J. Chem. Eng. Data 1985, 30, 91-94

Standard Potentials of Silver–Silver Iodide Electrode in Water + Propylene Glycol Mixtures by Electromotive Force Measurements and Related Thermodynamic Quantities

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The standard potentials of the silver–silver iodide electrode have been determined in the temperature range 15–45 °C in 20, 40, 75, and 90 wt % propylene glycol from emf measurements of the cells $Pt|H_2(g, 1\ atm)|HBO_2$ (m_1), $NaBO_2$ (m_2), KBr (m_3) (in water + propylene glycol mixtures)|AgBr|Ag and $Pt|H_2(g, 1\ atm)|HBO_2$ (m_1), $NaBO_2$ (m_2), CsI (m_3) (in water + propylene glycol mixtures)|AgI|Ag. The standard molal potentials, ${}_sE_m{}^\circ$, in the various solvent mixtures have been expressed as a function of temperature. The various thermodynamic parameters accompanying the transfer of HI from water to these solvents at 25 °C are reported. The variation of these parameters with solvent composition has been discussed in terms of the basicity of the solvent and the structural effects of the solvent mixtures on the transfer process. The transfer free energies of the proton and the iodide ion have been evaluated at 25 °C, on the basis of the ferrocene reference method in these media.

Introduction

In continuation of our earlier studies on the thermodynamics of hydrochloric and hydrobromic acids in water + propylene glycol (PG) mixtures (*1*, *2*), we have determined the standard potentials of the silver–silver iodide electrode in order to have a comprehensive understanding of the thermodynamic behavior of the hydrogen halides in these mixtures. An attempt was also made to utilize the proton medium effects determined earlier (*3*) in the various solvent mixtures, to elicit information on the acid–base nature of these media. Though studies on galvanic cells involving hydrogen and silver–silver iodide electrodes have been reported in a few amphiprotic media (*4–8*), to our knowledge no measurements of this nature have yet been made in water + propylene glycol mixtures.

In the method adopted, emf measurements were made on the buffered cells 1 and 2. In the composition range 20–90%

$$Pt|H_2(g,\ 1\ atm)|HBO_2\ (m_1),\ NaBO_2\ (m_2),\ KBr\ (m_3)\ in\ H_2O + propylene\ glycol|AgBr|Ag \quad (1)$$

$$Pt|H_2(g,\ 1\ atm)|HBO_2\ (m_1),\ NaBO_2\ (m_2),\ CsI\ (m_3)\ in\ H_2O + propylene\ glycol|AgI|Ag \quad (2)$$

wt % propylene glycol + water mixtures between the temperatures 15 and 45 °C and by combination of these data with the standard potentials of the Ag–AgBr electrode in these mixtures determined earlier (*2*), the standard potentials of the silver–silver iodide electrode were obtained.

Experimental Section

The solvents were purified as described previously (*9*). The hydrogen (*10*), silver–silver bromide, and silver–silver iodide electrodes were prepared according to the methods described elsewhere (*11*). Boric acid (AR, BDH) dried at 120 °C was used for the preparation of borate buffers. Sodium borate was prepared in situ by appropriately neutralizing the acid with sodium lyate which was always freshly prepared by dissolving freshly cut pieces of dry sodium in the desired solvent mixtures. The strength of the lyate solution was determined by titration against a standard aqueous HCl solution. KBr and CsI (BDH) reagent grade were used throughout. Stock solutions of sodium lyate, boric acid, and the salts KBr and CsI were suitably diluted by weight to get the buffer and test solutions of the required strength. The experimental setup and the general procedure used for emf measurements are identical with those described earlier (*8*). The cells were thermostated at each temperature with an accuracy of ±0.1 °C. Both Ag–AgBr and Ag–AgI electrodes were found to be stable over the entire temperature range and constancy of cell emf to ±0.05 mV over a period of 0.5 h was considered as an adequate criterion of equilibrium. The emf value at 25 °C was redetermined thrice during measurements as a check on the stability of the electrodes. All the values agreed within ±0.05 mV.

