Thermochemical Examination of NaI, $NaBPh_4$, and Ph_4PI in the Mixtures of Acetonitrile with *N*,*N*-Dimethylformamide and Dimethylsulfoxide at 298.15 K: Properties of Acetonitrile-Containing Mixtures as Solvents for Electrolytes[†]

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Dissolution enthalpies of NaI, $NaBPh_4$, and Ph_4PI in the mixtures of *N*,*N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) with acetonitrile (AN) over the whole composition range were measured at 298.15 K. From these data the single ion (Na^+, I^-, BPh_4^-, Ph_4P^+) enthalpies of transfer from AN to AN + cosolvent mixtures and the enthalpic pair interaction coefficients, h_{xy} (NaI−nonelectrolyte), in AN were determined and analyzed together with our earlier data concerning the mixtures of AN with methanol (MeOH), *N*, *N*-dimethylacetamide (DMA), propylene carbonate (PC), and 2-methoxyethanol (2-ME). The changes in electrolyte solvation were described with the use of Covington's preferential solvation (PS) model. The linear relationship between interaction coefficients, h_{xy}, of NaI−nonelectrolyte in AN and ln $K^{1/n}$ values from PS model for NaI molecule in the mixture of AN and DMA, 2-ME, DMF, and DMSO as well as for Na^+ ion in the mixture containing DMA, DMF, 2-ME, and MeOH was demonstrated. The behavior of the mixtures of water, MeOH, DMF, and AN with organic cosolvents when used as solvents for electrolytes was compared.

Introduction

Nonaqueous solutions of electrolytes perform a significant function in modern chemistry and technology. An excellent review of problems associated with these solutions was given by Barthel et al. in their paper published in 1978.[1] Despite the passing years, the issues presented in that publication have lost none of their relevance and importance.

In our laboratory, the systematic studies of thermochemical properties of electrolyte solutions in binary solvents have been carried out for many years. At first, we examined widely the dissolution enthalpies of electrolytes in mixtures of water with numerous organic solvents.[2,3] Then we have undertaken the examination of solutions of electrolytes in binary organic solvents containing methanol (protic, hydrogen-bonded solvent)[4−8] or *N*,*N*-dimethylformamide (DMF, aprotic, proton-acceptor, nonhydrogen-bonded solvent).[6−10] To obtain a more complete picture of these systems, the calorimetric data were supplemented by the results of volumetric investigations, for example, ref 12. As a continuation of these studies we have performed the calorimetric and densimetric investigations of electrolyte solutions in the mixtures of several organic solvents with acetonitrile (AN), which because of its polarity is a good solvent for both electrolytes and nonelectrolytes. Moreover, AN molecules, in contrast to the above-mentioned solvents, are not able to form H-bonds in a "classical" sense either as a proton-donor or as a proton-acceptor. Sodium iodide, sodium tetraphenylborate, and tetraphenylphosphonium iodide were selected for these studies as electrolytes. NaI was used because of its good solubility in the mixed solvents under examination and also because of numerous data concerning solutions of this electrolyte. The use of mentioned organic salts enabled us to determine the thermodynamic functions of solvation for individual ions. The results of our studies on electrolyte solutions in the mixtures of AN with propylene carbonate (PC), *N*,*N*-dimethylacetamide (DMA), and 2-methoxyethanol (2-ME) were published in one of our previous papers.[11,12] In this paper, we present new data concerning thermochemical investigations of the solutions of the same electrolytes in the mixtures of AN with DMF and dimethylsulfoxide (DMSO).

The analysis of thermodynamic functions in three-component systems containing a solute and binary solvent is complicated, as they describe the systems consisting of three kinds of molecules interacting with one another in a different way. Therefore, it is convenient to examine solutions of the selected electrolyte in a series of binaries containing one selected solvent and different cosolvents. Having at our disposal a large number of appropriate thermochemical data concerning the ternary systems,[2−10] we have additionally analyzed the effect of properties of water, methanol, DMF, and AN on the behavior of NaI solutions in two-component mixtures containing the above-mentioned solvents as one of their components.

Experimental Section

Sodium iodide (NaI), (Merck for analysis), was dried at 333.15 K and stored in a desiccator. Sodium tetraphenylborate ($NaBPh_4$; Merck for analysis) and tetraphenylphosphonium iodide (Ph_4PI; Aldrich for analysis) were dried for several days over phosphorus pentoxide under vacuum at 333.15 K. The salts were protected against light.

