

Reviews

Application of Volta chains to determine ionic components of real and chemical Gibbs energies of transfer of individual ions from water to aqueous-organic solvents

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The state of individual ions in individual and mixed solvents was described from the thermodynamic point of view using the method of Volta potential differences. This methodology provides a way of solving the problem of determination of thermodynamic characteristics of individual ions in solutions. The possibility of using the method of Volta potential differences to determine the ionic components of the real and chemical thermodynamic properties of individual ions in solutions and the surface potentials at gas–solution interface is substantiated.

Key words: ions, Gibbs energy, solvation, solutions.

The determination of thermodynamic characteristics of solvation of individual ions in solvents of different nature is topical due to the need of solving various theoretical problem and practical tasks. However, the problem has no unambiguous solution as yet. In the vast majority of experimental studies and theoretical calculations researchers use the so-called chemical thermodynamic properties obtained by separating the total characteristics of solvation of electrically neutral combinations of ions (stoichiometric mixtures). Modern theoretical methods of calculation of thermodynamic properties of individual ions are still far from being perfect. Moreover, the quality of such theoretical approximations is assessed by comparing

the results of calculations with "experimental" data obtained under various non-thermodynamic admissions based on the use of model compounds. At the same time despite the lack of a strict proof of the physical reality of activity, activity coefficient, and related thermodynamic properties of an individual ion, these characteristics are widely used. A possible way of determining the thermodynamic properties of individual ions is to use the method of Volta potential difference, which allows one to calculate the real energies of solvation of individual ions from experimental data.¹ To determine the chemical properties, one should know the surface potentials (χ) at gas–liquid interfaces.

The relation between the real ($\Delta_{\text{solv}}G_i^{0,\text{real}}$) and chemical ($\Delta_{\text{solv}}G_i^{0,\text{chem}}$) energies of solvation of individual ions is rather simple:

$$\Delta_{\text{solv}}G_{i(j)}^{0,\text{real}} = \Delta_{\text{solv}}G_{i(j)}^{0,\text{chem}} \pm z_{i(j)}F\chi, \quad (1)$$

where z is the charge, F is the Faraday constant, and the "minus" and "plus" signs refer to anions and cations, respectively.

The real energies of solvation of individual ions are meant² the changes in the energy of ions upon transition from the gaseous phase to solution with allowance for the overcoming of the surface potential (χ) at the gas—solution interface.

Clearly, exact determination of χ values is of key importance for solving the problem of calculations of chemical thermodynamic characteristics of individual ions.

The surface potentials of water and nonaqueous solvents

In a recent review,³ the surface potentials of water and aqueous electrolyte solutions at gas—solution interface reported by different authors were compared and the mechanism of the appearance of a surface potential at gas—liquid interface was considered for water and aqueous electrolyte solutions. This phenomenon is due to particular orientation of solvent molecules present in the surface layer at the interface.

Particular attention was paid³ to analysis of the surface potentials at the gaseous phase—water interface. The surface potential of water determined in that study³ was calculated using the method of Volta potential differences and compared with the corresponding potentials obtained by other methods. In spite of a great body of information on the surface potential of water accumulated to date, the sign and numerical value of this parameter is still debatable. The $\chi(\text{H}_2\text{O})$ values reported by different authors vary from -1.1 to $+0.5$ V.³

Analysis of these data suggests that the surface potential of water equal to $+0.10$ V seems to be the best approximation at the moment. The positive sign of this parameter is substantiated by the fact that the negative ends of water dipoles are oriented toward the gas phase while their positive ends are oriented toward the liquid phase.

In this work, interest in the $\chi(\text{H}_2\text{O})$ parameter is due to the fact that the procedure for calculating the surface potentials of the nonaqueous solvents under study³ implies the use of a reliable numerical value of the surface potential of water. Eventually, it is the $\chi(\text{H}_2\text{O})$ value accepted that determines the reliability of the surface potentials of solvents.