Results and Discussion

The determination of the standard potentials of the Ag–AgI electrode in these mixtures is based on Owen's method (*12*), which involves the use of buffered cells to prevent aerial oxidation of I^- to I_2. The pK_a values of boric acid in different solvent mixtures at various temperatures needed for the evaluation of $E_m{}^\circ$ of the Ag–AgI electrode were determined by using the emf data of cell 1 in combination with the standard potentials of the Ag–AgBr electrode in these mixtures as described previously (*13*). The emf's of cells 1 and 2, measured in various solvent mixtures and converted to a partial pressure of 1 atm of hydrogen gas, are given in Table I, a and b.

A function p(K_a') was defined as

$$p(K_a') = \frac{E - E^\circ}{k} + \log \frac{m_{HBO_2} m_{Br^-}}{m_{BO_2^-}}$$

$$= pK_a - \log \frac{\gamma_{HBO_2}\gamma_{Br^-}}{\gamma_{BO_2^-}}$$

or

$$pK_a' = pK_a + f(\mu) \quad (3)$$

where E is the measured emf of cell 1, E° is the standard potential of the silver–silver bromide electrode, $k = 2.303RT/F$, and μ is the ionic strength. The pK_a values of boric acid in these solvent mixtures have been obtained by extrapolating the linear plots of pK_a' against μ, to $\mu = 0$ and these data are recorded in Table II.

The standard potentials of the Ag–AgI electrode in different

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Table I. Emf Data of Cells 1 and 2 Corrected for 1 atm of Hydrogen from 15 to 45 °C in Various Water + Propylene Glycol Mixtures

(a) Cell 1

m_{HBO_2}/ (mol·kg^{-1})	m_{Br^-}/ (mol·kg^{-1})	$m_{BO_2^-}$/ (mol·kg^{-1})	emf, V			
			15 °C	25 °C	35 °C	45 °C
Water + 20 wt % Propylene Glycol (Ag–AgBr)						
0.007 99	0.007 99	0.007 99	0.685 12	0.705 78	0.724 72	0.742 63
0.008 99	0.009 16	0.008 99	0.681 32	0.701 01	0.720 89	0.739 02
0.010 02	0.009 99	0.009 99	0.676 83	0.696 78	0.715 96	0.734 59
0.014 01	0.015 00	0.014 99	0.668 67	0.688 12	0.706 39	0.724 11
0.020 00	0.019 99	0.019 99	0.664 31	0.683 31	0.702 11	0.719 65
Water + 40 wt % Propylene Glycol (Ag–AgBr)						
0.004 99	0.005 00	0.005 00	0.616 88	0.634 97	0.652 60	0.669 25
0.007 06	0.007 00	0.006 99	0.606 82	0.624 98	0.641 81	0.658 21
0.008 09	0.008 05	0.007 99	0.603 45	0.621 06	0.638 31	0.654 49
0.009 02	0.009 00	0.009 00	0.600 72	0.617 92	0.634 94	0.650 70
0.010 00	0.010 01	0.009 99	0.597 05	0.614 51	0.631 26	0.647 41
0.017 49	0.018 38	0.017 53	0.583 15	0.600 03	0.616 29	0.631 27
Water + 75 wt % Propylene Glycol (Ag–AgBr)						
0.005 00	0.005 00	0.004 99	0.566 85	0.580 15	0.591 07	0.604 79
0.006 03	0.006 01	0.006 01	0.561 30	0.573 28	0.585 75	0.598 29
0.006 98	0.007 01	0.007 01	0.556 29	0.568 35	0.579 54	0.591 74
0.007 98	0.008 02	0.008 00	0.554 15	0.565 94	0.578 32	0.590 18
0.008 99	0.009 00	0.009 00	0.550 91	0.562 81	0.574 73	0.585 10
0.010 00	0.009 99	0.010 00	0.546 72	0.558 36	0.570 56	0.582 83
0.020 49	0.020 01	0.020 01	0.532 56	0.544 26	0.555 46	0.566 50
Water + 90 wt % Propylene Glycol (Ag–AgBr)						
0.006 02	0.006 12	0.005 98	0.489 33	0.499 51	0.508 49	0.518 28
0.007 07	0.006 99	0.006 97	0.485 57	0.495 58	0.503 99	0.513 72
0.008 01	0.007 97	0.007 97	0.483 02	0.492 84	0.502 03	0.511 40
0.009 04	0.008 99	0.008 96	0.480 09	0.489 88	0.499 31	0.508 25
0.015 04	0.015 01	0.014 97	0.466 48	0.475 73	0.481 97	0.486 89

