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THERMODYNAMIC PROPERTIES OF SINGLE IONS IN PROPYLENE GLYCOL AND ITS AQUEOUS MIXTURES

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ABSTRACT

The standard absolute potentials of hydrogen and silver–silver halide (X = Cl, Br and I) electrodes in propylene glycol and its aqueous mixtures, over the full composition range of the solvent, have been determined at twelve different temperatures from 0 to 55°C by the new method reported recently. The temperature variation of the standard absolute potential has been utilized to evaluate the standard thermodynamic functions for the electrode reactions, and the standard transfer thermodynamic quantities of single ions from water to glycolic solvents. The chemical contributions to these transfer thermodynamic quantities have also been computed by using the new equation correlating the electrode potential with the dielectric constant of the solvent. The results have been analysed and discussed in the light of ion–solvent interactions as well as the structural changes of these solvents.

INTRODUCTION

The study of physico-chemical processes in mixed as well as non-aqueous solvents is of fundamental importance for better understanding of ion–ion, ion–solvent and solvent–solvent interactions [1,2]. Potentiometric studies reveal the nature of ion–solvent interactions [1–3]. Therefore, EMF measurements on galvanic cells involving hydrogen, silver–silver halide electrodes have been extensively used [4–11] not only to determine the thermodynamics of hydrogen halides in aqueous and non-aqueous media, but also to evaluate the thermodynamics of single ions in such media.

The study of the thermodynamic properties of single ions in pure or mixed solvents has recently been a subject of interest. Thus, in continuation of the author's studies on this subject [12–14], the present paper deals with the determination of the standard absolute potentials of the hydrogen and silver–silver halide (X = Cl, Br and I) electrodes in propylene glycol (PG) and its aqueous mixtures, over the full composition range of the solvent, at

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twelve different temperatures from 0 to 55 °C, in order to compute the thermodynamics of transfer of the ions from water to the glycolic solvents, with a view to a comprehensive understanding of the ion–solvent interactions as well as the thermodynamic properties of the single ions in these solvents.

RESULTS AND DISCUSSION

Standard absolute electrode potential

The new method, developed recently [12] for determination of absolute electrode potentials and the thermodynamics of single ions in solution, has been applied to our recently reported [11] EMF data of the cell

$$\mathrm{Pt}\,|\,\mathrm{H_2(g,\ 1\ atm)}\,|\,\mathrm{HX}(m),\ \mathrm{solvent}\,|\,\mathrm{AgX}\,|\,\mathrm{Ag} \tag{A}$$

in PG and its aqueous mixtures. As reported earlier [12,13], there are generally two possibilities for the variation of electrode potential with the radius (r) of the solvated ion on whose activity the potential depends: (I) the oxidation potential varies directly with r (method I), or (II) the reduction potential varies inversely with r (method II). Therefore, the cell EMF (E_m or E_m^0) is proportional to the radius of the solvated ion which is being varied in a series of electrolytes having a common ion [12]. Thus, in any solvent, the plot of the standard EMF (E_m^0) values of cells (A), where X = Cl, Br and I, against the radius of solvated anion, r^- (method I), or $1/r^-$ (method II) values, would yield a straight line according to eqn. (1-I) or (1-II), respectively, at any temperature.

$$E_m^0 = a_1^0 r^+ - a_1^0 r^- \tag{1-I}$$

$$E_m^0 = a_2^0/r^- - a_2^0/r^+ \tag{1-II}$$

In all solvents almost perfect straight lines were obtained at each of the twelve different temperatures. The least-squares results at 25 °C, for example, are collected in Table 1.

As would be expected [12,13], two different sets of values for standard absolute electrode potential (and thus related thermodynamic properties of single ions), based on different (oxidation or reduction) potential scales, are obtained (see Table 1). However, let us proceed through the following features seen in Table 1, to decide which set of data should be credited.

(1) At all temperatures and in all solvents, eqn. (1-I) fits better than eqn. (1-II), as indicated from the correlation coefficients (corr).

(2) The radius of the solvated H^+ ion (r^+), calculated by both methods I and II, decreases with increasing PG content of the solvent at any temper-

TABLE 1

The least-squares results of applying eqns. (1-I) and (1-II) to the recent EMF data [11] of cell (A) in propylene glycol–water solvents at 25 °C

