Monatshefte für Chemie 114, 891—905 (1983)

Monatshefte für Chemie
Chemical Monthly

Thermodynamic Studies of Hydriodic Acid in Ethylene Glycol—Water Mixtures from Electromotive Force Measurements

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(Received 30 June 1982. Accepted 2 December 1982)

The standard potentials of the Ag—AgI electrode in twenty ethylene glycol—water mixtures covering the whole range of solvent composition have been determined from the e.m.f. measurements of the cell

$$\mathrm{Pt}\,|\,\mathrm{H_2}\,(g,\ 1\,\mathrm{atm})\,|\,\mathrm{HO}Ac\,(m_1),\ \mathrm{NaO}Ac\,(m_2),\ \mathrm{KI}\,(m_3),\ \mathrm{solvent}\,|\,\mathrm{AgI}\,|\,\mathrm{Ag}$$

at nine different temperatures ranging from 15 to 55 °C. The temperature variation of the standard e.m.f. has been utilized to compute the standard thermodynamic functions for the cell reaction, the primary medium effects of various solvents upon HI, and the standard thermodynamic quantities for the transfer of HI from the standard state in water to the standard states in the respective solvent media. The chemical effects of solvents on the transfer process have been obtained by subtracting the electrostatic contributions from the total transfer quantities. The results have been discussed in the light of ion—solvent interactions as well as the structural changes of the solvents.

(Keywords: Electromotive force measurements; Ethylene glycol + water mixtures; Silver, silver iodide electrode; Standard electrode potentials; Thermodynamics)

Thermodynamische Untersuchungen über Jodwasserstoffsäure in Ethylenglycol—Wasser-Mischungen mittels EMK-Messungen

Es wurden die Standardpotentiale der Ag—AgI Elektrode in 20 Ethylenglycol—Wasser-Mischungen bei 9 Temperaturen (15—55 °C) mit der Zelle

$$\mathrm{Pt}\,|\,\mathrm{H_2}\,(g,\ 1\,\mathrm{atm})\,|\,\mathrm{HO}Ac\,(m_1),\ \mathrm{NaO}Ac\,(m_2),\ \mathrm{KI}\,(m_3),\ \mathrm{solvent}\,|\,\mathrm{AgI}\,|\,\mathrm{Ag}$$

gemessen. Aus der Temperaturabhängigkeit wurden die thermodynamischen Funktionen für die Zellenreaktion, die primären Lösungsmitteleffekte auf HI und die thermodynamischen Größen für den Transfer von HI aus dem Standardzustand in Wasser in den Standardzustand im entsprechenden Lösungsmittelgemisch errechnet; die chemischen Effekte erhielt man durch

0026-9247/83/0114/0891/$ 03.00

Abzug der elektrostatischen Beiträge zu den Gesamttransfergrößen. Die Ergebnisse werden sowohl im Licht von Ionen—Lösungsmittel-Wechselwirkungen als auch von Änderungen in der Lösungsmittelstruktur diskutiert.

Introduction

Kundu et al.[1,2] determined the standard potentials (E°_m) of the Ag—AgI electrode in 10, 30, 50, 70, 90 and 100 *wt*% ethylene glycol (*EG*) + water solvents in the temperature range 5–45 °C using the cell:

$$\mathrm{Pt}\,|\,\mathrm{H_2}\,(g,\ 1\,\mathrm{atm})\,|\,\mathrm{HO}Ac\,(m_1),\ \mathrm{NaO}Ac\,(m_2),\ \mathrm{KI}\,(m_3),\ \mathrm{solvent}\,|\,\mathrm{AgI}\,|\,\mathrm{Ag}\ (\mathbf{A})$$

However, when the reported[1] E°_m values for the 10% *EG* solvent are compared with the corresponding values in water[1] as the solvent, it is seen that the E°_m values for the 10% *EG* solvent are higher at 5–25 °C, whereas they are similar, within the experimental error, at 30–45 °C. This behaviour is not expected. Furthermore, it is very difficult to draw a smooth curve through the available points when E°_m is plotted against the solvent composition, at any temperature.

