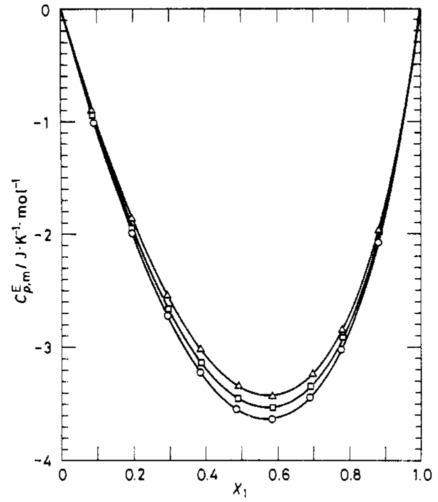

Figure 1. Molar excess heat capacities of benzene (1)–*n*-heptane (2) at (○) 293.15 K, (□) 298.15, (△) 303.15 K. Solid curves are least-squares representations calculated by eq 2.

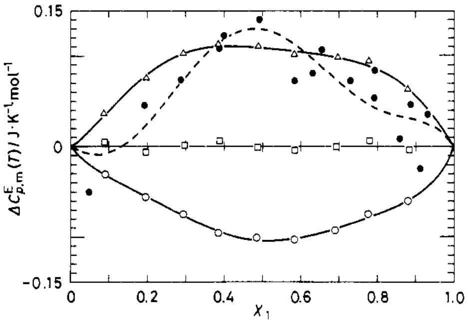

Figure 2. Variations of molar excess heat capacities $\Delta C^E_{p,m}(T)$ expressed by eq 3 for benzene (1)–*n*-heptane (2) at (○) 293.15 K, (□) 298.15 K, and (△) 303.15 K; (●), Karbalai Ghassemi and Grolier at 298.15 K (*4*).

are shown in Figure 2.

Karbalai Ghassemi and Grolier have measured $C^E_{p,m}$ for the preset system at 298.15 K by using the same calorimeter (*4*). Their results are plotted in Figure 2. Their values scatter with the standard deviation larger by about 7 times than the present work. Their smoothed values are less negative at the mole fraction $x_1 > 0.1$ and are closer to the present results at 303.15 K.

The molar excess heat capacities are negative at all the mole fractions with the minimum values of about −3.4 to −3.6 J·K^{-1}·mol^{-1}. The value of $C^E_{p,m}$ at a fixed composition varies linearly with temperature in the whole range of x, and $\partial C^E_{p,m}/\partial T$ is parabolic for x, with a value of 0.02 J·K^{-2}·mol^{-1} at the equimolar composition.

The heat capacities for the nonpolar mixtures containing *n*-alkanes as one component have been investigated from the view point of the structural change in *n*-alkanes (*5*, *6*). The negative $C^E_{p,m}$ and the positive $\partial C^E_{p,m}/\partial T$ for the present system are possibly attributed to an indication of the destruction of orientational order in the *n*-heptane by the benzene, according to the classification by Bhattacharyya and Patterson (*5*).

Glossary

$C_{p,m}$	molar heat capacity, J·K^{-1}·mol^{-1}
$C^E_{p,m}$	molar excess heat capacity, J·K^{-1}·mol^{-1}
c_1, c_2, ..., c_j	coefficients in representations of excess heat capacities by eq 2
T	thermodynamic temperature, K
x_i	mole fraction of component *i*
V_m	molar volume, cm^3·mol^{-1}

Greek Letters

σ	standard deviation calculated from eq 2

Superscripts

•	pure liquid

Subscripts

1	benzene
2	*n*-heptane

Registry No. Benzene, 71-43-2; heptane, 142-82-5.

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Densities of Some Alkali Halides in Water–Acetamide Mixtures at 298.15 K

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Densities of solutions of NaCl, NaI, KCl, KBr, and CsI in water–acetamide mixed solvents in the miscibility range at 298.15 K have been measured with the magnetic float densimeter. The apparent molal volumes, Φ_v, of the investigated electrolytes calculated from the experimental data were extrapolated to infinite dilution by means of the Masson equation. The dependence of the partial molal volumes of alkali halides and partial molal volumes of transfer from water to water–acetamide mixtures on the solvent composition is discussed.

Introduction

The study of partial molal volumes of electrolytes in mixed solvents has contributed to our knowledge about the interactions that occur in solution and helped gain a better understanding of electrolyte–nonelectrolyte–water interactions. The results of measurements of the enthalpy of solution of some electrolytes in water–acetamide mixtures (*1*) show that the structure of water–acetamide mixtures changes gradually.

