ba^{2+}(MP)}}$ = –300.3 J/(mol K) and $S^\circ_{\mathrm{Rb^{+}(MP)}}$ = –35.5 J/(mol K), which is evidence of stronger solvent ordering in the solvation sheath of the barium ion.

These effects are much less pronounced in solutions of $(C_4H_9)_4NI$. The large size of the $(C_4H_9)_4N^+$ ion and strong screening of the positive charge localized on nitrogen with alkyl groups result in the formation of one solvation shell and weak electrostriction.

The experimental C_p and ρ values were used to calculate the apparent molar heat capacities Φ_C and volumes Φ_V of barium and tetrabutylammonium iodides in MP. The corresponding concentration dependences are shown in Fig. 2. The $\Phi_C(BaI_2)$ values are described by a linear dependence on the root of the molal solution concentration m. For $(C_4H_9)_4NI$, the $\Phi_C = f(m^{1/2})$ dependence has a noticeable bend at $m \simeq 0.5$. The $\Phi_V = f(m^{1/2})$ dependences of the electrolytes are close to linear, but, similarly to the related $V = f(m)$ dependences considered above, have different slopes.

To determine the standard partial molar values $\overline{C^\circ_{p2}} = \Phi^\circ_C$ and $\overline{V^\circ_2} = \Phi^\circ_V$ corresponding to the state of infinitely dilute solutions, the $\Phi_V = f(m^{1/2})$ dependence for $(C_4H_9)_4NI$ was approximated by the equation

$$\Phi = \Phi^\circ + am^{1/2} + bm, \qquad (1)$$

where a and b are empirical coefficients, and the $\Phi_C(\Phi_V) = f(m^{1/2})$ dependences for BaI_2 and the linear portion of the $\Phi_C = f(m^{1/2})$ dependence for $(C_4H_9)_4NI$, by a linear regression equation taking into account the statistical weights of values depending on errors in ΔΦ. The $\overline{C^\circ_{p2}}$ and $\overline{V^\circ_2}$ values of barium and tetrabutylammonium iodides in MP are listed in Table 2. It is not surprising that the results do not correspond to the equations

$$\overline{C^\circ_{p2(i)}}(\mathrm{MP}) = -0.602\,\overline{C^\circ_{p2(i)}}(\mathrm{H_2O}), \qquad (2)$$

$$\overline{V^\circ_{2(i)}}(\mathrm{MP}) = 0.784\,\overline{V^\circ_{2(i)}}(\mathrm{H_2O}), \qquad (3)$$

obtained in [2] for 1–1 electrolytes and simple ions. Here, $\overline{C^\circ_{p2(i)}}$ and $\overline{V^\circ_{2(i)}}$ are the standard partial molar heat capacities and volumes of electrolytes and ions in MP and water. This is also evidence of the special features of the solutions under consideration (see above).

The separation of the $\overline{C^\circ_{p2}}$ and $\overline{V^\circ_2}$ values into ionic components was performed on the basis of the $\overline{C^\circ_{pi}}$ (MP) and $\overline{V^\circ_i}$ (MP) values for the iodide ion in MP [2, 3] and using the condition of the additivity of partial molar values. The results are listed in Table 2.

Table 2. Standard partial molar heat capacities ($\overline{C^\circ_{p2(i)}}$, J/(mol K)) and volumes ($\overline{V^\circ_{2(i)}}$, cm^3/mol) of barium and tetrabutylammonium iodides and ions in MP at 298.15 K

Value	BaI_2	$(C_4H_9)_4NI$	Ba^{2+}	$(C_4H_9)_4N^+$	I^-
$\overline{C^\circ_{p2(i)}}$	214 ± 5	558 ± 10	126 ± 5	514 ± 10	44 ± 2 [3]
$\overline{V^\circ_{2(i)}}$	56.9 ± 0.3	306.7 ± 0.3	8.5 ± 0.3	282.5 ± 0.3	24.2 ± 0.2 [2]

