values are compared with the measured results in Tables V and VI. Agreement may be considered good.

Acknowledgment

Glossary

a_{ij}	extended UNIQUAC binary interaction parameter related to τ_{ij}
F	objective function
P	total pressure
$P_i{}^s$	vapor pressure of pure component i
q_i	molecular geometric area parameter of pure component i
$q_i{}^*$	correction factor of interaction of pure component i
r_i	molecular volume parameter of pure component i
R	gas constant
T	absolute temperature
$v_i{}^L$	molar liquid volume of pure component i
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
Z	lattice coordination number, here equal to 10

Greek Letters

γ_i	activity coefficient of component i
θ_i	area fraction of component i
σ_P, σ_T	standard deviations in pressure and temperature
σ_x, σ_y	standard deviations in liquid and vapor mole fractions
τ_{ij}	extended UNIQUAC binary parameter defined as $\exp(-a_{ij}/T)$
ϕ_i	fugacity coefficient of component i
$\phi_i{}^s$	fugacity coefficient of pure component i at its saturation pressure and system temperature
Φ_i	segment fraction of component i

Registry No. Acetonitrile, 75-05-8; cyclohexane, 110-82-7; acetone, 67-64-1; benzene, 71-43-2.

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Standard Potential of the Ag/AgCl Electrode in 50 wt % 2-Methoxyethanol–Water Solvent from 5 to 45 °C

Carmen A. Vega* and **Sara Delgado**

Chemistry Department, University of Puerto Rico, Mayaguez, Puerto Rico 00708

Electromotive force measurements of cells of the type Pt,H$_2$|HCl(m) in 2-methoxyethanol + water|AgCl,Ag at nine temperatures ranging from 5 to 45 °C were used to derive the standard emf of the cells in 50 wt % 2-methoxyethanol (CH$_3$O–CH$_2$CH$_2$OH, methyl cellosolve). The molality of the acid used in the cell ranged from 0.01 to 0.10 mol kg^{-1}. The extended terms of the Debye–Hückel equation were used to obtain the standard emf. The standard emf of the cell varied with temperature (T, K) according to the equation $E_m{}^\circ = 0.02328 + (2.076 \times 10^{-3})T - (5.167 \times 10^{-6})T^2$ with a standard deviation to the fit of the polynomial $s = 0.26$ mV.

Introduction

The standard potential of the Ag/AgCl electrode has been studied in a variety of alcohol/water media (*1–17*).

Very little has been done with 2-methoxyethanol–water solvents. In 1970 Thun, Staples, and Bates (*16*) studied an 80 wt % mixture over a temperature range from 10 to 50 °C. In 1971 Sadek, Tadros, and El-Harakany (*17*) published their results with nine mixtures ranging from 0 to 80 wt % at temperatures from 25 to 45 °C. Sadek's calculated E° for the 80 wt % composition differ from Thun's results by more than 13 mV at 25 °C. Such discrepancies were the basis for our decision to study this solvent at a 50 wt % composition and extend the range of temperatures from 5 to 45 °C, using the cell

Pt,H$_2$(g,1 atm)|HCl(m)

in 50 wt % methoxyethanol–water|AgCl,Ag

where m represents the molality (moles of HCl per 1 kg of water plus 2-methoxyethanol).

Experimental Procedures

Spectral grade 2-methoxyethanol was obtained from Aldrich

Table I. Electromotive Force of Cell Pt,H$_2$(g,1 atm)|HCl(m) in 50 wt % 2-Methoxyethanol–Water|AgCl,Ag[a]