In the present investigation, attempts were made to determine the standard potentials of the Ag—AgI electrode and the relevant thermodynamic functions for HI in twenty EG + water solvents from e.m.f. measurements of cell (**A**) at nine different temperatures ranging from 15 to 55 °C.

Experimental

EG (Merck) was further purified by the method described elsewhere[3]. The characteristic physical properties of the product agreed well with those listed by *Kundu* et al.[4] for pure *EG*. The distilled *EG* was kept in an atmosphere of dry argon, redistilled freshly and used within a few hours. Acetic acid (Merck) was further purified[2] by partially freezing the sample, decanting off the liquid portion and then distilling the recrystallized sample before use. Potassium iodide (Merck) was dried in an oven kept at 200 °C. Triple-distilled water which had a conductivity of $0.7 \cdot 10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ was generally used, being prepared by distillation with alkaline $\mathrm{KMnO_4}$ in an all-glass apparatus. Sodium lyate solutions in the respective solvents were prepared as described earlier[2]. The buffer solutions were prepared by mixing weighed amounts of sodium lyate, acetic acid and KI solutions[2]. The cell solutions of the required ionic strengths were obtained by diluting the stock solution of the buffer with weighed amounts of the respective solvents. The molalities of HO*Ac*, NaO*Ac* and KI solutions ranged from 0.005 to 0.05 mol kg^{-1}. The compositions of the solvents were accurate to ± 0.03 wt%. All solutions were freshly prepared before taking measurements.

The Ag—AgI electrodes were thermally prepared as recommended by *Ives* and *Janz*[5]. The hydrogen gas electrodes were the typical platinum type[6]. The cell design and general experimental procedure have been described earlier[3,4]. The behaviour of the electrodes in the buffer mixtures was excellent and consistent within ±0.1 mV. The e.m.f. measurements were made at nine different temperatures in the range of 15 to 55 °C, at intervalls of 5 °C. The thermostat maintained a temperature within ± 0.01 °C. All measurements were taken by three Ag—AgI electrodes and three hydrogen electrodes for each solution. The cell measurements were made in triplicate, and the mean values of these observations recorded. The triplicates generally agreed within ± 0.2 mV. Vapour-pressure corrections for e.m.f. values were applied to convert the observed e.m.f. to 1 atm hydrogen pressure. Vapour pressures and densities of the solvents at different temperatures were obtained from the previous results[2,4,7]. The dielectric constants were taken from *Åkerlöf*'s data[8]. The pK_a values of acetic acid in the different solvents at the respective temperatures, needed for evaluation of the standard potential of the Ag—AgI electrode, were taken from earlier work[2,4,9].

Results and Discussion

The e.m.f. (E) of the cell (**A**) is given[1] by

$$E = E^\circ_m - k \log K_a - k \log (a_{\mathrm{HO}Ac} a_{\mathrm{I}^-} / a_{\mathrm{O}Ac^-}), \tag{1}$$

where E°_m is the standard potential of the Ag—AgI electrode on the molal scale, K_a is the dissociation constant of acetic acid in the particular solvent at the corresponding temperature, and k is $(RT \ln 10)/F$. Assuming complete dissociation of KI and NaO*Ac* in all the solvents, equ. (1) becomes

$$\begin{aligned} E' &= E - k\,(pK_a) + k \log (m_1 m_3/m_2) \\ &= E^\circ_m - k \log (\gamma_1 \gamma_3/\gamma_2) = E^\circ_m + f(\mu), \end{aligned} \tag{2}$$

where the subscripts 1, 2 and 3 refer to HO*Ac*, O*Ac*$^-$ and I$^-$ respectively[1].

Standard Electrode Potential

For each solvent at any temperature E°_m was obtained by the usual method of plotting E' against the ionic strength (μ) and extrapolating to $\mu = 0$. To get more precise value for E°_m the method of least squares was used, and the data are summarized in Table 1, for each solvent, together with the values for water as the solvent[6]. The values of E°_m, presented in Table 1, are accurate to better than ± 0.05, ± 0.1 and ± 0.2 mV for solvents containing 5-25, 30-60 and 65-100 wt% *EG*, respectively.