	PG (wt.%)									
	10	20	30	40	50	60	70	80	90	100
Results of method I										
$-$Corr (10^{-2})	99.9998	100.0000	100.0000	100.0000	99.9998	99.9996	99.9990	99.9972	99.9952	99.9828
a_1^0 (10^{10} V m^{-1})	1.05700	1.04414	1.03221	1.02008	1.00782	0.99370	0.97566	0.95458	0.92667	0.89636
r^+ (10^{-10} m)	2.013	2.009	2.005	2.000	1.993	1.986	1.976	1.959	1.922	1.772
${}^{\mathrm{Ox}}_{\mathrm{L}}E_m^0$ (V)	2.12806	2.09773	2.06918	2.03973	2.00903	1.97337	1.92748	1.86994	1.78083	1.58810
${}^{\mathrm{Ox}}_{\mathrm{R}}E_m^0$ (V) X = Cl	1.91318	1.88989	1.86831	1.84635	1.82415	1.79859	1.76594	1.72778	1.67726	1.62242
Br	2.06116	2.03607	2.01282	1.98916	1.96525	1.93771	1.90253	1.86142	1.80700	1.74791
I	2.28313	2.25534	2.22958	2.20338	2.17689	2.14638	2.10742	2.06188	2.00160	1.93615
Results of method II										
Corr (10^{-2})	99.8873	99.8785	99.8790	99.8821	99.8882	99.8923	99.8998	99.9125	99.9219	99.9527
a_2^0 (10^{-10} V m)	4.14629	4.09546	4.04871	4.00125	3.95340	3.89816	3.82771	3.74554	3.63644	3.51906
r^+ (10^{-10} m)	2.003	1.999	1.994	1.989	1.983	1.975	1.965	1.949	1.914	1.783
${}^{\mathrm{Red}}_{\mathrm{L}}E_m^0$ (V)	2.06998	2.04903	2.03022	2.01156	1.99368	1.97334	1.94774	1.92181	1.90028	1.97341
${}^{\mathrm{Red}}_{\mathrm{R}}E_m^0$ (V) X = Cl	2.29077	2.26269	2.23685	2.21063	2.18420	2.15368	2.11476	2.06936	2.00909	1.94423
Br	2.12630	2.10024	2.07626	2.05192	2.02738	1.99906	1.96293	1.92079	1.86484	1.80465
I	1.91958	1.89605	1.87440	1.85243	1.83028	1.80470	1.77209	1.73405	1.68354	1.62919
a_2^0/a_1^0 (10^{-20} m^2)	3.9227	3.9223	3.9224	3.9225	3.9227	3.9229	3.9232	3.9238	3.9242	3.9259

ature, or the temperature of any solvent system, i.e., with a decrease in the dielectric constant of the solvent. Thus, there may be a strong correlation between the r^+ values and the dielectric constant of the solvent. This may be so in view of an important feature seen later. However, at any temperature, the value of r^+ decreases first slowly up to 80% PG and thereafter rapidly with further additions of PG to the solvent. Thus, the solvation of the H^+ ion decreases generally as the water content of a solvent decreases in partially aqueous media, and the extent of solvation becomes minimum in the non-aqueous PG, or as the temperature of the medium increases. Similar results have been reported about the solvation of H^+ ion in methanol (MeOH)–water [12], ethylene glycol (EG)–water [13] and several amphiprotic solvent–water systems [1,3]. It is interesting to compare the values of r^+ in the non-aqueous amphiprotic solvents (such as PG, MeOH and EG), where the solvation becomes minimum in each. At 25°C, for example, the r^+ values (10^{-10} m) calculated by method I are 1.772, 1.798 and 1.837 (and those calculated by method II are 1.783, 1.804 and 1.838) in PG, MeOH [12] and EG [13], respectively. This increasing order in the r^+ values is parallel to, and in accordance with, that in the dielectric constants of the non-aqueous PG, MeOH and EG solvents; these are 31.0, 32.7 and 37.7, respectively [8,10]. Thus, it is again evident that the radius of the solvated ion (and also the electrode potential and its related thermodynamic quantities) are generally dependent upon, and/or related to, the dielectric constant of the medium. This important relationship will be considered and discussed in a following section.

(3) The ratio (a_2^0/a_1^0) is constant (3.923 ± 0.001) and independent of the solvent type and solvent composition, since the same result has been obtained not only in MeOH–water [12] and EG–water [13] solvents, but also in several solvent systems including both protic and aprotic, partially aqueous and non-aqueous solvents [15]. Thus, a_1^0 and a_2^0 appear to be universal constants for all electrodes, and dependent only on the temperature and the medium [12,13]. The values of these constants decrease with increasing PG content of the solvent system.

(4) The values of standard absolute electrode potentials at 25°C are included in Table 1 as an example. Results of method I show that as the PG content of the solvent increases, the solvation extent of H^+ ions decreases, and the oxidation potentials of both left-hand and right-hand electrodes, ${}^{\mathrm{Ox}}_{\mathrm{L}}E^0_m$ and ${}^{\mathrm{Ox}}_{\mathrm{R}}E^0_m$, respectively, decrease. On the other hand, results of method II show that although the r^+ value and thus the extent of solvation of H^+ ions decreases continuously in one direction, the reduction potential of the left-hand electrode $({}^{\mathrm{Red}}_{\mathrm{L}}E^0_m)$ decreases to a minimum at around 90% PG, and thereafter increases, whereas that of the right-hand electrode $({}^{\mathrm{Red}}_{\mathrm{R}}E^0_m)$ decreases, with increasing amounts of PG. This feature has been also observed in the MeOH–water [12] and EG–water [13] solvent systems at around 70% MeOH and 90% EG, respectively.

