

Thermodynamics of Hydrochloric Acid in 80 Weight Percent 2-Methoxyethanol and 20 Weight Percent Water From 10 to 50 °C

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(June 4, 1970)

Electromotive-force measurements of cells of the type Pt, H₂|HCl(*m*) in 2-methoxyethanol + H₂O|AgCl, Ag at nine temperatures ranging from 10 to 50 °C were used to derive (a) the standard emf of the cell in 80 weight percent 2-methoxyethanol (methylcellosolve), (b) the activity coefficient of HCl, (c) the relative partial molal enthalpy and heat capacity of HCl, and (d) the thermodynamic constants for the transfer of HCl from water to 80 weight percent methylcellosolve. The molality of the acid ranged from 0.006 to 0.106 mol kg⁻¹. To obtain the standard emf it was necessary to correct for ion-pair formation and to use the extended terms of the Debye-Hückel theory. The standard emf varied with temperature (*t*, °C) according to the equation $E_t^\circ = 0.14382 - 1.517 \times 10^{-3}t - 3.8317 \times 10^{-6}t^2 - 2.3838 \times 10^{-9}t^3$. Vapor pressures and dielectric constants for this mixture were measured over the temperature range. At 25 °C the solvent has a vapor pressure of 2506.5 Nm⁻² (18.8 mm Hg) and a dielectric constant of 31.5.

Key words: Activity coefficients; non-aqueous emf; standard emf; thermodynamic constants for HCl transfer.

1. Introduction

As a possible solvent for the determination of stability constants of metal ion complexes, 2-methoxyethanol (methylcellosolve) can be considered as very promising. It not only dissolves numerous organic compounds but also many inorganic salts such as several of the metal perchlorates including sodium perchlorate and the lanthanide perchlorates. Unfortunately, the pure solvent has a rather low dielectric constant (about 2.3 at 25 °C), and it therefore seemed preferable to examine a suitable mixture with water.

Simon et al. [1, 2]¹ have already carried out an impressive number of *pK* determinations for organic acids and bases in a mixture containing 80 wt % 2-methoxyethanol and 20 wt % water. A *pH* cell with glass electrode and calomel electrode was used. The *pH* scale in this medium has not been standardized, and consequently the measurements of Simon and his coworkers were based on the aqueous standard buffer solutions. In order to obtain unambiguous results in future electromotive-force studies on complex stabilities and *pK* values in 80 wt % methylcellosolve, it is necessary to establish a *pH* scale in this medium. The present study on the thermodynamics of HCl was

carried out as a first step toward the establishment of a standard acidity scale in a solvent containing 80 wt % 2-methoxyethanol and 20 wt % water.

Measurements of the emf of the cell

Pt; H₂(g), HCl(*m*) in 80 wt %

2-methoxyethanol, AgCl; Ag

were made from 10 to 50 °C at intervals of 5 °C and for six molalities of hydrochloric acid in the nominal range of 0.006 to 0.1 mol kg⁻¹. In order to correct the observed emf to the standard 1 atm partial pressure of hydrogen, it was necessary to measure the vapor pressure of the mixed solvent. The evaluation of the standard emf of the cell at each temperature further necessitated measurements of the dielectric constant ϵ and the density ρ_0 of the solvent. The procedure followed for the analysis of the emf data was very similar to the one adopted by Pool and Bates [3].

2. Experimental Procedure

The 2-methoxyethanol was obtained commercially, and gas chromatographic analysis showed the water content to be less than 0.03 percent. No other volatile impurities could be detected, and no further purification was attempted. The mixed solvent was prepared by weighing distilled water and the 2-methoxyethanol.

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¹ Figures in brackets indicate the literature references at the end of this paper.

The dielectric constant of the mixed solvent was measured at 10, 25, and 50 °C, using freshly distilled water and spectro-grade acetone as reference materials. The Multi-Dekameter instrument² was used for these measurements. The temperature of the cell was adjusted to within 0.1 °C of the nominal temperature of circulating water from a constant-temperature bath. The results are given in table 1.

TABLE 1. Dielectric constants of the 80 wt % 2-methoxyethanol solvent

<i>t</i>	ϵ
(°C)	
10	34.7
25	31.5
50	27.8

For the vapor pressure measurements, a flask containing the solvent was immersed in a water bath, the temperature of which was controlled to ± 0.01 °C. The flask was connected to a U-tube mercury manometer and the pumping system, which included a mercury diffusion pump. Because 2-methoxyethanol attacks the high-vacuum grease, Teflon stopcocks had to be used.

