Thermochimica Acta, 103 (1986) 371–385
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SOLVENT EFFECTS ON SINGLE ELECTRODE POTENTIAL AND RELATED THERMODYNAMIC QUANTITIES

MAHMOUD M. ELSEMONGY *

Chemistry Department, Faculty of Education, Umm Al-Qura University, City of Al-Taif, Shihar (Saudi Arabia)

FIKRY M. REICHA

Physics Department, Faculty of Science, Mansoura University, Mansoura (Egypt)

(Received 17 December 1985)

ABSTRACT

Studies have been extended to the ethylene glycol–water solvent system not only in support of the validity and general applicability of the new method developed for the determination of absolute electrode potentials and thermodynamics of single ions, but also to study the solvent effects on single electrode potential and related thermodynamic quantities, in such media. All results showed that the plots of standard transfer free energy or entropy against the reciprocal of the anionic or cationic radius, used earlier to obtain the thermodynamic properties of single ions, cannot be accepted.

INTRODUCTION

Recently, a new method has been developed [1] for the determination of absolute electrode potentials and the thermodynamics of single ions in solution. This method, relating the electrode potential to the radius of the solvated ion on whose activity the potential depends, has been successfully applied to the cells

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

$$\mathrm{M}\,|\,\mathrm{MX,\ solvent}\,|\,\mathrm{AgX}\,|\,\mathrm{Ag} \qquad \text{(B)}$$

in the aqueous and methanol–water systems. The single ion activities, activity coefficients, the radii of solvated cations, and their solvation extent have been also computed [1].

The new method [1] has the advantage that it does not involve any extrathermodynamic assumption for measurements or calculations, and thus

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* Author for correspondence.

many difficulties [2] which arise from different extrathermodynamic assumptions (which lead to contradictory results [2]) can be avoided.

In the present investigation, the studies have been extended to the ethylene glycol (EG)–water solvent system not only in support of the validity and general applicability of the new method, but also to study solvent effects on the standard single electrode potential and related thermodynamic quantities, in such media.

RESULTS AND DISCUSSION

The EMF data of cells of type (A), in partially aqueous and non-aqueous EG solvents reported by two independent groups of workers, (recent data of Elsemongy et al. [3–5] and those of Kundu et al. [6–9]) have been used for the present work. Plots of the standard EMF, E_{m}°, values of cells (A), where $\mathrm{X} = \mathrm{Cl}$, Br and I, against the radius of solvated anion, r^- (method I) or $1/r^-$ (method II) values [1] gave almost perfect straight lines, at all temperatures. The least-square results are summarized in Tables 1–8.

It should pointed out that there are [1] generally two possibilities (I and II) for the variation of the electrode potential with the radius of the solvated ion on whose activity the potential depends: I—the oxidation potential varies directly with the radius of the solvated ion (r); or II—the reduction potential varies inversely with r. Therefore, the cell EMF (E_{m} or E_{m}°) is proportional to the radius of the solvated ion which is being varied in a series of electrolytes having a common ion [1]. Thus, at any temperature, the plot of E_{m}° of cells (A) where $\mathrm{X} = \mathrm{Cl}$, Br and I against r^- (method I) or $1/r^-$ (method II), would yield a straight line according to eqns. (1-I) and (1-II), respectively, in any solvent [1].

$$E_{\mathrm{m}}^{\circ} = a_1^{\circ} r^+ - a_1^{\circ} r^- \qquad \text{(1-I)}$$

$$E_{\mathrm{m}}^{\circ} = a_2^{\circ}/r^- - a_2^{\circ}/r^+ \qquad \text{(1-II)}$$

Generally, one would expect that two different sets of values, for standard absolute electrode potential or radius of the solvated proton, based on different, oxidation or reduction, potential scales will be obtained. Of course, only one set of data should be credited for any. Thus, the question is which method (I or II) has to be applied to EMF data for the determination of absolute electrode potentials and then for the thermodynamics of single ions in solution.

However, inspection of Tables 1–4 reveals the following results.

(1) In all solvents and at all temperatures, 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 both with increasing the temperature of the solvent system and

TABLE 1

The least-squares results of applying eqn. (1) to the EMF data, of cells (A) in ethylene glycol–water solvents at 5–45°C, reported by Kundu et al. [6–9]

