Electromotive Force of the Silver–Silver Iodide, Hydrogen Iodide Hydrogen Cell and the Activity of Hydrogen Iodide in Water-Methanol Media

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The standard potentials of the Pt, H_2 (1 atm.) | HI, X% CH_3OH | AgI–Ag cell have been determined in 0, 15, 30, 45, 60, 75, 99, and 100 wt. % methanol at 25°, 35°, and 45° C. over a hydrogen iodide concentration range of 0.005 to 0.1*M*. The activity coefficients of hydriodic acid at these mixed solvents have been calculated at 25°, 35°, and 45° C. and the standard free energies, enthalpies, and entropies of the cell have also been calculated. These thermodynamic functions give evidence of the structural changes occurring in the solutions as the percentages of methanol increases. The effects can arise from the solvent properties and/or from the solvation properties of the ions in the different solvent mixtures.

HARNED and Ehlers measured the electromotive force of the cell H_2 (1 atm.) | HCl (m) | AgCl–Ag and determined the activity coefficients of hydrochloric acid in water over a broad temperature range (*6*). Oiwa (*11*) and Paabo, Bates, and Robinson (*13*) measured the electromotive forces of the cell H_2 (1 atm.) | HCl (m), *X*% CH_3OH, *y*% H_2O | AgCl–Ag at 25° C. and determined the activity coefficients of hydrochloric acid in the methanol-water mixtures at 25° C. Harned, Keston, and Donelson (*7*) measured the electromotive force of the cell H_2 (1 atm.) | HBr(m) | AgBr–Ag and determined the activity coefficients of hydrobromic acid in water over a broad temperature range. Feakins and Watson (*5*) studied the H_2 (1 atm.) | HBr(m), *X*% CH_3OH, *Y*% H_2O|AgBr–Ag cell at 25° C. for 10 and 43.12 wt. % CH_3OH, and also measured electromotive forces of the cell H_2 (1 atm.) | HBO_2(m), $NaBO_2$(m), KI (m), *X*% CH_3OH, *Y*% H_2O | AgI–Ag for 10 and 43.12% methanol with the buffered system. Feakins and his co-workers (*3*, *4*) have also studied this cell in a water-dioxane mixture of 20 and 45% dioxane and compared the results with the water-methanol results. Owen (*12*) made measurements of the same borate buffered cell and Hetzer, Robinson, and Bates (*9*) made measurements of the unbuffered cell in water at various temperatures from 0° to 50° C.

In this study, the electromotive forces of the cell Pt, H_2 (1 atm.) | HI (m), *X*% CH_3OH, *Y*% H_2O | AgI–Ag were measured at 25°, 35°, and 45° C. for 0, 15, 30, 45, 60, 75, 90, 99, and 100 wt. % methanol without a buffered system. The activity coefficients of hydriodic acid and the thermodynamic functions of the cell $\Delta G°$, $\Delta S°$, and $\Delta H°$ were determined.

EXPERIMENTAL PROCEDURE

The silver-silver iodide electrodes were prepared thermally by the method proposed by Ives and Janz (*10*). The dipping hydrogen electrodes used were the typical platinum type (*10*).

The solvents were prepared by adding weighed amounts of deionized, deoxygenated water stored under argon to anhydrous methanol (*2*) also stored under argon. The compositions of the solvents were accurate to ±0.01 wt. % and had a specific conductivity of less than 10^{-6} mhol. An aqueous solution of hydriodic acid was obtained by collecting the middle portion of the distillate of reagent grade hydriodic acid. The distillation was carried out under an argon atmosphere. The purified water and anhydrous methanol were added in the proper proportions to the aqueous solution of hydriodic acid to prepare the 15, 30, 45, 60, 75, and 90 wt. % methanol solutions. The 99 and 100 wt. % methanol solutions of hydriodic acid were prepared by bubbling dry hydrogen iodide (*15*) gas into the solvent. The solutions were all stored in dark bottles under an argon atmosphere. Solutions stored in this manner for over 3 months showed no decomposition of hydriodic acid. The hydriodic acid solutions were analyzed by titrating with potassium hydroxide to a phenolphthalein end point.