(b) Cell 2

m_{HBO_2}/ (mol·kg^{-1})	m_{I^-}/ (mol·kg^{-1})	$m_{BO_2^-}$/ (mol·kg^{-1})	emf, V			
			15 °C	25 °C	35 °C	45 °C
Water + 20 wt % Propylene Glycol (Ag–AgI)						
0.005 00	0.005 13	0.004 97	0.426 98	0.447 67	0.468 21	0.487 61
0.005 87	0.006 06	0.005 83	0.424 63	0.445 10	0.465 33	0.484 60
0.007 01	0.007 13	0.007 00	0.420 62	0.441 26	0.461 17	0.480 26
0.007 99	0.008 03	0.007 99	0.418 25	0.438 56	0.458 32	0.477 32
0.008 9	0.009 00	0.009 01	0.417 61	0.437 70	0.457 60	0.476 40
0.009 99	0.009 97	0.010 00	0.413 56	0.433 81	0.453 30	0.472 06
0.014 95	0.014 98	0.015 02	0.403 40	0.423 29	0.442 39	0.460 69
0.019 96	0.020 10	0.020 00	0.396 55	0.416 03	0.434 41	0.451 42
Water + 40 wt % Propylene Glycol (Ag–AgI)						
0.004 98	0.005 11	0.005 02	0.401 31	0.420 91	0.440 54	0.459 16
0.005 99	0.006 28	0.005 99	0.397 62	0.420 89	0.440 52	0.459 14
0.007 04	0.006 99	0.007 00	0.395 23	0.414 53	0.432 95	0.451 21
0.008 15	0.008 04	0.008 00	0.391 87	0.410 79	0.429 48	0.447 49
0.009 03	0.009 12	0.008 99	0.388 94	0.408 04	0.426 74	0.444 29
0.010 01	0.010 01	0.009 98	0.387 90	0.406 56	0.424 99	0.442 54
0.015 00	0.015 07	0.014 98	0.378 43	0.396 76	0.414 47	0.431 78
0.019 98	0.019 99	0.019 99	0.371 79	0.390 15	0.407 67	0.424 21
Water + 75 wt % Propylene Glycol (Ag–AgI)						
0.004 95	0.005 08	0.005 01	0.370 08	0.384 32	0.398 28	0.415 20
0.005 97	0.006 04	0.006 00	0.365 86	0.379 43	0.393 58	0.407 49
0.006 98	0.007 01	0.006 99	0.361 37	0.375 26	0.389 28	0.403 22
0.008 01	0.008 01	0.007 99	0.359 21	0.372 47	0.386 21	0.399 84
0.009 01	0.008 98	0.008 98	0.357 13	0.370 60	0.383 94	0.397 28
0.009 56	0.011 85	0.010 60	0.351 78	0.365 49	0.379 06	0.392 23
0.015 15	0.015 13	0.014 99	0.343 32	0.356 11	0.369 67	0.382 49
Water + 90 wt % Propylene Glycol (Ag–AgI)						
0.004 98	0.005 00	0.005 00	0.336 25	0.348 56	0.361 41	0.374 60
0.005 61	0.005 99	0.006 41	0.336 19	0.348 46	0.361 51	0.374 52
0.007 01	0.007 02	0.007 00	0.329 35	0.340 96	0.352 41	0.365 68
0.008 00	0.008 08	0.007 99	0.325 63	0.337 35	0.349 95	0.362 51
0.009 00	0.009 00	0.009 00	0.322 75	0.334 62	0.347 04	0.359 37
0.010 15	0.010 01	0.010 00	0.320 06	0.332 10	0.343 98	0.356 22
0.014 99	0.014 99	0.014 97	0.311 02	0.322 48	0.334 29	0.345 96
0.016 81	0.020 03	0.023 19	0.313 35	0.324 60	0.336 39	0.347 94

Table II. pK_a Data of Boric Acid in Various Water + Propylene Glycol Mixtures at Different Temperatures