Glycol (Wt.%)	10	30	50	70	90	100
Results of method I						
At 5°C						
$-$Corr (10^{-2})	99.9994	100.0000	99.9998	100.0000	99.9964	99.9921
a_1° (10^{10} V m^{-1})	1.06729	1.04962	1.02226	0.98004	0.91767	0.91218
r^+ (10^{-10} m)	2.022	2.015	2.009	2.001	1.963	1.862
At 15 °C						
$-$Corr (10^{-2})	99.9999	100.0000	99.9999	99.9997	99.9961	99.9954
a_1° (10^{10} V m^{-1})	1.05865	1.03996	1.01556	0.97402	0.91222	0.90872
r^+ (10^{-10} m)	2.019	2.011	2.004	1.993	1.951	1.850
At 25°C						
$-$Corr (10^{-2})	99.9998	99.9998	99.9998	99.9996	99.9959	99.9965
a_1° (10^{10} V m^{-1})	1.04917	1.02921	1.00835	0.96598	0.90820	0.90459
r^+ (10^{-10} m)	2.015	2.007	1.998	1.985	1.939	1.837
At 35°C						
$-$Corr (10^{-2})	100.0000	100.0000	100.0000	99.9998	99.9956	99.9991
a_1° (10^{10} V m^{-1})	1.03996	1.01808	0.99857	0.95977	0.90474	0.90045
r^+ (10^{-10} m)	2.010	2.002	1.991	1.975	1.926	1.824
At 45°C						
$-$Corr (10^{-2})	99.9999	99.9999	99.9999	100.0000	99.9973	99.9984
a_1° (10^{10} V m^{-1})	1.03019	1.00673	0.98989	0.95436	0.90038	0.89831
r^+ (10^{-10} m)	2.005	1.996	1.984	1.966	1.913	1.810
Results of method II						
At 5°C						
Corr (10^{-2})	99.8946	99.8820	99.8675	99.8767	99.9167	99.8085
a_2° (10^{-10} V m)	4.18698	4.11712	4.00919	3.84397	3.60091	3.57565
r^+ (10^{-10} m)	2.012	2.005	1.998	1.990	1.953	1.859
a_2°/a_1° (10^{-20} m^2)	3.9230	3.9225	3.9219	3.9223	3.9240	3.9199
At 15°C						
Corr (10^{-2})	99.8867	99.8799	99.8726	99.8896	99.9178	99.8264
a_2° (10^{-10} V m)	4.15271	4.07914	3.98315	3.82088	3.57957	3.56261
r^+ (10^{-10} m)	2.009	2.001	1.993	1.983	1.942	1.848
a_2°/a_1° (10^{-20} m^2)	3.9226	3.9224	3.9221	3.9228	3.9240	3.9205
At 25°C						
Corr (10^{-2})	99.8886	99.8872	99.8877	99.8916	99.9188	99.8337
a_2° (10^{-10} V m)	4.11563	4.03727	3.95544	3.78940	3.56383	3.54662
r^+ (10^{-10} m)	2.005	1.997	1.987	1.974	1.930	1.838
a_2°/a_1° (10^{-20} m^2)	3.9227	3.9227	3.9227	3.9229	3.9241	3.9207
At 35°C						
Corr (10^{-2})	99.8799	99.8749	99.8784	99.8882	99.9201	99.8560
a_2° (10^{-10} V m)	4.07914	3.99311	3.91672	3.76493	3.55031	3.53111
r^+ (10^{-10} m)	2.000	1.992	1.981	1.965	1.918	1.826
a_2°/a_1° (10^{-20} m^2)	3.9224	3.9222	3.9223	3.9227	3.9241	3.9215

TABLE 1 (continued)

Glycol (Wt.%)	10	30	50	70	90	100
At 45°C						
Corr (10^{-2})	99.8705	99.8716	99.8708	99.8750	99.9120	99.8485
a_2° (10^{-10} V m)	4.04042	3.94846	3.88237	3.74319	3.53286	3.52246
r^+ (10^{-10} m)	1.994	1.986	1.974	1.956	1.906	1.815
a_2°/a_1° (10^{-20} m^2)	3.9220	3.9221	3.9220	3.9222	3.9237	3.9212

the EG content in the solvent at any temperature. Thus, the solvation of the H^+ ion decreases as the temperature of the medium increases, or as the water content of a solvent decreases in partially aqueous media, and the extent of solvation reaches minima in the non-aqueous media. This feature is expected in view of previous results [10,11] and in accordance with those obtained in methanol–water solvents [1].

(3) The ratio (a_2°/a_1°) 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 methanol–water solvents [1], but also in several solvent systems [12] including both protic and aprotic, partially aqueous and non-aqueous solvents. Thus, a_1° and a_2° appear to be universal constants for all electrodes, and dependent only on the temperature and the medium [1]. The values of these constants decrease with increasing either the temperature or the EG content of the solvent system.

(4) The values of standard absolute electrode potentials at 25°C, for example, are given in Table 4. Results of method I show that as the EG content of the solvent increases, the oxidation potentials of both left and right electrodes decrease, the solvation extent of H^+ ions also decreases, and thus the transfer free energies of single ions increase (see Table 7). On the other hand, results of method II show that although the extent of solvation of H^+ ions decreases in one direction (Table 3), a minimum and its corresponding maximum have been observed at around 90% EG for ${}^{\mathrm{Red}}_{\mathrm{L}}E^\circ_{\mathrm{m}}$ (see Table 4) and $\Delta G_t^\circ(H^+)$ (see Table 8) values, respectively. The same feature has been observed in the methanol–water solvent system [1], at around 70% methanol. Also, it is evident from Table 4 that both the standard absolute oxidation potentials and reduction potentials decrease with increasing the temperature of the solvent system. For the electrode reactions, either the oxidation potential or reduction potential would decrease, with increasing temperature. This proves again [1] that only one of these methods (I or II) can be accepted for the calculation of a single electrode potential.