The cell used was an adaption of the one diagrammed by Ives and Janz (*10*). The cell was modified for the hydrogen electrodes. Instead of a vacuum system, as shown in the diagram, a tube fitted with a stopcock was extended nearly to the bottom of the cell so that solutions and solvents might be added or extracted. The cell was painted black and placed in a bath controlled to ±0.02° C.

The electrodes were placed in the cell, and the cell was purged with dry argon to remove any air present. The solution was then introduced, and the cell was allowed to come to equilibrium. If the e.m.f. measured did not change for a 1-hour period, the cell was assumed to be at equilibrium. The e.m.f. was measured with a Leeds and Northrup Type K-3 Universal potentiometer. A Weston cell that had been calibrated against an Eppley certified standard cell was used as the standardizing voltage for the potentiometer, and a G.M. Laboratories galvanometer Model 570-211 was used as a null indicator for the potentiometer. The literature values of the standard potentials for the cell in water at the various temperatures were reproduced and used as a criterion for the accuracy of the potentiometer. A sample of the solution was removed and analyzed after each measurement.

EXPERIMENTAL RESULTS

The measured electromotive forces corrected for pressure for the cells are listed in Table I with their respective molal concentration of hydriodic acid. The standard devia-

Table I. Electromotive Force Measurements of

25° C.		35° C.		45° C.	
Concn., *m*	E.m.f.	Concn., *m*	E.m.f.	Concn., *m*	E.m.f.
		100% H_2O			
0.1113	−0.02977	0.1272	−0.03867	0.09143	−0.02021
0.08141	−0.01418	0.08448	−0.01615	0.08380	−0.01908
0.05696	+0.00272	0.06737	−0.00576	0.07265	−0.00630
0.04414	+0.01563	0.04611	+0.01568	0.04692	+0.01689
0.03216	+0.03123	0.04031	+0.02177	0.02809	+0.04317
0.02155	+0.05072	0.02285	+0.05105	0.02170	+0.05676
0.01798	+0.06019	0.01605	+0.06982	0.01402	+0.07974
0.01012	+0.08810	0.00932	+0.09690	0.01084	+0.09816
				0.00708	+0.10680
		15% CH_3OH			
0.09572	−0.02057	0.09165	−0.01772	0.08703	−0.02108
0.06458	−0.00148	0.06476	−0.00040	0.04839	+0.00817
0.03469	+0.02865	0.03468	+0.02636	0.02059	+0.05087
0.01277	+0.07749	0.01330	+0.07906	0.00984	+0.08797
0.00571	+0.11711	0.00779	+0.10626	0.00484	+0.12421
		30% CH_3OH			
0.06801	−0.06374	0.06882	−0.00567	0.08117	−0.01456
0.05481	+0.00568	0.05879	+0.00295	0.05625	+0.00858
0.02906	+0.03627	0.02984	+0.03695	0.05253	+0.00771
0.02510	+0.04344	0.0223	+0.03784	0.03263	+0.03240
0.02494	+0.04410	0.01648	+0.06698	0.02958	+0.03745
0.01540	+0.06748	0.01624	+0.06750	0.02037	+0.05690
0.01329	+0.07464	0.00853	+0.10030	0.01657	+0.06740
0.00756	+0.10237			0.01051	+0.09106
				0.00643	+0.11801
		45% CH_3OH			
0.08707	−0.01606	0.09775	−0.02486	0.09164	−0.02656
0.05710	+0.00418	0.06334	−0.00434	0.06480	−0.00870
0.02124	+0.05222	0.03230	+0.03046	0.03101	+0.02912
0.01049	+0.08673	0.01547	+0.06730	0.01637	+0.06228
0.00482	+0.12499	0.00818	+0.09954	0.00595	+0.11505
		60% CH_3OH			
0.09344	−0.02053	0.09279	−0.02526	0.1227	
0.06801	−0.00433	0.06896	−0.01194	0.08948	

tions of the measured e.m.f. values are considered to be within ±0.1 mv. in all solutions.

