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THERMODYNAMIC STUDIES OF HYDROGEN IODIDE IN DIOXANE–WATER MIXTURES FROM ELECTROMOTIVE FORCE MEASUREMENTS

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ABSTRACT

The standard potentials of the silver–silver iodide electrode were measured in 10, 20, 30 and 40% (w/w) dioxane–water mixtures at 15, 25, 35 and 45 °C. These values have been used to determine the thermodynamic quantities ΔG_t°, ΔS_t°, ΔH_t° for the transfer of H^+I^- from water to various dioxane–water mixtures. The ionic ΔG_t° values for H^+, Cl^-, Br^- and I^- are determined using Feakins method. The chemical and electrical contributions of ΔG_t° are also calculated using the method proposed by Roy and co-workers. The significance of these thermodynamic functions is discussed in relation to the acid–base character of the solvents.

INTRODUCTION

In continuation of the previous studies on the standard potentials of silver–silver halide electrodes in dioxane–water mixtures at different temperatures[1, 2], investigation of the standard potentials of the silver–silver iodide electrode has been undertaken in 10, 20, 30 and 40% (w/w) dioxane–water mixtures at 15, 25, 35 and 45 °C from the study of the cell

$$\mathrm{Ag{-}AgBr}\ \left|\begin{array}{l|l} \mathrm{KBr}(x\ \mathrm{m}) & \mathrm{KI}(x\ \mathrm{m}) \\ \mathrm{KNO_3}\ (1-x)\ \mathrm{m} & \mathrm{KNO_3}\ (1-x)\ \mathrm{m} \\ \text{Dioxane (X)\%} & \text{Dioxane (X)\%} \\ \text{Water (Y)\%} & \text{Water (Y)\%} \end{array}\right|\ \mathrm{AgI{-}Ag} \qquad \text{(I)}$$

Feakins and Turner[3] have determined the standard potential of the silver–silver iodide electrode at 25 °C in 20 and 45% (w/w) dioxane–water mixtures using Owen's borate buffered cell. Mussini et al.[4] have also determined the standard potential of the silver–silver iodide electrode in dioxane–water mixtures. Both groups of workers have calculated the free energy of transfer ΔG_t° for the pair of ions H^+I^- from water to dioxane–water mixtures. But Feakins et al.[5] have not supported the value of ΔG_t° (H^+I^-) obtained by Mussini et al.[4]. The present work was undertaken to check the work of Feakins et al. and that of Mussini et al. using a different type of cell and also to extend the work to other solvent compositions at different temperatures. The solvent systems chosen were 10, 20, 30 and 40% (w/w) dioxane–water mixtures to correspond with the previous investigations on the silver–silver chloride electrode[1] and silver–silver bromide electrode[2] in the same compositions.

EXPERIMENTAL

The dioxane used was of B.D.H. Analar quality and was purified as described earlier[6]. Analar quality potassium nitrate, potassium bromide and potassium iodide were recrystallised four times from triple distilled water. Stock molal solutions of all these salts in water were prepared. A weighed quantity of the aqueous solution of the desired salt was taken and the aqueous content of this solution was calculated. The required amount of dioxane and water were weighed out in the same container so as to bring the solution to the required strength as well as to the desired solvent composition. Transference of the solutions was made under nitrogen pressure and exposure to air was avoided.

The silver–silver bromide and silver–silver iodide electrodes used were of the thermal type as described by Ives and Janz[7]. The silver–silver bromide electrodes were found to be stable for about a month whereas the silver–silver iodide electrodes were stable for about ten days. The electrodes having bias potential within ± 0.05 mV were used. Exposure of the electrodes to light was avoided. The electrode set-up consisted of two electrode vessels connected by a U-tube. One stopcock separated the two cell solutions. The stopcock was opened about 30 min before taking e.m.f. readings. The entire electrode assembly was made up of glass. The other experimental procedures were similar to those adopted with silver–silver chloride electrode described previously[1]. The cell potentials were measured with an accuracy of ± 0.05 mV by a Leeds Northrup K-2 potentiometer in conjugation with a matching galvanometer. The potentiometer was standardised against a certified Weston standard cell maintained at constant temperature. The cells attained equilibrium within 4 h. Duplicate experiments were performed simultaneously in each case and the duplicates generally agreed within ± 0.05 mV.

