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# Thermodynamics of $Na^+$ ion solvation in water–organic mixtures studied by the method of Volta potential differences

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**The features of the solvation of the $Na^+$ ion compared with the $Cl^-$ ion in mixtures of water with various organic solvents have been elucidated on the basis of the analysis of chemical Gibbs energies of $Na^+$ transfer from water to mixed solvents.**

The special interest to the thermodynamic characteristics of individual ions in solutions results from a wide range of theoretical and practical problems requiring information on the individual properties of solvated ions. All attempts at separating the experimental values that characterise interactions between solvents and electrolytes into contributions corresponding to ion–solvent interaction should use a model based on non-thermodynamic assumptions. An alternative approach is to develop methods for the theoretical calculations of resolvation functions.

Currently available theoretical methods for the calculation of thermodynamic characteristics of individual ions in solutions are inadequate. Moreover, they compare calculated data with the ‘experimental’ data obtained by making different extrathermodynamic assumptions.

The possibility of the determination of activity coefficients of individual ions based on the potentials of electrocapillary maximum of mercury was demonstrated.[1–3] The determination and analysis of thermodynamic characteristics of individual ions in water and non-aqueous solvents by the method of Volta potential differences were discussed.[4–6]

From our point of view, the solution of the above fundamental problem is the application of the conception of real thermodynamic properties of individual ions. The suggested conception[7] is based on analysis of the real thermodynamic characteristics of the solvation of individual ions ($\Delta_{solv}G_i^{o,r}$) and surface potentials ($\Delta\chi$) at the solution/gas phase interface. Chemical thermodynamic characteristics of the solvation of individual ions ($\Delta_{solv}G_i^{o,chem}$) can be calculated from the expression

$$\Delta_{solv}G_{i(j)}^{o,r} = \Delta_{solv}G_{i(j)}^{o,chem} \pm z_{i(j)}F\Delta\chi, \qquad (1)$$

where $F$ is the Faraday constant, and $z$ is the ion charge. It is clear that accurate values of $\Delta\chi$ are necessary. For the solvent studied and water, the $\Delta\chi$ values were determined earlier.[8]

A modern procedure for the determination of the compensating voltages of the Volta circuits containing electrolyte solutions[7] is similar to that described by Parsons[4,5] and Randles[9–11] and only differs from the later by some details of the glass part of an experimental unit and by the use of better measuring instruments.

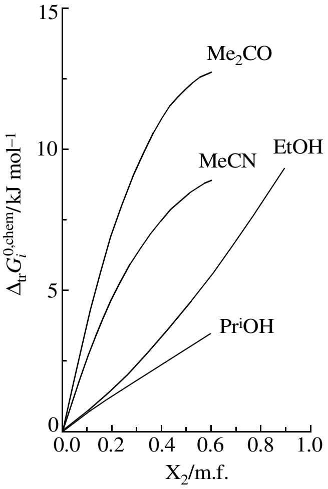

**Figure 1** The concentration dependence of $\Delta_{tr}G_i^{0,chem}$ ($Cl^-$, $H_2O \rightarrow S$) in the mixed solvents.

The real thermodynamic characteristics of individual ions were found from the experimental values of the compensating voltages ($\Delta V$) of Volta circuits.[†]

By the vertical jet method (the Kenrick method), the compensating voltages ($\Delta V$, $V$) of the folowing Volta circuits were measured:

$$\text{ISE(Na)} \mid \text{NaCl (m), S}(X) \mid \text{gas} \mid 0.05\ \text{m NaCl, } H_2O \mid \text{(Na)ISE.} \qquad (2)$$

Here, ISE is an ion selective electrode reversible to $Na^+$; m is the molality of the electrolyte ($2.5\times10^{-3}$–$5\times10^{-2}$ mol kg$^{-1}$); S refers to mixtures of water with ethanol (EtOH), isopropanol (Pr$^i$OH); acetone ($Me_2CO$) or acetonitrile (MeCN); $X$ is the molal fraction of a non-aqueous component in the mixture.

The calculation procedure of the real and chemical Gibbs energies of $Na^+$ transfer from water to water–organic mixtures was described previously.[3] The values of $\Delta_{tr}G_{Na^+}^{o,chem}$ ($H_2O \rightarrow S$) together with the reported data for the $Cl^-$ ion[4] allowed us to analyse the behaviour of $Na^+$ and $Cl^-$ ions in different solvents (Figures 1 and 2). Note that the behaviours of cations and anions were essentially different in several solvents.