The values of standard absolute potentials (V) of any electrode (${}_{\mathrm{E}}E^\circ_{\mathrm{m}}$), obtained in each solvent by both methods I and II, were fitted by the method of least-squares to eqn. (2).

$${}_{\mathrm{E}}E^\circ_{\mathrm{m}} = a + bT + cT^2 \tag{2}$$

TABLE 2

The least-squares results of applying eqn. (1-I) to the EMF data, of cells (A) in ethylene glycol–water solvents at 15–55°C, reported by Elsemongy et al. [3–5]

Temp. (°C)	Glycol (Wt.%)	10	20	30	40	50	60	70	80	90	100
15	$-$Corr (10^{-2})	99.9996	99.9999	99.9999	99.9993	99.9991	99.9982	99.9964	99.9954	99.9812	99.9953
	a_1° (10^{10} V m^{-1})	1.06692	1.05479	1.04223	1.03096	1.01924	1.00776	0.99289	0.96162	0.90706	0.90682
	r^+ (10^{-10} m)	2.018	2.015	2.011	2.008	2.003	1.997	1.988	1.975	1.949	1.850
25	$-$Corr (10^{-2})	99.9998	100.0000	99.9999	99.9994	99.9991	99.9980	99.9957	99.9943	99.9868	99.9970
	a_1° (10^{10} V m^{-1})	1.05725	1.04501	1.03146	1.01908	1.00671	0.99296	0.97501	0.94701	0.90676	0.90321
	r^+ (10^{-10} m)	2.014	2.011	2.007	2.003	1.998	1.991	1.982	1.967	1.938	1.837
35	$-$Corr (10^{-2})	100.0000	100.0000	100.0000	99.9994	99.9991	99.9979	99.9953	99.9937	99.9918	99.9980
	a_1° (10^{10} V m^{-1})	1.04758	1.03478	1.02028	1.00730	0.99298	0.97808	0.95885	0.93345	0.90555	0.90074
	r^+ (10^{-10} m)	2.010	2.006	2.002	1.998	1.992	1.985	1.975	1.959	1.926	1.824
45	$-$Corr (10^{-2})	100.0000	100.0000	100.0000	99.9997	99.9993	99.9984	99.9969	99.9958	99.9957	99.9989
	a_1° (10^{10} V m^{-1})	1.03697	1.02294	1.00815	0.99484	0.98030	0.96411	0.94420	0.92128	0.90440	0.90021
	r^+ (10^{-10} m)	2.004	2.001	1.997	1.992	1.985	1.978	1.966	1.948	1.914	1.810
55	$-$Corr (10^{-2})	100.0000	99.9998	99.9999	99.9998	99.9996	99.9991	99.9987	99.9982	99.9986	99.9992
	a_1° (10^{10} V m^{-1})	1.02562	1.01121	0.99608	0.98253	0.96688	0.95060	0.93174	0.91074	0.90225	0.90139
	r^+ (10^{-10} m)	1.999	1.995	1.990	1.985	1.978	1.969	1.957	1.937	1.901	1.796

TABLE 3

The least-squares results of applying eqn. (1-II) to the EMF data, of cells (A) in ethylene glycol–water solvents at 15–55°C, reported by Elsemongy et al. [3–5]

Temp. (°C)	Glycol (Wt.%)	10	20	30	40	50	60	70	80	90	100
15	Corr (10^{-2})	99.8913	99.8855	99.8843	99.8960	99.8984	99.9060	99.9164	99.9211	99.9551	99.8258
	a_2° (10^{-10} V m)	4.18539	4.13754	4.08819	4.04450	3.99865	3.95394	3.89606	3.77358	3.56117	3.55512
	r^+ (10^{-10} m)	2.008	2.005	2.001	1.997	1.992	1.986	1.978	1.965	1.940	1.848
	a_2°/a_1° (10^{-20} m^2)	3.9229	3.9226	3.9225	3.9230	3.9232	3.9235	3.9240	3.9242	3.9261	3.9204
25	Corr (10^{-2})	99.8876	99.8827	99.8863	99.8947	99.8984	99.9075	99.9199	99.9252	99.9453	99.8368
	a_2° (10^{-10} V m)	4.14728	4.09904	4.04606	3.99785	3.94946	3.89594	3.82607	3.71643	3.55945	3.54134
	r^+ (10^{-10} m)	2.004	2.001	1.997	1.992	1.987	1.981	1.972	1.957	1.929	1.838
	a_2°/a_1° (10^{-20} m^2)	3.9227	3.9225	3.9227	3.9230	3.9231	3.9236	3.9241	3.9244	3.9255	3.9208
35	Corr (10^{-2})	99.8827	99.8804	99.8821	99.8943	99.8980	99.9080	99.9213	99.9273	99.9334	99.8453
	a_2° (10^{-10} V m)	4.10913	4.05882	4.00203	3.95160	3.89560	3.83755	3.76270	3.66332	3.55409	3.53190
	r^+ (10^{-10} m)	1.999	1.996	1.992	1.987	1.981	1.974	1.964	1.949	1.918	1.826
	a_2°/a_1° (10^{-20} m^2)	3.9225	3.9224	3.9225	3.9230	3.9231	3.9236	3.9242	3.9245	3.9248	3.9211
45	Corr (10^{-2})	99.8774	99.8751	99.8779	99.8909	99.8959	99.9047	99.9141	99.9194	99.9200	99.8537
	a_2° (10^{-10} V m)	4.06728	4.01216	3.95429	3.90260	3.84575	3.78262	3.70490	3.61520	3.54898	3.53009
	r^+ (10^{-10} m)	1.994	1.990	1.986	1.981	1.975	1.967	1.956	1.939	1.906	1.815
	a_2°/a_1° (10^{-20} m^2)	3.9223	3.9222	3.9223	3.9228	3.9230	3.9234	3.9239	3.9241	3.9241	3.9214
55	Corr (10^{-2})	99.8763	99.8692	99.8698	99.8885	99.8921	99.8981	99.9019	99.9063	99.9029	99.8579
	a_2° (10^{-10} V m)	4.02274	3.96595	3.90663	3.85422	3.79296	3.72933	3.65551	3.57327	3.53985	3.53484
	r^+ (10^{-10} m)	1.988	1.984	1.980	1.974	1.968	1.959	1.947	1.928	1.894	1.803
	a_2°/a_1° (10^{-20} m^2)	3.9223	3.9220	3.9220	3.9228	3.9229	3.9231	3.9233	3.9235	3.9234	3.9215