AN (Aldrich, 99.89 % anhydrous), DMF (Aldrich, 99.8 %, anhydrous), and DMSO (Aldrich, 99.9 %, anhydrous) were dried and distilled according to the methods described in literature.[13] The water content in the solvents was determined by the method of Karl Fischer and was below $5 \cdot 10^{-2}$ weight percent.

Salts containing ampules were weighed with an accuracy of $\pm 1 \cdot 10^{-5}$ g; the mixtures of solvents were prepared in a dry chamber and weighed with an accuracy of $\pm 1 \cdot 10^{-2}$ g.

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Table 1. Standard Enthalpies of Solution $\Delta_{sol}H^0$ of NaI in AN (1) + Cosolvent (2) Mixtures at 298.15 K

	$\Delta_{sol}H^0$/kJ·mol^{-1}	
100 x_2	DMF	DMSO
0.0	−28.82	−28.82
2.5	−32.17	−32.81
5.0	−34.62	−35.89
7.5	−36.12	−38.89
10.0	−37.92	−40.18
12.5	−40.00	−41.15
15.0	−41.98	−42.81
20.0	−43.60	−44.60
30.0	−46.00	−46.40
50.0	−48.67	−47.58
70.0	−52.30	−48.97
80.0	−53.90[9]	−48.70
85.0		−48.94
87.5		−49.06
90.0	−55.22[9]	−49.14
92.5		−48.94
95.0	−55.82[9]	−48.89
97.5	−56.13[9]	−48.72
100	−56.40[9]	−48.88

Table 2. Standard Enthalpies of Solution $\Delta_{sol}H^0$ of $NaBPh_4$ and Ph_4PI in AN (1) + Cosolvent (2) Mixtures at 298.15 K

	$\Delta_{sol}H^0$/kJ·mol^{-1}			
	DMF		DMSO	
100 x_2	$NaBPh_4$	Ph_4PI	$NaBPh_4$	Ph_4PI
0.0	−43.42	16.03	−43.42	16.03
2.5	−46.10	16.09		
5.0	−48.67	15.97		
7.5	−52.25	15.95		
10.0	−54.97	15.89	−55.31	17.93
12.5				
25.0			−58.23	16.95
30.0	−62.96	13.60		
50.0	−66.71	10.21	−59.22	15.06
70.0	−69.22	7.26		
75.0			−59.34	15.65
85.0	−70.54	6.43		
90.0			−59.50	14.89
100	−72.25	4.48	−59.49	15.73

The dissolution enthalpies were measured over the whole range of the mixed solvent composition at a temperature of 298.15 K using an "isoperibol" type calorimeter.[14] The measurements were carried out for a $1.5\cdot10^{-3}$ mol·kg^{-1} to $8\cdot10^{-3}$ mol·kg^{-1} salt concentration range in binary solvents. The relative error in the calorimetric measurements was estimated to be ± 0.01 of the measured value. The uncertainty in the mixed solvent composition was ± 0.001 of the mole fraction and that for the temperature of the experiment ± 0.02 K.

Results and Discussion

Dissolution and Transfer Enthalpies. The standard dissolution enthalpies $\Delta_{sol}H^0$ of NaI, $NaBPh_4$, and Ph_4PI in each examined mixture were determined by extrapolation of the measured enthalpies of solution $\Delta_{sol}H$ to infinitely diluted solution according to the formula:

$$\Delta_{sol}H = \Delta_{sol}H^0 + Am^{1/2} \quad (1)$$

where A is an experimental slope and m is molality.

The values of $\Delta_{sol}H^0$ in all of the mixtures under study are presented in Tables 1 and 2.

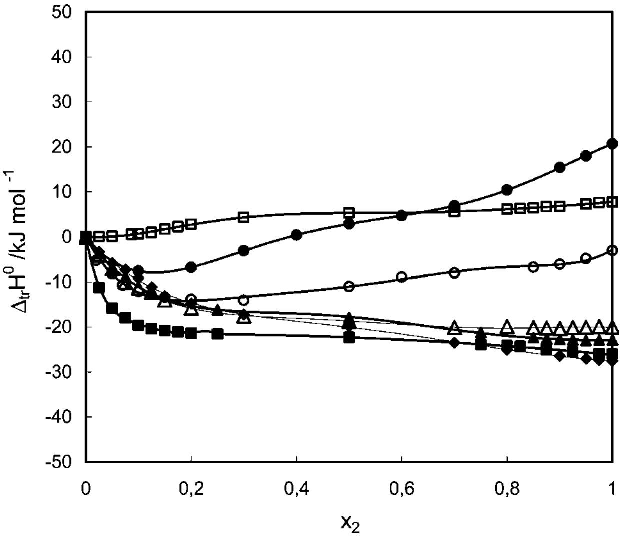

Figure 1. Enthalpies of transfer of NaI from AN to AN + cosolvent mixtures. □, PC; ■, 2-ME; ▲, DMA; ○, ME; ●, W; ◆, DMF; △, DMSO.