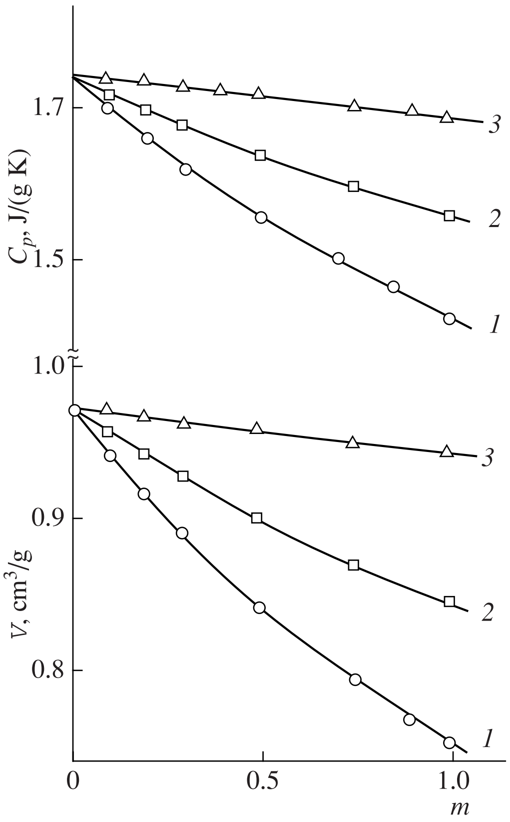

Fig. 1. Concentration dependences of the specific heat capacities and volumes of (*1*) barium, (*2*) rubidium, and (*3*) tetrabutylammonium iodides in MP at 298.15 K.

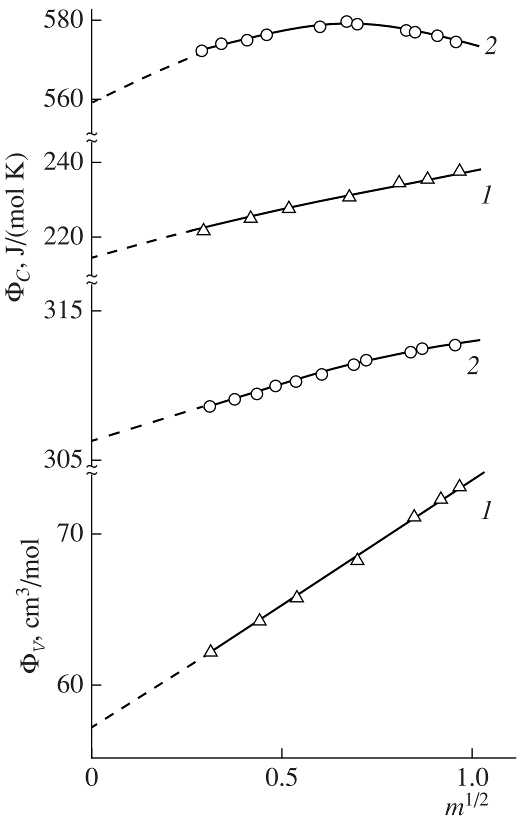

Fig. 2. Concentration dependences of the apparent molar heat capacities and volumes of (*1*) barium and (*2*) tetrabutylammonium iodides in MP at 298.15 K.

According to [14–17], the standard partial molar heat capacities and volumes of large-sized tetraalkylammonium ions in various nonaqueous solvents are close to each other. Table 3 contains the literature data on $\overline{C_{pi}^{\circ}}$ [12] and $\overline{V_i^{\circ}}$ [16] of the tetrabutylammonium cation in aprotic solvents whose properties are similar to those of MP, namely, dimethylformamide (DMFA), dimethylsulfoxide (DMSO), propylene carbonate (PC), acetonitrile (AN), and dimethylacetamide (DMAA). Note that the $\overline{C_{pi}^{\circ}}$ and $\overline{V_i^{\circ}}$ values for MP closely agree with those for the other solvents, especially considering that these values were obtained using different methods for the division of the $\overline{C_{p2}^{\circ}}$ and $\overline{V_2^{\circ}}$ values obtained for tetrabutylammonium iodide into ionic components. The $\overline{C_{pi}^{\circ}}$ and $\overline{V_i^{\circ}}$ values (Table 3) were calculated according to the tetraphenylarsonium–tetraphenyl borate (TATB) and tetraphenylphosphonium–tetraphenyl borate (TPTB) assumptions extensively used for nonaqueous solutions [14–20]. The scale of $\overline{C_{pi}^{\circ}}$ and $\overline{V_i^{\circ}}$ values in MP is based on dependences (2) and (3) [2–4]. Agreement between the values obtained for the $(C_4H_9)_4N^+$ ion in various nonaqueous solvents is in our view evidence that the scale of ionic components $\overline{C_{pi}^{\circ}}$ and $\overline{V_i^{\circ}}$ developed by us is close to the scale based on the TATB–TPTB approach.

Table 3. Standard partial molar heat capacities ($\overline{C_{p\,i}^{\circ}}$, J/(mol K)) and volumes ($\overline{V_i^{\circ}}$, cm^3/mol) of the tetrabutylammonium cation in aprotic dipolar solvents at 298.15 K

Value	MP	DMSO	DMFA	PC	AN	DMAA
$\overline{C_{p\,i}^{\circ}}$	514	–	517	496	513	–
$\overline{V_i^{\circ}}$	282.5	282	281	283	276	278

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