TABLE 2

Values of the parameters a (10^{-2} V), b (10^{-5} V K^{-1}) and c (10^{-5} V K^{-2}) of eqn. (2) for evaluation of ${}_{\mathrm{E}}E^{0}_{m}$ values in propylene glycol–water solvents at 0–55°C

	PG (wt.%)									
	10	20	30	40	50	60	70	80	90	100
Hydrogen electrode										
a	229.619	207.816	184.485	158.080	123.583	74.616	−6.408	−88.595	−296.933	−608.086
b	127.261	266.257	414.826	585.356	813.602	1136.099	1666.192	2191.761	3493.923	5322.005
c	0.616	0.871	1.139	1.447	1.859	2.430	3.348	4.251	6.375	9.223
Ag/AgCl electrode										
a	217.529	199.901	179.732	157.972	128.891	88.836	20.811	−44.818	−232.564	−519.718
b	−2.352	110.090	238.476	378.641	571.002	834.196	1278.024	1694.034	2867.022	4606.005
c	0.287	0.492	0.720	0.970	1.313	1.774	2.534	3.234	5.113	7.777
Ag/AgBr electrode										
a	234.454	215.449	193.605	170.100	138.552	95.716	22.503	−48.186	−250.857	−559.969
b	−3.230	118.003	257.109	408.520	617.233	898.629	1376.303	1824.393	3090.856	4962.578
c	0.308	0.529	0.776	1.046	1.418	1.911	2.729	3.483	5.512	8.379
Ag/AgI electrode										
a	259.724	238.473	214.773	188.303	153.716	106.192	24.913	−53.460	−277.823	−620.407
b	−3.702	131.914	282.663	453.308	682.078	994.305	1524.595	2021.422	3423.372	5497.953
c	0.341	0.588	0.856	1.160	1.568	2.115	3.023	3.859	6.105	9.283

For the electrode reactions, either the oxidation potential or the reduction potential would decrease with increasing either PG content in the solvent or the temperature of the solvent system [12]. This proves again [12,13] that only one of the methods (I or II) can be accepted for the calculation of a single electrode potential. All the interesting results and conclusions obtained in several protic and aprotic partially aqueous and non-aqueous solvents [12–15], reflecting the same general features gained in the present work, proved that method I should be applied to the EMF data for the determination of absolute electrode potentials as well as the thermodynamic properties of single ions in solution, and thus its set of data (Table 1) should be credited. At the same time, these results shed more light on the inapplicability of method II for such calculations, and gave much evidence that the plots of standard transfer free energy or entropy against the reciprocal of anionic or cationic radius, used earlier [1–11] to obtain the thermodynamic properties of single ions, cannot be accepted. Therefore in the following sections the results of calculations by method I only will be taken into consideration. These further substantiate our conclusions.

The values of standard absolute potentials (V) of any electrode (${}_{\mathrm{E}}E_m^0$) obtained in each solvent by method I were fitted by the method of least-squares to eqn. (2):

$${}_{\mathrm{E}}E_m^0 = a + bT - cT^2 \tag{2}$$

where T is the thermodynamic temperature. The values of the parameters a, b and c are listed in Table 2, for each electrode. The values of ${}_{\mathrm{E}}E_m^0$ computed by eqn. (2) and the original values agree within ±0.27 mV on average, at 0–55 °C.

Standard thermodynamic functions for the half-cell reactions

The standard free energy, ΔG_{E}^0, enthalpy, ΔH_{E}^0, and entropy, ΔS_{E}^0 changes involved in the half-cell reactions are essentially related to the standard absolute electrode potentials and their temperature coefficients. Hence, the standard thermodynamic functions of the half-cell reaction were computed on the molal scale using the usual thermodynamic relations [12]. The results so computed at 25 °C are given in Table 3 as an example. The values of ΔG_{E}^0 are accurate to ± 50 J mol^{-1}. The standard thermodynamic functions associated with the overall cell reaction can be computed as the difference between those for half-cell reactions, both based on the same (oxidation) potential scale [12].

An inspection of Table 3 shows that the thermodynamic functions for the electrode reactions, computed by method I and based on the oxidation potential scale, are all negative. However, since the oxidation reactions of the electrodes are known to be exothermic [1,3], the values of ΔH_{E}^0 should

TABLE 3

Standard molal thermodynamic functions [ΔG_E^0 and ΔH_E^0 (kJ mol^{-1}); ΔS_E^0 (J K^{-1} mol^{-1})] of the electrode reactions at 25 °C, calculated by method I, in propylene glycol–water solvents