TABLE 4

Standard molal absolute potentials of cell (A) electrodes in ethylene glycol–water solvents at 25°C, computed from the recent reported EMF data [3–5]

Glycol (Wt.%)		10	20	30	40	50	60	70	80	90	100
Results of method I											
${}^{\mathrm{Ox}}_{\mathrm{L}}E^{\circ}_{\mathrm{m}}$ (V)		2.12956	2.10147	2.07028	2.04113	2.01113	1.97717	1.93256	1.86323	1.75738	1.65921
${}^{\mathrm{Ox}}_{\mathrm{R}}E^{\circ}_{\mathrm{m}}$ (V)	X=Cl	1.91363	1.89146	1.86695	1.84454	1.82214	1.79726	1.76477	1.71408	1.64123	1.63482
	Br	2.06164	2.03776	2.01135	1.98721	1.96308	1.93628	1.90127	1.84666	1.76817	1.76127
	I	2.28366	2.25722	2.22796	2.20122	2.17449	2.14480	2.10602	2.04554	1.95859	1.95094
Results of method II											
${}^{\mathrm{Red}}_{\mathrm{L}}E^{\circ}_{\mathrm{m}}$ (V)		2.06947	2.04882	2.02629	2.00646	1.98738	1.96695	1.94055	1.89876	1.84521	1.92717
${}^{\mathrm{Red}}_{\mathrm{R}}E^{\circ}_{\mathrm{m}}$ (V)	X=Cl	2.29131	2.26466	2.23539	2.20876	2.18202	2.15245	2.11385	2.05327	1.96654	1.95654
	Br	2.12681	2.10207	2.07490	2.05018	2.02536	1.99792	1.96209	1.90586	1.82536	1.81607
	I	1.92004	1.89770	1.87318	1.85086	1.82845	1.80367	1.77133	1.72057	1.64789	1.63951

TABLE 5

Values of the parameters a, b and c of eqn. (2) for the evaluation of ${}_{\mathrm{E}}E_{\mathrm{m}}^{\circ}$ in ethylene glycol–water solvents at 15–55°C, and the standard molal thermodynamic functions of the half-cell reactions at 25°C, all calculated by method I, using the recent reported EMF data [3–5]