Before the flask was connected to the vacuum line, the temperature of the solvent was lowered to -72 °C in an ethanol–solid carbon dioxide mixture, so that the evacuation of the system would not cause any change in the composition of the liquid. To avoid condensation of vapors in the manometer, the latter was placed in a controlled air bath with a transparent plastic panel. In this way, the manometer could be kept at 56 °C throughout the measurements. The rest of the apparatus, except for the flask, was wrapped with heating tape and kept at a temperature well above 50 °C. Before starting the measurements, the pressure in the apparatus was reduced below 1 $\mu\text{m Hg}$. The readings were taken with a cathetometer giving a precision of 0.05 mm Hg.

The measured values for the vapor pressure of the 80 wt percent 2-methoxyethanol solvent under study in the temperature range 10 to 50 °C are given in table 2. They were fitted to the following equation

TABLE 2. Vapor pressures of the 80 wt % 2-methoxyethanol solvent

<i>t</i>	Pressure		σ
	<i>Nm</i> ⁻²	<i>mm Hg</i>	
°C			
10	973.3	(7.3)	(0.1)
15	1346.6	(10.1)	(0.2)
20	1813.2	(13.6)	(0.2)
25	2506.5	(18.8)	(0.3)
30	3373.1	(25.3)	(0.2)
35	4479.6	(33.6)	(0.1)
40	5919.5	(44.4)	(0.2)
45	7732.7	(58.0)	(0.4)
50	10052.	(75.4)	(0.6)

² Multi-Dekameter, Type MDK-06, Wiss. Techn. Werkstätten, Weilheim, Obb., Germany. Reference to trade name is made only for identification and does not imply in any way the endorsement of the product by the National Bureau of Standards.

$$\log p = 9.061 - \frac{2321.7}{T} \quad (1)$$

by the method of least squares. In this equation, *T* is the thermodynamic temperature $t(^{\circ}\text{C}) + 273.15$.

The densities of the mixed solvent were measured with a pycnometer. The results are presented in table 3.

TABLE 3. Density of the 80 wt % 2-methoxyethanol solvent

<i>t</i>	Density
°C	<i>g cm</i> ⁻³
10	0.9997
15	.9955
20	.9910
25	.9868
30	.9824
35	.9781
40	.9739
45	.9693
50	.9647

High-purity hydrochloric acid was used to make a stock solution, of molality approximately 0.1 mol kg⁻¹, in the mixed solvent. The hydrochloric acid was tested for the presence of bromide and found to be satisfactory (< 0.002 mole percent). Solutions of six different molalities *m* were prepared by weighing the stock solution and diluting it with a weighed amount of the mixed solvent.

The design of the cells, preparation of electrodes, purification of the hydrogen gas, and other experimental details have been described previously [4, 5].

The values of the emf were corrected to 1 atm partial pressure of hydrogen and are given in table 4. Each entry in the table represents the average of three replicate cells prepared for each molality of hydrochloric acid. Each cell was measured at all nine temperatures. The lowest and highest emf values for replicate cells differed, at most, by 0.1 mV. The emf at 25 °C was recorded three times, namely, at the beginning, middle, and end of the run. The three values usually agreed within 0.05 mV.

3. Standard Emf of the Cell

The standard emf (E°) of the cell used is derived from the measured emf (E) by the Nernst equation:

$$E^{\circ} = E + (2RT/F) \ln (m\gamma_{\pm}) = E + (2RT/F) \ln (m'\gamma'_{\pm}) \quad (2)$$

where *m* and γ_{\pm} are the stoichiometric molality and mean molal activity coefficient of HCl in the solvent under study, and *m'* and γ'_{\pm} are the actual molality of ionized HCl and the true mean activity coefficient. In a first attempt to derive E° , γ_{\pm} was calculated by a form of the Debye-Hückel equation

$$-\log \gamma_{\pm} = \frac{A(m\rho_0)^{1/2}}{1 + B\hat{a}(m\rho_0)^{1/2}} \quad (3)$$

TABLE 4. *Emf (in volts) of the cell Pt; H₂ (g, 1 atm), HCl (m) in 80 wt % 2-methoxyethanol, AgCl; Ag*