The E°_m values at different temperatures in the respective solvents can be expressed in the form of equations of the type

$$E^\circ_m = a - b\,(t - 35) - c\,(t - 35)^2, \tag{3}$$

Table 1. *Standard molal potentials* ($-E^\circ_m$/V) *of the* Ag—AgI *electrode in ethylene glycol + water solvents at temperatures from 15 to 55 °C*

Glycol wt%	$-E^\circ_m$/V 15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C
0	0.14920	0.15062	0.15225	0.15398	0.15588	0.15787	0.15990	0.16188	0.16399
5	0.15002	0.15149	0.15312	0.15484	0.15665	0.15856	0.16057	0.16260	0.16478
10	0.15091	0.15238	0.15394	0.15567	0.15744	0.15933	0.16135	0.16336	0.16553
15	0.15189	0.15333	0.15475	0.15642	0.15826	0.16019	0.16204	0.16411	0.16642
20	0.15272	0.15421	0.15567	0.15736	0.15912	0.16104	0.16290	0.16502	0.16733
25	0.15374	0.15512	0.15663	0.15825	0.16002	0.16185	0.16382	0.16597	0.16836
30	0.15473	0.15607	0.15754	0.15916	0.16098	0.16280	0.16479	0.16712	0.16942
35	0.15575	0.15714	0.15860	0.16023	0.16204	0.16394	0.16593	0.16822	0.17048
40	0.15688	0.15836	0.15981	0.16152	0.16330	0.16527	0.16729	0.16956	0.17185
45	0.15829	0.15977	0.16132	0.16298	0.16478	0.16679	0.16893	0.17118	0.17359
50	0.15992	0.16133	0.16301	0.16469	0.16651	0.16858	0.17077	0.17306	0.17558
55	0.16181	0.16335	0.16488	0.16667	0.16853	0.17069	0.17293	0.17536	0.17784
60	0.16402	0.16549	0.16712	0.16888	0.17089	0.17306	0.17548	0.17812	0.18098
65	0.16659	0.16797	0.16967	0.17149	0.17365	0.17598	0.17861	0.18149	0.18464
70	0.16962	0.17106	0.17273	0.17467	0.17693	0.17959	0.18238	0.18575	0.18916
75	0.17283	0.17448	0.17638	0.17856	0.18112	0.18406	0.18737	0.19099	0.19482
80	0.17676	0.17904	0.18149	0.18423	0.18723	0.19067	0.19422	0.19830	0.20247
85	0.18210	0.18533	0.18874	0.19228	0.19615	0.20029	0.20451	0.20918	0.21385
90	0.18982	0.19486	0.20002	0.20526	0.21060	0.21617	0.22178	0.22742	0.23331
95	0.21899	0.22394	0.22921	0.23444	0.24002	0.24569	0.25159	0.25756	0.26394
100	0.28225	0.28716	0.29230	0.29771	0.30327	0.30917	0.31533	0.32179	0.32846

Table 2. *Values of the constants a, b, and c of equ. (3) for evaluation of* E_m° *in ethylene glycol + water solvents at 15-55 °C, and the standard potentials of the* Ag—AgI *electrode on the molar* (E_c°/V) *and mole fraction* (E_N°/V) *scales at 25 °C*

Glycol wt%	$-10^2 a$/ V	$10^4 b$/ V (°C)$^{-1}$	$10^6 c$/ V (°C)$^{-2}$	25 °C $-E_c^\circ$/V	$-E_N^\circ$/V
0	15.589	3.791	1.767	0.15240	0.35865
5	15.665	3.710	1.853	0.15293	0.35766
10	15.744	3.670	1.967	0.15343	0.35655
15	15.827	3.660	2.047	0.15391	0.35536
20	15.911	3.638	2.193	0.15450	0.35420
25	16.006	3.617	2.387	0.15514	0.35298
30	16.099	3.655	2.527	0.15572	0.35163
35	16.204	3.688	2.647	0.15646	0.35031
40	16.330	3.741	2.760	0.15735	0.34904
45	16.475	3.811	3.073	0.15854	0.34794
50	16.650	3.899	3.240	0.15994	0.34688
55	16.850	4.014	3.527	0.16150	0.34584
60	17.089	4.203	4.020	0.16345	0.34500
65	17.366	4.495	4.827	0.16574	0.34427
70	17.693	4.882	6.347	0.16856	0.34383
75	18.110	5.499	7.020	0.17198	0.34372
80	18.721	6.413	6.227	0.17688	0.34477
85	19.614	7.946	4.720	0.18394	0.34762
90	21.060	10.879	2.560	0.19503	0.35408
95	24.003	11.221	3.467	0.22403	0.37796
100	30.325	11.518	5.340	0.28694	0.43512