Glycol	a	b	c	Δ	$-\Delta G_{\mathrm{E}}^{\circ}$	$-\Delta H_{\mathrm{E}}^{\circ}$	$-\Delta S_{\mathrm{E}}^{\circ}$
(Wt.%)	(V)	(10^{-3} V K^{-1})	(10^{-6} V K^{-2})	(mV)	(kJ mol^{-1})		(J K^{-1} mol^{-1})
Hydrogen electrode							
0	2.53955	−0.24637	−3.45993	0.18	208.3	274.7	222.8
20	1.89451	3.89163	−10.7234	0.52	202.8	274.8	241.5
40	2.45793	0.09153	−4.99371	0.24	197.0	280.0	278.5
60	3.17763	−4.51101	1.62188	0.32	190.7	292.7	341.9
80	3.75958	−9.14754	9.34585	0.20	179.8	282.6	344.9
100	3.29919	−9.28476	12.6895	0.26	160.1	209.5	165.8
Ag, AgCl electrode							
0	2.39263	−1.38332	−0.48903	0.18	186.9	235.0	161.6
20	1.80948	2.38597	−7.07957	0.48	182.5	235.3	177.1
40	2.31120	−0.97676	−1.97161	0.22	178.0	239.9	207.7
60	2.99797	−5.37451	4.51562	0.29	173.4	250.5	258.8
80	3.56894	−9.89031	12.3038	0.21	165.4	238.8	246.4
100	3.12042	−9.41876	14.8758	0.24	157.7	173.5	52.9
Ag, AgBr electrode							
0	2.57855	−1.49630	−0.51647	0.20	201.3	253.2	174.0
20	1.94849	2.57660	−7.63677	0.51	196.6	253.5	190.8
40	2.48883	−1.04500	−2.13589	0.23	191.8	258.5	223.7
60	3.23060	−5.79506	4.87289	0.31	186.8	269.9	278.8
80	3.84686	−10.66758	13.2756	0.23	178.2	257.3	265.5
100	3.36235	−10.15132	16.0334	0.27	169.9	186.9	57.0
Ag, AgI electrode							
0	2.85545	−1.65212	−0.58101	0.22	223.0	280.5	192.8
20	2.15708	2.86225	−8.47268	0.57	217.8	280.8	211.3
40	2.75631	−1.15400	−2.37163	0.25	212.4	286.3	247.8
60	3.57891	−6.42167	5.40152	0.35	206.9	299.0	308.8
80	4.26046	−11.81175	14.6974	0.25	197.3	285.0	294.1
100	3.72403	−11.24163	17.7552	0.29	188.2	207.0	63.1

where T is the thermodynamic temperature. The values of the parameters a, b and c are recorded in Tables 5 and 6, for each electrode. Values of ${}_{\mathrm{E}}E_{\mathrm{m}}^{\circ}$ calculated by eqn. (2) and the original values agree within ±0.30 mV on average, at 15–55°C, and the maximum difference between these values, $\pm\Delta$(mV), is given in Tables 5 and 6, for each electrode.

Standard thermodynamic functions for the half-cell reactions

The standard thermodynamic functions associated with the cell reaction can be calculated as the difference between those for half-cell reactions, both

TABLE 6

Values of the parameters a, b and c of eqn. (2) for the evaluation of $_{\mathrm{E}}E^{\circ}_{\mathrm{m}}$ in ethylene glycol–water solvents at 15–55°C, and the standard molal thermodynamic functions of the half-cell reactions at 25°C, all calculated by method II, using the recent reported EMF data [3–5]

Glycol	a	b	c	Δ	$-\Delta G^{\circ}_{\mathrm{E}}$	$-\Delta H^{\circ}_{\mathrm{E}}$	$-\Delta S^{\circ}_{\mathrm{E}}$
(Wt.%)	(V)	(10^{-3} V K^{-1})	(10^{-6} V K^{-2})	(mV)	(kJ mol^{-1})		(J K^{-1} mol^{-1})
Hydrogen electrode							
0	2.71893	−2.83618	2.45361	0.22	201.8	241.3	132.5
20	2.06307	1.43482	−4.97172	0.55	197.7	241.7	147.6
40	2.60500	−2.17527	0.56495	0.25	193.6	246.5	177.4
60	3.37418	−7.10254	7.98811	0.30	189.8	257.0	225.7
80	4.01095	−12.14673	16.9767	0.24	183.2	241.4	195.2
100	3.52778	−11.27024	19.7915	0.28	185.9	170.6	−51.3
Ag, AgCl electrode							
0	2.87339	−1.70365	−0.51970	0.22	223.8	281.7	194.3
20	2.15601	2.93350	−8.61559	0.58	218.5	281.9	212.6
40	2.76037	−1.11886	−2.45018	0.27	213.1	287.3	248.9
60	3.56128	−6.24312	5.08718	0.34	207.6	300.0	309.7
80	4.20533	−11.38574	13.9759	0.23	198.1	285.9	294.5
100	3.71560	−11.16266	17.6481	0.29	188.7	207.1	61.7
Ag, AgBr electrode							
0	2.66805	−1.58758	−0.47223	0.21	207.7	261.5	180.3
20	2.00013	2.72994	−8.00832	0.54	202.8	261.7	197.4
40	2.56175	−1.03575	−2.27870	0.25	197.8	266.7	231.0
60	3.30435	−5.78668	4.70852	0.32	192.7	278.4	287.4
80	3.90437	−10.57456	12.9827	0.22	183.9	265.4	273.3
100	3.44901	−10.36255	16.3834	0.28	175.2	192.3	57.2
Ag, AgI electrode							
0	2.40804	−1.42918	−0.43296	0.18	187.5	236.1	162.8
20	1.80700	2.45574	−7.21529	0.49	183.1	236.2	178.2
40	2.31266	−0.93493	−2.05724	0.22	178.6	240.8	208.6
60	2.98516	−5.23758	4.27275	0.28	174.0	251.4	259.5
80	3.52457	−9.54504	11.7180	0.20	166.0	239.6	246.8
100	3.11298	−9.35041	14.7829	0.25	158.2	173.6	51.7

based on the same potential scale [1]. The standard free energy, $\Delta G^{\circ}_{\mathrm{E}}$, enthalpy, $\Delta H^{\circ}_{\mathrm{E}}$, and entropy, $\Delta S^{\circ}_{\mathrm{E}}$ changes involved in the half-cell reactions are essentially related to the standard electrode potentials and their temperature coefficients. Hence, the standard thermodynamic functions of the half-cell reaction were calculated on the molal scale using the usual thermodynamic relations [1]. The results so calculated at 25°C are also included in Tables 5 and 6. The values of $\Delta G^{\circ}_{\mathrm{E}}$ are accurate to ± 60 J mol^{-1}.