| | | | | | E, V | | | | |
m_{HCl}	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C
0.019 01	0.4016	0.4011	0.4003	0.3995	0.3986	0.3974	0.3958	0.3940	
0.030 12		0.3794	0.3783	0.3771	0.3753	0.3740	0.3721	0.3697	0.3675
0.031 46	0.3793	0.3784	0.3773	0.3760	0.3746	0.3729	0.3711	0.3691	0.3668
0.036 42	0.3730	0.3720	0.3707	0.3693	0.3677	0.3662	0.3642	0.3621	0.3597
0.047 08	0.3614		0.3587	0.3572		0.3535			
0.049 34		0.3587	0.3572		0.3540	0.3518	0.3494		0.3444
0.056 62	0.3532	0.3519	0.3534			0.3447			
0.057 04	0.3534	0.3521	0.3506	0.3489	0.3471	0.3451	0.3429	0.3405	0.3379
0.065 05	0.3476	0.3462	0.3446	0.3429	0.3409	0.3389	0.3366	0.3341	0.3313
0.067 74		0.3447	0.3430	0.3412	0.3393		0.3348	0.3321	0.3294
0.070 22					0.3376		0.3332	0.3305	0.3275
0.076 49	0.3401	0.3385	0.3369	0.3350	0.3330				
0.078 01	0.3395	0.3380					0.3265	0.3239	0.3213
0.084 21	0.3357	0.3341		0.3303	0.3283	0.3260			
0.086 07	0.3348	0.3331	0.3314		0.3272	0.3250	0.3225	0.3197	0.3170
0.088 48	0.3339	0.3323	0.3305	0.3285	0.3264	0.3234			
0.094 99	0.3309	0.3292	0.3273	0.3253	0.3231	0.3207			
0.097 04					0.3214	0.3197	0.3171	0.3145	0.3117

[a] Values corrected to 1 atm of hydrogen partial pressure.

Table II. Properties of the Solvent, Debye–Hückel Constants A and B, and Values for the Vapor Pressures of the 50 wt % 2-Methoxyethanol–Water Solvent

t, °C	ϵ	d, g cm^{-3}	A	B	vap press., torr
5	57.42	1.0206	0.913 39	0.401 99	6.20
10	55.97	1.0166	0.922 74	0.402 76	8.52
15	54.52	1.0130	0.932 86	0.403 84	11.95
20	53.07	1.0106	0.945 48	0.405 33	16.43
25	51.61	1.0058	0.958 89	0.406 59	21.88
30	50.16	1.0036	0.975 04	0.408 56	29.34
35	48.71	0.9991	0.991 92	0.410 27	37.57
40	47.26	0.9946	1.010 93	0.412 27	51.25
45	45.81	0.9927	1.033 39	0.415 02	68.28

Chemical Co. and purified by two fractional distillations. Doubly distilled hydrochloric acid was used to make stock solutions of the desired concentrations. The cell solutions were prepared by diluting the stock solutions with doubly distilled water and adding the necessary calculated amounts of 2-methoxyethanol by weight. The cells were of all-glass construction of a design described earlier (18). The preparation of the hydrogen electrodes and the silver–silver chloride electrodes followed the instructions given by Bates (19). Hydrogen gas was purified by passage through a De-Oxo catalytic purifier. The Ag/AgCl electrodes were intercompared in a dilute solution of HCl and only those whose bias potentials were within 0.1 mV of the average of the set were used. Temperature measurements were made with a calibrated thermometer. Measurements of emf were made with the aid of a Fluke potentiometer, Model 8800A. The accuracy of the Fluke 8800A was checked on a regular basis by using a Weston standard cell from Eppley Laboratory, Inc., Newport, RI (E = 1.019 32 V). Other experimental details were essentially the same as described earlier (20–21).

Initial measurements of the emf were made at 25 °C, after which the temperature of the water bath was lowered to 5 °C and raised gradually to 45 °C, waiting until equilibrium was attained at each of the selected temperatures. After the reading at 45 °C was taken, at the conclusion of the run, the cells were brought back to 25 °C to test their stability. On the average, the initial and the final values at 25 °C differed by 0.1 mV.

