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Standard Potential of the Ag/AgCl Electrode and Dissociation Constant of Protonated Tris(hydroxymethyl)aminomethane in 50 wt % Ethanol/Water Solvent from 25 to –10 °C

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Measurements of electromotive force (emf) of cells of the type Pt;H_2(g, 1 atm)|HCl(m) in 50 wt % ethanol/water|AgCl;Ag were carried out at molalities (m) over the range 0.05–0.005 and at temperatures from 25 to –10 °C in order to determine the standard potential ($E°_m$) of the Ag/AgCl electrode under these conditions. Further measurements of the cells Pt;H_2(g, 1 atm)|Tris(m),Tris–HCl(m) in 50 wt % ethanol/water|AgCl;Ag led to pK values of protonated tris(hydroxymethyl)aminomethane [2-amino-2-(hydroxymethyl)-1,3-propanediol] (Tris-H^+) in the mixed solvent over the same temperature range. The $E°_m$ data were fitted to a second-order equation in temperature resulting in a standard error, s = 0.02 mV, over the range studied. The pK data were fitted to the equation pK = $A/T + B + C \ln T$ (s = 0.0008 pK units). Pertinent thermodynamic quantities were calculated for the dissociation process based on these results. Conventional pH (pa_H) values for the equimolal buffer (m = 0.05) in the mixed solvent are reported at 5-deg intervals over the temperature range studied.

Introduction

Buffer solutions composed of tris(hydroxymethyl)aminomethane [2-amino-2-(hydroxymethyl)-1,3-propanediol] (Tris) and its hydrochloride salt have been widely used in clinical laboratories as working standards of acidity in the pH range 7–9. The acid–base behavior of Tris has been extensively investigated in aqueous media (*1*, *2*) and in certain nonaqueous and mixed solvents (*3*, *4*).

The importance of acidity control in ethanol/water media at low temperatures has been pointed out by Sankar et al. (*5*), for example, pH control in the separation of blood proteins by the Cohn method (*6*). Bates and co-workers (*7*) have determined the pK values of acetic acid and primary phosphate ion in 10, 20, and 40 wt % ethanol/water from 25 to –10 °C, results which suggest that these buffers could provide suitable reference points for pH standardization below 0 °C. We have now determined the pK of Tris-H^+ in 50 wt % ethanol/water by making electromotive force (emf) measurements of the cell

Pt;H_2(g, 1 atm)
|Tris–HCl(m),Tris(m) in 50 wt % C_2H_5OH/H_2O|AgCl;Ag (A)

where m is molality, at 5-deg intervals over the temperature range from 25 to –10 °C.

In order to calculate pK values, it was first necessary to determine the standard potential ($E°$) of the silver–silver chloride electrode under these conditions. This was accomplished by making emf measurements of similar cells, but containing hydrochloric acid in the mixed solvent:

Pt;H_2(g, 1 atm)|HCl(m) in 50 wt % C_2H_5OH/H_2O|AgCl;Ag (B)

These results are also reported here.

Table I. Properties of 50 wt % Ethanol/Water Solvent from 25 to –10 °C

				Debye–Hückel const	
T, K	p_{solv}, mmHg	ϵ	density, g/mL	A	B
298.15	49.7	49.02	0.9098	0.9852	0.3968
293.15	36.8	50.38	0.9138	0.9720	0.3956
288.15	26.9	51.81	0.9178	0.9585	0.3943
283.15	19.6	53.26	0.9216	0.9460	0.3931
278.15	14.1	54.75	0.9254	0.9342	0.3920
273.15	9.9	56.28	0.9292	0.9230	0.3910
268.15	6.8	57.86	0.9328	0.9121	0.3899
263.15	4.6	59.48	0.9365	0.9019	0.3890

Experimental Section

Anhydrous absolute ethanol was obtained from U.S. Industrial Chemicals Co. and used without further purification. Tris–HCl (Alfa, 99+%) and Tris base (Sigma, 99+%) were dried at 80 °C overnight and stored over anhydrous $CaSO_4$ until use. A stock buffer solution approximately 0.1 m was prepared by weighing the dried salts and diluting with 50 wt % ethanol/water solvent. Further dilutions were prepared by weight. Deionized water containing less than 0.4 ppm dissolved salts (as NaCl) was distilled once in an all-glass still. Constant-boiling HCl was distilled twice, retaining the middle fraction each time; its concentration was determined by weighing silver chloride.