The nonaqueous components of mixed solvents used in this work possess significantly different chemical properties. Following Kolthoff,⁴ these are amphiprotic (from methyl to *n*-butyl alcohol), protophobic aprotic

Table 1. Surface potentials of organic solvents (χ)*

Solvent	$-\chi/\text{V}$	
	I	II
MeOH	0.18	0.13 ¹⁰ , 0.18 ¹¹ , 0.23 ¹² , 0.31 ¹³ , 0.20 ¹⁴
EtOH	0.26	0.29 ¹⁰ , 0.12 ¹¹ , 0.30 ¹⁵ , 0.31 ¹³ , 0.27 ¹⁴ , 0.26 ¹⁶
Pr ⁿ OH	0.27	—
Pr ⁱ OH	0.28	—
Bu ⁿ OH	0.28	—
MeCN	0.11	0.1 ¹⁷
DMSO	0.24	0.21 ¹⁰ , 0.29 ¹¹
DMF	0.44	0.46 ¹⁰ , 0.26 ¹¹ , 0.54 ¹⁸
Acetone	0.34	0.40 ¹⁰ , 0.34 ¹¹ , 0.36 ¹³ , 0.33 ¹⁹

* I — our data, II — data reported by other researchers.

(MeCN, acetone), and protophilic aprotic solvents (DMSO, DMF).

The surface potentials of organic solvents were calculated by the method of Volta potential differences.⁵ The procedure for experimental data processing and calculations of the changes in the surface potentials at the gaseous phase—solution interface $\Delta\chi(\text{H}_2\text{O} \rightarrow \text{S})$ (S stands for nonaqueous solvent) was reported earlier.⁶ The key moment in $\Delta\chi(\text{H}_2\text{O} \rightarrow \text{S})$ calculations is to reach a constant value of this parameter^{7–9} starting with a particular concentration of the nonaqueous component in mixed aqueous-organic solvent. The surface potentials of organic solvents studied in this work are listed in Table 1.

Real and chemical thermodynamic properties of individual ions in solutions

In order to determine the thermodynamic properties of individual ions by the method of Volta potential differences, the compensating voltages of Volta circuits in sodium and potassium chloride, bromide, and iodide solutions in mixed solvents (mixtures of water with EtOH, PrOH, PrⁱOH, acetone, MeCN, DMSO, and DMF) were measured.^{20–29} Based on the results obtained, the standard real and chemical Gibbs energies of transfer of individual ions, $\Delta_{\text{tr}}G_i^0(\text{H}_2\text{O} \rightarrow \text{S})$, in the solvents studied were calculated. The experimental procedure and the method of $\Delta_{\text{tr}}G_i^{0,\text{real}}(\text{H}_2\text{O} \rightarrow \text{S})$ computations were reported earlier.^{26,27}

The ionic components of the chemical Gibbs energies of transfer, $\Delta_{\text{tr}}G_i^{0,\text{chem}}(\text{H}_2\text{O} \rightarrow \text{S})$, of Na^+ , K^+ , Cl^- , Br^- , and I^- ions from water to mixed solvents are plotted vs. compositions of aqueous-organic mixtures (X is the mole fraction of the nonaqueous component) in Figs 1 and 2. The $\Delta_{\text{tr}}G_i^{0,\text{chem}}(\text{H}_2\text{O} \rightarrow \text{S})$ values were calculated by Eq. (1).

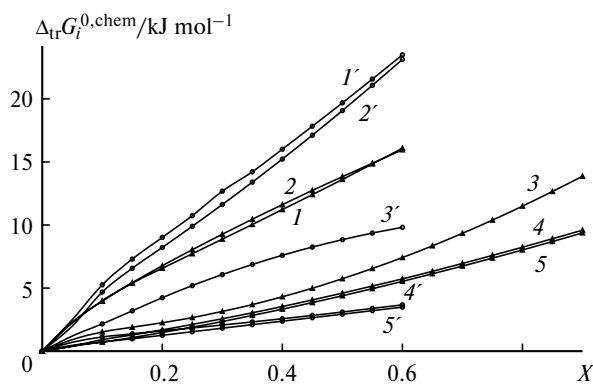


Fig. 1. Ionic components of chemical Gibbs energies ($\Delta_{tr}G_i^{0,chem}$) of transfer of K^+ (1, 1'), Na^+ (2, 2'), I^- (3, 3'), Br^- (4, 4'), and Cl^- ions (5, 5') from water to H_2O –EtOH (1–5) and H_2O –PrⁱOH (1'–5') mixtures plotted vs. compositions of mixed solvents.