It must be interesting to examine whether comparable information can be obtained from a determination of molal vol-

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Table I. Density of NaCl Solutions in Water–Acetamide Mixtures at 298.15 K

m	*d*	*m*	*d*	*m*	*d*
AcNH$_2$, 15 wt %, 5.10 mol %					
0.0000	1.006 952	0.1003	1.011 111	0.2047	1.015 417
0.0212	1.007 833	0.1199	1.011 920	0.2241	1.016 211
0.0402	1.008 622	0.1401	1.012 753	0.2551	1.017 494
0.0607	1.009 472	0.1613	1.013 626		
0.0799	1.010 265	0.1822	1.014 495		
AcNH$_2$, 30 wt %, 11.55 mol %					
0.0000	1.017 151	0.0796	1.020 401	0.2011	1.025 315
0.0148	1.017 759	0.0999	1.021 228	0.2244	1.026 249
0.0299	1.018 377	0.1238	1.022 195	0.2502	1.027 288
0.0401	1.018 792	0.1502	1.023 258		
0.0602	1.019 612	0.1751	1.024 266		
AcNH$_2$, 50 wt %, 23.36 mol %					
0.0000	1.030 245	0.0806	1.033 466	0.2004	1.038 202
0.0148	1.030 840	0.1002	1.034 244	0.2252	1.039 170
0.0282	1.031 378	0.1247	1.035 218	0.2499	1.040 118
0.0399	1.031 846	0.1504	1.036 241		
0.0611	1.032 693	0.1748	1.037 194		

Table II. Density of NaI Solutions in Water–Acetamide Mixtures at 298.15 K

m	*d*	*m*	*d*	*m*	*d*
AcNH$_2$, 15 wt %, 5.10 mol %					
0.0000	1.006 952	0.0820	1.016 167	0.2001	1.029 326
0.0092	1.007 989	0.1007	1.018 258	0.2262	1.032 214
0.0201	1.009 217	0.1253	1.021 029	0.2514	1.035 001
0.0406	1.011 523	0.1502	1.023 783		
0.0611	1.013 824	0.1749	1.026 530		
AcNH$_2$, 30 wt %, 11.55 mol %					
0.0000	1.017 151	0.0803	1.026 058	0.2004	1.039 227
0.0102	1.018 288	0.1001	1.028 241	0.2255	1.041 952
0.0227	1.019 678	0.1247	1.030 948	0.2499	1.044 599
0.0404	1.021 643	0.1503	1.033 775		
0.0617	1.024 002	0.1752	1.036 477		
AcNH$_2$, 50 wt %, 23.36 mol %					
0.0000	1.030 245	0.0812	1.039 052	0.1991	1.051 629
0.0099	1.031 328	0.0989	1.040 953	0.2246	1.054 314
0.0207	1.032 506	0.1229	1.043 525	0.2537	1.057 358
0.0414	1.034 753	0.1517	1.046 594		
0.0599	1.036 756	0.1746	1.049 030		

Table III. Density of KCl Solutions in Water–Acetamide Mixtures at 298.15 K

m	*d*	*m*	*d*	*m*	*d*
AcNH$_2$, 15 wt %, 5.10 mol %					
0.0000	1.006 952	0.0606	1.009 819	0.1753	1.015 194
0.0126	1.007 550	0.0711	1.010 312	0.2011	1.016 394
0.0250	1.008 138	0.1002	1.011 679	0.2498	1.018 657
0.0355	1.008 635	0.1247	1.012 829		
0.0495	1.009 296	0.1422	1.013 649		
AcNH$_2$, 30 wt %, 11.55 mol %					
0.0000	1.017 151	0.0678	1.020 328	0.1708	1.025 078
0.0106	1.017 651	0.0855	1.021 149	0.2041	1.026 684
0.0245	1.018 305	0.1015	1.021 892	0.2512	1.028 759
0.0303	1.018 576	0.1289	1.023 162		
0.0498	1.019 487	0.1518	1.024 216		
AcNH$_2$, 50 wt %, 23.36 mol %					
0.0000	1.030 245	0.0642	1.033 164	0.1718	1.037 884
0.0102	1.030 718	0.0811	1.033 916	0.2002	1.039 107
0.0214	1.031 230	0.1077	1.035 090	0.2503	1.041 222
0.0305	1.031 644	0.1203	1.035 633		
0.0405	1.032 097	0.1446	1.036 707		

