

Thermodynamic characteristics of the resolution of K⁺ and Cl[−] ions in mixtures of water with aprotic solvents

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DOI: 10.1070/MC2005v015n05ABEH002140

The solvation of K⁺ and Cl[−] ions in water mixtures with aprotic solvents (acetone, acetonitrile, dimethylsulfoxide and dimethylformamide) was studied based on the analysis of primary effects of the medium of K⁺ and Cl[−] and the chemical Gibbs energies of transfer of these ions from water to the mixed solvents at 298.15 K obtained from Volta potential differences.

The thermodynamic characteristics of resolution (or a primary medium effect) $\Delta_{tr}G_i^0(1 \rightarrow 2)$ at isothermal transfer of ions from an infinitely dilute solution in solvent (I) to an infinitely dilute solution in solvent (II) is of considerable interest. To solve a wide range of theoretical and practical problems, information on the individual properties of solvated ions is required.¹

The determination and analysis of the thermodynamic characteristics of individual ions in water and non-aqueous solvents by the method of Volta potential differences is well known.^{2–7} An important feature of this method is the possibility of determining real thermodynamic functions of individual ions directly from experimental data (the primary effect of the medium of ions $\lg \gamma_{oi}^0$ and the real Gibbs energies of transfer of ions from water to a mixed solvent $\Delta_{tr}G_i^{0,r}$). A clear distinction between the real and chemical solvation energies was made by Lange and Mishchenko.⁸

The method of Volta potential differences provides an opportunity to calculate the surface potential $\Delta\chi$ at the solvent/gas interface. If the surface potential is known, we can pass from the real thermodynamic to the chemical characteristics of separate ions $\lg \gamma_{oi}^{chem}$ and $\Delta_{tr}G_i^{0,chem}$.

It is clear that accurate values of $\Delta\chi$ are necessary. For water and the test solvents, the values of $\Delta\chi$ have been determined earlier. The investigation of the change of potentials at the phase interface was described in detail^{9–11} in terms of physical, chemical and structural aspects of the interface.

A modern procedure for the determination of compensating voltages of the Volta circuits containing electrolyte solutions is similar to that described previously.^{2,3,12,13}

The real thermodynamic characteristics of individual ions were calculated from the experimental compensating voltages ($\Delta E_i/V$) of Volta circuits, obtained by the vertical jet method (the Kenrick method¹⁴):

$$\text{ISE} | \text{KCl (m), S(X)} | \text{GAS} | 0.05 \text{ m KCl, H}_2\text{O} | \text{ISE} \quad (1)$$

Here, ISE is a selective electrode reversible to K⁺ or Cl[−]; m is the molality of electrolyte (2.5×10^{-3} – 5×10^{-2} mol kg^{−1}); S refers to mixtures of water with acetone (Me₂CO), acetonitrile

(MeCN), dimethyl sulfoxide (DMSO) and dimethylformamide (DMF); X is the mole fraction of a non-aqueous component in the mixture (m.f.).

The chloride-reversible electrode was a pasted silver chloride electrode characterised by a high stability and a good voltage reproducibility in aqueous organic media.¹⁵ We also used an ESL-91-07 glass electrode with a potassium function. The function of the ion selective electrodes (ISLs) was checked by measuring the emf of chains without transfer. The difference of the electrode potentials was not greater than 0.1 mV. Prior to measurements in mixed solvents, all electrodes were held for a day in working solutions.¹⁶

The difference of the compensation voltages of circuits (1) in water and a non-aqueous solvent is related to the activities of K⁺ and Cl[−] in the non-aqueous solvent and water as

$$\Delta E_i(\text{H}_2\text{O}) - \Delta E_i(\text{S}) = E_{oi}^{\text{H}_2\text{O}} - E_{oi}^{\text{S}} + \theta \lg \frac{a_i^r(\text{H}_2\text{O})}{a_i^r(\text{S})} \pm \Delta\chi, \quad (2)$$

where $E_{oi}^{\text{H}_2\text{O}}$ and E_{oi}^{S} are the standard electrode potentials in water and the non-aqueous solvent, respectively, and $\Delta\chi$ is the difference of the surface potentials at the solution/gas interface.