The values of $\Delta_{sol}H^0$ for electrolytes in pure solvents determined in this work agree very well with the literature data: in AN for NaI $\Delta_{sol}H^0 = -28.82$ kJ·mol^{-1} (−28.84 kJ·mol^{-1},[7] −29.2 kJ·mol^{-1}),[15] for $NaBPh_4$ $\Delta_{sol}H^0 = -43.42$ kJ·mol^{-1} (−43.5 kJ·mol^{-1},[16−19] −42.05 kJ·mol^{-1},[20] for Ph_4PI $\Delta_{sol}H^0 = 16.03$ kJ·mol^{-1} (15.69 kJ·mol^{-1});[21] in DMF, for NaI $\Delta_{sol}H^0 = -56.40$ kJ·mol^{-1} (−56.82 kJ·mol^{-1},[9] −56.90 kJ·mol^{-1},[22] −55.31 kJ·mol^{-1},[23] −56.40 kJ·mol^{-1}),[7] for $NaBPh_4$ $\Delta_{sol}H^0 = -72.25$ kJ·mol^{-1} (−72.38 kJ·mol^{-1},[22] −71.70 kJ·mol^{-1},[24] −72.16 kJ·mol^{-1},[25] −72.35 kJ·mol^{-1}),[6] for Ph_4PI $\Delta_{sol}H^0 = 4.48$ kJ·mol^{-1} (2.45 kJ·mol^{-1});[6] in DMSO, for NaI $\Delta_{sol}H^0 = -48.88$ kJ·mol^{-1} (−48.20 kJ·mol^{-1},[22] −48.24 kJ·mol^{-1},[22] −48.37 kJ·mol^{-1},[22] −48.10 kJ·mol^{-1},[24] −48.35 kJ·mol^{-1},[24] −48.11 kJ·mol^{-1});[24] for $NaBPh_4$ $\Delta_{sol}H^0 = -59.49$ kJ·mol^{-1} (−59.43 kJ·mol^{-1},[20] −59.80 kJ·mol^{-1}).[22]

The standard dissolution enthalpies of Ph_4PI in DMSO could not be compared with appropriate literature data as the latter were not available.

A convenient function to describe solutions in binary solvents is the enthalpy of transfer, $\Delta_{tr}H^0$, of the solute from an individual solvent (in our case, AN) to the mixed solvent (M) of various compositions. The mentioned function illustrates the difference in energetic effects of solute solvation in the solvent chosen as a reference and in the mixture and can be calculated as a difference of appropriate dissolution enthalpies.

$$\Delta_{tr}H^0 = \Delta_{solv}H^0(\mathrm{M}) - \Delta_{solv}H^0(\mathrm{AN}) = \Delta_{sol}H^0(\mathrm{M}) - \Delta_{sol}H^0(\mathrm{AN}) \quad (2)$$

The calculated enthalpies of transfer are presented as a function of the mixed solvent composition in Figures 1 to 3. For the sake of comparison, analogous data for the examined earlier mixtures of AN with DMA,[11] 2-ME,[11] PC,[11] methanol,[21] and water[16] are also given in Figures 1 to 3.

The transfer enthalpies of NaI examined here in mixtures of AN with DMF and with DMSO as a function of the mixed solvent composition have an almost identical shape as that for AN + DMA mixtures examined earlier.[11] It is characterized by a sharp decrease in the $\Delta_{tr}H^0$ values in the range of high AN content ($0 < x_2 < 0.3$) and then a smooth, almost linear run of the transfer enthalpy until the $\Delta_{tr}H^0$ value characteristic of pure cosolvent. It has to be mentioned here that the analogous course of the $\Delta_{tr}H^0 = f$ (mixed solvent composition) function with the very rapid fall of the solution enthalpy along with the AN content decrease was observed in the case of NaI solutions in almost all binary mixtures containing AN examined until now.