where t is the temperature in °C. The constants of equ. (3) for the different solvents were obtained by the method of least squares and are given in Table 2. The maximum difference between the observed values of E_m° and those calculated from equ. (3) at the nine temperatures is 0.12 mV for the various *EG* + water solvents.

The values of the standard potentials at 25 °C on the molar and molefraction scales, E_c° and E_N°, respectively, were computed from E_m° by the usual relations[6], and are also included in Table 2.

Reported standard potentials of the Ag—AgI electrode in *EG* + water solvents[1,2] and our corresponding new values are collected in Table 3 for comparison. The new E_m° values are in excellent agreement with those obtained by *Kundu* et al.[1,2] for the 30% *EG* solvent at 20, 30, 35, 40 and 45 °C, for the 70% *EG* solvent at 35 °C, for the 90% *EG* solvent at 15, 20, 25, 30, 35, 40 and 45 °C and for the anhydrous *EG* at 30 and 35 °C. The differences range from 0.0 to 0.19 mV. The reported

Table 3. *Comparison between the new E°_m values and previously reported ones* ($-E^\circ_m$/V)

Glycol wt%		$-E^\circ_m$/V 15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C
10	Ref.[1]	0.1494	0.1508	0.1522	0.1540	0.1558	0.1578	0.1600
	this work	0.15091	0.15238	0.15394	0.15567	0.15744	0.15933	0.16135
30	Ref.[1]	0.1545	0.1560	0.1573	0.1590	0.1609	0.1627	0.1.648
	this work	0.15473	0.15607	0.15754	0.15916	0.16098	0.16280	0.16479
50	Ref.[1]	0.1589	0.1611	0.1634	0.1659	0.1685	0.1712	0.1741
	this work	0.15992	0.16133	0.16301	0.16469	0.16651	0.16858	0.17077
70	Ref.[1]	0.1624	0.1658	0.1693	0.1730	0.1770	0.1811	0.1855
	this work	0.16962	0.17106	0.17273	0.17467	0.17693	0.17959	0.18238
90	Ref.[1]	0.1898	0.1948	0.1999	0.2052	0.2106	0.2161	0.2217
	this work	0.18982	0.19486	0.20002	0.20526	0.21060	0.21617	0.22178
100	Ref.[2]	0.2828	0.2877	0.2928	0.2979	0.3032	0.3079	0.3146
	this work	0.28225	0.28716	0.29230	0.29771	0.30327	0.30917	0.31533

E_m° values for the 30% *EG* solvent at 15 and 25 °C, and for the 50% *EG* solvent at 20 °C are in fair agreement with the new ones. The differences range from 0.23 to 0.24 mV. On the other hand, the agreement between new E_m° values and the reported ones for the rest of the solvents is poor.

Standard Thermodynamic Functions for the Cell Reaction

The standard thermodynamic functions ΔG°, ΔH° and ΔS° for the cell reaction,

$$\tfrac{1}{2}\,\mathrm{H_2}\,(g,\ 1\,\mathrm{atm}) + \mathrm{AgI}\,(s) = \mathrm{Ag}\,(s) + \mathrm{HI}\ (\text{solvated}), \tag{4}$$

have been calculated from the temperature variation of the standard molal potential in *EG* + water solvents, by using the usual relations[9]. The calculated thermodynamic functions of the cell at 15-55 °C are recorded in Table 4. The values of ΔG° are accurate to within $\pm 19\,\mathrm{J\,mol^{-1}}$. The free energy changes (which are all positive) increase with increasing either the *EG* content in the solvent or the temperature of the solvent system. On the other hand, the standard enthalpy and entropy changes for the cell reaction decrease with increasing temperature, in any solvent.