[PG]/ wt %	pK_a			
	15 °C	25 °C	35 °C	45 °C
20	8.75	8.79	8.84	8.88
40	7.49	7.60	7.64	7.71
75	7.20	7.27	7.34	7.41
90	6.72	6.83	6.91	7.00

Table III. $_sE_m°$ at Different Temperatures and $_sE_c°$ and $_sE_N°$ at 25 °C for Ag–AgI Electrode in Various Water + Propylene Glycol Mixtures

[PG]/ wt %	$_sE_m°$					
	15 °C	25 °C	35 °C	45 °C	$_sE_c°_{25\ °C}$	$_sE_N°_{25\ °C}$
0[a]	–0.1495	–0.1524	–0.1559		–0.1526	–0.3589
20	–0.2030	–0.2067	–0.2109	–0.2157	–0.2059	–0.4046
40	–0.1581	–0.1632	–0.1655	–0.1708	–0.1617	–0.3509
75	–0.1731	–0.1823	–0.1916	–0.1992	–0.1803	–0.3451
90	–0.1798	–0.1920	–0.2022	–0.2128	–0.1901	–0.3387
100[b]	–0.3332	–0.3468	–0.3609	–0.3749	–0.3451	–0.4791

[a] From ref *18*. [b] From ref *19*.

solvent mixtures were obtained from a plot of the function $E°'$ defined by

$$E°' = E - k(\mathrm{p}K_a) + k \log \frac{m_{\mathrm{HBO_2}} m_{\mathrm{I^-}}}{m_{\mathrm{BO_2^-}}}$$

$$= {}_sE_m°(\mathrm{Ag/AgI}) - k \log \frac{\gamma_{\mathrm{HBO_2}} \gamma_{\mathrm{I^-}}}{\gamma_{\mathrm{BO_2^-}}}$$

$$E°' = {}_sE_m°(\mathrm{Ag/AgI}) + f(\mu) \qquad (4)$$

against, μ, the ionic strength, by extrapolating to $\mu = 0$. In equation 4, E represents the emf of cell 2, m's and γ's represent the molality and activity coefficients of the respective species, and $k = 2.303RT/F$. For calculating μ, it was assumed that CsI and $NaBO_2$ are completely dissociated in all solvent mixtures. A representative plot of $E°'$ against μ in 40 wt % propylene glycol at different temperatures is shown in Figure 1.

The standard potentials $_sE_m°$ of the Ag–AgI electrode on the molal scale were converted to those on the mole fraction scale ($_sE_N°$) and molar scale ($_sE_c°$) by employing the usual expressions (*14*). The $_sE_m°$ values at different temperatures, together with those of $_sE_N°$ and $_sE_c°$, at 25 °C in different solvent mixtures are recorded in Table III. The standard error in $_sE_m°$ is about (±0.2) mV. The variation of $_sE_m°$ of the Ag–AgI electrode with temperature in different solvent mixtures has been expressed in the form

$$_sE_m° = {}_sE_m°_{25\ °C} + b(t - 25) + c(t - 25)^2 \qquad (5)$$

where t is the temperature in degrees Celsius, b and c are empirical coefficients which are summarized in Table IV. The standard deviation in $_sE_m°$ calculated from eq 5 was found to be within ±0.2 mV in all solvent mixtures.

The standard free energy change, $\Delta G_t°(\mathrm{HI})_{w\to s}$ associated with the transfer of 1 mol of HI from water to the various solvent mixtures at infinite dilution

$$\mathrm{HI(water)} = \mathrm{HI(water + PG)} \qquad (6)$$

has been calculated on the mole fraction scale at 25 °C from the expression

$$\Delta G_t°(\mathrm{HI})_{w\to s} = F({}_wE_N° - {}_sE_N°) \qquad (7)$$

where $_wE_N°$ and $_sE_N°$ represent the standard potentials of the Ag–AgI electrode in water and mixed solvent, respectively, on the mole fraction scale. The transfer process, eq 6, is associated with a transfer of charged species (H^+ and I^- ions) from water to the mixed solvent, at infinite dilution, and it is generally agreed (*15*) that it consists of an electrostatic part, $\Delta G_t°{}_{el}$ and a nonelectrostatic part, $\Delta G_t°{}_{nonel}$. While the electrostatic transfer free energy arises mainly due to the differences in the dielectric constants of the solvents, the nonelectrostatic transfer free energy reflects the contributions of solvation and other specific ion–solvent interactions which depend on the basicity of the solvent. Thus

