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The enthalpic characteristics of individual ions in the mixed solvent *N,N*-dimethylformamide–water

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Abstract

The enthalpic characteristics of individual ions in mixed solvent DMF–water were determined from the data on the dissolution enthalpies of tetraalkylammonium salts derived from a quantitative account of the various contributions to the solvation enthalpy of the ion. The universal constituent is shown to make the basic contribution to the transfer enthalpy of the Bu_4N^+ ion. For the organic ions Ph_4P^+ and Ph_4B^- which are similar in size, the differences in the enthalpies of their transfer were determined by the sign of the ionic charge. The influence of the mixture composition on the solvation of halide ions is conditioned by the change in its electron acceptability and by the differences in the electron donicity of the anions.

INTRODUCTION

The interest in systems based on amides derives from their use as model compounds in biochemistry and relates to the possibility of tracing the influence of various functional groups of molecules of amides on the thermodynamics of the solvation of ions [1].

The experimental material on the thermochemistry of dissolution of electrolytes in water mixtures with *N,N*-dimethylformamide (DMF) that is available in the literature assumes its different interpretations. On the basis of the thermochemical investigation of dissolution of tetraalkylammonium salts, Karpenko [2] and Rouw and Somsen [3] have come to conclusions concerning the stabilizing influence of DMF on the structure of water due to the hydrophobic interaction between the components of the mixed solvent. The stabilization of the water structure by the addition of DMF results in a weakening of the solvation of the electrolytes, which is manifested as endothermicity maxima in the $\Delta_{soln}H^{\ominus} = f(X)$ isotherms in the $X_{DMF} = 0.2$–0.3 m.f. (molar fraction) region.

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Vyugin [4] measured the heat capacity characteristics of the solutions of organic salts. The data obtained were explained on the basis of assuming the destructive action of organic cations on the structure of the mixed solvent water–DMF.

Gusev et al. [5] obtained the enthalpic characteristics of individual ions in mixtures of water with dimethylformamide, assuming the equality between the transfer enthalpies of the Ph_4P^+ and Ph_4B^- ions. The authors consider that the increase in the exothermicity of the transfer enthalpies from water into the mixed solvent water–DMF of Na^+ and Ni^{2+} ions reflects the strengthening of the solvating power of the mixture with respect to the cation; this is determined by the increasing electron-donicity of the mixture with increasing content of the non-aqueous component. The differences in the solvation of different anions are explained by the authors by the different polarizabilities of the anions.

From an investigation of the thermodynamic characteristics of solvation of a series of electrolytes in water–DMF solvent, Toropov [6] concluded that the decrease in its solvating power with increasing amide concentration is conditioned by the entropic factor.

Boou and Somsen [7] obtained the enthalpic characteristics of individual ions based on the assumption that in mixed solvent water–DMF, the ratio $\Delta_{tr}H^0(Na^+)//\Delta_{tr}H^{\ominus}(Br^-)$ remained constant for all the compositions of the mixture. For the transfer from DMF into water, the authors used the Cs^+–I^- assumption. Considering that Na^+ and Br^- ions are not specifically solvated and criticizing the Ph_4P^+–Ph_4B^- assumption [8], the investigators explained the differences in the solvation of Ph_4P^+ and Ph_4B^- ions by the steric effects in solution and by their different polarizability. Here, the chemical individuality of the ions and the donor–acceptor ability of the mixed solvent were not taken into account [9].

The above stresses the need to obtain the enthalpic characteristics of individual ions on the basis of more correct and physically substantiated approaches to the resolution of this task.

APPROACH

In the present paper, the enthalpic characteristics of individual ions in mixed solvent DMF–water were determined using the approach which is being developed by us [10–13]. The transfer enthalpy of the ion (i) from one to the other solvent is represented as a sum of the universal and charge contribution

$$\Delta_{tr}H^{\ominus}(i) = \Delta_{tr}^{un}H^{\ominus}(i) + \Delta_{tr}^{ch}H^{\ominus}(i) \tag{1}$$