Primary Medium Effect

The primary medium effect ($\log {}_w^s\gamma_\pm^\circ$) represents the difference in ion-solvent interaction for HI at the standard state in the particular solvent and in water. It is a measure of the change of *Gibbs* free energy which accompanies the transfer of one mole of HI from the standard state in water to the standard state in the respective solvent. Thus, the primary medium effect measures the change in escaping tendency of HI in the transfer from a standard state in one solvent to a standard state in another solvent. The primary medium effects (molal scale) of various glycolic solvents upon HI have been computed, by the usual relation[6], at 15-55 °C. The values of $\log {}_w^s\gamma_\pm^\circ$, presented in Table 5, show that the escaping tendency of HI is greater in glycolic solvents than in pure water, because the primary medium effect of glycolic solvents on HI becomes greater with gradual addition of *EG*.

Standard Thermodynamic Quantities for the Transfer Process

The standard thermodynamic quantities for the transfer of one mole of HI from the standard state in water to the standard states of glycolic solvents,

$$\mathrm{HI}\ (\text{in water}) = \mathrm{HI}\ (\text{in } EG + \text{water solvents}), \tag{5}$$

Table 4. *Standard molal thermodynamic functions of the cell reaction in various ethylene glycol + water solvents at 15-55 °C*

Glycol wt%	0	10	20	30	40	50	60	70	80	90	100
						ΔG°/J mol^{-1}					
15 °C	14378	14558	14734	14925	15141	15437	15832	16374	17066	18319	27242
25 °C	14692	14855	15022	15205	15422	15720	16122	16661	17504	19295	28199
35 °C	15041	15191	15352	15533	15756	16065	16488	17071	18063	20320	29259
45 °C	15424	15564	15724	15910	16144	16472	16933	17603	18742	21394	30422
55 °C	15841	15975	16138	16336	16584	16942	17454	18258	19541	22518	31688
						ΔH°/J mol^{-1}					
15 °C	5802	6542	7058	7575	7810	8202	8617	9859	6162	—9081	1159
25 °C	4803	5431	5818	6144	6248	6367	6342	6268	2638	—10529	—1863
35 °C	3769	4279	4536	4665	4635	4472	3992	2557	—1005	—12027	—4986
45 °C	2701	3089	3211	3140	2966	2515	1563	—1279	—4766	—13574	—8214
55 °C	1599	1864	1844	1563	1243	495	—945	—5238	—8651	—15170	—11543
						$-\Delta S^\circ$/J K^{-1} mol^{-1}					
15 °C	29.8	27.8	26.6	25.5	25.4	25.1	25.0	22.6	37.8	95.1	90.5
25 °C	33.2	31.6	30.9	30.4	30.8	31.4	32.8	34.9	49.9	100.0	100.8
35 °C	36.6	35.4	35.1	35.3	36.1	37.6	40.6	47.1	61.9	105.0	111.1
45 °C	40.0	39.2	39.3	40.1	41.4	43.9	48.3	59.4	73.9	109.9	121.4
55 °C	43.4	43.0	43.6	45.0	46.7	50.1	56.1	71.6	85.9	114.8	131.7

Table 5. *Primary medium effect,* $\log {}_w^s\gamma_\pm^\circ$ *(molal scale), of ethylene glycol + water solvents on* HI *at 15–55 °C, and values of the constants A, B, and C of equ. (6) for evaluation of thermodynamic quantities for transfer of* HI *from water to ethylene glycol + water media*