Table IV. Density of KBr Solutions in Water–Acetamide Mixtures at 298.15 K

m	*d*	*m*	*d*	*m*	*d*
AcNH$_2$, 15 wt %, 5.10 mol %					
0.0000	1.006 952	0.0892	1.014 359	0.2011	1.023 434
0.0151	1.008 221	0.1002	1.015 258	0.2348	1.026 160
0.0298	1.009 451	0.1292	1.017 638	0.2768	1.029 503
0.0448	1.010 696	0.1501	1.019 345		
0.0625	1.012 161	0.1744	1.021 292		
AcNH$_2$, 30 wt %, 11.55 mol %					
0.0000	1.017 151	0.0861	1.024 228	0.2002	1.033 351
0.0098	1.017 970	0.1013	1.025 456	0.2284	1.035 574
0.0305	1.019 685	0.1248	1.027 344	0.2547	1.037 646
0.0489	1.021 197	0.1502	1.029 377		
0.0644	1.022 462	0.1751	1.031 372		
AcNH$_2$, 50 wt %, 23.36 mol %					
0.0000	1.030 245	0.0831	1.036 962	0.2004	1.046 153
0.0116	1.031 201	0.1007	1.038 361	0.2241	1.047 988
0.0251	1.032 300	0.1242	1.040 219	0.2502	1.049 973
0.0421	1.033 677	0.1505	1.042 288		
0.0616	1.035 242	0.1739	1.044 094		

Table V. Density of CsI Solutions in Water–Acetamide Mixtures at 298.15 K

m	*d*	*m*	*d*	*m*	*d*
AcNH$_2$, 15 wt %, 5.10 mol %					
0.0000	1.006 952	0.0751	1.022 019	0.2004	1.046 832
0.0112	1.009 210	0.1048	1.027 939	0.2202	1.050 713
0.0264	1.012 267	0.1238	1.031 711	0.2507	1.056 674
0.0352	1.014 033	0.1503	1.036 960		
0.0531	1.017 622	0.1712	1.041 083		
AcNH$_2$, 30 wt %, 11.55 mol %					
0.0000	1.017 151	0.0749	1.032 279	0.1999	1.057 341
0.0153	1.020 243	0.1015	1.037 632	0.2252	1.062 397
0.0251	1.022 225	0.1249	1.042 335	0.2491	1.067 144
0.0394	1.025 114	0.1502	1.047 407		
0.0502	1.027 296	0.1747	1.052 312		
AcNH$_2$, 50 wt %, 23.36 mol %					
0.0000	1.030 245	0.0602	1.042 415	0.1504	1.060 574
0.0108	1.032 428	0.0749	1.045 381	0.1740	1.065 306
0.0226	1.034 814	0.0903	1.048 488	0.2002	1.070 565
0.0332	1.036 957	0.1015	1.050 746		
0.0453	1.039 405	0.1251	1.055 493		

umes. For this reason we report in this paper the partial molal volumes of NaCl, NaI, KCl, KBr, and CsI in water–acetamide mixtures at 298.15 K.

Experimental Section

Reagents. Analytically pure NaCl, KCl, and KBr (POCH, Gliwice) were recrystallized from doubly distilled water and dried for a day at 383 K. NaI A.R. (POCH, Gliwice) was recrystallized from a 1:1 water–acetone mixture and dried under vacuum for 6 h at 333 K. Laboratory grade CsI (BDH) was used without further purification and dried under vacuum for 6 h at 323 K. All the salts were stored in a desiccator before being used. Analytically grade acetamide (Xenon, Lodz) was crystallized from methanol and dried under vacuum for 10 h at 323 K. The melting point of acetamide was 354–355 K which is in accordance with literature data (*2*). The mixed solvents used for investigations were prepared by mixing the weighed amounts of acetamide with doubly distilled water. All solutions were prepared by weighing appropriate amounts of salt and adding it to a weighed amount of mixed solvent.

Procedure of Measurements. The density measurements were performed with a magnetic float densimeter. The magnetic float densimeter and a review of the development of the magnetic float method has been described elsewhere (*3*, *4*). The densimeter was placed in a water bath controlled to ±0.01 K. The total uncertainty in density is about 5 ppm. The accuracy of the densimeter was tested by measurements on dilute solutions of KCl in water at 298.15 K. The results yield for KCl $\bar{V}_2{}^0$ = 26.7 ± 0.5 cm^3 mol^{-1}. The agreement with literature value 26.8 (*5*) is satisfactory. All measurements were made at 298.15 ± 0.01 K.