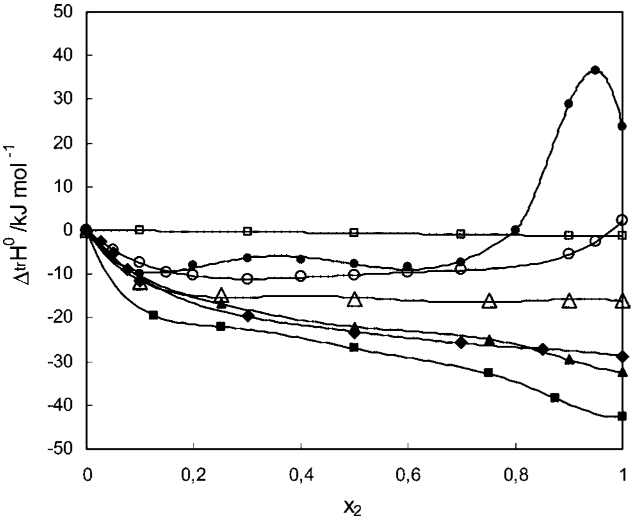

Figure 2. Enthalpies of transfer of $NaBPh_4$ from AN to AN + cosolvent mixtures. □, PC; ■, 2-ME; ▲, DMA; ○, ME; ●, W; ◆, DMF; △, DMSO.

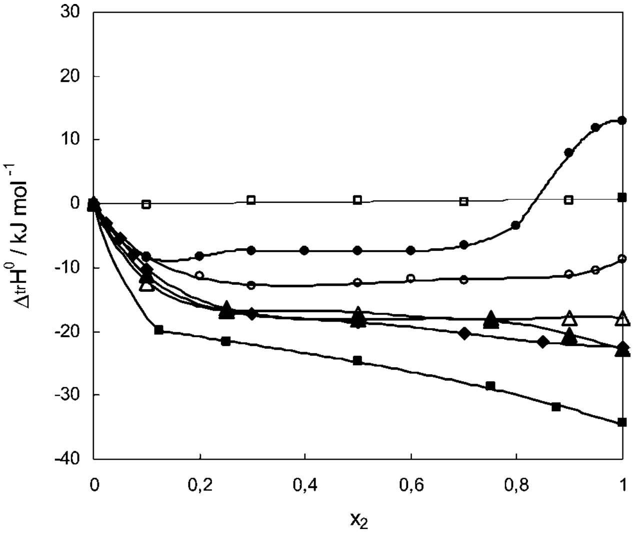

Figure 4. Enthalpies of transfer of the sodium ion from AN to AN + cosolvent mixtures. □, PC; ■, 2-ME; ▲, DMA; ○, ME; ●, W; ◆, DMF; △, DMSO.

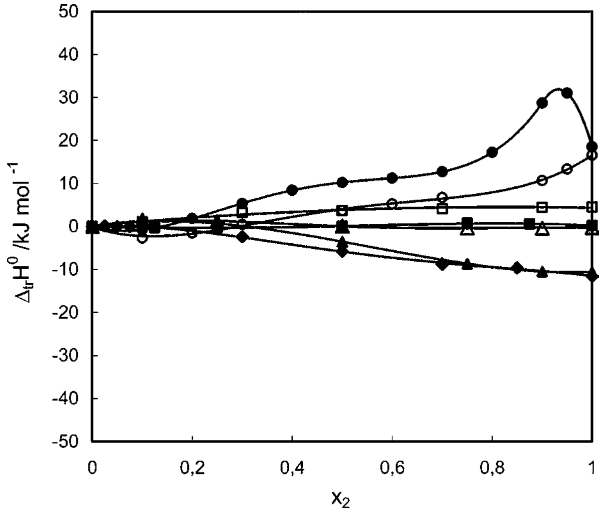

Figure 3. Enthalpies of transfer of Ph_4PI from AN to AN + cosolvent mixtures. □, PC; ■, 2-ME; ▲, DMA; ○, ME; ●, W; ◆, DMF; △, DMSO.