RESULTS AND DISCUSSION

The e.m.f. of the cell I is given by the expression

$$E = E^0 + \frac{RT}{F}\ln\left(\frac{a_{\mathrm{I}^-}}{a_{\mathrm{Br}^-}}\right) \pm E_j = E^0 + k\log\left(\frac{a_{\mathrm{I}^-}}{a_{\mathrm{Br}^-}}\right) \pm E_j$$

$$= E^0 + k\log\left(\frac{m_{\mathrm{I}^-}}{m_{\mathrm{Br}^-}}\right) + k\log\left(\frac{\lambda_{\mathrm{I}^-}}{\lambda_{\mathrm{Br}^-}}\right) \pm E_j \qquad (1)$$

where E^0 is the standard potential of the cell I, E_j is the unknown liquid junction potential, a_{Br^-}, m_{Br^-}, λ_{Br^-} and a_{I^-}, m_{I^-}, λ_{I^-} are, respectively, the activities, molalities and activity coefficients of Br^- and I^- ions and k equals 2.3026 RT/F. Since the molalities of Br^- and I^- are equal, eqn. (1) can be written as

$$E = E^0 + k \log \left(\frac{\lambda_{I^-}}{\lambda_{Br^-}} \right) \pm E_j \tag{2}$$

Keeping m constant, the e.m.f. was determined at different values of x and the value obtained $x \to 0$, by extrapolating the plot of E against x, gives the e.m.f. without liquid junction potential,

$$\underset{x \to 0}{E} = E^0 + k \log \left(\frac{\lambda_{I^-}}{\lambda_{Br^-}} \right) \tag{3}$$

Generally, ions of the same valency have almost equal values of the activity coefficient. So the ratio of $\lambda_{I^-}/\lambda_{Br^-}$ will be almost equal to unity and thus the term containing the activity coefficients in eqn. (3) is expected to be zero. If not, the value of E obtained by extrapolation against x at constant m, should differ from E^0 only by the term $[k \log(\lambda_{I^-}/\lambda_{Br^-})]_{x=0}$ which is proportional to m. The E^0 of cell I can therefore be determined by extrapolation of the E against m plot to $m = 0$, i.e.

$$\underset{\substack{x \to 0 \\ m \to 0}}{E} = E^0 \tag{4}$$

The e.m.f. of cell I was measured at 15, 25, 35 and 45 °C in 10, 20, 30 and 40% (w/w) dioxane–water mixtures with four different values of x. These e.m.f. values are given in Table 1.

For each value of m, E was plotted against x to get $\underset{x \to 0}{E}$ at different solvent compositions and different temperatures. The $\underset{x \to 0}{E}$ values are also given in Table 1. The values obtained in this way were plotted against m and these graphs were extrapolated to zero (i.e. $m = 0$) to get $\underset{\substack{x \to 0 \\ m \to 0}}{E}$ values which are the E^0 values of cell I according to eqn. (4). The E^0 values are given in Table 2. The average standard deviation in E^0 values is ± 0.2 mV for 10, 20, 30% (w/w) dioxane–water mixtures and ± 0.3 mV for 40% (w/w) dioxane–water mixtures. The standard electrode potentials (E_m°) of the silver–silver iodide electrode in 10, 20, 30 and 40% (w/w) dioxane–water mixtures at 15, 25, 35 and 45 °C were obtained by subtracting the E_m° values of the silver–silver bromide electrode reported from this laboratory[2] from E^0 of cell I. The E_m° of the silver–silver iodide electrode are given in Table 3.

The standard thermodynamic quantities (ΔG_t°, ΔS_t° and ΔH_t°) for the process H^+I^- (in water) → H^+I^- (in various dioxane–water media) were calculated from the standard e.m.f. of cell

H_2(1 atm) | HI soln. | AgI–Ag (II)

in water and in respective dioxane–water media in mole fraction scale using the Feakins and Watson method[8]. The e.m.f. of cell II is equal to the standard potential of the silver–silver iodide electrode. The standard potentials of cell II in water used here were taken from the work of Owen[9]. The ΔG_t°, ΔS_t°, ΔH_t° values so calculated are given in Table 4.