Table VI. Partial Molal Volume of Alkali Halides in Water-Acetamide Mixtures at 298.15 K

		$AcNH_2$		
salt	water (7)	15 wt %, 5.10 mol %	30 wt %, 11.55 mol %	50 wt %, 23.36 mol %
NaCl	16.6	17.0	17.7	18.7
NaI	35.0	37.6	39.5	42.1
KCl	26.8	27.1	27.5	28.2
KBr	33.7	34.7	35.7	37.3
CsI	57.5	59.0	60.3	62.0

Results

The experimental results are given in Tables I-V. Each value of density is the mean of four series of six measurements. The apparent molal volumes were calculated from

$$\Phi_v = \frac{M}{d} - \frac{1000(d - d_0)}{dd_0m} \quad (1)$$

Within experimental error, the Φ_v shows a linear dependence on the square root of the molarity according to the Masson equation (*6*)

$$\Phi_v = \Phi_v^0 + S_v^e c^{1/2} \quad (2)$$

where Φ_v^0 is the apparent molal volume at infinite dilution equal to the partial molal volume, $\bar{V}_2^0$, and S_v^e is the experimental slope. The values of the partial molal volume of investigated electrolytes in water-acetamide mixtures obtained by a linear extrapolation eq 2 are given in Table VI.

Discussion

As is seen from Table VI the partial molal volume of alkali halides in water-acetamide mixed solvents increases linearly with the amount of acetamide in the mixed solvent. This increase is largest in case of NaI and small for NaCl and KCl. It seems that the partial molal volume of transfer ($\bar{V}_{tr}^0$) is the function which better reflects the interactions between dissolved electrolyte and solvent. Using the values $\bar{V}_2^0$ of alkali halides in water-acetamide mixtures, we can calculate the partial molal volume of transfer, $\bar{V}_{tr}^0$, from water to water-acetamide mixtures from the equation

$$\bar{V}_{tr}^0 = \bar{V}_{2(ms)}^0 - \bar{V}_{2(w)}^0 \quad (3)$$

where $\bar{V}_{2(ms)}^0$ is the partial molal volume of electrolyte in mixed solvent and $\bar{V}_{2(w)}^0$ is the partial molal volume of electrolyte in water. As can be seen from Table VII the partial molal volume of transfer of alkali halides in water-acetamide mixtures is nearly proportional to the mole fraction of acetamide in the mixed solvent. Therefore, one can draw the conclusion that the interactions among water and acetamide molecules are weak and the structure of water-acetamide mixtures changes gradually. Moreover, it can be noticed that the partial molal volume of transfer is positive and it increases with the increase of size for anions and decreases for cations. Hence, it can be presumed that the largest interactions of the ion with the mixed solvent are in the case of Na^+ and decrease for K^+ and Cs^+ ions. For anions the largest interactions between ion and water-acetamide mixture are observed for the I^- ion. These interactions increase with the amount of acetamide in the mixed solvent. From this it follows that the structure of water-acetamide mixtures is looser than that of pure water.

Table VII. Partial Molal Volume of Transfer of Alkali Halides from Water to Water-Acetamide Mixtures at 298.15 K

	$AcNH_2$		
salt	15 wt %, 5.10 mol %	30 wt %, 11.55 mol %	50 wt %, 23.36 mol %
NaCl	0.4	1.1	2.1
NaI	2.6	4.5	7.1
KCl	0.3	0.7	1.4
KBr	1.0	2.0	3.6
CsI	1.5	2.8	4.5

Glossary

Φ_v	apparent molal volume, $cm^3\ mol^{-1}$
M	molecular weight
d	density of solution, $g\ cm^{-3}$
d_0	density of solvent, $g\ cm^{-3}$
m	molality, $mol\ kg^{-1}$
Φ_v^0	apparent molal volume at infinite dilution, $cm^3\ mol^{-1}$
$\bar{V}_{tr}^0$	partial molal volume of transfer, $cm^3\ mol^{-1}$
$\bar{V}_{2(ms)}^0$	partial molal volume of electrolyte in mixed solvent, $cm^3\ mol^{-1}$
$\bar{V}_{2(w)}^0$	partial molal volume of electrolyte in water, $cm^3\ mol^{-1}$

Registry No. NaCl, 7647-14-5; NaI, 7681-82-5; KCl, 7447-40-7; KBr, 7758-02-3; CsI, 7789-17-5; acetamide, 60-35-5.

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