Glycol wt%	15 °C	25 °C	$\log {}_w^s\gamma_\pm^\circ$ 35 °C	45 °C	55 °C	$10^{-2}A$/ J mol^{-1}	B/ J K^{-1} mol^{-1}	$10^2 C$/ JK^{-2} mol^{-1}
10	0.0150	0.0143	0.0128	0.0115	0.0118	23.4167	14.2854	1.9297
20	0.0308	0.0289	0.0265	0.0238	0.0256	46.6851	29.3539	4.1102
30	0.0484	0.0447	0.0417	0.0387	0.0417	78.5941	50.4865	7.3328
40	0.0672	0.0639	0.0607	0.0585	0.0604	99.6131	65.0854	9.5809
50	0.0937	0.0909	0.0869	0.0861	0.0890	141.9797	93.8379	14.2122
60	0.1296	0.1257	0.1227	0.1234	0.1305	208.6392	139.2237	21.7380
70	0.1786	0.1731	0.1721	0.1781	0.1933	407.4748	273.2378	44.1899
80	0.2410	0.2471	0.2564	0.2718	0.2955	360.8800	253.8613	43.0321
90	0.3552	0.4037	0.4475	0.4901	0.5323	—85.2984	—4.2984	7.6512
100	1.1635	1.1837	1.2053	1.2311	1.2630	239.7948	158.4821	34.4739

were obtained from the standard potential of the cell, in water[6] and in the glycolic solvent, together with the variation of E_N° with temperature. The effect of solvent on the free energy of transfer should, however, be more clearly reflected in the mole fraction scale, because that will eliminate free energy changes due to concentration changes[2,10-12]. Thus the standard changes of *Gibbs* free energy (ΔG_t°) can be represented as a function of temperature (in K) by equ. (6).

$$F\,({}^{w}E_N^\circ - {}^{s}E_N^\circ) = \Delta G_t^\circ = A - B\,T + C\,T^2 \tag{6}$$

The standard thermodynamic quantities for *EG* + water solvents were computed by applying the usual thermodynamic relations[9,11] to equ. (6). The least squares values of the constants A, B and C are given in Table 5, and the values of the transfer thermodynamic quantities at 15–55 °C are listed in Table 6. ΔG_t° values are accurate to within $\pm 38\,\mathrm{J\,mol^{-1}}$.

The standard *Gibbs* free energy of transfer, ΔG_t°, has negative values, which increase in magnitude as the proportion of *EG* increases, and after passing through a minimum around 80 wt% *EG* (at 15 °C, for example) ultimately go over to positive values. Thus, although the transfer of HI from water to anhydrous *EG* and *EG*-rich media is non-spontaneous, the process is thermodynamically favourable so long as the extreme *EG*-rich region is not reached, and the spontaneity of transfer increases up to about 80 wt% *EG* (at 15 °C, for example). Obviously, at least two opposing factors are operating. The observed values of ΔG_t° include the electrostatic contribution, which necessarily becomes more positive as the dielectric constant decreases with increasing proportion of *EG*. Similar behaviour was also observed by *Kundu* et al.[1] in their studies of HI in *EG* + water solvents. They[1] compute the standard free energy of transfer for the individual ions, $\Delta G_t^\circ(i)$. For HI, however, for the media containing smaller proportions of *EG*, the positive magnitude of $\Delta G_t^\circ(\mathrm{I}^-)$ is too small to counteract the negative magnitude of $\Delta G_t^\circ(\mathrm{H}^+)$, so that the over-all free energy of transfer, ΔG_t°, remains negative till very high *EG* concentration is attained.

The standard entropy and enthalpy changes accompanying the transfer of one mole of HI from water to the glycolic solvent appear to be positive for water-rich solvents at lower temperatures and negative for the *EG*-rich solvents at higher temperatures. At 15 °C, for example, the values of ΔH_t° and ΔS_t° are found to be increasingly positive and after passing through maxima at around 70% *EG*, the values tend to be less positive and thereafter decrease to negative values passing through minima at around 90% *EG*.

Table 6. *Free energy, enthalpy, entropy and heat capacity of transfer of* HI *from water to ethylene glycol + water solvents at 15-55 °C*