For the water–alcohol mixtures in water-rich regions, the ions mainly hydrated[5] because of the lesser solvating ability of alcohols as compared with water. The process of resolvation occurs with an increase in the alcohol concentration. For [$H_2O$–EtOH] and [$H_2O$–Pr$^i$OH] systems, an increase in $\Delta_{tr}G_{Na^+}^{o,chem}$ ($H_2O \rightarrow S$) values was greater by ~16 and 23 kJ mol$^{-1}$, respectively, with an increase in alcohol concentration up to 0.6 m.f. The rise of $\Delta_{tr}G_{Na^+}^{o,chem}$ ($H_2O \rightarrow S$) values for the $Cl^-$ ion is significantly smaller and falls sharply from ethanol to isopropanol. It may be concluded that the cation gives the main contribution to the total energy of resolvation of chlorides on the addition of protic solvents to water. Moreover, the weakening of the solvation of cations is more pronounced than that of anions. Obviously, the replacement of water molecules by alcohol molecules in the solvate shell of the anion occurs less intensely than that for the cation. The solvate shells of anions mainly consist of water. Probably, it may be due to the ability of anions to form bonds with water molecules similar to hydrogen bonds. These bonds complete with water–water hydrogen bonds.[6]

The comparison of $\Delta_{tr}G_i^{o,chem}$ ($H_2O \rightarrow Me_2CO$) for cations with those for anions indicates that the contributions of ions with opposite signs to the total energy of resolvation are approximately equal over the whole concentration range studied. This fact confirms the following assumption: the composition of solvate shells of ions in water–acetone mixtures changes exemplarily in proportion to the changing of solvent composition in the bulk.

However, for water–acetonitrile mixtures, the behaviour of ions essentially changes. The $\Delta_{tr}G_i^{o,chem}$ ($H_2O \rightarrow MeCN$) values for $Na^+$ became greater by 4 kJ mol$^{-1}$ and for $Cl^-$ ions, by 8 kJ mol$^{-1}$, as the acetonitrile concentration increased up to $X = 0.6$ mole fraction. Thus, in water–organic mixtures with a polar aprotic solvent like acetonitrile as a non-aqueous component, anions give the main contribution to the total energy of resolvation of the electrolytes studied. Note that $\Delta_{tr}G_{Cl^-}^{o,chem}$ ($H_2O \rightarrow MeCN$) at $X_{MeCN} = 0.6$ m.f. is twice as high as an analogous value in water–alcohol mixtures. The opposite behaviour is observed for cations.

The results may be explained by the weak solvating ability of acetonitrile in relation to cations. Their solvate shells, at least in the neighbouring surrounding, mainly consist of water molecules even at relatively high MeCN concentrations. Moreover, according to published data,[7] the strength of cation–water bonds increases by the addition of acetonitrile. On the other hand, acetonitrile can form donor–acceptor bonds with metal ions.[8] Therefore, the replacement of water by MeCN molecules in the solvate shell leads to the compensation of a positive contribution of dehydration effects to $\Delta_{\rm solv}G_i^{\rm o,chem}$ by a negative contribution of cation solvation by the molecules of a polar aprotic solvent.

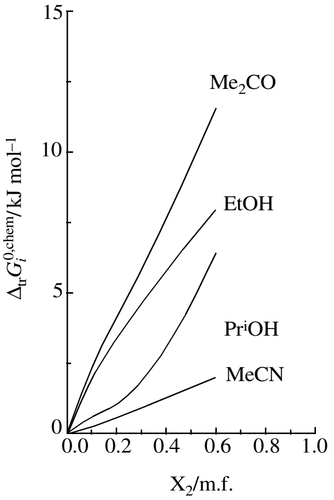

**Figure 2** The concentration dependence of $\Delta_{\rm tr}G_i^{0,\rm chem}$ (Na$^+$, H$_2$O→S) in the mixed solvents.

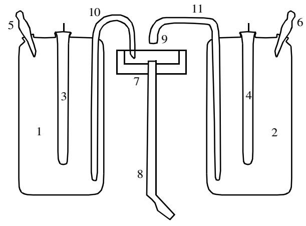

**Figure 3** Scheme of the glass part of a unit for measuring compensation voltages of Volta cirquits by the Kenrick method.