Results

The recorded values of the emf were corrected to a hydrogen partial pressure of 1 atm (101.325 kPa) in the usual way. The correction (ΔE) to be added is given by

$$\Delta E = \frac{RT}{2F} \ln \frac{760}{p_{H_2}} \qquad (1)$$

were p_{H_2}, the partial pressure of hydrogen, is the barometric pressure in torr less the vapor pressure of the solvent, R = 8.31433 J K^{-1} mol^{-1}, F = 96 487.0 C mol^{-1}, and T is the temperature in K. Solvent vapor pressures at the various temperatures were calculated from extrapolation of the values for pure water (23), 80 wt % 2-methoxyethanol–water (16), and pure 2-methoxyethanol (24) (see Table II). The corrected emf data are listed in Table I.

Apparent values, $E^{\circ\prime}$, of the standard emf, E°, were calculated by the equation

$$E^{\circ\prime} = E^\circ - 2k\beta m = E + 2k \log m - 2k\frac{am^{1/2}}{1 + Ba^\circ m^{1/2}} \qquad (2)$$

in which the extended Debye–Hückel expression has been substituted for the mean activity coefficient of HCl, and k is written for $(RT \ln 10)/F$. The "true" value of E° is the limit of $E^{\circ\prime}$ at m = 0. The Debye–Hückel constants A and B for the solvent mixture were calculated by the equations given elsewhere (19, p 248) with the aid of the solvent densities and dielectric constants for the nine temperatures studied. The ion-size parameter a° was chosen as 4.3 Å, the value characteristic of HCl in water at 25 °C (21) and in several mixed solvent media as well.

Using these parameters, $E^{\circ\prime}$ was found to be essentially a linear function of the molality m, and the intercept E° was obtained by linear regression methods. The dielectric constants (ϵ), densities (d) of the solvent, the Debye–Hückel constants A and B, and the calculated vapor pressures are given in Table II. Densities of the solvent mixture were measured with a calibrated 25-mL pycnometer. The dielectric constants were measured and furnished by Dr. S. D. Klein (22). The values of E° (molality scale) together with the standard deviation of the intercept, s, are given in Table V.

Primary measurements, e.g., the immediately measured emf values together with the barometric pressure readings, are reported in Table III. These values should allow one to recalculate the results using any correction procedure.

Table III. Electromotive Force of Cell Pt,H₂(g,1 atm)|HCl(m) in 50 wt % 2-Methoxyethanol-Water|AgCl,Ag[a]