Table IV. Coefficients of Empirical Equation

$_sE_m° = {}_sE_m°_{25\ °C} + b(t - 25) + c(t - 25)^2$

[PG]/wt %	a	-10^4b	-10^6c
0[a]	–0.1524	3.190	2.840
20	–0.2067	3.955	2.750
40	–0.1623	3.990	0.500
75	–0.1826	9.160	–4.000
90	–0.1916	11.320	–4.000
100[b]	–0.3468	13.800	1.130

[a] From ref *18*. [b] From ref *19*.

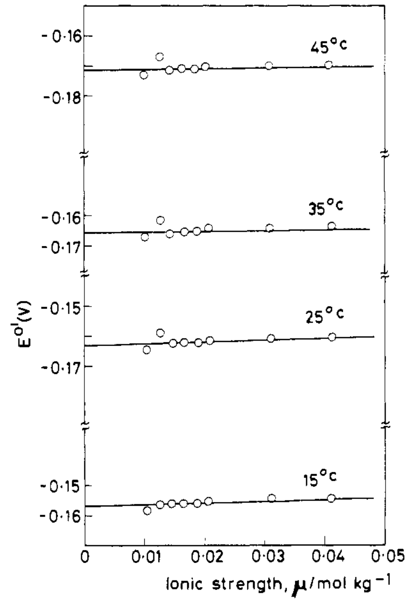

Figure 1. Extrapolation of $E°$ (V) against μ (eq 3) in water + 40 mass % propylene glycol mixture at different temperatures.

$$\Delta G_t°{}_{w\to s} = \Delta G_t°{}_{el} + \Delta G_t°{}_{nonel} \qquad (8)$$

The standard entropy of transfer $\Delta S_t°(\mathrm{HI})_{w\to s}$ and standard enthalpy of transfer $\Delta H_t°(\mathrm{HI})_{w\to s}$ on the mole fraction scale were obtained at 25 °C in the usual way as described earlier (*15*). All these thermodynamic quantities are recorded in Table V. The $\Delta G_t°(\mathrm{HI})_{w\to s}$ values are accurate to ±40 J·mol^{-1} and the expected errors in $\Delta S_t°(\mathrm{HI})_{w\to s}$ and $\Delta H_t°(\mathrm{HI})_{w\to s}$ are ±0.5 J·K^{-1} mol^{-1} and ±160 J·mol^{-1}, respectively.

It is seen from Table V that $\Delta G_t°(\mathrm{HI})_{w\to s}$ initially increases up to about 20 wt % propylene glycol and then decreases, the value becoming increasingly negative up to about 90 wt % propylene glycol, and finally attains a large positive value in pure propylene glycol. Thus, the transfer of HI from water to these solvent mixtures is a thermodynamically favorable process in the region 20–90 wt % propylene glycol. The variation of $\Delta G_t°{}_{w\to s}$ with solvent composition can be qualitatively explained from eq 8, where $\Delta G_t°{}_{el}$ becomes positive due to the decrease in dielectric constant of the solvent with increasing addition of propylene glycol while $\Delta G_t°{}_{nonel}$ possibly decreases under the same conditions. An examination of $\Delta H_t°(\mathrm{HI})_{w\to s}$ indicates that it passes through an endothermic maximum at about 20 wt % propylene glycol as in the case of HCl and HBr but subsequently

Table V. Standard Free Energy, Entropy, and Enthalpy of Transfer (Mole Fraction Scale) of HI from Water to Water + Propylene Glycol Mixtures at 25 °C

[PG]/wt %	$\Delta G_t°(\mathrm{HI})_{w\to s}$/ (J·mol^{-1})	$\Delta S_t°(\mathrm{HI})_{w\to s}$/ (J·K^{-1}·mol^{-1})	$\Delta H_t°(\mathrm{HI})_{w\to s}$/ (J·mol^{-1})
20	4410	−4.7	+3 009
40	−772	−1.7	−1 279
75	−1332	−43.5	−14 302
90	−1949	−59.2	−19 600
100[a]	+11599	−78.44	−11 788

[a] Calculated with data from ref *19*.