A comparative analysis of the effect of composition of the mixed solvent on the thermodynamic parameters of solvation of individual ions revealed correlations between the changes in these characteristics and the properties and structural features of aqueous-organic mixtures and the nature of ions. Note that cations and anions behave quite differently in certain solvents.

In aqueous-alcohol solvents with high content of water, ions are mainly hydrated³⁰ because alcohols show a

lower solvating ability compared to water. As the content of alcohol in the mixed solvent increases, resolution occurs. Heteroselective solvation in electrolyte solutions in methanol (tetraalkylammonium bromides) is indicated by the fact that the partial molal entropies of cations and anions depend on the solvent composition in an opposite fashion.³¹ In this work we showed that cations in the solvent under study are mainly hydrated while anions are mostly solvated. Similar conclusions were made in a Monte Carlo study of clusters $Na^+ + 9 H_2O + 9 MeOH$ and $Cl^- + 12 H_2O + 12 MeOH$.³² The results of calculations show that replacement of H_2O molecules in the solvation shell of Cl^- ions by MeOH molecules in an equimolar mixture is energetically favorable. The reverse holds for Na^+ . This is consistent with the conclusions based on experimental data.^{30,31,33}

The situation changes significantly on going to other alcohols. As the concentration of the alcohol in the H_2O –EtOH and H_2O –PrⁱOH systems (see Fig. 1) increases to $X = 0.60$, the parameters $\Delta_{tr}G_i^{0,chem}(Na^+, H_2O \rightarrow S)$ and $\Delta_{tr}G_i^{0,chem}(K^+, H_2O \rightarrow S)$ increase by ~ 16 and 23 kJ mol^{-1} , respectively. For anions, the $\Delta_{tr}G_i^{0,chem}(H_2O \rightarrow S)$ values increase to a much lesser extent, being abruptly decreased for Cl^- and Br^- ions while increased for I^- on going from EtOH to PrⁱOH. This casts some doubt upon the conclusion, according to which isopropyl alcohol is the predominant solvating component of the solvent for both cations and anions in the H_2O –PrⁱOH system.

Based on these facts, one can suggest that the major contribution to the total energy of resolution of sodium and potassium halides upon the addition of protic solvents to water comes from cation. Here, solvation of cations weakens to a greater extent compared to solvation of anions. Probably, displacement of H_2O molecules by the alcohol molecules for anions is not so intense as for cations in the concentration range studied, and their solvation shells remain mainly built of water molecules. It seems likely that an important role is played by specificity of hydration of anions, which manifests itself in their ability to form hydrogen bonds with water molecules. These bonds compete with water–water hydrogen bonds in strength.³⁴

Comparison of the $\Delta_{tr}G_i^{0,chem}(H_2O \rightarrow Me_2CO)$ values (see Fig. 2, a) for cations and anions shows that the contributions of the unlikely charged ions to the total energy of resolution are nearly the same in the whole range of compositions. This can be treated as substantiation of the admission that the composition of the solvation shells of ions in water–acetone mixtures changes nearly proportionally to the change in the composition of bulk solvent. In other words, as the content of Me_2CO in the mixture changes, the acetone molecules gradually and nearly equally replace water molecules in the solvation shells of both cations and anions. Abrupt changes in the behavior

