Electromotive Force Measurements of the Cell-Pt/H_2: HCl(m): AgCl/Ag-, in 1-Propanol–Water Mixtures

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The e.m.f. of the cell, -Pt/H_2; HCl(m): AgCl/Ag-, in-1-propanol–water mixtures of 10, 20, 40, 60, and 80% by weight, has been measured at 0°, 25°, and 40° C. The activity coefficients of HCl solutions in these mixtures have been calculated for concentrations ranging from 0.01 to 0.1 molal.

RECENT STUDIES (*2, 3*) of dissociation constants of acetylacetone in mixed solvents emphasized the desirability of having available in the literature, activity coefficient data for HCl in 1-propanol–water solutions at various temperatures. For this reason, this study was undertaken.

MATERIALS

Reagent grade 1-propanol was purified by fraction distillation. All solutions were prepared with conductivity water which had a conductivity of approximately 0.7×10^{-6} ohm^{-1} cm.^{-1} at 25° C. Electrolytic H_2 was passed through traps containing Ascarite, Drierite, and anhydrous magnesium perchlorate and finally through a saturator containing the same solution as that to be measured, at the same temperature as the measurement cell. The solutions were prepared by adding the calculated amount of conductivity water and 1-propanol to a known amount of standardized hydrochloric acid. All solutions were freshly prepared before taking measurements.

ELECTRODES

The hydrogen electrode consisted of platinum foil 1.0×0.7 cm. attached to a platinum wire fused into a soft glass tube. The electrical contact was made by a copper wire attached to the platinum wire. After every three to five measurements the hydrogen electrode was recoated with platinum black. For this purpose the old coating was dissolved in aqua regia and the shiny platinum foil plated with platinum black by electrolysis in a 3% solution of chloroplatinic acid in 1*M* HCl for 5 minutes. After washing the electrode in distilled water, the electrolysis was continued in dilute sodium hydroxide solution for a few seconds, and then for 5 minutes in 10% H_2SO_4 to remove chlorine and to saturate the platinum black with H_2. The electrode was rinsed several times with conductivity water and stored in dilute HCl solution. The silver-silver chloride electrode was a helix of a platinum wire fused into a soft glass tube and coated with a layer of silver and silver chloride (*5*). When not in use the electrode was stored in conductivity water. Before using, both electrodes were rinsed three times with the solution to be measured and then immersed in this solution overnight.

APPARATUS

The cell was of borosilicate glass in the form of an H recommended by Harned and Fleysher (*6*) and Lucasse (*7*).

The e.m.f. measurements were made with a type K2, Leeds and Northrup potentiometer. The mirror-type galvonometer had a sensitivity of ±0.00002 volt per division. The Eppley standard cell was calibrated by the National Bureau of Standards. All of the electrical connections were shielded.

Table I. E.M.F. Data and Mean Activity Coefficients of HCl in 10% 1-Propanol–Water Mixtures

	0 ° C. $E^0 = 0.22852$		25° C. $E^0 = 0.21413$		40° C. $E^0 = 0.20349$	
m_{HCl}	E_{cell}	$\sigma\pm$	E_{cell}	$\sigma\pm$	E_{cell}	$\sigma\pm$
0.0010	0.55522	0.962	0.57115	0.960	0.57849	0.957
0.0015	0.53646	0.956	0.55075	0.952	0.55701	0.950
0.0020	0.52333	0.948	0.53626	0.946	0.54159	0.948
0.0030	0.50445	0.944	0.51597	0.936	0.52052	0.934
0.0050	0.48142	0.924	0.49063	0.920	0.49403	0.916
0.0100	0.45008	0.900	0.45659	0.892	0.45827	0.888

Table II. E.M.F. Data and Mean Activity Coefficients of HCl in 1-Pronanol–Water Mixtures