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[†] Measurements of the compensating voltages of Volta circuits refer to measurements of the voltages of current sources whose total resistance is ~$10^{12}$ Ω.[10] It follows that the measuring instrument used for this purpose should have a fairly high input resistance. We used an ITN-7 electrometer. The internal resistance of this instrument was ~$10^{15}$ Ω, and its input resistance was virtually determined by the quality of insulating input terminals and the dynamic capacitor; it could reach $10^{16}$–$10^{17}$ Ω. The measurement range of the electrometer covered by 11 scales was $5\times10^{-5}$–30 V. The main error of voltage measurements did not exceed ±10% in the range up to $3\times10^{-4}$ V, ±4% up to $1\times10^{-3}$ and $3\times10^{-3}$ V, and 1.5% in the other measurement ranges.

The unit for measuring the compensating voltages of Volta circuits by the Kenrick method consists of a glass part containing cells for solutions and electrode sensors (3,4), a metallic box, which simultaneously serves as a screen and an air thermostat, a recording instrument (an ITN-7 electrometer), and a system for supplying solutions. To remove disturbances induced by external electromagnetic fields, the screen thermostat and all metallic parts within it (stands, holders, *etc*.). were thoroughly grounded. A well-shielded cable from the high-resistance electrometer input was introduced into the thermostat through its top wall. This cable was used to connect the electrodes to the instrument. The glass part of the unit was placed inside the thermostat and fixed in stands by fluoroplastic holders for electric insulation purposes. This part is shown in Figure 3.

The test solutions (~200 ml) were introduced into cell 1 through ground-glass joint 5. The cell was connected to a system for supplying compressed air through a branch pipe in ground-glass joint 5 and a flexible tube. Compressed air transferred the test solution from cell 1 through pipe 10 to fluoroplastic funnel 7. Cell 1 contained indicator electrode 3 fixed in a ground-glass joint; through this electrode, the test solution was connected to a grounded terminal of the electrometer. Tube 8 fixed by a special holder was introduced into funnel 7 through a hole in its bottom. The length of the vertical part of the tube was 130–140 mm, its inside diameter was ~6 mm. The bottom tube portion was bent at a 45° angle, and the bend contained a hole through which a flow of a reference solution passed.

During experiments, the test solution fills fluoroplastic funnel 7 and runs down inside glass tube walls 8 completely wetting them and forming a hollow liquid cylinder. Simultaneously, a reference solution was supplied under the action of compressed air from vessel 2 of volume ~200 ml through tube 11 and capillary 9. The reference solution runs down along the axis of tube 8. The test solution and the reference solution formed something like two cylindrical capacitor plates. An electric field arose in the space between the solutions that formed the cylindrical capacitor. Drops into which the stream flowing from capillary 9 separated carried away an excess electric charge, which charged the mobile plate of the dynamic capacitor and generated a potential difference between its plates.

The reference solution ($m_{\rm ref}$) was a dilute NaCl solution with a concentration of 0.05 mol kg$^{-1}$; this solution was loaded into cell 2 through ground-glass joint 6. Cell 2 was connected to a system for supplying compressed air through a branch pipe in ground-glass joint 6. Reference electrode 4 connected to the signal electrometer terminal was fixed in cell 2 with the use of a ground-glass joint. In Volta circuit compensation voltage measurements, special attention should be given to the purity of tube 8 inside walls. Tube 8 should be kept in a potassium bichromate–sulfuric acid mixture between measurements to remove contaminants that may cause incomplete wetting of its walls by the flowing down test solution. The tube should be thoroughly washed first with distilled water and then with the test solution before measurements. In preparing the unit for measurements, capillary 9 and tube 8 were fixed in such a way that the stream of the reference solution from capillary 9 was strictly vertical and directed along the axis of tube 8.

To check the correctness of electrometer and electrode system operations, the same reference solution was loaded into vessels 1 and 2 before a series of measurements, two calibrated silver chloride electrodes were introduced, and the compensation voltage of the Volta circuit

$$\mathrm{Ag,AgCl}\,|\,\mathrm{HCl}(m_{\rm ref})\,|\,\mathrm{air}\,|\,\mathrm{HCl}(m_{\rm ref})\,|\,\mathrm{AgCl,Ag} \qquad (3)$$

was measured. Ideally, this voltage should be zero. In practice, some small finite voltage (≈0.1–0.5 mV) called asymmetry potential by Randles[10] was observed. In subsequent measurements with test solutions, this value was taken as the origin.