TABLE 1

E.M.F. READINGS OF CELL I (IN V) AT DIFFERENT VALUES OF x AND m

m	x	*Temperature (°C)*			
		15	*25*	*35*	*45*
10% Dioxane					
0.02	0.2	0.2192	0.2188	0.2159	0.2112
	0.4	0.2209	0.2200	0.2171	0.2127
	0.6	0.2225	0.2217	0.2183	0.2143
	0.7	0.2227	0.2218	0.2199	0.2151
	0.8	0.2230	0.2228	0.2198	0.2167
	→0	0.2180	0.2170	0.2135	0.2090
0.03	0.2	0.2204	0.2184	0.2153	0.2105
	0.4	0.2218	0.2201	0.2174	0.2114
	0.6	0.2224	0.2212	0.2185	0.2129
	0.7	0.2237	0.2223	0.2191	0.2136
	0.8	0.2241	0.2225	0.2202	0.2141
	→0	0.2190	0.2170	0.2140	0.2090
0.04	0.2	0.2196	0.2180	0.2152	0.2109
	0.4	0.2207	0.2196	0.2170	0.2125
	0.6	0.2219	0.2204	0.2186	0.2135
	0.7	0.2226	0.2217	0.2190	0.2146
	0.8	0.2229	0.2224	0.2201	0.2151
	→0	0.2185	0.2165	0.2140	0.2095
0.06	0.2	0.2205	0.2195	0.2155	0.2119
	0.4	0.2221	0.2209	0.2176	0.2135
	0.6	0.2235	0.2224	0.2184	0.2151
	0.7	0.2241	0.2230	0.2193	0.2159
	0.8	0.2249	0.2238	0.2199	0.2172
	→0	0.2190	0.2180	0.2140	0.2100
20% Dioxane					
0.02	0.2	0.2150	0.2134	0.2101	0.2094
	0.4	0.2164	0.2147	0.2112	0.2054
	0.5	0.2169	0.2154	0.2121	0.2065
	0.6	0.2176	0.2159	0.2125	0.2071
	0.8	0.2189	0.2174	0.2134	0.2083
	→0	0.2140	0.2120	0.2090	0.2030
0.03	0.2	0.2150	0.2134	0.2101	0.2044
	0.4	0.2162	0.2145	0.2109	0.2052
	0.5	0.2168	0.2150	0.2111	0.2059
	0.6	0.2174	0.2156	0.2116	0.2065
	0.8	0.2185	0.2170	0.2129	0.2076
	→0	0.2140	0.2120	0.2090	0.2035
0.04	0.2	0.2152	0.2130	0.2104	0.2049
	0.4	0.2170	0.2139	0.2116	0.2064
	0.5	0.2076	0.2146	0.2121	0.2071
	0.6	0.2081	0.2150	0.2125	0.2077
	0.8	0.2092	0.2163	0.2136	0.2084
	→0	0.2145	0.2120	0.2095	0.2040
0.05	0.2	0.2152	0.2141	0.2109	0.2051
	0.4	0.2170	0.2150	0.2120	0.2069
	0.5	0.2176	0.2151	0.2127	0.2074
	0.6	0.2181	0.2158	0.2134	0.2083
	0.8	0.2189	0.2173	0.2145	0.2099
	→0	0.2145	0.2125	0.2095	0.2040

TABLE 1 *(continued)*

m	*x*	*Temperature (°C)*			
		15	*25*	*35*	*45*
30% Dioxane					
0.02	0.2	0.2093	0.2071	0.2000	0.1929
	0.4	0.2103	0.2079	0.2009	0.1939
	0.5	0.2109	0.2085	0.2016	0.1943
	0.7	0.2124	0.2092	0.2024	0.1952
	0.8	0.2129	0.2101	0.2030	0.1960
	→0	0.2080	0.2060	0.1995	0.1920
0.03	0.2	0.2099	0.2079	0.2002	0.1933
	0.4	0.2112	0.2088	0.2020	0.1951
	0.5	0.2121	0.2098	0.2023	0.1959
	0.7	0.2134	0.2107	0.2034	0.1975
	0.8	0.2143	0.2118	0.2043	0.1977
	→0	0.2085	0.2060	0.1995	0.1920
0.05	0.2	0.2112	0.2081	0.2020	0.1942
	0.4	0.2124	0.2100	0.2038	0.1956
	0.5	0.2128	0.2108	0.2047	0.1970
	0.7	0.2144	0.2123	0.2064	0.1983
	0.8	0.2151	0.2132	0.2071	0.1992
	→0	0.2090	0.2065	0.2000	0.1925
0.06	0.2	0.2101	0.2081	0.2020	0.1943
	0.4	0.2113	0.2107	0.2038	0.1957
	0.5	0.2126	0.2108	0.2043	0.1959
	0.7	0.2138	0.2131	0.2064	0.1972
	0.8	0.2147	0.2133	0.2072	0.1978
	→0	0.2090	0.2070	0.2005	0.1930
40% Dioxane					
0.02	0.2	0.2039	0.1984	0.1898	0.1789
	0.4	0.2054	0.1995	0.1911	0.1801
	0.5	0.2060	0.1999	0.1923	0.1814
	0.6	0.2064	0.2010	0.1924	0.1819
	0.8	0.2077	0.2018	0.1938	0.1833
	→0	0.2030	0.1980	0.1885	0.1780
0.03	0.2	0.2043	0.1998	0.1901	0.1788
	0.4	0.2058	0.2007	0.1919	0.1802
	0.5	0.2063	0.2020	0.1924	0.1803
	0.6	0.2066	0.2027	0.1932	0.1807
	0.8	0.2083	0.2041	0.1947	0.1823
	→0	0.2030	0.1985	0.1890	0.1780
0.04	0.2	0.2022	0.1997	0.1899	0.1788
	0.4	0.2068	0.2012	0.1908	0.1797
	0.5	0.2070	0.2023	0.1919	0.1806
	0.6	0.2083	0.2028	0.1923	0.1807
	0.8	0.2096	0.2041	0.1936	0.1817
	→0	0.2035	0.1985	0.1890	0.1785
0.06	0.2	0.2026	0.2003	0.1919	0.1803
	0.4	0.2063	0.2022	0.1934	0.1817
	0.5	0.2069	0.2030	0.1947	0.1823
	0.6	0.2080	0.2038	0.1952	0.1827
	0.8	0.2087	0.2052	0.1970	0.1846
	→0	0.2040	0.1990	0.1995	0.1790