Glycol wt%	10	20	30	40	50	60	70	80	90	100
					$-\Delta G_t^\circ/\mathrm{J\ mol^{-1}}$					
15 °C	172	377	600	838	1041	1204	1295	1332	938	−6937
25 °C	202	430	675	927	1146	1322	1436	1348	447	−7373
35 °C	228	474	735	997	1223	1396	1490	1278	−60	−7878
45 °C	250	510	781	1048	1271	1427	1454	1121	−582	−8453
55 °C	268	538	812	1080	1291	1414	1331	879	−1120	−9096
					$-\Delta H_t^\circ/\mathrm{J\ mol^{-1}}$					
15 °C	−739	−1256	−1771	−2006	−2398	−2815	−4056	−358	14883	4644
25 °C	−626	−1015	−1341	−1445	−1564	−1540	−1466	2165	15331	6666
35 °C	−509	−766	−896	−864	−703	−222	1214	4774	15795	8756
45 °C	−388	−508	−437	−264	188	1139	3981	7469	16274	10915
55 °C	−264	−243	37	356	1106	2544	6837	10250	16769	13143
					$\Delta S_t^\circ/\mathrm{J\ K^{-1}\ mol^{-1}}$					
15 °C	3.2	5.7	8.2	9.9	11.9	13.9	18.6	5.9	−48.4	−40.2
25 °C	2.8	4.8	6.8	8.0	9.1	9.6	9.7	−2.7	−49.9	−47.1
35 °C	2.4	4.0	5.3	6.0	6.2	5.3	0.9	−11.3	−51.5	−54.0
45 °C	2.0	3.2	3.8	4.1	3.4	0.9	−7.9	−20.0	−53.0	−60.9
55 °C	1.6	2.4	2.4	2.2	0.6	−3.4	−16.8	−28.6	−54.5	−67.8
					$-\Delta C_p^\circ/\mathrm{J\ K^{-1}\ mol^{-1}}$					
15 °C	11.1	23.7	42.3	55.2	81.9	125.3	245.7	248.0	44.1	198.7
25 °C	11.5	24.5	43.7	57.1	84.7	129.6	263.5	256.6	45.6	205.6
35 °C	11.9	25.3	45.2	59.0	87.6	134.0	272.3	265.2	47.2	212.5
45 °C	12.3	26.2	46.7	61.0	90.4	138.3	281.2	273.8	48.7	219.4
55 °C	12.7	27.0	48.1	62.9	93.3	142.7	290.0	282.4	50.2	226.3

Now, all structure-forming processes, e.g. solvation, are expected to be exothermic and accompanied by a decrease in entropy, whereas structure-breaking processes should be endothermic and lead to an increase in entropy[1]. The process of transfer of an ion from water to another solvent (*SH*) should involve the following structural changes: a) Breaking down of the structure of the hydration shell around the hydrated ion in water. b) Building up of the liquid structure by the water molecules released by process a). c) Breaking down of the liquid structure of the solvent (*SH*), if any, so that the molecules may be free to solvate the incoming ion. d) Building up of the solvation shell around the ion in the solvent (*SH*) by the molecules released by process c). For the respective steps ΔH_t° as well as ΔS_t° are positive for a) and c), and negative for b) and d). The sign and magnitude of the over-all entropy or enthalpy changes will depend on the relative magnitudes of the individual steps.

The positive ΔS_t° value suggests that the amount of order[12] created by HI in these solvents is less. Since addition of small amounts of *EG* to water enhances the three-dimensional hydrogen bonded polymeric form of water[12], there will be relatively more structure to break than to promote. The negative values of ΔH_t° and ΔS_t° suggest that when a sufficient quantity of *EG* is added to a highly polar water molecule, the glycolic solvent becomes less associated than pure water. Thus, hydriodic acid breaks more structure in pure water than in glycolic solvents[12].

The values of ΔC_p° are all negative, and decrease as the temperature increases for any solvent. At 15 °C, for example, ΔC_p° decreases, passes through a minimum at around 80% *EG*, then increases to a maximum at around 90% *EG*, and thereafter decreases again, with increasing the *EG* concentration in the solvent.