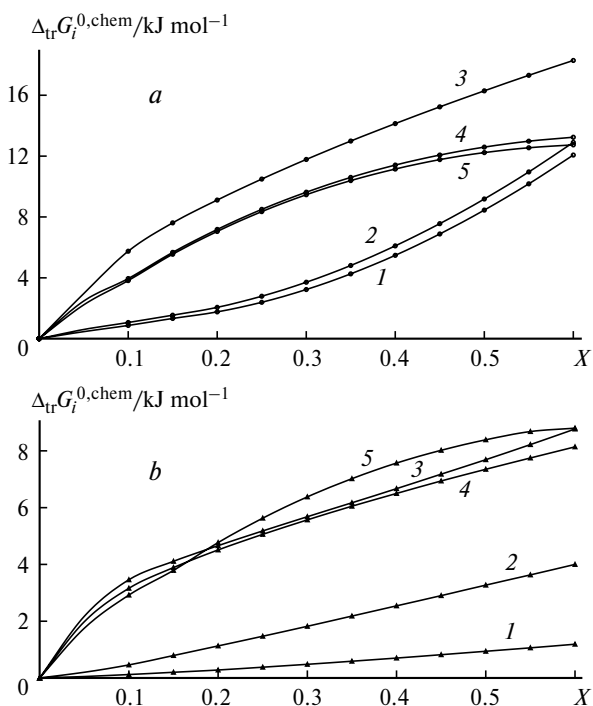


Fig. 2. Ionic components of chemical Gibbs energies ($\Delta_{tr}G_i^{0,chem}$) of transfer of K^+ (1), Na^+ (2), I^- (3), Br^- (4), and Cl^- ions (5) from water to H_2O – Me_2CO (a) and H_2O –MeCN (b) mixtures plotted vs. compositions of mixed solvents.

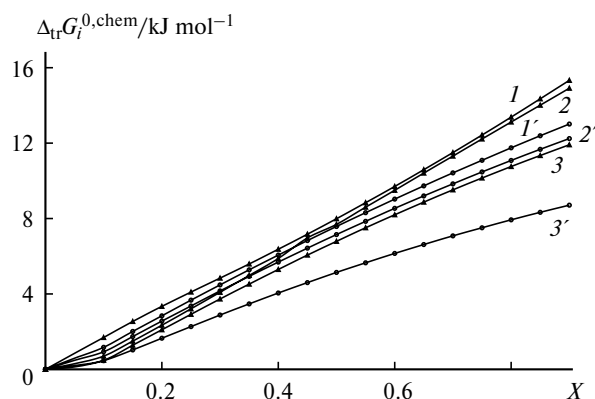


Fig. 3. Ionic components of chemical Gibbs energies ($\Delta_{tr}G_i^{0,chem}$) of transfer of I^- (1, 1'), Br^- (2, 2'), and Cl^- ions (3, 3') from water to water–DMSO (1–3) and water–DMF (1'–3') mixtures plotted vs. compositions of mixed solvents.

of the $\Delta_{tr}G_i^{0,chem}$ vs. X_{Me_2CO} curves at $0.2 < X_{Me_2CO} < 0.3$ are due to the fact that the greatest structural rearrangements in the water–acetone mixture occur at $X_{Me_2CO} < 0.25$ (see Refs 35 and 36).

The picture significantly changes on going to aprotic solvents MeCN (see Fig. 2, b), DMSO, and DMF (Fig. 3). An increase in the content of the nonaqueous component of the water–MeCN mixture to $X = 0.60$ causes the $\Delta_{tr}G_i^{0,chem}(H_2O \rightarrow MeCN)$ values to increase by 4 and 1.2 kJ mol^{−1} for Na^+ and K^+ ions, respectively, and by 8–9 kJ mol^{−1} for Cl^- , Br^- , and I^- ions. Thus, unlike the mixtures of water with protic solvents (alcohols), in aqueous-organic mixtures containing the polar aprotic solvent (MeCN) as the nonaqueous component the major contribution to the total energy of resolution of the electrolytes under study comes from the anion. It should be noted that the chemical Gibbs energy of resolution of halide ions at $X_{MeCN} = 0.6$ is two or three times higher than the corresponding values for aqueous-alcohol solvents. The reverse holds for cations. The results obtained can be explained by weak solvating ability of MeCN with respect

to cations whose solvation shells, at least in the nearest environment, are built of water molecules even at relatively high MeCN concentrations. Moreover, the cation–water bond becomes somewhat stronger in the presence of MeCN.³⁷ At the same time MeCN, DMSO, and DMF are solvents whose molecules can be coordinated by metal ions through donor-acceptor bonds.³⁸ Because of this replacement of water molecules in the solvation shell by MeCN, DMSO, and DMF molecules will lead to compensation of the positive contribution of the dehydration effect to $\Delta_{solv}G_i^{0,chem}$ by negative contribution of the effect of solvation of the cation by the molecules of aprotic electron-donating solvent. We believe this is the best explanation for the mechanism and energy characteristics of resolution, which is also consistent with modern hypotheses of a common nature of solvation and complexation.³⁹

Anions capable of forming hydrogen bonds with proton-donor solvents are weakly solvated in aprotic solvents. For this reason displacement of water molecules from solvation shells of anions by the aprotic solvent molecules is accompanied by essentially positive resolution effects.