TABLE 2

E^0 (IN V) OF CELL I

Dioxane (Wt. %)	*Temperature (°C)* 15	25	35	45
10	0.2178	0.2162	0.2135	0.2084
20	0.2136	0.2120	0.2086	0.2024
30	0.2076	0.2054	0.1989	0.1916
40	0.2024	0.1976	0.1880	0.1774

TABLE 3

STANDARD MOLAL POTENTIAL (E_m^0 IN V) OF SILVER–SILVER IODIDE ELECTRODE IN DIOXANE–WATER MIXTURES

Dioxane (Wt. %)	*Temperature (°C)* 15	25	35	45
10	−0.1480	−0.1509	−0.1551	−0.1573
20	−0.1488	−0.1519	−0.1552	−0.1579
30	−0.1506	−0.1557	−0.1560	−0.1583
40	−0.1538	−0.1591	−0.1598	−0.1599

TABLE 4

STANDARD THERMODYNAMIC QUANTITIES FOR THE TRANSFER OF H^+I^- FROM WATER TO DIOXANE–WATER MIXTURES

t (°C)	ΔG_t^0 *(J mole^{-1})*	ΔH_t^0 *(J mole^{-1})*	ΔS_t^0 *(J K^{-1} mole^{-1})*
10% Dioxane			
15	−531	104	2.18
25	−560	105	2.18
35	−511	107	2.18
45	−724	109	2.19
20% Dioxane			
15	−878	−250	2.71
25	−897	−256	2.70
35	−965	−263	2.69
45	−1148	−270	2.68
30% Dioxane			
15	−1187	−296	4.00
25	−1023	−309	3.98
35	−1399	−322	3.96
45	−1640	−336	3.93
40% Dioxane			
15	−1409	−240	5.23
25	−1245	−257	5.20
35	−1592	−274	5.17
45	−2055	−291	5.14

The standard free energies of transfer, ΔG_t°, for the pair of ions (H^+I^-) are found to be negative for all the solvent compositions studied and they decrease with increase in temperature. But in the case of HCl (ref. 10) and HBr (ref. 2) it was found to be positive in these solvent media. Feakins and Turner[3] have found that ΔG_t° for the pair of ions (H^+I^-) is negative for 20% (w/w) dioxane–water but positive for 45% (w/w) dioxane-water at 25 °C. In the present study, negative ΔG_t° values are obtained at all temperatures and the solvent mixtures studied containing less than 45 wt.% dioxane. So the results at 25 °C in 20% dioxane–water are in agreement with those of Feakins and co-workers and who used a borate buffered cell. The ΔH_t° values are seen to be positive for 10% dioxane and negative for 20, 30 and 40% dioxane. The ΔH_t° values are positive at all the temperatures for all the solvent mixtures studied and these values remain almost same in a particular solvent mixture at all the temperatures. The ΔS_t° values for HCl (ref. 10) and HBr (ref. 2) in these solvent media were negative. The positive ΔS_t° can be interpreted as the ordering of the solvent mixture is not favoured for the pair of ions (H^+I^-) specially because of the large size of the iodide ion.