Although the values obtained by method I (Table 5) are based on the oxidation potential scale, whereas those by method II (Table 6) are on the

TABLE 7

Values of the parameters *A*, *B* and *C* of eqn. (3) for the evaluation of standard thermodynamic quantities (molal scale) for the transfer of individual ions from water to glycolic solvents at 15–55°C and their values at 25°C, calculated by method I, using the recent reported EMF data [3–5]

Glycol (Wt.%)	*A* (10^2 J mol^{-1})	*B* (J K^{-1} mol^{-1})	*C* (10^{-2} J K^{-2} mol^{-1})	ΔG_t°	ΔH_t°	ΔS_t° (J K^{-1} mol^{-1})
				(kJ mol^{-1})		
Hydrogen ion						
20	622.368	−399.253	70.081	5.50	−0.06	−18.6
40	78.749	−32.602	14.799	11.31	−5.28	−55.6
60	−615.649	411.472	−49.032	17.53	−17.98	−119.1
80	−1177.142	858.825	−123.556	28.51	−7.88	−122.1
100	−732.934	872.065	−155.817	48.20	65.22	57.1
Chloride ion						
20	562.650	−363.678	63.589	4.36	−0.26	−15.5
40	78.571	−39.227	14.305	8.88	−4.86	−46.1
60	−584.062	385.088	−48.287	13.48	−15.48	−97.2
80	−1134.959	820.793	−123.431	21.50	−3.77	−84.8
100	−702.205	775.296	−148.247	29.15	61.56	108.7
Bromide ion						
20	607.917	−392.972	68.700	4.70	−0.28	−16.7
40	86.568	−43.543	15.625	9.56	−5.23	−49.6
60	−629.123	414.764	−51.999	14.53	−16.69	−104.7
80	−1223.720	884.887	−133.072	23.16	−4.08	−91.4
100	−756.246	835.076	−159.681	31.41	66.32	117.1
Iodide ion						
20	673.816	−435.567	76.142	5.20	−0.30	−18.5
40	95.651	−48.061	17.277	10.59	−5.79	−55.0
60	−698.033	460.188	−57.722	16.09	−18.49	−116.0
80	−1355.623	980.247	−147.413	25.66	−4.52	−101.2
100	−838.042	925.240	−176.916	34.79	73.46	129.7

different reduction scale, the thermodynamic functions for the half-cell reactions are all negative (except ΔS_E° for the hydrogen electrode in non-aqueous EG, calculated by method II). However, since the oxidation reactions of the half-cells are known to be exothermic [1,10,11], the ΔH_E° values must 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. This conclusion has been found in the methanol–water solvent system [1]. Thus, this may lend further support to the validity and general applicability of method I, and at the same time give evidence against the applicability of method II, for such calculations.

TABLE 8

Values of the parameters A, B and C of eqn. (3) for the evaluation of standard thermodynamic quantities (molal scale) for the transfer of individual ions from water to glycolic solvents at 15–55°C and their values at 25°C, calculated by method II, using the recent reported EMF data [3–5]

Glycol (Wt.%)	A (10^2 J mol^{-1})	B (J K^{-1} mol^{-1})	C (10^{-2} J K^{-2} mol^{-1})	ΔG_t° (kJ mol^{-1})	ΔH_t° (kJ mol^{-1})	ΔS_t° (J K^{-1} mol^{-1})
Hydrogen ion						
20	632.799	−412.086	71.643	4.10	−0.41	−15.1
40	109.927	−63.768	18.223	8.18	−5.21	−44.9
60	−632.221	411.638	−53.399	12.04	−15.75	−93.2
80	−1246.603	898.324	−140.125	18.61	−0.10	−62.8
100	−780.420	813.757	−167.284	15.87	70.66	183.8
Chloride ion						
20	692.161	−447.413	78.113	5.26	−0.22	−18.4
40	109.046	−56.423	18.626	10.64	−5.65	−54.6
60	−663.712	437.989	−54.098	16.13	−18.28	−115.4
80	−1285.121	934.172	−139.860	25.68	−4.19	−100.2
100	−812.602	912.648	−175.291	35.02	74.56	132.6
Bromide ion						
20	644.436	−416.574	72.712	4.88	−0.19	−17.0
40	102.556	−53.243	17.430	9.87	−5.24	−50.7
60	−613.932	405.148	−49.986	14.97	−16.96	−107.1
80	−1192.860	867.105	−129.819	23.84	−3.88	−93.0
100	−753.510	846.649	−162.631	32.51	69.22	123.1
Iodide ion						
20	579.915	−374.835	65.439	4.40	−0.18	−15.4
40	92.024	−47.687	15.672	8.92	−4.73	−45.8
60	−556.827	367.452	−45.403	13.51	−15.32	−96.7
80	−1077.283	783.099	−117.238	21.52	−3.51	−84.0
100	−680.160	764.276	−146.810	29.35	62.49	111.1