The available data on thermodynamic characteristics of transfer (resolution) of individual ions^{40–44} and their stoichiometric mixtures (total thermodynamic characteristics)^{45–47} refer to pure solvents, which precludes a correct comparison of our data with the results obtained by other researchers. In this connection here we compared the total Gibbs energies of transfer of potassium and sodium chlorides from water to EtOH–water, acetone–water, MeCN–water, and DMSO–water mixtures with the published data^{48–52} (Tables 2–5). Analysis showed that a reasonable convergence of these values, which can serve as a criterion for correctness of our data.

The aforesaid suggests that the experimentally determined (obtained by the method of Volta potential differences) ionic components of real thermodynamic characteristics of transfer of individual ions and the correspond-

Table 2. Total Gibbs energies of transfer ($\Delta_{tr}G^0(H_2O \rightarrow S)/kJ\ mol^{-1}$)* for the KCl (NaCl)–H₂O–DMSO system at $T = 298.15\ K$

X_{DMSO}	$\Delta_{tr}G_{Cl^-}^{0,real}$ (± 0.1)	$\Delta_{tr}G_{Cl^-}^{0,chem}$ (± 0.4)	$-\Delta_{tr}G_{Na^+}^{0,real}$ (± 0.1)	$\Delta_{tr}G_{Na^+}^{0,chem}$ (± 0.4)	$-\Delta_{tr}G_{K^+}^{0,real}$ (± 0.1)	$\Delta_{tr}G_{K^+}^{0,chem}$ (± 0.4)	$\Delta_{tr}G_{NaCl}^0$		$\Delta_{tr}G_{KCl}^0$	
							I (± 0.4)	II	I (± 0.4)	II
0.1	35.3	0.5	31.3	2.5	30.9	3.0	3.5	3.8	3.9	4.2
0.2	37.0	2.2	28.1	5.7	27.7	6.4	8.4	8.1	9.0	8.9
0.3	38.4	3.6	26.9	6.8	25.5	8.3	10.7	11.0	12.4	12.6
0.4	40.2	5.4	26.3	7.5	24.5	9.2	13.4	13.6	15.1	15.4
0.5	41.7	6.9	26.0	7.8	23.9	9.9	15.2	15.3	17.3	17.8
0.6	43.0	8.2	25.7	8.0	22.4	11.3	16.6	16.4	20.2	19.4
0.7	43.8	9.0	25.6	8.1	22.2	11.6	17.5	—	20.5	—
0.8	45.2	10.4	23.6	10.2	20.5	13.3	20.9	—	24.2	—
0.9	46.9	12.1	22.4	11.4	18.1	15.7	24.0	—	27.3	—

* I — our data, II — data taken from Ref. 51.

Table 3. Total Gibbs energies of transfer ($\Delta_{tr}G^0(\text{H}_2\text{O} \rightarrow \text{S})/\text{kJ mol}^{-1}$)* for the KCl–H₂O–EtOH system at $T = 298.15$ K

X_{EtOH}	$\Delta_{tr}G_{\text{Cl}^-}^{0,\text{real}}$ (± 0.1)	$\Delta_{tr}G_{\text{Cl}^-}^{0,\text{chem}}$ (± 0.4)	$\Delta_{tr}G_{\text{K}^+}^{0,\text{real}}$ (± 0.1)	$\Delta_{tr}G_{\text{K}^+}^{0,\text{chem}}$ (± 0.4)	$\Delta_{tr}G_{\text{KCl}}^0$	
					I	II
					(±0.4)	
0.08	36.5	0.2	32.0	3.8	3.6	3.4
0.1	36.6	0.8	31.8	4.0	4.7	4.3
0.12	36.7	0.9	31.6	4.3	5.2	4.9
0.16	36.9	1.1	30.0	5.8	6.9	6.5
0.2	37.3	1.5	29.0	6.9	8.3	7.9
0.4	39.2	3.4	24.9	11.0	14.3	14.4
0.6	41.3	5.5	19.7	16.1	21.6	20.8
0.9	44.8	11.2	13.3	20.2	31.5	32.1

* I — our data, II — data taken from Refs 50–52.