The universal charge contribution is equal to the transfer enthalpy of a non-polar particle of the corresponding size-model (M)

$$\Delta_{tr}^{un}H^{\ominus}(i) = \Delta_{tr}H^{\ominus}(M) \tag{2}$$

The charge contribution is determined by the near interaction solvent-ion, by the structural effects (in the solvents that are associated by H bonds), and by far-range forces [13]

$$\Delta_{tr}^{ch}H^{\ominus}(i) = \Delta_{tr}^{near}H^{\ominus}(i) + \Delta_{tr}^{str}H^{\ominus}(i) + \Delta_{tr}^{far}H^{\ominus}(i) \tag{3}$$

To calculate the far-range contribution, the Born–Bjerrum equation was used

$$\Delta_{solv}^{Born}H^{\ominus}(i) = -N_A z e^2/8\pi\varepsilon_0 r(1 - 1/\varepsilon - T/\varepsilon(d \ln \varepsilon/dT) \tag{4}$$

where N_A is Avogardro's number, z is the ionic charge, e is the elementary charge, ε_0 is the electric constant, ε is the relative dielectric permeability of the medium, and $r = r_i + \delta_s$ is the "effective" radius formed by the sum of the ionic radius r_i and thickness of the solvent layer δ_s; beyond this radius, the solvent dielectric permeability can be assumed to be equal to its macroscopic dielectric permeability.

It is found that at δ_s values above 0.25 nm, the Born contribution to the transfer enthalpy of ions becomes practically constant [13]. This is correct for a great number of solvents. Here, for an (R_4N^+) ion of $(C_nH_{2n+1})_4N^+$

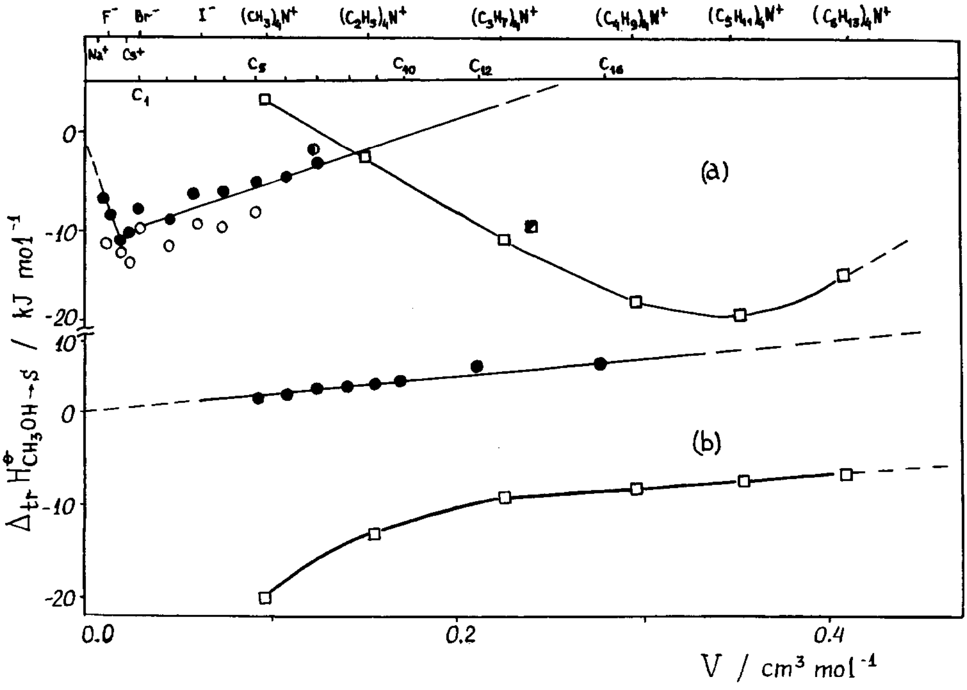


Fig. 1. Dependences of the transfer enthalpies of non-polar substances (●) [14–16], (○) [15] and tetraalkylammonium bromides (□) [17] from methanol to water (a) and from methanol to DMF (b) on the size of the molecule or cation. The values $V = N_A 4/3\pi r^3$ were determined from literature data [18, 19]. (◐), Cyclohexane [20]: (▨), tetramethylpentane [20]. The reference temperature is 298.15 K.