However, Tables 5 and 6 show that, for the Ag, AgX electrodes on the oxidation or reduction potential scale, ΔG_E° values increase whereas both ΔH_E° and ΔS_E° decrease to minima at around 60% EG and thereafter increase, with increasing EG content in the solvent. For the hydrogen electrode, results of method I, based on the oxidation potential scale, show that ΔG_E° values increase, whereas those of ΔH_E° and ΔS_E° decrease to minima at around 60 and 80% EG, respectively, and thereafter increase, with increasing EG concentration in the solvent. On the other hand, results of method II, based on the reduction potential scale, show that ΔG_E° values reach a maximum at around 80% EG and thereafter decrease, while ΔH_E° and ΔS_E° values pass through minima at around 60% EG and thereafter increase, with successive addition of EG to the solvent.

Standard transfer thermodynamic quantities of single ions

The standard transfer Gibbs free energy of a single ion, $\Delta G_{\rm t}^{\circ}(i)_{\rm m}$, can be expressed as a function of temperature [1] by eqn. (3).

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

The standard transfer thermodynamic quantities of single ions can then be obtained by applying the usual thermodynamic relations [1] to eqn. (3), where all refer to the molal scale. The results of calculations on the basis of oxidation and reduction potential scales (methods I and II, respectively) are collected in Tables 7 and 8, respectively. The $\Delta G_{\rm t}^{\circ}(i)_{\rm m}$ values are accurate to ± 120 J mol^{-1}

The single ion free energies of transfer provide a clearer understanding of ion–solvent interactions than do the free energies of the transfer of the HX acids. The transfer free energies of ions are all positive. For the transfer of the $\rm H^+$ ions from water to glycolic solvents, the values obtained by method I increase, whereas those obtained by method II increase to a maximum at around 90% EG and thereafter decrease, with increasing EG content in the solvent. The free energies of halide ions calculated by both methods increase in the same direction. The positive values of $\Delta G_{\rm t}^{\circ}(i)_{\rm m}$ support the view that the transfer of ions from water to glycolic solvents is not spontaneous.

Although the transfer thermodynamic quantities calculated by method I are based on the oxidation potential scale, whereas those calculated by method II on the reduction potential scale, the transfer enthalpies and entropies of ions from water to glycolic solvents show the same trend, with increasing EG concentration in the solvent. Their values decrease negatively to minima at around 60% EG (for $\Delta S_{\rm t}^{\circ}(\rm H^+)_{\rm m}$ values calculated by method I, the minimum at 90% EG), thereafter increase negatively, with increasing EG content in the aqueous solvent and finally become highly positive in the non-aqueous EG.

The structural features of the ion–solvent interactions in EG–water solvents are reflected by $\Delta H_{\rm t}^{\circ}(i)_{\rm m}$ and $\Delta S_{\rm t}^{\circ}(i)_{\rm m}$ values. The positive entropy and enthalpy of the transfer of ions from water to non-aqueous EG can be attributed to a greater structure breaking by the ion in this solvent than in water. The non-aqueous EG solvent is therefore a more structured solvent than water. The negative $\Delta H_{\rm t}^{\circ}(i)_{\rm m}$ and $\Delta S_{\rm t}^{\circ}(i)_{\rm m}$ values for the aqueous glycolic solvents assume that ions are more effective at breaking the structure in water than in these solvents. This is further supported by the view [6,11] that the structure-forming processes, including solvation of ions, are exothermic and are accompanied by an entropy decrease while the structure-breaking processes are endothermic and lead to an entropy increase.

However, further discussion of the thermodynamics of single ions in EG–water solvents will be reserved until chemical contributions to the transfer thermodynamic properties are computed by a new method developed by Elsemongy [12], where the results also support the validity and general applicability of method I for the determination of thermodynamic properties of single ions in solution.

Cell (B) and thermodynamic properties of single ions

As will be seen later [13], several experimental studies have been made in our lab on cell (B) (where M = Li, Na and K and where X = Cl, Br and I) in EG–water solvents. Treatment of the data [13], together with all other data [14] in these solvents, by method I shows that the extent of solvation, in any solvent, increases in the expected well known order: $K^+ < Na^+ < Li^+$, and that the Li^+ ion is always highly solvated. On the other hand, method II treatment of the data indicates that the solvation increases in the order: $Li^+ < K^+ < Na^+$ which, as is well known, is not the case. This interesting feature, again [1], shed more light on the inapplicability of method II for such calculations, and gave further strong evidence that all thermodynamic calculations based on r^{-1} relationships may be inadequate, and need a major revision. Further discussion of thermodynamic properties of single ions related to cell (B) will be presented later [13].