EVALUATION OF DATA

The standard potentials of the silver–silver iodide electrodes were calculated by the equation

$$E^\circ_m = E + 2k \log m + 2K \log \gamma_\pm \tag{1}$$

where E is the e.m.f. after correction for the hydrogen pressure by adding the value of $(RT/2F) \ln 760/(P - p_w)]$ to the measured e.m.f. P is barometric pressure and p_w is the vapor pressure of the solvent (*8*). The pressure corrections were essentially negligible at low alcohol compositions but made major contributions at high alcohol compositions. The molality is m, k is 2.3026 RT/F, and

$$\log \gamma_\pm = -\frac{A(d_0 m)^{1/2}}{1 + Ba(d_0 m)^{1/2}} - \log\left(1 + \frac{2M_{xy}}{1000}\right) + E_{ext} + bm \tag{2}$$

Here A and B are constants of the Debye-Hückel theory, dependent on the temperature and the dielectric constant of the solvent, and d_0 is the measured density of the solvent. The symbols a and b are, respectively, the ion size parameter and an adjustable parameter. M_{xy} is the mean molecular weight of the solvent defined by

$$M_{xy} = \left(\frac{100}{\frac{X}{M_x} + \frac{Y}{M_y}}\right) \tag{3}$$

M_x and M_y are the molecular weight of the solvents. X and Y are the respective compositions of solvent in weight per cent. E_{ext} denotes the Debye-Hückel extended terms taken from Harned and Owen (*8*). The values of the standard potentials are tabulated in Table II. These were obtained from a least square statistical analysis of the measured data. Owen's value of E°_m in water at 25° C. was −0.15225 and at 35° C. was −0.15586, which agrees with the data in this paper (*12*). The value of E°_m in water at 45° C. also agrees with Hetzer, Robinson, and Bates' value of −0.15998 (*9*).

The thermodynamic functions of the cell were calculated from the values of the standard potentials. The values of Gibb's free energy, ΔG°, were given by

$$\Delta G^\circ = -nFE^\circ_m \tag{4}$$

where n is the number of electrons transferred in the reaction and F is a faraday [23,061 cal. (absolute volt)$^{-1}$ (mole)$^{-1}$]. The enthalpies were obtained from

Hydriodic Acid in Methanol-Water Solvents

25° C.		35° C.		45° C.	
Concn., *m*	E.m.f.	Concn., *m*	E.m.f.	Concn., *m*	E.m.f.
		60% CH_3OH			
0.05277	+0.00808	0.04939	+0.00535	0.05599	−0.00923
0.02649	+0.04050	0.02528	+0.03820	0.04455	−0.00269
0.01453	+0.06984	0.01491	+0.06523	0.02246	+0.03771
0.01030	+0.08662	0.01201	+0.07533	0.01163	+0.05398
0.00668	+0.10484	0.00658	+0.10556	0.00930	+0.08377
				0.00643	+0.10205
		75% CH_3OH			
0.09234	−0.02493	0.09362	−0.03439	0.09466	−0.04330
0.04464	+0.00892	0.03560	+0.01286	0.03589	+0.00479
0.02065	+0.04521	0.02165	+0.03701	0.02067	+0.03263
0.01244	+0.06956	0.01354	+0.05991	0.01441	+0.05068
0.00817	+0.08946	0.00724	+0.09054	0.00792	+0.08102
		90% CH_3OH			
0.07780	−0.05388	0.07755	−0.06512	0.07890	−0.07810
0.05787	−0.04073	0.06737	−0.05970	0.07265	−0.07826
0.03750	−0.02258	0.03444	−0.02726	0.04055	−0.04662
0.01840	+0.00944	0.02114	−0.00390	0.02410	−0.02149
0.00889	+0.04338	0.01166	+0.02466	0.01248	+0.01071
0.00409	+0.08170	0.00757	+0.04524	0.00809	+0.03221
		0.00440	+0.07202	0.00539	+0.05256
		99% CH_3OH			
0.1091	−0.15035	0.08138	−0.15017	0.09143	−0.17063
0.05696	−0.12097	0.06896	−0.14215	0.07265	−0.15888
0.03988	−0.10445	0.04031	−0.11631	0.02809	−0.11198
0.01932	−0.07118	0.01926	−0.08017	0.01872	−0.09026
0.00776	−0.02911	0.00819	−0.03898	0.00790	−0.04726
0.00450	−0.00299	0.00450	−0.00995	0.00454	−0.01990
0.00323	+0.01233	0.00315	+0.00829	0.00286	+0.00337
		100% CH_3OH			
0.08969	−0.16803	0.08448	−0.17685	0.08380	−0.18918
0.08141	−0.16332	0.06820	−0.16519	0.04692	−0.16052
0.05049	−0.14188	0.04264	−0.14273	0.03757	−0.14924
0.03405	−0.12376	0.03512	−0.13429	0.03430	−0.14472
0.01260	−0.07801	0.01395	−0.08977	0.01218	−0.09338
0.00671	−0.04831	0.00743	−0.05798	0.00635	−0.05981
0.00401	−0.02400	0.00426	−0.03059	0.00365	−0.03191