<i>m</i>	Temperature, °C								
	10	15	20	25	30	35	40	45	50
<i>mol kg⁻¹</i>									
0.006012	0.39176	0.38873	0.38550	0.38212	0.37840	0.37471	0.37086	0.36674	0.36240
.010897	.36671	.36333	.35976	.35614	.35221	.34823	.34425	.33991	.33557
.02183	.33804	.33432	.33045	.32650	.32231	.31807	.31365	.30897	.30448
.04213	.31188	.30768	.30353	.29928	.29486	.29028	.28564	.28073	.27575
.07855	.28714	.28283	.27834	.27370	.26888	.26408	.25921	.25411	.24902
.10620	.27509	.27063	.26596	.26131	.25647	.25150	.24641	.24111	.23591

where ρ_0 is the solvent density, \bar{a} is the ion-size parameter, and the Debye-Hückel constants A and B took into account the temperature and dielectric constant of the solvent. From these γ_{\pm} values, the apparent E° was calculated according to

$$E^{\circ'} = E^\circ + \beta m = E + (2RT/F) \ln (m\gamma_{\pm}). \quad (4)$$

Least squares treatment of E° as a function of m permitted extrapolation to zero ionic strength and yielded preliminary values for E° . However, straight lines could not be obtained, suggesting that the hydrochloric acid was not completely ionized in the medium under investigation. There were no results available for the ion-pair dissociation constant K_d for HCl in this medium, so an empirical treatment had to be used, as was the case in earlier work in 95 percent ethanol [3].

The following procedure was used. The mean activity coefficient γ_{\pm} was derived from eq (3) and values of m' were calculated for each stoichiometric molality (m) by the equation

$$K_d = \frac{(m'\gamma_{\pm})^2}{(m-m')}. \quad (5)$$

A reasonable value of K_d in the range 0.01 to 1.0 was chosen. With these estimates of m' , the true molality of dissociated HCl, new values for the γ_{\pm} "true" activity coefficient were calculated by an extended form of eq (3):

$$-\log \gamma'_{\pm} = \frac{A(m'\rho_0)^{1/2}}{1 + B\bar{a}(m'\rho_0)^{1/2}} + \log (1 + 0.002m'\bar{M}) \quad (6)$$

where \bar{M} is the mean molar mass of the mixed solvent (46.273 g mol⁻¹). The γ'_{\pm} so obtained was substituted in a modified form of eq (5)

$$K_d = \frac{(m'\gamma'_{\pm})^2}{(m-m')} \quad (7)$$

and used to obtain a new m' . This iterative procedure was repeated n times, until the difference

$$|\gamma'_{\pm n} - \gamma'_{\pm n-1}| \leq 10^{-5}.$$

From these values of γ_{\pm} and m' , E° was calculated by the method of least squares from $E^{\circ'}$ defined by

$$E^{\circ'} = E^\circ + \beta m' = E + (2RT/F) \ln (m'\gamma'_{\pm}). \quad (8)$$

For each value of K_d chosen, a set of \bar{a} values was used to calculate m' , γ'_{\pm} , and $E^{\circ'}$. Decreasing ranges of both K_d and \bar{a} were selected until values were found that produced the minimum standard deviation of $E^{\circ'}$ values from a linear function of m' . These were taken to be the true values of K_d and \bar{a} . The resulting intercept (E°) of the plot of $E^{\circ'}$ as a function of m' seemed to vary only a few hundredths of a millivolt with changes in K_d of 0.005 and changes in \bar{a} of 0.05 Å. The final E° at each temperature is given together with the "best" values of K_d and \bar{a} . Ion-pairing seems to be less extensive in 80 wt % methylcellosolve ($K_d = 0.204$) than in 95 percent ethanol ($K_d = 0.033$ [3]). This conclusion is consistent with the slightly higher dielectric constant and the considerably larger amount of water in the methylcellosolve-water solvent. The standard emf can be represented by the equation

$$E_t^\circ = 0.14382 - 0.001517t - 3.8317 \times 10^{-6}t^2 - 2.3838 \times 10^{-9}t^3 \quad (9)$$

where t is the temperature in °C. Values of E° calculated by eq (9) are also compared with the experimental values in table 5.

TABLE 5. *Summary of results for the standard emf (E°) of the cell in 80 wt % 2-methoxyethanol solvent*

<i>t</i>	K_d	(\bar{a})	E°	${}^a\sigma_d$	E° calc. ^b	ΔE°
°C			V	mV		mV
10	0.366	4.59	0.12822	0.04	0.12827	0.05
15	.306	4.79	.12027	.04	.12019	.08
20	.227	4.73	.11192	.03	.11193	.01
25	.204	4.60	.10353	.04	.10344	.09
30	.130	4.60	.09466	.08	.09479	.13
35	.116	4.37	.08589	.08	.08592	.03
40	.089	4.36	.07693	.10	.07685	.08
45	.071	4.41	.06763	.10	.06757	.05
50	.058	4.21	.05804	.17	.05808	.04

^a Standard deviation of E° .

^b By eq (9).