CONCLUSION

Now, it is evident that the results gained through the present work in the EG–water solvent system as well as those obtained in various solvent systems [1,12,13] lend further strong support to the validity and general applicability of method I for the determination of the thermodynamics of single ions in solution, and all gave evidence that the plots of standard transfer free energy or entropy against the reciprocal of anionic or cationic radius, used earlier [6–11] to obtain the thermodynamic properties of single ions, cannot be accepted. Thus, method I should be applied to the EMF data for the determination of absolute electrode potential as well as thermodynamics of single ions in solution.

Simultaneous extrapolations and thermodynamic quantities for individual ions

The method of "simultaneous extrapolations" has long been used [6–11] for evaluating the thermodynamic quantities for the individual ions. According to this method [6,11], to a first approximation, the free energy of transfer $\Delta G_t^\circ(HX)$ is a linear function of $(r_{X^-})^{-1}$, the reciprocal of the radius of the X^- ion, the limiting value of $\Delta G_t^\circ(HX)$, as $(r_{X^-})^{-1}$ tends to zero, would furnish a measure of the negative free energy of the transfer of the hydrogen ion, since $\Delta G_t^\circ(X^-)$ for an ion of infinite radius when $(r_{X^-})^{-1} = 0$, should approach a value of negligible magnitude [6]. This may be represented by

$$\Delta G_t^\circ(\mathrm{HX}) = \Delta G_t^\circ(\mathrm{H}^+) + m(r_{\mathrm{X}^-})^{-1} \tag{4}$$

Similarly, the plots of $\Delta G_t^\circ(\mathrm{Cl}^- - \mathrm{X}^-)$ against $(r_{\mathrm{X}^-})^{-1}$ would lead to a positive value [6,11] of $\Delta G_t^\circ(\mathrm{Cl}^-)$ at $(r_{\mathrm{X}^-})^{-1} = 0$. This may be represented by

$$\begin{aligned}\Delta G_t^\circ(\mathrm{HCl}) - \Delta G_t^\circ(\mathrm{HX}) = \Delta G_t^\circ(\mathrm{Cl}^- - \mathrm{X}^-) &= m(r_{\mathrm{Cl}^-})^{-1} - m(r_{\mathrm{X}^-})^{-1} \\ &= \Delta G_t^\circ(\mathrm{Cl}^-) - m(r_{\mathrm{X}^-})^{-1} \end{aligned} \tag{5}$$

Actually, eqn. (5) is another form of eqn. (4), where in both cases m is the same slope of the lines.

As in the case of free energy values, the thermodynamic quantities $\Delta S_t^\circ(\mathrm{HX})$ and $\Delta H_t^\circ(\mathrm{HX})$, if plotted [6] against $(r_{\mathrm{X}^-})^{-1}$, should yield the values of $\Delta S_t^\circ(\mathrm{H}^+)$ and $\Delta H_t^\circ(\mathrm{H}^+)$ at $(r_{\mathrm{X}^-})^{-1} = 0$.

However, it should pointed out that the second extrapolation (eqn. (5)), may involve a greater uncertainty (the left hand side is a difference between two different values, each with a certain accuracy) as compared with the first extrapolation. Simply, a comparison between eqns. (4) and (5) shows that there is no need at all for the second extrapolation, since the product of the slope (m) of the line obtained by eqn. (4) and $(r_{\mathrm{Cl}^-})^{-1}$ would yield the value of $\Delta G_t^\circ(\mathrm{Cl}^-)$. Similarly, the values of $\Delta G_t^\circ(\mathrm{Br}^-)$ and $\Delta G_t^\circ(\mathrm{I}^-)$ could be obtained as $m(r_{\mathrm{Br}^-})^{-1}$ and $m(r_{\mathrm{I}^-})^{-1}$, respectively. Thus, the first extrapolation (eqn. (4)) is sufficient to obtain the least discrepancies in the values of $\Delta G_t^\circ(\mathrm{H}^+)$ and $\Delta G_t^\circ(\mathrm{X}^-)$ with respect to the experimental values of $\Delta G_t^\circ(\mathrm{HX})$.

As previously reported [1], the EMF values, and also the transfer free energies for the halogen acids from water to any solvent, may vary linearly with either r^- (case I) or $(r^-)^{-1}$ (case II). Although three points only are available, the correlation coefficients obtained [1,12,13] always indicate that the variables are closely related in the wider range ($r^- = 1.81$–2.16) of case I than those values do in the narrower range ($(r^-)^{-1} = 0.463$–0.552) of case II, where the extrapolation to $(r^-)^{-1} = 0$ involves considerable uncertainty.

Kundu et al. [6] reported that the method of "simultaneous extrapolations" employed for evaluating the thermodynamic quantities for the individual ions involves a great deal of uncertainty, and the very basis may be open to question, so that the values obtained by extrapolation should not be credited with exact quantitative significance [6]. Really, this may be so in view of the present results and conclusions.

ACKNOWLEDGEMENT

The authors are very indebted to Mrs. Laila Abu Elela for encouragement and fruitful discussion.

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