$$\Delta H^\circ = \frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial\left(\frac{1}{T}\right)} \tag{5}$$

by plotting $(\Delta G^\circ)/T$ *vs.* $1/T$ and taking the slope. The entropies were obtained from

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{6}$$

The calculated values of ΔG°, ΔH°, and ΔS° are tabulated in Table II. ΔH° *vs.* weight per cent CH_3OH at 35° C., and ΔS° *vs.* weight per cent CH_3OH at 35° C. are plotted in Figures 1 and 2, respectively.

The activity coefficients were obtained from Equation 2, and the values of $-\log \gamma_\pm$ *vs.* *m* are tabulated in Table III.

DISCUSSION

The characteristic curves of E°_m at 25° C. *vs.* solvent composition for the three cells H_2 (1 atm.) | HCl (m) | AgCl-Ag, H_2 (1 atm.) | HBr(m) | AgBr-Ag, (*16*) and H_2 (1 atm.) | HI(m) | AgI-Ag, are compared in Figure 3. The curves at lower methanol composition are almost linear,

Table II. Tabulated Values of Derived Quantities in Different Solvents and at Different Temperatures

Solvent	Temp., ° C.	E°, V.	ΔG°, Cal. Mole	ΔH°, Cal. Mole	ΔS°, E.U.
H_2O	25	−0.15224	3487		
	35	−0.15586	3621	−209	−12.43
	45	−0.15994	3735		
15% CH_3OH	25	−0.15306	3530		
	35	−0.15724	3626	+103	−11.44
	45	−0.16378	3777		
30% CH_3OH	25	−0.15387	3547		
	35	−0.15862	3658	−506	−13.52
	45	−0.16562	3819		
45% CH_3OH	25	−0.15398	3551		
	35	−0.16201	3736	−2634	−20.67
	45	−0.17195	3966		
60% CH_3OH	25	−0.15640	3607		
	35	−0.16809	3876	−4970	−28.71
	45	−0.18132	4181		
75% CH_3OH	25	−0.16655	3841		
	35	−0.18060	4165	−5800	−32.35
	45	−0.19462	4488		
90% CH_3OH	25	−0.21153	4878		
	35	−0.22578	5208	−6490	−37.98
	45	−0.24462	5641		
99% CH_3OH	25	−0.29193	6732		
	35	−0.30627	7063	−5010	−39.20
	45	−0.32609	7520		
100% CH_3OH	25	−0.31786	7330		
	35	−0.33101	7633	−3458	−36.01
	45	−0.34926	8054		