	Wt. % Organic Solvent							
	20		40		60		80	
	0° C.							
	$E^0 = 0.22543$		$E^0 = 0.21240$		$E^0 = 0.19092$		$E^0 = 0.15264$	
$m_{\text{HCl.}}$	E_{cell}	$\sigma\pm$	E_{cell}	$\sigma\pm$	E_{cell}	$\sigma\pm$	E_{cell}	$\sigma\pm$
0.0050	0.47951	0.902						
0.0100	0.44754	0.889	0.43721	0.840	0.42116	0.748	0.39129	0.626
0.0200	0.41746	0.843	0.40719	0.795	0.39253	0.688	0.36468	0.551
0.0300	0.39882	0.835	0.39010	0.762	0.37612	0.650	0.34907	0.512
0.0500	0.37661	0.804	0.36774	0.736	0.35532	0.607	0.32938	0.467
0.0700	0.36194	0.784	0.35282	0.722	0.34098	0.588	0.31670	0.437
0.1000	0.34528	0.783	0.33675	0.711	0.32501	0.578	0.29921	0.443
	25° C.							
	$E^0 = 0.20781$		$E^0 = 0.18862$		$E^0 = 0.15896$		$E^0 = 0.10939$	
0.0050	0.48533	0.902						
0.0100	0.45134	0.874	0.43523	0.823	0.41207	0.725	0.37257	0.597
0.0200	0.41818	0.833	0.40307	0.770	0.38154	0.657	0.34549	0.505
0.0300	0.39882	0.807	0.38451	0.726	0.36447	0.611	0.33004	0.455
0.0500	0.37469	0.777	0.36126	0.695	0.34251	0.562	0.30949	0.407
0.0700	0.35826	0.764	0.34579	0.670	0.32778	0.534	0.29630	0.376
0.1000	0.34156	0.740	0.32899	0.651	0.31129	0.516	0.27939	0.366
	40° C.							
	$E^0 = 0.19514$		$E^0 = 0.17292$		$E^0 = 0.13995$		$E^0 = 0.08094$	
0.0050	0.48642	0.903						
0.0100	0.45042	0.880	0.43276	0.809	0.40661	0.713	0.35944	0.572
0.0200	0.41671	0.822	0.39915	0.754	0.37488	0.642	0.33170	0.479
0.0300	0.39642	0.798	0.37998	0.717	0.35681	0.598	0.31553	0.431
0.0500	0.37119	0.765	0.35572	0.675	0.33385	0.549	0.29531	0.376
0.0700	0.35444	0.745	0.33967	0.649	0.31855	0.521	0.28155	0.347
0.1000	0.33665	0.726	0.32244	0.625	0.30156	0.450	0.26557	0.326

The measurements at 25° and 40° C. were made in water baths thermostated to ±0.05° C. At 0° C., a mixture of ice and water stirred by a magnetic stirrer was used.

PROCEDURE

The depth of the hydrogen electrode varied from 1.5 to 2.0 cm. The cell and the saturator were placed in the temperature bath, and the H_2 flow rate was adjusted to 1 to 2 bubbles per second, and the first e.m.f. reading was taken 1 hour later. Readings were then taken every 15 minutes until the potential became constant within ±0.05 mv. for at least 1 hour. Since the solvents studied have appreciable vapor pressures, the pressure of H_2 at the electrode was corrected for these pressures. The vapor pressures were determined by method of Smith and Menzies (*8*).

RESULTS

Listed in Tables I and II are the values of the measured e.m.f., the mean activity coefficients and E_T^0 of HCl in a variety of 1-propanol–water mixtures. The $\sigma\pm$ were determined by standard methods (*4*). Values of E' were calculated from the equation:

$$E_T + \lambda \log m - \lambda\,(m)^{1/2} = E_T^0 - \lambda \mathrm{B}\, m \qquad (1)$$

where E' is used to represent the value of the left side of Equation 1. Equation 1 results from the expression:

$$E = E^0 - 4.606\ (\mathrm{RT/F}) \log m - 4.606\ (\mathrm{RT/F}) \log \sigma\pm,$$

where $\log \sigma\pm$ is assumed to equal to $-\alpha\ (m)^{1/2} + \mathrm{B}\ m$. The Debye-Hückel constant α has been evaluated for the various solvents at various temperatures and by employing the dielectric constants determined by Akeloef (*1*).

Table III. Vapor Pressure (mm.) of Various 1-Propanol–Water Mixtures at 0°, 25° and 40° C.

Temp. °C.	Wt. % Organic Solvent					
	0	10	20	40	60	80
0.0	4.5	5.3	6.2	6.7	6.5	6.3
25.0	23.7	29.0	32.6	34.0	35.4	33.3
40.0	55.5	73.7	81.1	84.5	85.6	84.3

Table III lists the vapor pressure of the various solvent systems employed in this study. The values are reliable to ±0.5 mm. of Hg.

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