The only exception is the AN + PC mixture for which the transfer enthalpy runs almost linearly within the whole mixed solvent composition.[11] The possible reasons of such behavior were discussed in detail in our previous paper.[11] Therefore, one can repeat here that after the addition of the first portions of the cosolvent to AN the replacement of the AN molecules in the NaI solvation shells by cosolvent molecules starts immediately. It happens because of the weak solvation ability of AN toward the electrolyte. As a result of this oversolvation, the enthalpy of solvation (and the enthalpy of transfer) becomes more exothermic within the range of the mixed solvent composition under discussion.

Similar observations to those in the case of NaI may be made in relation to the enthalpy of transfer of $NaPh_4$ from AN to the mixtures examined until now. The rapid drop in the enthalpy of solvation (or transfer) due to the addition of cosolvent to solution can be attributed to the replacement of AN molecules within the coordination zone of electrolyte by stronger solvating molecules of cosolvent. Also in this case, the mixture of AN and PC is an exception, probably due to the comparably weak capacity for the solvation of ions by both solvents.[11]

The enthalpy of Ph_4PI transfer in AN + DMSO mixtures is almost independent of the composition of mixture within its whole range. On the other hand, in AN + DMSO mixtures, one can observe almost a linear drop in the solvation enthalpy with the increase of the DMSO content. Such a “linear behavior” suggests that the structure of both mixtures is labile and no molecular complexes with a specified composition are formed. The dissolved ions are very weakly solvated, and the composition of their solvation sheaths changes gradually with the change in the mixed solvent composition.

From the above analysis it also follows that the rapid change in the solvation effect of the sodium salts examined within the AN-rich range is connected basically with the behavior of sodium ion in these mixtures. To verify this opinion, it will be helpful to determine the single ion transfer enthalpy.

Single Ion Transfer Enthalpies. The transfer enthalpies of single ions (Na^+, I^-, BPh_4^-, Ph_4P^+) were calculated in accordance with the tetraphenylphosphonium tetraphenylborate (TPTB) method assumptions[26−28] according to the equation:

$$\Delta_{tr}H^0(Ph_4P^+) = \Delta_{tr}H^0(BPh_4^-) = 1/2[\Delta_{tr}H(NaBPh_4) + \Delta_{tr}H(Ph_4PI) - \Delta_{tr}H(NaI)] \quad (3)$$

The calculated standard transfer enthalpies of single ions as a function of the mixed solvent composition in the system under investigation are shown in Figures 4 to 6 together with analogous literature data concerning other mixtures of AN with organic cosolvents.[16,21]

As can be seen in these figures, the enthalpy of Na^+ solvation in the mixtures of AN with DMF and DMSO changes very similarly to the enthalpy of solvation of NaI and $NaBPh_4$ in the same mixtures as well as in the examined earlier mixtures of AN with DMA, 2-ME, and MeOH within the whole range of the mixed solvent composition. In AN + water mixtures, the $\Delta_{tr}H^0(Na^+)$ also exhibits a characteristic sharp decrease in the AN-rich region. On the other hand, the enthalpies of solvation of iodide anion in the mixture of AN with DMF and DMSO and also with PC, DMA, 2-ME, and MeOH[21] change almost linearly within the wide range of the mixed solvent composition. Therefore, the observed changes of $\Delta_{sol}H^0$ of sodium salts in the range of high AN content are due to the preferential solvation (PS) of the sodium cation.

Preferential Solvation. For a quantitative description of the enthalpic effect of PS, it is possible to use the simplest version

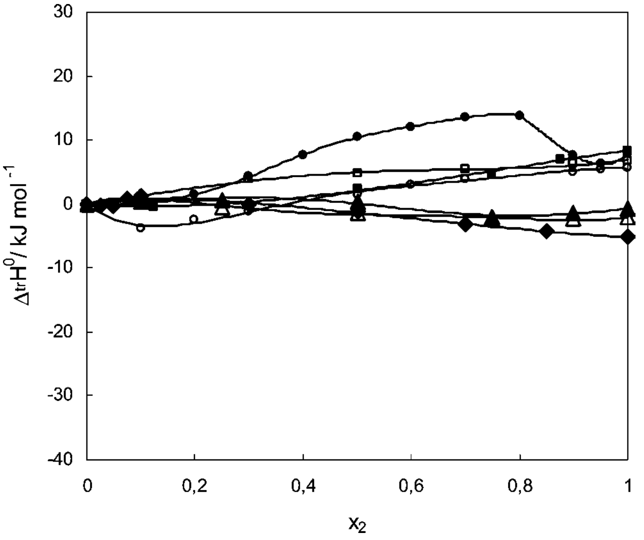

Figure 5. Enthalpies of transfer of the iodide ion from AN to AN + cosolvent mixtures. □, PC; ■, 2-ME; ▲, DMA; ○, ME; ●, W; ◆, DMF; △, DMSO.