Let us introduce the notation

$$E_{oi}^{\text{H}_2\text{O}} - E_{oi}^{\text{S}} \pm \Delta\chi(\text{H}_2\text{O} \rightarrow \text{S}) = \Delta_i, \quad (3)$$

We can write

$$\Delta E_i(\text{H}_2\text{O}) - \Delta E_i(\text{S}) = \Delta_i + \theta \lg \frac{a_i^r(\text{H}_2\text{O})}{a_i^r(\text{S})}. \quad (4)$$

The Δ_i values were determined graphically as the distances between the $\Delta E_i = f(-\lg m)$ straight lines at $\lg m = 0$. The $\Delta_{tr}G_i^0(1 \rightarrow 2)$ Gibbs energy of transfer at a given temperature is determined by the difference of the standard chemical potentials of type 'i' ions in solvents I and II. In accordance with the IUPAC recommendations, a standard solution is the ideal hypothetical solution with $(a_k c_k^0/c_k)^\infty = 1$, where c_k^0 is the standard concentration, a_k is the activity, and k is an arbitrary solution component except the solvent whose partial molar energy characteristics are the same as in an infinitely dilute solution. In the

Table 1 Experimental real primary medium effects of potassium ions $\lg \gamma_{0K^+}$ at 298.15 K.

X (m.f.)	$-\lg \gamma_{0K^+}$			
	Me ₂ CO	MeCN	DMSO	DMF
0	0	0	0	0
0.08	7.41	4.02	5.50	6.17
0.10	7.40	3.68	5.41	6.15
0.12	7.39	3.67	5.25	6.07
0.16	7.31	3.66	5.03	6.03
0.20	7.21	3.65	4.87	6.01
0.30	7.93	3.54	4.47	5.83
0.40	6.65	3.49	4.31	5.54
0.50	6.22	3.40	4.19	5.20
0.60	5.47	3.36	3.94	5.03
0.70	—	—	3.89	4.85
0.80	—	—	3.59	4.72
0.90	—	—	3.18	4.62

Table 2 Experimental real primary medium effects of chloride ions $\lg \gamma_{0Cl^-}$ at 298.15 K.

X (m.f.)	$-\lg \gamma_{0Cl^-}$			
	Me ₂ CO	MeCN	DMSO	DMF
0	0	0	0	0
0.08	8.15	4.22	6.15	9.25
0.10	8.25	4.23	6.19	9.36
0.12	8.37	4.24	6.25	9.41
0.16	8.52	4.36	6.37	9.46
0.20	8.81	4.51	6.49	9.51
0.30	9.15	4.84	6.73	9.69
0.40	9.53	5.12	7.05	9.85
0.50	9.72	5.18	7.31	10.15
0.60	9.83	5.26	7.54	10.42
0.70	—	—	7.68	10.53
0.80	—	—	7.93	10.64
0.90	—	—	8.22	10.73

infinitely dilute solution, the coefficient of activity of a solute is accepted to be unity. We used the assumption

$$\lg \frac{a_i^r(\text{H}_2\text{O})}{a_i^r(\text{S})} = 0,$$

which gave

$$\Delta E_i(\text{H}_2\text{O}) - \Delta E_i(\text{S}) = \Delta_i. \quad (5)$$

The Δ_i values allowed us to calculate the real primary medium effects of the separate ions under consideration

$$\lg \gamma_{oi}^r = \frac{\Delta_i}{\theta}, \quad (6)$$

where $\theta = 2.303RT/zF$, and z is the ion charge.

The real primary medium effects of K^+ and Cl^- $\lg \gamma_{oi}^r$ calculated directly from the experimental ΔE_i values are given in Tables 1 and 2 (error of 0.05). The $\lg \gamma_{oi}^r$ values are positive for chloride and negative for potassium ions over the whole range of mixed solvent compositions. The changes in $\lg \gamma_{oi}^r$ depend on surface and volume, and they are caused by a surface factor in the region of small amounts of organic components and by a volume factor in the region of high concentrations. Starting with the concentration $X = 0.1$ mole fractions, changes in the surface potential of solutions at the solution/gas interface become constant, and the rate at which $\lg \gamma_{oi}^r$ increases substantially lowers.