TABLE 1

Contributions to the transfer enthalpies of ions from DMF into its mixtures with water (kJ $\mathrm{mol^{-1}}$)

X_w	$\Delta_{tr}^{un}H^{\ominus}$		$\Delta_{tr}^{Born}H^{\ominus}$ [a]		$\Delta_{tr}^{near+str}H^{\ominus}$	
	Bu_4N^+	Br^-	Bu_4N^+	Br^-	Bu_4N^+	Br^-
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	3.3	0.5	0.7	0.7	0.0	−1.9
0.3	11.0	1.2	1.2	1.1	0.0	−5.2
0.5	20.5	2.1	1.4	1.4	0.0	−10.5
0.7	30.5	3.2	1.6	1.6	0.0	−19.5
0.9	19.5	1.2	1.7	1.7	0.0	−22.9
1.0	2.5	−10.8 [b]	1.7	1.7	−5.9	−10.3

[a] The Born contribution was calculated for the Bu_4N^+ ion at $r = r_i$, and for the Br^- ion at $r = r_i + 0.25$ nm.

[b] $\Delta_{tr}^{un}H^{\ominus}(Br^-)$ from DMF to water was determined from the data shown in Fig. 1.

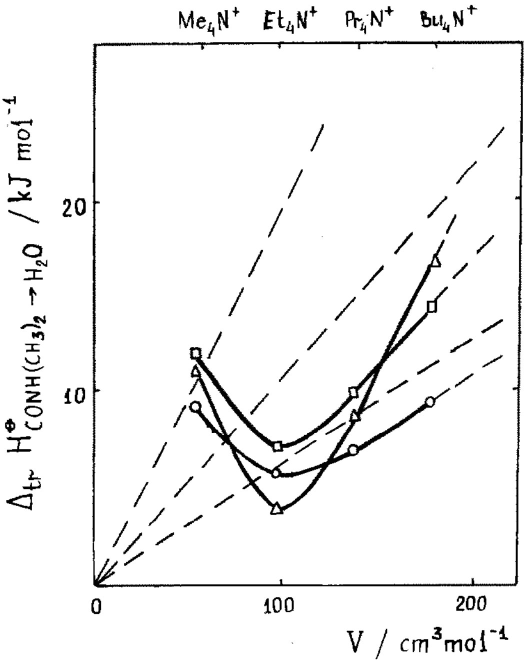


Fig. 2. Dependences of the transfer enthalpies of tetraalkylammonium bromides from DMF to its mixtures with water on the size of cation. Literature data [17] were used. The dashed lines correspond to the molar fractions of water: (○), 0.3; (□), 0.5; (△), 0.7.

type, beginning with a definite value of n, the correlations given below are correct.

$$\Delta_{\mathrm{tr}}^{\mathrm{near}}H^{\ominus}(\mathrm{R_4N^+}) = \Delta_{\mathrm{tr}}^{\mathrm{str}}H^{*}(\mathrm{R_4N^+}) \approx 0 \qquad (5)$$

$$\Delta_{\mathrm{tr}}^{\mathrm{ch}}H^{\ominus}(\mathrm{R_4N^+}) = \Delta_{\mathrm{tr}}^{\mathrm{fan}}H^{\ominus}(\mathrm{R_4N^+}) = \Delta_{\mathrm{tr}}^{\mathrm{Born}}H^{\ominus}(\mathrm{R_4N^+}) = \text{constant} \qquad (6)$$

Here, the calculation for such an ion is derived from eqn. (4) at $r = r_{\mathrm{i}}$. Then

$$\Delta_{\mathrm{tr}}H^{\ominus}(\mathrm{R_4N^+}) = \Delta_{\mathrm{tr}}H^{\ominus}(\mathrm{M}) + \Delta_{\mathrm{tr}}^{\mathrm{Born}}H^{\ominus}(\mathrm{R_4N^+}) \qquad (7)$$

$$\Delta_{\mathrm{tr}}H^{\ominus}(\mathrm{X^-}) = \Delta_{\mathrm{tr}}H^{\ominus}(\mathrm{R_4N^+}, \mathrm{X^-}) - \Delta_{\mathrm{tr}}H^{\ominus}(\mathrm{R_4N^+}) \qquad (8)$$