Table III. Activity Coefficients of Hydriodic Acid in Methanol-Water Solvent

25° C.		35° C.		45° C.	
Concn., m	$-\log \gamma_\pm$	Concn., m	$-\log \gamma_\pm$	Concn., m	$-\log \gamma_\pm$
100% H_2O					
0.1113	0.0817	0.1272	0.0629	0.09143	0.0836
0.08141	0.0778	0.8448	0.0693	0.07265	0.0782
0.05696	0.0655	0.06737	0.0656	0.04692	0.0720
0.04414	0.0626	0.04611	0.0668	0.02809	0.0574
0.03216	0.0581	0.04031	0.0582	0.02170	0.0529
0.02155	0.0478	0.02285	0.0511	0.01402	0.0452
0.01798	0.0508	0.01605	0.0512	0.00852	0.0432
0.01012	0.0353	0.00932	0.0365		
15% CH_3OH					
0.09572	0.1014	0.09165	0.1028	0.08703	0.1027
0.06458	0.0912	0.06476	0.0935	0.04839	0.0876
0.03469	0.0762	0.03468	0.0781	0.02059	0.0671
0.01277	0.0544	0.01330	0.0566	0.00984	0.0493
0.00571	0.0400	0.00779	0.0463	0.00484	0.0392
30% CH_3OH					
0.06801	0.0795	0.06882	0.0889	0.08117	0.1059
0.05481	0.0876	0.05879	0.0907	0.05254	0.0933
0.02906	0.0706	0.02984	0.0743	0.03263	0.0821
0.02510	0.0676	0.02923	0.0726	0.02958	0.0795
0.02494	0.0704	0.01648	0.0621	0.02037	0.0715
0.01540	0.0599	0.01624	0.0599	0.01657	0.0650
0.01329	0.0551	0.00853	0.0480	0.01051	0.0547
0.00756	0.0446			0.00643	0.0548
45% CH_3OH					
0.08707	0.1056	0.09775	0.1120	0.09164	0.1135
0.05710	0.0943	0.06334	0.1003	0.06480	0.1037
0.02124	0.0704	0.03230	0.0829	0.03101	0.0845
0.01049	0.0550	0.01547	0.0653	0.01637	0.0686
0.00482	0.0408	0.00818	0.0518	0.00595	0.0474
60% CH_3OH					
0.09343	0.1190	0.09279	0.1356	0.1227	0.1366
0.06801	0.1181	0.06896	0.1157	0.08948	0.1284
0.05227	0.1086	0.04930	0.1121	0.05599	0.1112
0.02649	0.0868	0.02528	0.0909	0.04455	0.1064
0.01453	0.0747	0.01491	0.0817	0.02246	0.0863
0.01030	0.0671	0.01201	0.0703	0.00930	0.0682
0.00668	0.0331	0.00658	0.0563	0.00643	0.0527
75% CH_3OH					
0.09234	0.1622	0.09362	0.1676	0.09466	0.1743
0.04464	0.1306	0.03560	0.1297	0.03589	0.1347
0.02065	0.1051	0.02165	0.1156	0.02067	0.1140
0.01244	0.0887	0.01354	0.0979	0.01441	0.1009
0.00819	0.0760	0.00724	0.0765	0.00792	0.0810
90% CH_3OH					
0.07780	0.2236	0.07755	0.2036	0.07890	0.2161
0.05787	0.2062	0.06737	0.1863	0.07265	0.1789
0.03750	0.1712	0.03444	0.1607	0.04055	0.1763
0.01840	0.1327	0.02114	0.1398	0.02410	0.1494
0.00889	0.1037	0.01166	0.1149	0.01248	0.1186
0.00409	0.0904	0.00757	0.0956	0.00809	0.1009
		0.00440	0.0788	0.00539	0.0857
99% CH_3OH					
0.1091	0.2346	0.08138	0.1872	0.09143	0.1924
0.05690	0.2007	0.06896	0.1809	0.07265	0.1856
0.03988	0.1843	0.04031	0.1590	0.02809	0.1445
0.01932	0.1520	0.01926	0.1339	0.01872	0.1403
0.00776	0.1115	0.00819	0.0994	0.00790	0.1062
0.00452	0.0975	0.00450	0.0767	0.00454	0.0824
0.00323	0.0811	0.00315	0.0710	0.00286	0.0660
100% CH_3OH					
0.08969	0.2192	0.08448	0.1875	0.08380	0.1912
0.08141	0.2171	0.06820	0.1900	0.04692	0.1664
0.05049	0.1921	0.04269	0.1699	0.03757	0.1591
0.03405	0.1728	0.03512	0.1554	0.03430	0.1554
0.01260	0.1279	0.01395	0.1176	0.01218	0.1124
0.00671	0.1051	0.00743	0.1040	0.00635	0.0935
0.00407	0.0871	0.00426	0.0864	0.00365	0.0760

and the slopes of the lines decrease in the order HCl > HBr > HI. Harned and Owen (*8*) attributed the great deviation from theory at low dielectric constants to the replacement of the hydronium ion H_3O^+ by (solvent) H^+ according to the reaction H_3O + (solvent) ⇌ H_2O + (solvent) H . Amis (*1*) proposed the equation