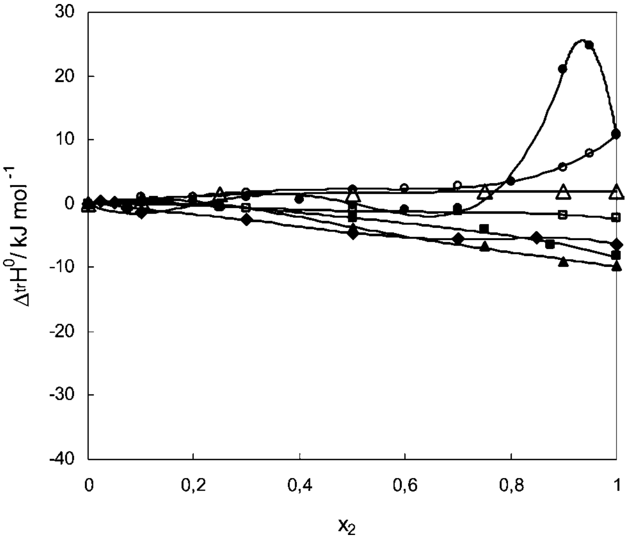

Figure 6. Enthalpies of transfer of the tetraphenylborate (tetraphenylphosphonium) ion from AN to AN + cosolvent mixtures. □, PC; ■, 2-ME; ▲, DMA; ○, ME; ●, W; ◆, DMF; △, DMSO.

of the PS thermodynamic theory by Covington and Thain[29] in the form proposed by Balk and Somsen.[30] According to this theory, for a given solute X in a mixture of solvent components S and Y the change in the composition of the solvation shell of X along with the change of the mixed solvent composition is described by a successive series of "n" equilibriums, where n is the solvation number:

$$X(S_{n+1-i}Y_{i-1}) + Y \overset{K_i}{\rightleftarrows} X(S_{n-i}Y_i) + S \qquad (1 \le i \le n) \tag{4}$$

The final equation for the excess enthalpic effect of PS has the following form:[30]

$$\Delta_{tr}H^{E}_{PS}(M) = nRT[\{(1 - x_s)/\{(1 - x_s) + K^{1/n}x_s\}\} - (1 - x_s)] \ln K^{1/n} \tag{5}$$

where K is the equilibrium constant for the process of ionic solvation shell change when the mixed solvent composition changes, n is the solvation number, and $K^{1/n}$ is the equilibrium constant describing the exchange of one solvent molecule in ionic solvation shell.

Table 3. PS Parameters, $K^{1/n}$ and n for NaI and Na$^+$ in the Mixtures of AN with DMF, DMSO, DMA, 2-ME, and MeOH

	NaI		Na$^+$	
cosolvent	$K^{1/n}$	n	$K^{1/n}$	n
DMF	8.6	3.3	7.7	4.2
DMSO	9.1	4.2	16.5	2.8
DMA[11]	11.6	3.0	9.6	3.5
2-ME[11]	46.4	2.3	31.8	1.8
MeOH[11]	14.6	3.4	6.4	5.2

This function is negative over the whole mole fraction region ($K^{1/n} > 0$), thus resulting in an exothermic contribution to the enthalpy of solution. When $K < 1$, the electrolyte is preferentially solvated by solvent S (AN), while $K > 1$ means that the electrolyte is preferentially solvated by cosolvent Y.

It appeared that the PS model proposed by Covington describes well the thermodynamic properties of the systems examined in our work. On the basis of experimental data, there were calculated parameters $K^{1/n}$ and n describing the selective solvation of the NaI molecule and Na$^+$ ion in AN + DMF and AN + DMSO mixtures. These parameters were compared with the values obtained for the mentioned previously examined systems, for which it was possible to describe the course of $\Delta_{tr}H^E$ by means of the PS model[11] (Table 3).

The values of the reaction equilibrium constants for all of the systems presented in Table 3 are higher than unity ($K > 1$), which indicates the preferential ion solvation by the cosolvent in the mixtures of AN with these cosolvents. The reaction equilibrium of solvent molecule exchange in the ionic solvation shell is shifted to the right-hand side in all cases. The strongest shift of the examined equilibrium has been observed in the case of the AN mixtures with 2-ME. What concerns the systems examined in this work is that this shift is stronger in the mixtures containing DMSO than in the mixtures with DMF {$K^{1/n}$(AN + DMSO) > $K^{1/n}$(AN + DMF)}.