E, V

m_{HCl}	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C
0.019 01	0.40147 (759.6)	0.40096 (759.6)	0.40012 (759.3)	0.39924 (759.2)	0.39820 (759.3)	0.39683 (760.2)	0.39512 (760.8)	0.39308 (761.1)	
0.030 12	0.37922 (759.5)	0.37925 (759.9)	0.37811 (763.4)	0.37678 (759.9)	0.37495 (759.9)	0.37345 (759.9)	0.37142 (759.9)	0.36877 (759.9)	0.36617 (759.9)
0.031 46		0.37824 (759.5)	0.37707 (759.6)	0.37572 (759.8)	0.37420 (760.8)	0.37243 (760.7)	0.37043 (760.6)	0.36815 (761.1)	0.36556 (761.1)
0.036 42	0.37292 (759.5)	0.37183 (759.5)	0.37046 (759.6)	0.36904 (759.8)	0.36736 (760.8)	0.36567 (760.7)	0.36358 (760.6)	0.36118 (761.1)	0.35842 (761.1)
0.047 08	0.36129 (759.5)	0.35854 (759.9)	0.35849 (759.6)	0.35695 (759.8)	0.35359 (759.9)	0.35297 (760.7)			
0.049 34			0.35705 (759.9)			0.35123 (759.9)	0.34870 (759.9)		0.34311 (759.9)
0.056 62	0.35326 (758.0)	0.35194 (759.1)	0.35315 (758.0)	0.34865 (760.4)	0.34672 (760.8)	0.34460 (759.7)	0.34223 (759.7)	0.33956 (760.1)	0.33660 (760.1)
0.057 04	0.35310 (760.2)	0.35172 (760.2)	0.35038 (760.2)	0.34261 (760.4)	0.34059 (760.8)	0.34417 (758.0)	0.33592 (759.7)	0.33310 (760.1)	0.32998 (760.1)
0.065 05	0.34754 (760.2)	0.34610 (760.2)	0.34442 (760.2)	0.34095 (759.9)	0.33890 (759.9)	0.33838 (759.7)	0.33410 (759.9)	0.33113 (761.0)	0.32806 (759.9)
0.067 74		0.34457 (759.9)	0.34284 (759.9)		0.33730 (760.8)		0.33249 (759.7)	0.32953 (760.1)	0.32618 (760.1)
0.070 22				0.33470 (759.1)	0.33256 (759.1)				
0.076 49	0.33996 (759.1)	0.33837 (759.1)	0.33666 (759.1)						
0.078 01	0.33936 (760.2)	0.33783 (760.2)		0.33004 (759.1)					
0.084 21	0.33561 (759.1)	0.33395 (759.1)	0.33112 (758.0)		0.32788 (759.1)	0.32545 (759.1)	0.32576 (759.7)	0.32292 (760.1)	0.31999 (760.1)
0.086 07	0.33466 (758.0)	0.33296 (758.0)	0.33025 (759.1)		0.32682 (758.8)	0.32449 (758.8)			
0.088 48	0.33378 (759.1)	0.33211 (759.1)	0.32708 (759.1)	0.32820 (759.1)	0.32598 (759.1)	0.32290 (759.1)	0.32173 (757.0)	0.31872 (757.0)	0.31558 (756.4)
0.094 99	0.33076 (759.1)	0.32899 (759.1)		0.32502 (759.1)	0.32267 (759.1)	0.32020 (759.1)			
0.097 04					0.31848 (761.2)	0.31918 (761.3)	0.31648 (761.1)	0.31358 (761.1)	0.31042 (760.4)

[a] Primary measurements; barometric pressure in parentheses.

Table IV. Standard Potential of Ag/AgCl Electrode at Several Solvent Compositions

	temp, °C		
wt %	10	25	45
0[a]	0.231 48	0.222 40	0.208 41
50	0.196 9	0.183 1	0.160 6
80[b]	0.128 21	0.103 251	0.067 61

[a] Values for $E^\circ_{Ag/AgCl}$ in pure water obtained in our laboratory. [b] Values obtained by Thun, Staples, and Bates (16).

Table V. Standard Emf for the Ag/AgCl Electrode in 50 wt % 2-Methoxyethanol-Water Solvent from 5 to 45 °C

t, °C	E°, V	s(E°),[a] mV	t, °C	E°, V	s(E°),[a] mV
5	0.2011	0.20	30	0.1778	0.26
10	0.1969	0.24	35	0.1724	0.24
15	0.1922	0.21	40	0.1669	0.23
20	0.1877	0.23	45	0.1606	0.27
25	0.1831	0.24			

[a] s = standard deviation of the intercept.

Discussion

The values of E_m° (molality scale) as a function of temperature (T, K) are given by the quadratic equation

$$E_m^\circ = 0.02328 + (2.076 \times 10^{-3})T - (5.167 \times 10^{-6})T^2 \quad (3)$$

with s = 0.26 mV, where s is the standard deviation of the fit to the polynomial. The standard potentials for the Ag/AgCl electrode in pure water (0 wt %) and 50 and 80 wt % 2-methoxyethanol-water solvent for 10, 25, and 45 °C are given in Table IV. With these data anyone can calculate the standard thermodynamic quantities for the transfer process of HCl from pure water to 50 wt % 2-methoxyethanol-water mixture.

Acknowledgment

Registry No. CH₃O-CH₂CH₂OH, 109-86-4; AgCl, 7783-90-6; HCl, 7647-01-0; Ag, 7440-22-4.

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