$$E^\circ = E_1^\circ - \frac{NZ_aZ_be^2}{nFDrK} \tag{7}$$

to account for the solvent's effect on the standard potential. E_1° is the potential freed from charge effect and the second term represents the electrostatic contribution. Z_a and Z_b are the ionic charges, e is the charge of an electron, N is Avagadro's number, n is the number of electrons involved in the electrode process, F is the faraday, D is the dielectric constant, $K = 10^7$ ergs per joule, and r is the separation distance between ion a and ion b. A plot of E° *vs.* $1/D$ gives a fairly linear slope at high dielectric constant and a value of $r = 0.5$ A. is calculated from the slope. This value is low, but it is comparable with the value of $r = 0.64$ A. for HCl in methanol-water solvents calculated in the same manner. Amis explained the curvature of E° *vs.* $1/D$ at lower dielectric constants in the case of cells containing hydrochloric acid as probably due to the selective solvation of, or selective solvent binding, by the ions of higher dielectric, more polar, component of the solvent. In like manner, the present data indicate that the values of the standard potentials in various solvent compositions of low dielectric constants are influenced by selective solvation of the H^+ and I^- ions.

The increase in curvature from Cl^- to Br^- to I^- must be the result of the change in solvation of the different halide ions alone, but this is not readily explained since the ionic radii of Cl^-, Br^- and I^-, namely 1.8, 2.0, and 2.2 A., respectively, as well as the hydrated ionic radii based on mobilities (~2.8 A.) are all about the same. The small differences in radii appear to be significant, or some specific effect is important.

The activity coefficients of hydriodic acid in various methanol-water mixtures in Table III show the generally expected decreasing trend as the acid concentration is increased and as the dielectric constant of the solvent decreases.

The enthalpies for H_2 (1 atm.) | HCl (m) | AgCl-Ag cell at 25° and 35° C. were calculated from the data reported by Robinson and Stokes (*14*). These values are compared in Figure 1 with the H_2 (1 atm.) | HI (m) | AgI-Ag cell. The shapes are consistent with each other. Owing to the limited available data on the thermodynamic functions in regard to the influence of the solvent on the electrode reactions, the solvation of the ions, the solvations of HI molecules, and the degree of association of HI, it is impossible to distinguish the relative influences which make up

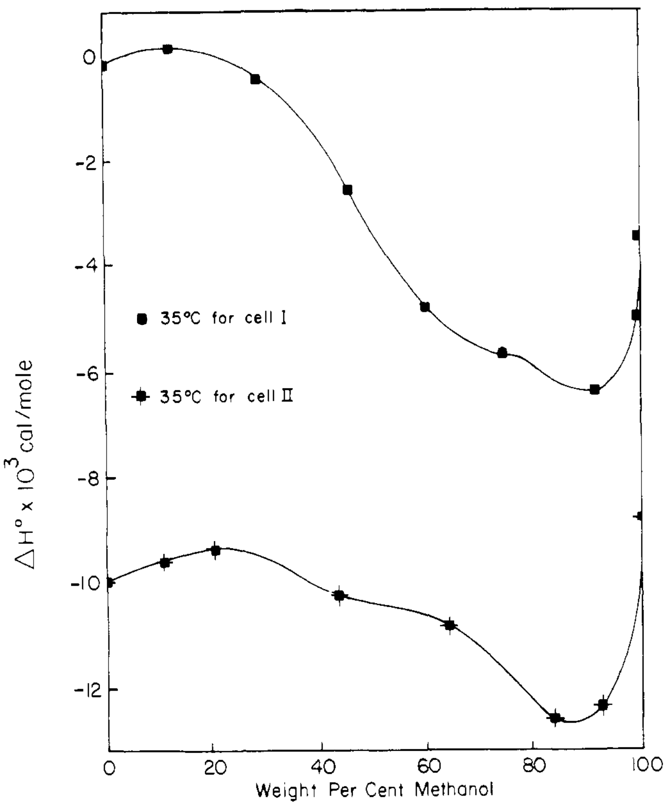

Figure 1. Enthalpies for the Pt, H_2| HI (m)| AgI–Ag cell (I) and the Pt, H_2| HCl (m)| AgCl–Ag cell (II) as functions of methanol-water compositions