The results of our calorimetric studies have also been examined with the use of the enthalpic pair interaction coefficients concept.[9] These coefficients derived from McMillan–Mayer's theory[31] can be regarded as a measure of the heat effect (i.e., enthalpy of interaction) when two solute particles approach each other in dilute solutions. In our earlier papers,[11] it was demonstrated that in three-component systems containing electrolyte X, solvent S, and cosolvent Y, the enthalpic pair interaction coefficients, h_{xy}, illustrate the heat effect of replacing the solvent molecule by the cosolvent one in the ionic solvation shell.

The enthalpic pair interaction coefficients, h_{xy}, for NaI–nonelectrolyte (cosolvent) pairs in AN solutions have been calculated on the basis of the transfer enthalpies in the AN + organic cosolvent mixtures, using the formula:

$$\Delta_{sol}H^0(M) - \Delta_{sol}H^0(AN) = 2h_{xy}m_y + 3h_{xyy}m_y^2 \tag{6}$$

where $\Delta_{sol}H^0$ is the standard molar enthalpy of solution of NaI (X) in AN (S) + cosolvent (Y) mixtures and $\Delta_{sol}H^0(H_2O)$ is the standard enthalpy of solution of NaI in AN. Parameter h_{xyy} denotes the enthalpic triplet interaction coefficient.

Coefficients h_{xy} obtained were then divided into "linear" and "specific" or "excess" contributions according to the concept presented in the paper.[9]

$$h_{xy} = h_{xy}^{*} + h_{xy}^{E} \qquad (7)$$

The first "linear" contribution, $h_{xy}^* = (M_S/2)\Delta_{tr}H^0(S \rightarrow Y)$ is derived on the basis of the assumption about the linearity of the dissolution enthalpy of electrolyte in the mixed solvents, and it illustrates the effect of gradual changes in the solute solvation shell structure. The "specific" contribution, h_{xy}^E, gives the effect arising from the specific interactions in the system under investigation (e.g., PS).[9,11]

The results of these calculations are given in Table 4.

The calculated values of the enthalpic pair interaction coefficients for NaI−nonelectrolyte pairs in AN are negative for almost all systems examined so far. The only exception is the system containing PC for which the h_{xy} value is close to zero. The highly negative values of the "specific" contributions confirm our earlier conclusions that the NaI−cosolvent molecule interactions leading to the replacement of the solvent molecules by the cosolvent ones in the NaI solvation shell are dominating in the AN solution. For this reason we expected that the h_{xy} coefficients would be correlated with the parameters illustrating the PS in the same system. As it can be seen in Figure 7, the enthalpic interaction coefficients in AN for the pairs containing NaI and DMF, DMA, DMSO, or 2-ME are linearly correlated with the values of ln $K^{1/n}$ derived from Covington's PS model for the same systems. As $K^{1/n}$ is the equilibrium constant for the process of exchange of the AN molecule to the cosolvent molecule in the ionic solvation shell, the obtained correlation confirms the above-mentioned interpretation of the enthalpic interaction coefficients in AN. The correlation obtained made it also possible to calculate the PS equilibrium constant $K^{1/n}$ for NaI in AN + PC mixtures. It amounts to 1.3, which confirms the earlier conclusion that in this system the structure of ionic solvation shells changes gradually along with the change of the mixed solvent composition.[11]

The point corresponding to AN + MeOH mixtures lies outside of the correlation line. It is probably due to the non-negligible contribution of the methanol−iodide anion solvation effect. Figure 8, which presents the analogous correlation of ln $K^{1/n}$ for solvation of the Na^+, confirms the above suggestion.