Feakins and Watson[8] have assumed that the free energy of transfer is inversely proportional to the radius of the ion which is being varied in a series of electrolytes having a common ion; say halogen acids according to

$$\Delta G_t^0 = \Delta G_t^0(H^+) + Kr_-^{-1} \qquad (5)$$

where $\Delta G_t^\circ(H^+)$ is the free energy of transfer of proton, K is an empirical constant and r_- is the radius of the anion. In a similar manner, the $\Delta G_t^\circ(H^+)$ values in the solvent mixtures are obtained from the ΔG_t° values for HCl (ref. 10), HBr (ref. 2) and HI. The $\Delta G_t^\circ(H^+)$ values are given in Table 5 and these are found to be negative. Feakins and Turner[3] have also found that $\Delta G_t^\circ(H^+)$ is negative for 20 and 45% dioxane-water mixtures like methanol–water mixtures[11]. So the proton is in a lower free energy state in dioxane–water mixtures than in water, i.e. dioxane–water mixtures are more basic than water.

To obtain the free energy of transfer for single ions, i.e. for Cl^-, Br^- and I^-, the $\Delta G_t^\circ(H^+)$ was subtracted from the respective values for HCl, HBr and HI. This is possible since Feakins et al.[5] have shown that the ΔG_t° values for ions in an electrolyte is additive. The ionic ΔG_t° values for Cl^-, Br^- and I^- are given in Table 6. These are

TABLE 5

ΔG_t^0 (H^+) VALUES (IN J) FROM WATER TO VARIOUS DIOXANE–WATER MIXTURES

Dioxane	*Temperature (°C)*			
(Wt. %)	*15*	*25*	*35*	*45*
10	−5540	−5500	−11800	−19800
20	−28800	−10400	−11300	−12900
30	−14800	−10600	−20800	−28400
40	−21000	−24000	−32400	−41500

TABLE 6

FREE ENERGIES OF TRANSFER (ΔG_t^0/J) FOR Cl^-, Br^-, I^- FROM WATER TO VARIOUS DIOXANE–WATER MIXTURES

	Temperature (°C)			
	15	*25*	*35*	*45*
10% Dioxane				
Cl^-	7310	5920	13570	22910
Br^-	5846	5665	12106	20215
I^-	5029	4940	11289	19076
20% Dioxane				
Cl^-	29903	11409	12403	14105
Br^-	29128	10630	11628	13477
I^-	27835	9503	10335	11752
30% Dioxane				
Cl^-	17290	11500	23290	32140
Br^-	15635	11334	21635	29524
I^-	13401	9577	19401	26760
40% Dioxane				
Cl^-	25600	27330	37000	47370
Br^-	22687	25271	34087	43576
I^-	19408	22755	30808	39445

TABLE 7

CHEMICAL AND ELECTRICAL PARTS OF THE FREE ENERGY OF TRANSFER

Temperature (°C)	$\Delta G_{t_{el}}^0$ *(J mole^{-1})*	$\Delta G_{t_{ch}}^0$ *(J mole^{-1})*
10% Dioxane		
15	359	−890
25	388	−948
35	419	−930
45	443	−1167
20% Dioxane		
15	831	−1709
25	890	−1787
35	943	−1910
45	1015	−2163
30% Dioxane		
15	1460	−2647
25	1566	−2589
35	1668	−3067
45	1783	−3423
40% Dioxane		
15	2630	−4036
25	2523	−3768
35	2691	−4283
45	2872	−4927

found to be positive for all the temperatures in the solvent mixtures studied. So anions are in higher free energy state than in water.

The ΔG_t° values are split into two parts, a "non-electrostatic" or "chemical" contribution ($\Delta G_{t_{ch}}^\circ$) and an "electrostatic" contribution $\Delta G_{t_{el}}^\circ$ as has been done by Roy et al.[12]. The details of this are given in our investigation on the silver–silver bromide electrode[2]. The $\Delta G_{t_{ch}}^\circ$ and $\Delta G_{t_{el}}^\circ$ values are given in Table 7. It is clearly evident from an examination of these tables that the chemical contribution of the free energy of transfer $\Delta G_{t_{ch}}^\circ$ is negative for all the three cases except for HCl in 20 and 40% dioxane–water. $\Delta G_{t_{ch}}^\circ$ appears to be a solvent parameter that measures the increase in the basicity of the dioxane–water mixtures. So, considering only the chemical contribution of the free energy, $\Delta G_{t_{ch}}^\circ$, which has negative values, the dioxane–water mixtures appear to be more basic than water. The same conclusion was also drawn by considering Feakins and Watson arguments[8]. So, whether the arguments of Feakins and co-workers or those of Roy et al. are taken into consideration, the conclusions arrived at for the basicity of the solvent mixtures do not alter, even though both groups of workers have made extra thermodynamic assumptions of different natures.

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