TABLE 6. Stoichiometric mean activity coefficient (γ_{\pm}) of hydrochloric acid in 80 wt % 2-methoxyethanol from 10 to 50 °C

<i>t</i>	<i>m</i> (HCl), mol kg ⁻¹					
	0.006012	0.010897	0.02183	0.04213	0.07855	0.10620
°C						
10	0.751	0.692	0.621	0.551	0.490	0.464
15	.747	.687	.615	.545	.482	.456
20	.740	.679	.606	.535	.472	.446
25	.735	.672	.598	.526	.464	.437
30	.728	.663	.587	.514	.454	.425
35	.723	.656	.578	.506	.444	.416
40	.717	.648	.570	.496	.434	.407
45	.711	.640	.561	.487	.424	.398
50	.704	.629	.548	.476	.413	.386

4. Thermodynamic Properties of Hydrochloric Acid

With the aid of eq (2) and the stoichiometric molalities, the stoichiometric activity coefficients γ_{\pm} were derived from E° and the measured values of E . These values are shown in table 6. For each molality, $\log \gamma_{\pm}$ was fitted to a power series of the form

$$-\log \gamma_{\pm} = A + BT + CT^2 \quad (10)$$

where T is the thermodynamic temperature, $t(^{\circ}\text{C}) + 273.15$.

The constants of this equation are given in table 7, together with the standard deviations of the calculated values of $\log \gamma_{\pm}$.

TABLE 7. Constants of the equation $-\log \gamma_{\pm} = A + BT + CT^2$

<i>m</i>	<i>A</i>	<i>B</i> × 10 ³	<i>C</i> × 10 ⁶	$\sigma \times 10^3$
mol kg ⁻¹				
0.006012	0.195708	-1.0828	2.9359	0.5
.010897	.518064	-3.2864	7.1346	.4
.02183	.41377	-2.5559	6.4359	.9
.04213	.409875	-2.4130	6.6281	1.0
.07855	.675343	-4.0528	9.7507	0.5
.10620	.402071	-2.2042	6.9208	.8

The relative partial molal enthalpy \bar{L}_2 and the relative partial molal heat capacity \bar{J}_2 of hydrochloric acid in the medium studied were calculated from the constants B and C of eq (10) by the following formulas:

$$\bar{L}_2 = (2RT^2 \ln 10) (B + 2CT) \quad (11)$$

and

$$\bar{J}_2 = (4RT \ln 10) (B + 3CT). \quad (12)$$

The values obtained for \bar{L}_2 at 10, 25, and 50 °C and for \bar{J}_2 at 25 °C are summarized in table 8.

The standard thermodynamic quantities for the transfer process

TABLE 8. Relative partial molal enthalpy (\bar{L}_2) and relative partial molal heat capacity (\bar{J}_2) of hydrochloric acid in 80 wt % 2-methoxyethanol

<i>t</i>	<i>m</i> (HCl), mol kg ⁻¹					
	0.006012	0.010897	0.02183	0.04213	0.07855	0.1062
	\bar{L}_2 , J mol ⁻¹					
10	1780	2315	3342	4115	4509	5121
25	2273	3295	4363	5239	5995	6519
50	3257	5297	6412	7480	8992	9307
	\bar{J}_2 , J K ⁻¹ mol ⁻¹					
25	35	71	73	80	107	100

HCl (in H₂O) = HCl (in 80 wt %

2-methoxyethanol-20 wt % water)

can be derived from the standard emf (E°) of the cell in water [6] and in 80 wt % 2-methoxyethanol together with the variation of E° with temperature. From eq (9) the standard Gibbs energy of transfer (ΔG_t°) is found to be

$$\Delta G_t^{\circ} = -31338.1 + 254.465T - 0.607549T^2 + 7.90581 \times 10^{-4}T^3 \quad (13)$$

and

$$\Delta S_t^{\circ} = +254.465 - 1.21510T + 2.37174 \times 10^{-3}T^2 \quad (14)$$

while

$$\Delta H_t^{\circ} = \Delta G_t^{\circ} + T\Delta S_t^{\circ}. \quad (15)$$

For 25 °C the thermodynamic functions for the transfer of HCl have the following values:

$$\Delta G_t^{\circ} = 11477.0 \text{ J mol}^{-1}$$

$$\Delta S_t^{\circ} = -103.0 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta H_t^{\circ} = -19237.0 \text{ J mol}^{-1}$$

The large positive value for the transfer free energy suggests that the affinity of 2-methoxyethanol for HCl is less than that of water, or, in other words, that water is the more basic component of the solvent mixture. In view of the structural changes characteristic of alcohol-water mixtures [7], however, judgments of this sort must be made with caution.

5. References

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(Paper 74A5-627)