Table VI. Transfer Free Energies of H^+, Cl^-, Br^-, and I^- Ions in Water + Propylene Glycol Mixtures (Mole Fraction Scale) at 25 °C Based on Ferrocene Reference Method

[PG]/ wt %	$\Delta G_t°$-$(H^+)_{w\to s}$/ (J·mol^{-1})	$\Delta G_t°$-$(Cl^-)_{w\to s}$/ (J·mol^{-1})	$\Delta G_t°$-$(Br^-)_{w\to s}$/ (J·mol^{-1})	$\Delta G_t°$-$(I^-)_{w\to s}$/ (J·mol^{-1})
20	−2 939	3 604	3 267	7349
40	−4 166	5 270	4 533	3394
75	−10 731	13 475	12 381	9399
90	−13 792	20 248	18 308	11 843
100	−13 473	30 874	28 961	25073

it decreases, becoming increasingly negative, with the addition of propylene glycol. However, $\Delta H_t°_{w\to s}$ increases in the pure solvent although the value is still negative. The significance of the existence of the endothermic maximum at 20 wt % of propylene glycol which is similar to that observed in the case of other aquoorganic mixtures has been discussed earlier (*4–8*, *16*).

The continuous decrease of $\Delta H_t°_{w\to s}$ with increase in weight percent of organic solvent is associated with structure-making ion–solvent interactions. Examination of $\Delta S_t°(\mathrm{HI})_{w\to s}$ (Table V) values, which are in general increasingly negative with the addition of propylene glycol, supports the above conclusions. The large negative $\Delta S_t°_{w\to s}$ values beyond 40 wt % propylene glycol indicate the net structure-making effect of the ions which is aided by the strong electrostatic fields in media of low dielectric constant.

The Gibbs transfer energies of the proton, $\Delta G_t°(H^+)_{w\to s}$, determined earlier (*3*) in these solvent mixtures on the basis of the ferrocene reference method were utilized to evaluate the transfer free energies of the halide ions from the relation

$$\Delta G_t°(\mathrm{HX})_{w\to s} = \Delta G_t°(H^+)_{w\to s} + \Delta G_t°(X^-)_{w\to s} \qquad (9)$$

where $X^- = Cl^-$, Br^-, or I^-. These results on the mole fraction scale are recorded in Table VI. It is seen that $\Delta G_t°(H^+)_{w\to s}$ decreases continuously with the addition of propylene glycol, passes through a minimum at about 90 wt % propylene glycol, and then slightly increases although the value is still negative in the pure solvent. The transfer energies of the halide ions are all positive and in general they decrease in the order $Cl^- > Br^- > I^-$ except in 20 wt % propylene glycol in the case of I^-. The results in 40–90 wt % propylene glycol + water mixtures are in general agreement for the transfer of halide ions from water to other mixed aqueous amphiprotic solvents and also to pure solvents like methanol (*16*). The order of the transfer free energies observed as above may be ascribed to the increasing radius of the halide ions from chloride to iodide and hence their decreasing capacity to act as hydrogen-bond acceptors (*16*). The large $\Delta G_t°(I^-)_{w\to s}$ in water + 20 wt % propylene glycol as compared to that of Cl^- and Br^- is however surprising and presumably other factors such as the mutual polarizability (*17*) between the iodide ion and the solvent molecules also affects the energetics of the transfer process, although this should be of minor importance in the present case as only a transfer from water to another amphiprotic solvent mixture is involved.

The transfer of the proton, from water to these solvent mixtures, is however spontaneous in all solvent mixtures and is most favorable for the solvent containing 90 wt % propylene glycol. Thus, all water + propylene glycol mixtures including the pure solvent are more basic than water. The present results suggest that the halide ions are hydrophilic whereas H^+ ions are glycophilic (*6*) in nature. Similar results have been reported in other aquoorganic mixtures (*4–8*).

Registry No. AgI, 7783-96-2; HI, 10034-85-2; HBO_2, 13460-50-9; $NaBO_2$, 7775-19-1; CsI, 7789-17-5; Ag, 7440-22-4; H^+, 12408-02-5; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; propylene glycol, 57-55-6.

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Received for review February 21, 1984. Accepted June 22, 1984.