To study the ion-solvent interaction, the method adopted by *Khoo* and *Chan*[10] was followed. In this method, consider a function $\Delta G_t^{\circ\prime}$ on the mole-fraction scale given[10] by

$$\Delta G_t^{\circ\prime} = \Delta G_t^\circ(\mathrm{HCl}) - \Delta G_t^\circ(\mathrm{HI}) = \Delta G_t^\circ(\mathrm{Cl}^-) - \Delta G_t^\circ(\mathrm{I}^-) \qquad (7)$$

The difference between the free energies of transfer of hydrochloric[11] and hydriodic acids gives the difference between the free energies of transfer of the chloride and iodide ions. The values of $\Delta G_t^{\circ\prime}$ calculated at 25 °C are given in Table 7. $\Delta G_t^{\circ\prime}$ is positive and increases with increasing concentration of *EG* in the solvents. This is qualitatively in agreement with the *Born* theory which predicts that the iodide ion should be in lower free energy states than the chloride ion in the mixed solvents of lower dielectric constants than water[10]. Therefore, the *Born* equation

Table 7. *Electrical and chemical parts of the thermodynamic quantities accompanying the transfer of* HI *from water to ethylene glycol + water solvents and the difference between the free energies of transfer of the chloride and iodide ions* (ΔG_t°/J mol^{-1}) *at 25 °C*

Glycol wt%	ΔG_t°	ΔG_{el}°	$-\Delta G_{ch}^{\circ}$	$-\Delta H_{el}^{\circ}$	ΔH_{ch}°	$-\Delta S_{el}^{\circ}$	ΔS_{ch}°
10	429	28	230	38	664	0.2	3.0
20	848	57	487	77	1092	0.5	5.3
30	1307	91	766	133	1474	0.8	7.6
40	1714	130	1057	201	1646	1.1	9.1
50	2152	177	1323	270	1834	1.5	10.6
60	2596	235	1557	329	1869	1.9	11.5
70	3184	318	1754	395	1861	2.4	12.1
80	4131	432	1780	438	−1727	2.9	0.2
90	5476	581	1028	471	−14860	3.5	−46.4
100	5681	790	−6583	519	−6147	4.4	−42.7

may be be expected to fit increasingly better as the *EG* content of the solvent is increased.

Since the process involves the transfer of charged particles, the hydrogen ion and the iodide ion, from water to another solvent having a different dielectric constant, the related thermodynamic quantities comprise two parts: electrostatic (*el*) and nonelectrostatic or chemical (*ch*). Thus for free energy change

$$\Delta G_t^\circ = \Delta G_{el}^\circ + \Delta G_{ch}^\circ \tag{8}$$

and so for the other thermodynamic quantities, ΔS_t° and ΔH_t°. The nonelectrostatic contribution reflects the chemical nature of the solvent with respect to water which includes the basicity as well as the solvating capacity of the solvent. The electrostatic as well as the chemical parts of the standard thermodynamic quantities for the transfer process were calculated by using the usual relations[11], and the values so computed at 25 °C are also included in Table 7.

The chemical part of the *Gibbs* free energy change, which appear to be negative for aqueous glycolic solvents, decreases, passes through a minimum at around 80% *EG*, and thereafter increases with increasing glycol content in the solvent and becomes positive in the anhydrous *EG*. Insofar as ΔG_{ch}° is a criterion of the changes in the acidity or basicity of the medium, the negative ΔG_{ch}° values show that the chemical reaction in the transfer process is spontaneous, and the spontaneity increases, with increasing *EG* concentration in the solvent, and reachs a maximum at around 80% *EG*. On the other hand, the more positive value of ΔG_{ch}° obtained for the anhydrous glycol indicates that the transfer process is favourable.

The electrostatic parts of the enthalpy and entropy changes for the transfer process have negative values, whereas their chemical contributions which have negative values only for *EG*-rich solvents, increase passing through maxima (at around 60 and 70 wt% *EG* for ΔH_{ch}° and ΔS_{ch}°, respectively), then decrease passing through minima at around 90 wt% *EG* and thereafter increase with increasing *EG* concentration in the solvent. The large negative ΔH_{ch}° value, for the 90% *EG* solvent, reflect the smaller enthalpy changes involved in creating a correct configurational change of the solvent on the transfer process. This view is further supported by the large negative value of ΔS_{ch}°, which is associated with the structural changes as far as the chemical interaction or solvation on the transfer process is concerned. This phenomenon produces an over-all order and hence ΔS_{ch}° value is negative.

Acknowledgements

The authors are indebted to. Mrs. *Laila Abu Elela* for technical assistance and preliminary calculations.

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