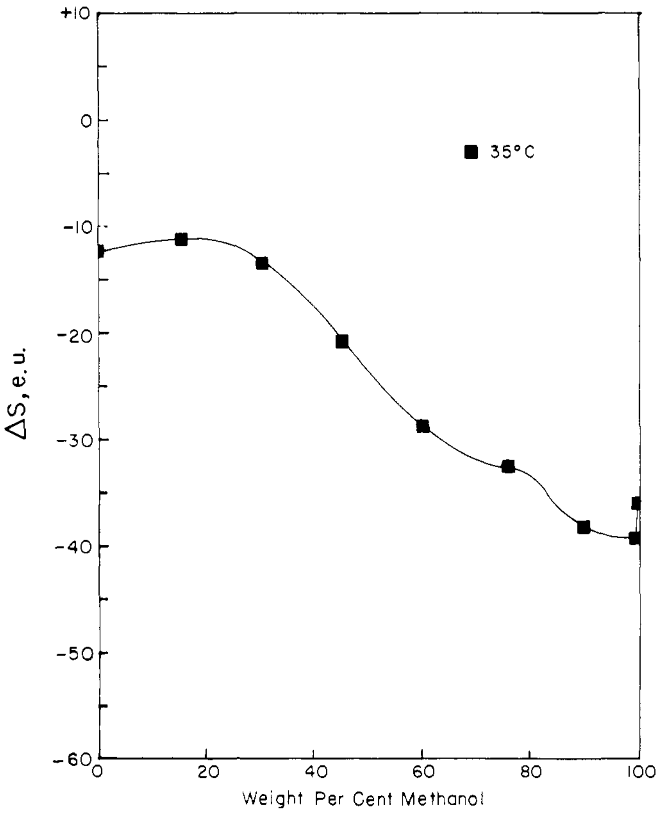

Figure 2. Entropies for the Pt, H_2| HI (m)| AgI–Ag cell as functions of methanol-water compositions

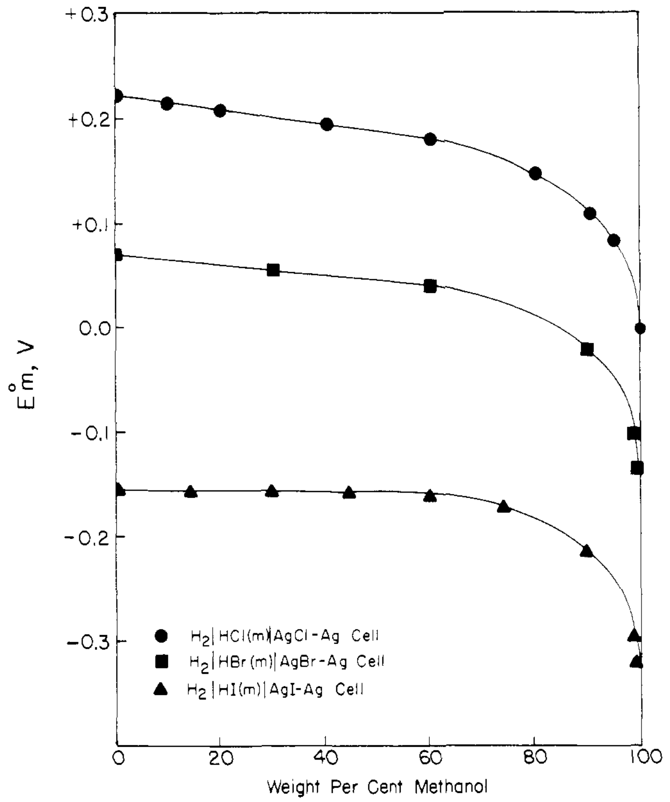

Figure 3. Standard potentials at 25° C. as functions of methanol-water compositions

the enthalpies and entropies. Therefore, no further attempt will be made to explain these curves, with one exception. Steric hindrance, owing to solvation by methanol, may account for the decrease in exothermisity at higher compositions.

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