	PG (wt.%)									
	10	20	30	40	50	60	70	80	90	100
Hydrogen electrode										
$-\Delta G_E^0$	205.32	202.40	199.64	196.80	193.84	190.40	185.98	180.42	171.82	153.22
$-\Delta H_E^0$	274.38	275.21	275.69	276.63	278.68	280.41	280.97	279.12	260.28	204.33
$-\Delta S_E^0$	231.6	244.2	255.1	267.7	284.6	301.9	318.9	331.0	296.7	171.4
Ag/AgCl electrode										
$-\Delta G_E^0$	184.59	182.35	180.26	178.15	176.01	173.53	170.39	166.70	161.83	156.53
$-\Delta H_E^0$	234.50	235.07	235.17	235.61	236.97	237.87	237.42	234.13	214.15	165.57
$-\Delta S_E^0$	167.4	176.8	184.2	192.7	204.5	215.8	224.8	226.2	175.5	30.3
Ag/AgBr electrode										
$-\Delta G_E^0$	198.87	196.45	194.21	191.93	189.62	186.96	183.57	179.60	174.35	168.64
$-\Delta H_E^0$	252.63	253.25	253.36	253.83	255.30	256.25	255.77	252.24	230.72	178.37
$-\Delta S_E^0$	180.3	190.5	198.4	207.6	220.3	232.4	242.2	243.6	189.1	32.6
Ag/AgI electrode										
$-\Delta G_E^0$	220.28	217.61	215.12	212.59	210.04	207.09	203.34	198.94	193.12	186.80
$-\Delta H_E^0$	279.84	280.52	280.64	281.17	282.80	283.86	283.32	279.40	255.56	197.59
$-\Delta S_E^0$	199.8	211.0	219.8	230.0	244.0	257.5	268.2	269.9	209.4	36.2

be negative, and the oxidation potentials of the single electrodes should decrease with increasing temperature. This is in agreement with the results obtained from method I calculations, and contradictory to those of method II where the reduction potentials decrease with increasing temperature, in any solvent. This conclusion has also been found in the MeOH–water [12] and EG–water [13] solvent systems. Thus, this may lend further support to the validity and general applicability of method I for such calculations.

However, it is evident from Table 3 that for any electrode reaction the values of $\Delta G_{\mathrm{E}}^{0}$ increase, whereas those of both $\Delta H_{\mathrm{E}}^{0}$ and $\Delta S_{\mathrm{E}}^{0}$ decrease slowly to minima (at around 70 and 80% PG, respectively, for the hydrogen electrode reaction, and at around 60% and 80% PG, respectively, for the Ag | AgX electrode reactions), and thereafter increase rapidly with increasing amounts of PG in the solvent.

Standard transfer thermodynamic quantities of single ions

The standard transfer Gibbs free energy of a single ion, $\Delta G_{\mathrm{t}}^{0}(\mathrm{i})$, can be expressed as a function of temperature [12] by eqn. (3):

$$F({}_{\mathrm{E}}^{\mathrm{w}}E_{m}^{0} - {}_{\mathrm{E}}^{\mathrm{s}}E_{m}^{0}) = \Delta G_{\mathrm{t}}^{0}(\mathrm{i}) = A - BT + CT^{2} \tag{3}$$

The standard transfer thermodynamic quantities of single ions can then be obtained by applying the usual thermodynamic relations [12] to eqn. (3), where all refer to the molal scale. The results of calculations on the basis of oxidation potential scale (method I) are collected in Table 4. The values of $\Delta G_{\mathrm{t}}^{0}(\mathrm{i})$ are accurate to ± 90 J mol^{-1}.

The standard Gibbs free energy of the transfer is an important index of the differences in interactions of the ions and the solvent molecules in the two different media, and the single ion free energies of transfer provide a clearer understanding of ion–solvent interactions than do the free energies of transfer of the HX acids [6,7]. Table 4 shows that for all ions the values of $\Delta G_{\mathrm{t}}^{0}(\mathrm{i})$ increase positively with increasing proportions of PG in the solvent. The observed positive increase in $\Delta G_{\mathrm{t}}^{0}(\mathrm{i})$ values suggests that the transfer of ions from water to the glycolic solvents is increasingly unfavourable. The positive $\Delta G_{\mathrm{t}}^{0}(\mathrm{i})$ values indicate that the ions are in higher free energy states in the glycolic solvents than in water, and therefore the transfer process is not spontaneous.

However, the increasingly high positive $\Delta G_{\mathrm{t}}^{0}$ values for the proton in solvents containing 90–100% PG are reflected by the significantly rapid decrease in r^{+} values in these media. Therefore, the increasingly positive $\Delta G_{\mathrm{t}}^{0}$ values reflect increased desolvation of ions, with increasing amounts of PG. Thus, as it appears from this relationship, if the transfer free energy of single ions is largely influenced by the solvation of ions, $\Delta G_{\mathrm{t}}^{0}$ should reflect the solvating capacities of the solvent concerned and water toward this ion.

TABLE 4

Standard molal thermodynamic quantities [ΔG_t^0 and ΔH_t^0 (J mol^{-1}); ΔS_t^0 and ΔC_p^0 (J K^{-1} mol^{-1})] for the transfer of single ions from water to propylene glycol–water solvents at 25 °C