Table 4. Enthalpic Pair Interaction Coefficients h_{xy} and "Linear" h_{xy}* and "Specific" h_{xy}^E Contributions to h_{xy} for NaI−Nonelectrolyte Interactions in AN

nonelectrolyte	h_{xy} $J \cdot kg \cdot mol^{-2}$	h_{xy}* $J \cdot kg \cdot mol^{-2}$	h_{xy}^E $J \cdot kg \cdot mol^{-2}$
DMF	−2925	−283	−2642
DMSO	−3050	−206	−2844
DMA	−3337[11]	−235	−3102
PC	3[11]	80	−77
2-ME	−5493[11]	−267	−5226
MeOH	−2370[21]	−31	−2339
W	−2704[a]	212	−2916

[a] Calculated from literature data.[16]

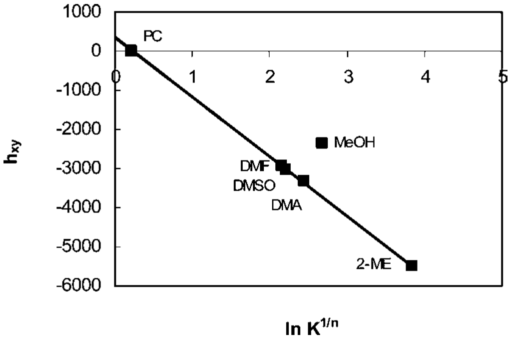

Figure 7. Correlation of the enthalpic pair interaction coefficients h_{xy} for NaI−nonelectrolyte pairs and ln $K^{1/n}$ from Covington's PS model in AN solution.

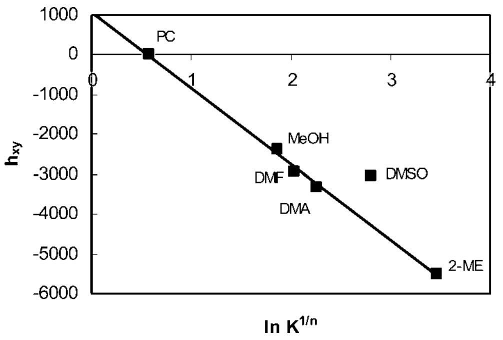

Figure 8. Correlation of the enthalpic pair interaction coefficients h_{xy} for Na^+−nonelectrolyte pairs and ln $K^{1/n}$ from Covington's PS model in AN solution.

It is noteworthy that the conclusions drawn on the basis of the thermochemical functions for the salts and ions in all examined AN + cosolvent mixtures are fully consistent with those drawn from our examinations of volumetric properties concerning these solutions.[12] Hence, the analysis of thermochemical and volumetric functions of NaI solutions in the mixed solvents containing AN has demonstrated that the characteristic changes in their values are connected mainly with the PS of the sodium cation by the cosolvent (DMA, DMF, DMSO, 2-ME, MeOH, water) molecules; in the mixtures of AN with PC, the structure of solvation sheaths of the examined ions varies proportionally to the change in the mixed solvent composition. 2-ME in electrolyte solutions with AN behaves very similarly to aprotic solvents (like in solutions with water, methanol, and DMF). The behavior of the electrolyte−AN + cosolvent systems observed generally reflects the properties of the cosolvent, and it is not dominated by the properties of AN.

Conclusions

AN as a component of the mixed solvent shows a very strong differentiating ability with regards to the properties of cosolvent.

AN is a good reference solvent for electrolyte solutions, especially in the case of inorganic cations.

AN weakly differentiates anions; hence, it seems to be particularly suitable in studies on the effect of cations on the behavior of the system.

The results of extensive studies on the solutions of electrolytes in binary solvents carried out in our laboratory as well as appropriate literature data make it possible to draw some more general conclusions concerning the behavior of various mixtures in relation to simple, noncoordinating electrolytes dissolved in them.

Water + Organic Solvent. The effect of ion solvation, at least within the water-rich region of the mixed solvent, is dominated by the water−organic solvent interactions, that is, by the hydration of organic solvent. Within the organic solvent-rich range only, its influence on the solvation of ions becomes dominating or at least considerable.

DMF + Organic Solvent. DMF differentiates the properties of cosolvents relatively weakly. A decisive part in the behavior of electrolyte solutions within the DMF-rich region in the system is played by the properties of DMF as a solvent that solvates ions relatively strongly.

MeOH + Organic Solvent. The addition of an organic solvent (or water) to methanol, since its first portions are already added, modifies the properties of methanol as the solvent of the electrolytes. Depending on the kind of cosolvent, we observe the PS of ions by methanol or cosolvent.

AN + Organic Solvent. The observed behavior of the system reflects mainly the properties of cosolvent, especially the cation−cosolvent interactions. A dominating part in the behavior of electrolyte solutions within the AN-rich region is played by the PS of electrolyte, especially cations by the cosolvent, and relatively weak interaction between the mixed solvent components.

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