Table 4. Total Gibbs energies of transfer ($\Delta_{tr}G^0(\text{H}_2\text{O} \rightarrow \text{S})/\text{kJ mol}^{-1}$)* for the KCl–H₂O–Me₂CO system at $T = 298.15$ K

$X_{\text{Me}_2\text{CO}}$	$\Delta_{tr}G_{\text{Cl}^-}^{0,\text{real}}$ (± 0.1)	$\Delta_{tr}G_{\text{Cl}^-}^{0,\text{chem}}$ (± 0.4)	$\Delta_{tr}G_{\text{K}^+}^{0,\text{real}}$ (± 0.1)	$\Delta_{tr}G_{\text{K}^+}^{0,\text{chem}}$ (± 0.4)	$\Delta_{tr}G_{\text{KCl}}^0$	
					I	II
					(±0.4)	
0.08	46.5	3.2	42.2	1.0	4.2	4.2
0.10	47.1	3.7	42.2	1.0	4.9	5.0
0.12	47.7	4.5	42.1	1.1	5.6	5.7
0.16	49.7	6.4	41.7	1.6	8.0	7.3
0.20	50.3	7.0	41.6	1.7	8.7	8.9
0.40	54.3	11.0	37.9	5.4	16.4	17.1
0.60	56.1	12.2	31.2	12.1	24.3	25.5

* I — our data, II — data taken from Ref. 50.

Table 5. Total Gibbs energies of transfer ($\Delta_{tr}G^0(\text{H}_2\text{O} \rightarrow \text{S})/\text{kJ mol}^{-1}$)* for the KCl (NaCl)–H₂O–MeCN system at $T = 298.15$ K

X_{MeCN}	$\Delta_{tr}G_{\text{Cl}^-}^{0,\text{real}}$ (± 0.1)	$\Delta_{tr}G_{\text{Cl}^-}^{0,\text{chem}}$ (± 0.4)	$-\Delta_{tr}G_{\text{Na}^+}^{0,\text{real}}$ (± 0.1)	$\Delta_{tr}G_{\text{Na}^+}^{0,\text{chem}}$ (± 0.4)	$-\Delta_{tr}G_{\text{K}^+}^{0,\text{real}}$ (± 0.1)	$\Delta_{tr}G_{\text{K}^+}^{0,\text{chem}}$ (± 0.4)	$\Delta_{tr}G_{\text{NaCl}}^0$		$\Delta_{tr}G_{\text{KCl}}^0$	
							I	II	I	II
							(±0.4)		(±0.4)	
0.08	23.7	2.7	20.8	0.4	21.2	0.1	3.3	2.9	2.7	2.6
0.10	24.1	3.0	20.6	0.5	21.0	0.1	3.5	3.0	3.1	2.7
0.12	24.2	3.1	20.4	0.7	20.9	0.2	3.8	3.2	3.3	2.9
0.16	24.9	3.8	20.3	0.8	20.9	0.2	4.6	3.6	4.0	3.2
0.20	25.7	4.6	20.2	0.9	20.8	0.3	5.5	4.1	4.9	3.9
0.40	29.3	8.1	18.4	2.7	19.9	1.2	10.9	9.8	9.3	9.0
0.60	32.9	9.8	13.5	5.8	18.9	3.7	19.4	20.1	14.3	15.1

* I — our data, II — data taken from Ref. 52.

ing chemical properties of the same ions calculated with allowance for the surface potentials of the solvents under study provide information on specific features of solvation of individual ions in various classes of solvents and can be used for thermodynamic description of the state of individual ions in nonaqueous and mixed solvents.

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