	PG (wt.%)									
	10	20	30	40	50	60	70	80	90	100
Hydrogen ion										
ΔG_t^0	2948	5871	8629	11466	14428	17875	22295	27852	36447	55048
ΔH_t^0	314	−521	−996	−1936	−3989	−5716	−6276	−4428	14414	70361
ΔS_t^0	−8.8	−21.4	−32.3	−45.0	−61.8	−79.1	−95.8	−108.3	−73.9	51.4
$-\Delta C_p^0$	145	292	446	623	860	1189	1717	2236	3458	5097
Chloride ion										
ΔG_t^0	2279	4523	6606	8722	10863	13336	16479	20165	25038	30333
ΔH_t^0	550	−24	−120	−567	−1927	−2819	−2370	914	20902	69474
ΔS_t^0	−5.8	−15.3	−22.6	−31.2	−42.9	−54.2	−63.2	−64.6	−13.9	131.3
$-\Delta C_p^0$	127	245	376	520	717	982	1419	1822	2903	4436
Bromide ion										
ΔG_t^0	2455	4872	7117	9397	11701	14367	17753	21724	26973	32680
ΔH_t^0	586	−32	−141	−620	−2086	−3040	−2560	975	22497	74845
ΔS_t^0	−6.3	−16.4	−24.3	−33.6	−46.2	−58.4	−68.1	−69.6	−15.0	141.4
$-\Delta C_p^0$	137	264	406	561	775	1059	1530	1963	3131	4780
Iodide ion										
ΔG_t^0	2721	5398	7885	10409	12964	15914	19666	24064	29878	36199
ΔH_t^0	650	−37	−150	−684	−2307	−3369	−2825	1091	24931	82899
ΔS_t^0	−6.9	−18.2	−27.0	−37.2	−51.2	−64.7	−75.4	−77.1	−16.6	156.6
$-\Delta C_p^0$	151	293	447	622	857	1171	1694	2175	3467	5295

The positive values of ΔG_t^0 for all ions presumably indicate that the glycolic solvents possess smaller solvating capacities (which decrease with increasing amounts of PG in the solvent) toward ions than water. Besides, the relative magnitudes of ΔG_t^0 for the halide ions show that the relative degree of solvation in any glycolic solvent decreases from Cl^- through Br^- to I^-. This sequence is an agreement with that of the decreasing force field around the ion because of its increasing size and consequent decreasing charge density which should largely influence the solvation of the ion [8]. Thus, the values of ΔG_t^0 indicate that, so far as any ion is concerned, water is a stronger solvating agent than the glycolic solvents.

The transfer enthalpies pass through a slight endothermic maximum at around 10% PG, then become increasingly negative (exothermic) up to 70% PG for the transfer of the proton and 60% for the halide ions, thereafter increasing to positive values in the PG-rich solvents, and subsequently attaining large positve values in the non-aqueous PG. The transfer entropies of ions from water to aqueous glycolic solvents are all negative. Their values decrease negatively to minima at around 80% PG, thereafter increasing negatively, with increasing amounts of PG in the aqueous solvent, and finally becoming highly positive in the non-aqueous PG. Such variation of ΔH_t^0 and ΔS_t^0 values with solvent composition has been observed [4–8,12–15] in many organic solvent–water mixtures.

According to Franks and Ives [16] and Feakins and Voice [9], the effect of ionic fields on the structure of the solvent will appear as a compensating contribution in ΔH_t^0 and ΔS_t^0, and they [9,16] have emphasized the importance of these quantities in explaining the structural effects of the solvents on the transfer process. However, the endothermic maximum in ΔH_t^0 at around 10% PG is due to the structure-breaking effect of the ions on the ordered structure in solvents of low PG content when the ions are transferred from water to these media. This is because addition of small amounts of alcohols is known [16] to promote the hydrogen-bonded structure of water and any ion is a better structure-breaker in the glycolic solvent than in water. The decrease of ΔH_t^0 beyond 10% PG is associated with the structure-making ion–solvent interactions, accompanied by an entropy decrease, at this composition. Thus, the negative and decreasing values of ΔH_t^0 and ΔS_t^0 assume that ions are more effective at breaking the structure in water than in the aqueous glycolic solvents. Water is therefore a more structured solvent than these glycolic solvents. On the other hand, the large positive entropy and enthalpy of transfer of ions from water to the non-aqueous PG can be attributed to a greater structure-breaking by the ion in this solvent than in water. This is further supported by the view [1,4–8] that structure-making processes are exothermic and are accompanied by an entropy decrease while structure-breaking processes are endothermic and lead to an entropy increase.

Table 4 also shows that the values of the heat capacity (ΔC_p^0) for the transfer of any ion from water to the respective glycolic solvents are all negative and decrease with increasing PG content in the solvent.

Chemical contributions to standard transfer thermodynamic quantities of single ions

The transfer process involves the transfer of charged species H^+ and X^- ions from water to the glycolic solvents in the standard states. It is therefore reasonable to expect that the standard Gibbs energy of transfer ΔG_t^0 (and similarly ΔH_t^0, ΔS_t^0 or ΔC_p^0) consists of an electrostatic part ΔG_{el}^0 and a non-electrostatic or chemical part ΔG_{ch}^0:

$$F\left({}^{w}_{E}E^0_m - {}^{s}_{E}E^0_m\right) = \Delta G_t^0(i) = \Delta G^0_{el} + \Delta G^0_{ch} \tag{4}$$