The data illustrated in Fig. 1 explain the above statements. It can be seen that the dependences of the transfer enthalpies of alkanes and tetraalkylammonium salts on the size of the molecule or cation join the parallel straight lines: for the transfer from methanol to H_2O, beginning with $\mathrm{Am_4N^+}$ ion; and for that from methanol into DMF, beginning with $\mathrm{Pr_4N^+}$ ion. Analogous regularities occur for the transfer in both non-aqueous [20] and mixed (for example, alcohol–water [13]) solvents. It is important to stress here that for alkanes (A), the dependences $\Delta_{\mathrm{tr}}H^{\ominus}(\mathrm{A}) = f(v)$ are described by the straight-line equations beginning at the coordinate origin for both non-aqueous [21, 22] and mixed solvents [13, 23, 24]. It is noteworthy that the $\Delta_{\mathrm{tr}}H^{\ominus}(\text{methanol} \rightarrow \text{DMF, A}) = f(v)$ dependence includes the cyclic and branched alkanes (Fig. 1), and, for the solvents, for which experimental data are available, also for inorganic gaseous substances. This is discussed in detail elsewhere [22]. For water, as seen in Fig. 1, the dependence discussed is of extremal character.

The determination of the enthalpic characteristics of individual ions in mixed solvent DMF–water using this approach is illustrated by the data in the table and in Figs. 1–4. Figure 2 shows how the universal contribution to the transfer enthalpy of the $\mathrm{Bu_4N^+}$ ion was determined. The broken lines in the figure correspond to the supposed transfer enthalpies of the model compounds for a definite composition of the mixed solvent (compare with Fig. 1).

DISCUSSION

The data of Table 1 show that the universal constituent of the transfer enthalpy for the $\mathrm{Br^-}$ ion, is insignificant, except for the transfer from DMF into water. The Born contribution is also small. The magnitudes of $\mathrm{d}(\ln \varepsilon)/\mathrm{d}T$ for the mixed solvent were calculated here according to the additive scheme, using the data taken from ref. 25. The negative values of $\Delta_{\mathrm{tr}}^{\mathrm{near+str}}H^{\ominus}(\mathrm{Br^-})$ suggest that reaction (9) is accompanied by a gain in

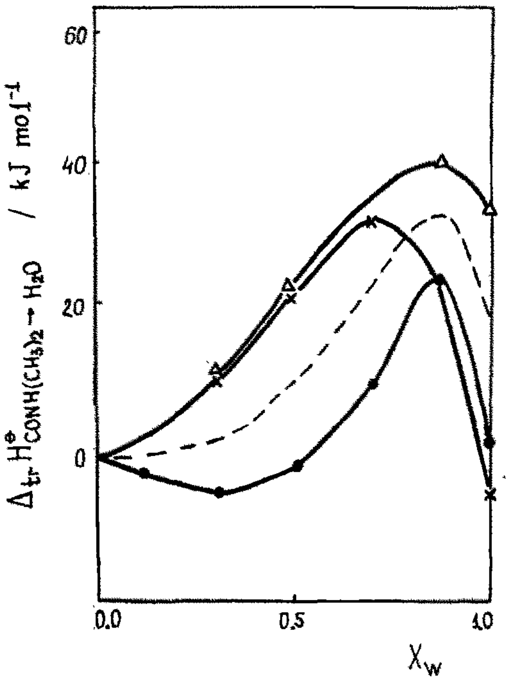
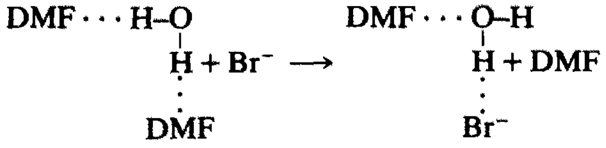


Fig. 3. The transfer enthalpies of Ph_4P^+ (△), Bu_4N^+ (×) and Ph_4B^- (●) ions from DMF to its mixtures with water: (——), our data; (– – –), Ph_4P^+–Ph_4B^- assumption.

energy



$$\begin{array}{l} \mathrm{DMF\cdots H{-}O} \\ \qquad\quad \mathrm{H + Br^-} \longrightarrow \\ \qquad\quad \vdots \\ \qquad \mathrm{DMF} \end{array} \qquad \begin{array}{l} \mathrm{DMF\cdots O{-}H} \\ \qquad\quad \mathrm{H + DMF} \\ \qquad\quad \vdots \\ \qquad\quad \mathrm{Br^-} \end{array} \tag{9}$$

It follows that the Br^- ion is a somewhat stronger electron donor than the DMF molecule.