The method for calculating the chemical primary medium effects of individual ions $\lg \gamma_{oi}^{\text{chem}}$ is based on using the real primary medium effects of individual ions and $\Delta\chi$ on the interface. The real primary medium effect is related to the chemical effect by the equation

$$\lg \gamma_{oi}^r = \lg \gamma_{oi}^{\text{chem}} \pm \frac{\Delta\chi}{\theta}. \quad (7)$$

We calculated the values of $\Delta\chi$ for some organic solvents and water^{17,18} (Table 3) (error of 0.003 V).

The surface potentials of organic solvents are negative, unlike the surface potential of water. This means that the molecules of these solvents are oriented so that their polar functional groups are directed toward the liquid phase, whereas apolar hydrocarbon radicals, toward the gaseous phase. In the case of water–organic mixtures, the gradual replacement of water molecules in the surface layer by the molecules of organic components leads to the change in sign of surface potential.

Surface-active organic solvent molecules are adsorbed on the surface of water. Therefore, the gas phase potential becomes more negative. As a result, the double layer of adsorbed non-aqueous solvent molecules hinders the transfer of Cl^- ions from the solution to the gas phase through the interface and, conversely, facilitates the transfer of potassium ions. This results in the difference in sign between the $\lg \gamma_{oi}^r$ values for the cation and anion.

The primary chemical medium effects of Cl^- and K^+ ions are positive and increase with solvent concentration. This is evidence that water solvates both cations and anions more strongly than non-aqueous solvents.

The real $\Delta_{tr}G_i^{0,r}$ and chemical $\Delta_{tr}G_i^{0,\text{chem}}$ Gibbs energies of transfer of chloride and potassium ions from water to mixed solvents were calculated by the equations

$$\Delta_{tr}G_i^{0,r} = 2.303RT \lg \gamma_{oi}^r \quad (8)$$

$$\Delta_{tr}G_i^{0,\text{chem}} = 2.303RT \lg \gamma_{oi}^{\text{chem}}. \quad (9)$$

These values are positive for both the cation and the anion and increase with the concentration of the organic solvent. The

Table 4 Gibbs energies $\Delta_{tr}G_{\text{KCl}}^0$ of KCl transfer from water to the mixed solvents at 298.15 K (published data^{19–21} are given in parentheses).

X (m.f.)	$\Delta_{tr}G_{\text{KCl}}^0 / \text{kJ mol}^{-1}$		
	Me_2CO	MeCN	DMSO
0.08	4.2 (4.2)	2.7 (2.6)	3.3 (3.0)
0.10	4.9 (5.0)	3.1 (2.7)	3.9 (4.2)
0.12	5.6 (5.7)	3.3 (2.9)	4.4 (5.1)
0.16	8.0 (7.3)	4.0 (3.2)	7.8 (8.1)
0.20	8.7 (8.9)	4.9 (3.9)	9.0 (8.9)
0.30	12.7 (13.0)	7.2 (6.9)	12.4 (12.6)
0.40	16.4 (17.1)	9.3 (9.0)	15.5 (15.4)
0.50	20.4 (21.3)	12.2 (12.2)	17.7 (17.8)
0.60	24.3 (25.5)	14.3 (15.1)	20.2 (19.4)

ions are predominantly hydrated in the region rich in water because organic solvents have lower solvating abilities as compared with water.

The reliability of the results is supported by the agreement of the thermodynamic characteristics of transfer of a stoichiometric ion mixture ($\Delta_{tr}G_{\text{KCl}}^0$) from water to a mixed solvent with published data^{19–21} (Table 4).

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Table 3 Surface potentials $\Delta\chi$ of water and organic solvents.

Solvent	$\Delta\chi/\text{V}$
H_2O	+0.100
Me_2CO	−0.337
MeCN	−0.108
DMSO	−0.238
DMF	−0.434

Received: 24th January 2005; Com. 05/2463