While the electrostatic transfer free energy arises from the differences in the dielectric constants of the solvents, the chemical transfer free energy reflects the contributions of solvation and other specific ion–solvent interactions which depend on the chemical affinity of the solvent for the ions [1–11]. Since the transfer thermodynamic quantities of single ions from water to the respective glycolic solvents have been calculated, it is of considerable interest to compute the chemical contributions to the standard thermodynamic properties of single ions. However, these computations have been made using the new procedure developed recently by Elsemongy [14]. According to this procedure, the electrode potential ${}_{E}E^0_m$ (on the molal scale), in any solvent at different temperatures, can be correlated with the corresponding dielectric constant D of the solvent by the new general relation [14]:

$${}_{E}E^0_m = A_1 + B_1(\ln D) + C_1(\ln D)^2 \tag{5}$$

or,

$$\left({}_{E}E^0_m\right)^{1/2} = a_1 + b_1(\ln D) \tag{6}$$

where A_1, B_1, C_1, a_1 and b_1 are constants for the electrode in each solvent. Equation (6), for example, predicts that, for any solvent at various temperatures, $({}_{E}E^0_m)^{1/2}$ will vary linearly with (ln D). This has actually been verified in all PG–water solvents, as well as in partially aqueous and non-aqueous protic and aprotic solvent systems [14,15] over a wide range of D values. In all cases, plots of $({}_{E}E^0_m)^{1/2}$ against (ln D) gave almost perfect straight lines in each solvent.

For the transfer process from water to any (aqueous or non-aqueous) solvent, when the water (at one temperature) and the solvent (at another temperature) both have the same dielectric constant D, i.e., a transfer process from water of dielectric constant D to a solvent (at another temperature) of the same D, the electrostatic contribution to the transfer

TABLE 5

Chemical contributions to standard thermodynamic quantities for the transfer of single ions from water to propylene glycol–water solvents at two different dielectric constant values [ΔG^0 and ΔH^0 (J mol^{-1}); ΔS^0 and ΔC_p^0 (J K^{-1} mol^{-1})]

PG	$D = 40$				$D = 60$			
(wt.%)	ΔG^0_{ch}	ΔH^0_{ch}	ΔS^0_{ch}	$-(\Delta C_p^0)_{\mathrm{ch}}$	ΔG^0_{ch}	ΔH^0_{ch}	ΔS^0_{ch}	$-(\Delta C_p^0)_{\mathrm{ch}}$
Hydrogen ion								
10	5944	−21120	−68.6	205	1839	−5323	−26.8	163
20	10920	−39794	−132.6	403	2804	−8189	−46.7	317
30	10337	−48095	−170.8	584	1835	−4917	−47.0	461
40	7101	−49442	−191.6	770	60	3840	−29.0	607
50	5052	−52776	−218.5	1017	−1906	18959	11.9	786
60	1223	−48555	−225.1	1335	−2768	46213	97.9	1012
70	−3648	−32255	−196.5	1817	650	98943	283.1	1338
80	−8939	17441	−58.5	2186	12777	172146	561.1	1567
90	−5937	118010	256.8	3128	48122	315047	1108.5	2276
100	23685	307489	871.5	4277	121009	541815	1956.7	3192
Chloride ion								
10	5455	−19910	−62.0	183	1694	−5766	−25.5	146
20	9897	−36353	−116.3	346	2701	−9338	−44.8	274
30	10425	−46531	−155.1	508	2210	−8459	−49.8	403
40	8710	−50469	−178.4	667	1047	−3056	−40.0	528
50	7633	−55774	−206.1	880	−353	7451	−11.8	686
60	5004	−54362	−215.6	1144	−916	27952	53.2	875
70	1447	−43296	−197.0	1553	2006	69778	200.6	1156
80	−2718	−3857	−84.6	1842	11775	127704	421.6	1336
90	−912	81049	189.2	2700	41882	253940	909.7	1980
100	16986	244958	756.6	3811	100171	458394	1711.5	2856
Bromide ion								
10	5892	−21513	−67.0	197	1829	−6242	−27.5	158
20	10681	−39248	−125.5	373	2914	−10101	−48.4	296
30	11274	−50335	−167.7	549	2389	−9190	−53.9	436
40	9428	−54608	−192.8	721	1136	−3366	−43.3	571
50	8277	−60428	−223.0	952	−374	7975	−12.8	742
60	5425	−58733	−232.8	1233	−980	30047	57.1	944
70	1595	−46804	−212.6	1674	2166	75080	215.8	1246
80	−2890	−4332	−91.6	1985	12687	137467	453.8	1440
90	−945	87164	203.5	2912	45154	273659	980.5	2135
100	18341	263742	814.7	4107	107936	493810	1843.8	3078
Iodide ion								
10	6497	−23667	−73.7	217	2023	−6856	−30.3	174
20	11832	−43503	−139.1	414	3226	−11181	−53.6	328
30	12417	−55340	−184.6	605	2639	−10069	−59.3	479
40	10424	−60421	−213.4	798	2153	−3681	−47.8	632
50	9126	−66660	−246.2	1051	−419	8876	−14.1	819

TABLE 5 (*continued*)