It is interesting that the values of $\Delta_{tr}^{near+str}H^{\ominus}(Br^-)$ are proportional to X_w within the range $0 < X_w < 0.5$. The complexes 1DMF:1H_2O correspond to the composition 0.5 m.f. (molar fraction). In addition, there is a sharp increase in the exothermicity of the $4_{tr}^{near+str}H^{\ominus}(Br^-)$ values up to the concentration $X_w \approx 0.7$ m.f. (1DMF:2H_2O). The maximum energy of the donor–acceptor interaction of the solvent anion corresponds to compositions of mixed solvent in the range 0.7–0.9 m.f.

Figure 3 shows that the solvation of the Bu_4N^+ ions becomes weaker at the transition from DMF into its mixtures with water ($X_w = 0.0$–0.7 m.f.), illustrated by the increase in the universal constituent of the transfer enthalpy of this cation (see Table 1). The value of the Born contribution for the ions Bu_4N^+, Ph_4P^+, and Ph_4B^-, which are close in size, is

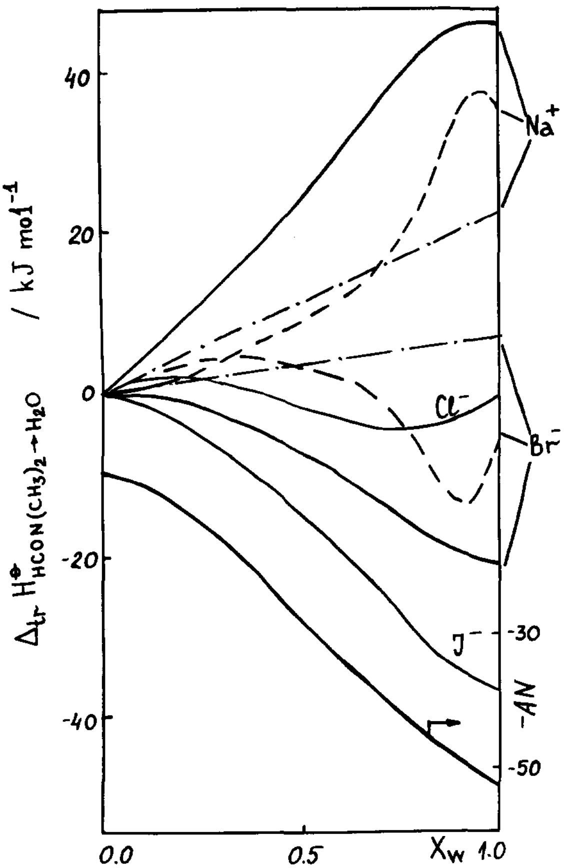


Fig. 4. The transfer enthalpies of ions from DMF to its mixtures with water, obtained from different division methods: (——), our data; (– – –) Ph_4P^+–Ph_4B^- assumption; (– · –), Na^+/Br^- assumption [7]; (●), electron acceptability of the mixture DMF-water [26].

insignificant. The differences in the solvation of the ions discussed (Fig. 3) cannot be explained as proceeding from the electrostatic nature of the solvent–ion interactions alone. The weakening of the universal solvation (relative to DMF) at $X_w = 0.5$–0.7 m.f. is characteristic of all three ions. The less endothermic values of $\Delta_{tr}H^{\ominus}$ for the Ph_4B^- ion, compared to those of Ph_4P^+, over the entire interval of compositions, can be explained by the electron-donating ability of the Ph_4B^- ion, which is conditioned by the displacement of the electronic density of the boron atom towards the ionic periphery. In the case of Ph_4P^+, the π electrons of the benzene rings, while interacting with the d orbitals of the central atom, delocalize the ionic charge; therefore, the organic cation is solvated, this being the particle with low surface density of the electric charge. Maximum differences in the solvation of the Ph_4B^- and Ph_4P^+ ions (relative to DMF) are observed at $X_w = 0.5$–0.7 m.f. and in water.