PG (wt.%)	$D = 40$				$D = 60$			
	ΔG^0_{ch}	ΔH^0_{ch}	ΔS^0_{ch}	$-(\Delta C^0_p)_{ch}$	ΔG^0_{ch}	ΔH^0_{ch}	ΔS^0_{ch}	$-(\Delta C^0_p)_{ch}$
60	5975	−64855	−257.2	1364	−1094	33304	63.3	1043
70	1737	−51690	−235.1	1853	2396	83231	239.3	1379
80	−3232	−4645	−101.1	2199	14053	152369	503.0	1595
90	−1077	96701	225.8	3224	50008	303166	1086.1	2364
100	20285	292321	902.9	4549	119566	547117	2042.8	3409

free energy would be zero, and the chemical contribution ΔG^0_{ch} can thus be obtained [14] from eqns. (4) and (5) by

$$\Delta G^0_{ch} = A_2 + B_2(\ln D) + C_2(\ln D)^2 \qquad (7)$$

Similarly, the chemical contributions to other standard transfer thermodynamic properties of single ions, at any dielectric constant D, could be obtained as before [14], and the values so computed at $D = 40$ and $D = 60$, as an illustration , are recorded in Table 5.

For the transfer of any ion to media of high dielectric constant (e.g., $D = 60$), the chemical contributions to transfer free energies increase positively to maxima at around 20% PG, then decrease to negative values (at around 50–60% PG) and minima at around 60% PG, and thereafter increase again positively, with increasing PG content in the solvent. A comparison of ΔG^0_{ch} values at $D = 60$ and $D = 40$ (Table 5) shows that, for the transfer to media of low dielectric constant ($D = 40$), the values of ΔG^0_{ch} reflect the same trend observed at $D = 60$, but while the maxima are displaced to 30% PG for the halide ions, the negative minima are displaced to 80% PG for all ions. A similar situation has been found in different solvent systems [14,15].

It is, however, noteworthy that while ΔG^0_{ch} values vary in this manner, those of ΔG^0_t are increasingly positive for all ions. Therefore, as can be expected, the values of ΔG^0_{el} will be increasingly positive, due to the resulting decrease in the dielectric constant, with increasing PG content in the solvent. The increasingly positive values of ΔG^0_t presumably indicate a dominant contribution of the electrostatic over the chemical interactions, causing an unfavourable effect on the overall transfer process. Obviously, the dielectric constant of the medium plays a dominant role in the process of transfer.

Insofar as ΔG^0_{ch} is a criterion of the changes in the chemical affinity of medium for ions, the positive values of ΔG^0_{ch} indicates that the transfer process (e.g., $D = 60$) from water to the glycolic solvents containing 10–40 or 70–100% PG is not favoured, i.e., water has more chemical affinity for the ions than these glycolic solvents. The unfavourable effect increases to maxima for the 20% PG or non-aqueous PG solvents. Thus, as far as chemical reaction or solvation is concerned, any ion is in a lower Gibbs free energy state in water than in such glycolic media. On the other hand, the negative values of ΔG^0_{ch} show that the transfer process is only favourable for aqueous solvents containing 50–60% PG. This suggests that these solvents have greater chemical affinity for the ions than water, and any ion interacts strongly with these solvents. A maximum chemical affinity for the ions (and thus maximum ion–solvent interactions) is noticed for the 60% PG solvent, and further addition of either PG or water tend to decrease it.

The maxima and minima in ΔG^0_{ch} values reflect compensation effects between at least two opposing operating factors. In water- and PG-rich solvents, the increasing factor predominates and thus ΔG^0_{ch} values increase, whereas the decreasing factor predominates in solvents of moderate PG content leading to a decrease in ΔG^0_{ch} values, with increasing amounts of PG in the solvent. This may be so since the chemical interaction includes the breakdown of one type of solvation shell and the creation of another [5,17]. However, to understand this point more clearly, let us examine the values of ΔS^0_{ch} and ΔH^0_{ch} for the single ions. Greater insight into the transfer process is available from these values which reflect contributions from the effects of the ions on the structure of the solvents.

The chemical contributions to transfer enthalpies and entropies of the single ions show similar trends, with increasing PG content in the solvent (Table 5). Thus, for the transfer to media of high dielectric constant (e.g., $D = 60$), the values of ΔH^0_{ch} and ΔS^0_{ch} decrease negatively to minima at around 20 and 30% PG, respectively, thereafter increasing to positive values with increasing amounts of PG, and becoming highly positive for the PG-rich solvents. The negative minima of ΔH^0_{ch} and ΔS^0_{ch} values are displaced to 50 and 60% PG, respectively, for transfer to media of low dielectric constant (e.g., $D = 40$).

Since all structure-forming processes including solvation of ions are exothermic and accompanied by a decrease in entropy, whereas structure-breaking processes including desolvation of ions are endothermic and lead to an increase in entropy, the process of transfer of an ion from water to another solvent should involve [5,8] the following structural changes: (1) breaking down of the structure of the hydration shell around the hydrated ion in water; (2) building up of the liquid structure by the water molecules released by process (1); (3) breaking down of the liquid structure of the solvent, if any, so that the molecules may be free to solvate the incoming ion; (4) building up of the solvation shell around the ion in the solvent by the molecules released by process (3). For the respective steps ΔH^0 and ΔS^0 are positive for (1) and (3), and negative for (2) and (4). The sign and magnitude of the overall entropy or enthalpy changes will depend on the relative magnitudes of the individual steps [5,8].

In water-rich solvents the negative and decreasing values of ΔH^0_{ch} and ΔS^0_{ch} show the net structure-making effect of the ions which is aided by strong ionic fields in media of low dielectric constants. On the other hand, the net structure-breaking effect of the ions in PG-rich solvents is indicated by the positive and increasing values of ΔH^0_{ch} and ΔS^0_{ch}. This effect is more pronounced in media of high dielectric constants. Therefore, PG-rich solvents appear to be more structured solvents than water, which is also a more structured solvent than the water-rich solvents, as far as the chemical interaction on the transfer process is concerned. Moreover, the large positive values of ΔH^0_{ch} and ΔS^0_{ch} for anhydrous PG reflect the larger enthalpy and entropy changes involved in creating a correct configurational change of the solvent on the transfer process.

Furthermore, it is evident from Tables 4 and 5 that in solvents less structured than water the values of ΔS^0_t (in any aqueous glycolic solvent) and ΔS^0_{ch} (in water-rich solvents) decrease negatively from Cl^- through Br^- to I^-. On the other hand, those of ΔS^0_t (in the non-aqueous PG) and ΔS^0_{ch} (in PG-rich solvents) increase positively from Cl^- through Br^- to I^-, in solvents more structured than water. As concluded earlier [5,14], these ideal orders are in better accord with the fundamental tenets of ion-solvation and solvent structure theory [5]. This conclusion, however, lends further proof to the validity of the results obtained from method I calculations, based on the oxidation potential scale.

The values of $(\Delta C^0_p)_{ch}$ are all negative and decrease continuously with increasing PG concentration in the solvent (Table 5), a behaviour similar to that of ΔC^0_p, for the transfer of any ion from water to the respective glycolic solvents (Table 4). However, the value of $(\Delta C^0_p)_{ch}$ becomes more negative on transfer to any glycolic solvent with a lower dielectric constant, and in all cases it decreases from Cl^- through Br^- to I^-.

Finally, it is evident from Tables 4 and 5 that different trends are observed if the values of ΔG^0_{ch}, ΔH^0_{ch} and ΔS^0_{ch} are compared with those of ΔG^0_t, ΔH^0_t and ΔS^0_t, respectively, for any ion. This again reflects [14] the importance of computing the chemical contribution to the standard transfer thermodynamic quantities from water to any solvent.

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REFERENCES

1 D. Feakins, in F. Franks (Ed.), Physico-Chemical Processes in Mixed Aqueous Solvents, Heinemann, London, 1969, and references therein.

2 H.P. Bennetto and D. Feakins, in A.K. Covington and P. Jones (Eds.), Hydrogen-Bonded Solvent Systems, Taylor and Francis, London, 1968, and references therein.

3 R.G. Bates, in J.F. Coetzee and C.D. Ritchie (Eds.), Solute–Solvent Interactions, Dekker, New York, 1969, Chap. 2.
4 V.V. Sastry and C. Kalidas, J. Chem. Eng. Data, 28 (1983) 5.
5 K. Bose, A.K. Das and K.K. Kundu, J. Chem. Soc., Faraday Trans. 1, 71 (1975) 1838; 74 (1978) 1051.
6 B.K. Das and P.K. Das, J. Chem. Soc., Faraday Trans. 1, 74 (1978) 22.
7 K.H. Khoo and C. Chan, Aust. J. Chem., 28 (1975) 721.
8 K.K. Kundu, D. Jana and M.N. Das, J. Phys. Chem., 74 (1970) 2625; Electrochim. Acta, 18 (1973) 95; J. Chem. Eng. Data, 19 (1974) 329.
9 D. Feakins and P.J. Voice, J. Chem. Soc., Faraday Trans. 1, 68 (1972) 1390.
10 K.K. Kundu, P.K. Chattopadhyay, D. Jana and M.N. Das, J. Chem. Eng. Data, 15 (1970) 209.
11 M.M. Elsemongy, A.A. Abdel-Khalek and M.A. Hussein, Z. Phys. Chem. Neue Folge, 134 (1983) 215; Thermochim. Acta, 66 (1983) 303; 68 (1983) 187.
12 M.M. Elsemongy, Thermochim. Acta, 80 (1984) 239.
13 M.M. Elsemongy and F.M. Reicha, Thermochim. Acta, 103 (1986) 371.
14 M.M. Elsemongy, Thermochim. Acta, 103 (1986) 387.
15 M.M. Elsemongy and F.M. Reicha, Thermochim. Acta, 108 (1986) 115.
16 F. Franks and D.J.G. Ives, Q. Rev., Chem. Soc., 20 (1966) 1.
17 U. Sen, K.K. Kundu and M.N. Das, J. Phys. Chem., 71 (1967) 3665.