Figure 4 shows the transfer enthalpies of inorganic ions obtained from different division methods. The increase in exothermicity of the transfer enthalpies of anions in the series I^-, Br^-, Cl^- with increasing water content is determined by the increase in electron–donicity over the same ionic series [12]. It is noteworthy that the enthalpic characteristic of the bromide ion, assuming that $\Delta_{tr}H^{\ominus}(Na^+)/4_{tr}H^{\ominus}(Br^-) = \text{constant}$ [7], does not agree with the increase in electron–acceptability of the mixed solvent with increasing water content 26] (Fig. 4). It can be seen that the Ph_4P^+–Ph_4B^- and Na^+/Br^- assumptions do not take into account (each to differing degrees) the donor–acceptor nature of ion–molecular interactions and the structural effects in solution.

REFERENCES

1 V.N. Vandyshev and V.P. Korolyov, Collected papers: Ivanovo Institute of Chemistry and Technology, (1987) 111.
2 G.V. Karpenko, Izv. Vuzov, Khim. Khim. Tekhnol., 19 (1976) 1714.
3 A.C. Rouw and G. Somsen, J. Solution Chem., 10 (1981) 533.
4 A.I. Vyugin, Ph.D. Thesis, Ivanovo Institute of Chemistry and Technology, 1977.
5 V.D. Gusev, V.A. Shormanov and G.A. Krestov, Collected papers: Ivanovo Institute of Chemistry and Technology, (1988) 109.
6 V.V. Toropov, Ph.D. Thesis, Institute of Non-aqueous Solution Chemistry of Russian Academy of Sciences, (1984).
7 M. Boou and G. Somsen, Electrochim. Acta, 18 (1985) 1883.
8 C.V. Krishnan and H.L. Friedman, J. Phys. Chem., 71 (1971) 2487.
9 G.A. Krestov, Zh. Vses. Khim. Ova., 29 (1984) 482.
10 G.A. Krestov, V.P. Korolyov and V.N. Vandyshev, Dokl. Akad. Nauk SSSR, 302 (1988) 132.
11 V.P. Korolyov, Collected papers: Ivanovo Institute of Chemistry and Technology, (1988) 120.
12 G.A. Krestov, V.P. Korolyov and V.N. Vandyshev, Dokl. Akad. Nauk SSSR, 131 (1990) 641.
13 N.G. Manin, V.P. Korolyov and G.A. Krestov. Collected papers: Institute of Non-aqueous Solution Chemistry of Russian Academy of Sciences, (1990) 45.
14 M.H. Abraham, J. Am. Chem. Soc., 104 (1982) 2085.
15 S.F. Dec and S.J. Gill, J. Solution Chem., 14 (1985) 417.
16 W.K. Stephenson and R. Fuchs, Can. J. Chem., 63 (1985) 336.
17 G.M. Poltoratsky, Thermodynamic Characteristics of Non-Aqueous Solutions of Electrolytes, Khimiya, Leningrad, 1984.
18 A. Bondi, J. Phys. Chem., 68 (1964) 441.
19 M.H. Abraham and Y. Marcus, J. Chem. Soc. Faraday Trans. 1, 10 (1986) 3255.
20 R. Fuchs and W.K. Stephenson, Can. J. Chem., 14 (1985) 336.
21 V.N. Vandyshev, V.P. Korolyov and G.A. Krestov, Thermochim. Acta, 169 (1990) 57.
22 V.P. Korolyov, O.A. Antonova, D.V. Batov and G.A. Krestov, Collected papers: Institute of Non-aqueous Solution Chemistry of Russian Academy of Sciences, (1990) 104.
23 C.V. Krishnan and H.L. Friedman, J. Phys. Chem., 75 (1971) 3598.
24 Y. Kondo, R. Uematsu, Y. Nakamura and S. Kusabayashi, J. Chem. Soc. Faraday Trans. 1, 84 (1988) 111.
25 Ya.Yu. Akhadov, Dielectric Properties of Pure Liquids, Izd-vo standartov, 1972, 412 pp.
26 U. Mayer, W. Gerger and V. Gutmann, Monatsh. Chem., 108 (1977) 489.