The electrodes were prepared as described elsewhere (*8*). The silver–silver chloride electrodes were stored in 0.01 m NaCl (50 wt % ethanol/water solvent) for at least 24 h before use. Bias potentials among the electrodes never exceeded 0.02 mV. The cells were of all-glass construction with a triple saturator for the entering hydrogen gas. Hydrogen was purified with a De-oxo (Engelhard) catalytic purifier. Constant temperature was maintained by immersion of the cells in an insulated bath equipped with a refrigerated circulating unit and a proportional heater/controller. The bath solution was a 50% mixture of ethylene glycol–water. All emf measurements were run in duplicate and the results averaged. Measurements were made initially at 25 °C. The cells were then allowed to attain –10 °C overnight, after which readings were taken at 5-deg intervals, returning to 25 °C. The cells displayed excellent stability, the initial and final values at 25 °C differing by no more than 0.05 mV on the average.

Results

The emf values obtained were corrected to 1 atm (101.325 kPa, 760 mmHg) partial pressure of hydrogen by adding the quantity ΔE

$$\Delta E = \frac{RT}{2F} \ln \left[\frac{760}{\mathrm{bp} - p_{solv}} \right] \qquad (1)$$

where bp and p_{solv} are the corrected barometric pressure and vapor pressure of the solvent, respectively (in mmHg). At 25 °C we chose to use the value of 49.7 mmHg (*9*) for p_{solv}.

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Table II. Corrected EMF Values for the Cell Pt;H_2(g, 1 atm)|HCl(m) in 50 wt % C_2H_5OH/H_2O|AgCl;Ag from 25 to −10 °C

m	25 °C	20 °C	15 °C	10 °C	5 °C	0 °C	−5 °C	−10 °C
0.004995	0.46504	0.46420	0.46389	0.46296	0.46183	0.46044	0.45883	0.45708
0.01190	0.42369	0.42383	0.42378	0.42348	0.42298	0.42222	0.42132	0.42022
0.01697	0.40710	0.40755	0.40772	0.40768	0.40742	0.40695	0.40626	0.40542
0.02301	0.39292	0.39361	0.39399	0.39415	0.39410	0.39380	0.39334	0.39270
0.03199	0.37768	0.37858	0.37921	0.37960	0.37978	0.37973	0.37948	0.37904
0.04088	0.36648	0.36754	0.36831	0.36886	0.36919	0.36931	0.36924	0.36895
0.05014	0.35721	0.35830	0.35921	0.35990	0.36036	0.36063	0.36070	0.36058

Table III. Standard Potential ($E°_m$) of the Ag;AgCl Electrode in 50 wt % Ethanol/Water from 25 to −10 °C

T, °C	$E°_m$, V	å,[a] Å	s,[b] mV
25	0.18550 (0.18588)[c]	4.2	0.02
20	0.18977	3.5	0.04
15	0.19386	3.6	0.02
10	0.19773	3.9	0.03
5	0.20138	4.1	0.02
0	0.20478	4.5	0.03
−5	0.20795	4.5	0.02
−10	0.21098	4.8	0.03

[a] Best-fit ion-size parameter from eq 3. [b] Standard deviation of the intercept. [c] Harned's data for å = 4.3 Å, ref *9*.

Values used at the other temperatures were "ideal" values derived from the partial pressure contributions, x_1P_1 and x_2P_2, for water and ethanol, respectively,

$$(p_{\mathrm{solv}})_t = (p_{\mathrm{solv}})_{25}\left[\frac{(x_1P_1 + x_2P_2)_t}{(x_1P_1 + x_2P_2)_{25}}\right] \tag{2}$$

The mole fractions x_1 and x_2 take the values 0.719 and 0.281 for 50 wt % ethanol/water. The pure solvent vapor pressures P_1 and P_2 are available in the literature (*10*) for temperatures above 0 °C. Values for temperatures below 0 °C were obtained by extrapolation of the pressure/temperature curves at the higher temperatures. The values of $(p_{\mathrm{solv}})_t$ calculated from eq 2 are given in Table I. The correction to the measured emf ranged from 0.03 mV at −10 °C to 0.80 mV at 25 °C.

*1. **Standard Potentials***. The results of emf measurements leading to the standard potential of the silver-silver chloride electrode are given in Table II. Seven cell solutions containing HCl at molalities ranging from 0.05 to 0.005 m were tested. The standard potential on the molality scale, $E°_m$, was obtained by extrapolation of the function ($E°'$) of the emf, E, to m = 0:

$$E°' \equiv E°_m - bm = E + 2k \log m - \frac{2kAm^{1/2}}{1 + B\mathring{a}m^{1/2}} \tag{3}$$

This function is derived from the Nernst equation, where a Debye–Hückel expression has been included to approximate the mean activity coefficient of HCl. The term k is written for RT ln 10/F and the Debye–Hückel constants A and B (molality scale) were calculated by the usual equations (*11*) from the densities and dielectric constants of the solvent, and the thermodynamic temperature. The density of the solvent below 0 °C was obtained by extrapolation of the data at higher temperatures (*10*). The dielectric constants, ϵ, at the various temperatures were approximated by using the equation and constants given by Akerlöf (*12*) for 50 wt % ethanol/water mixtures. These physical data are tabulated in Table I at each temperature.

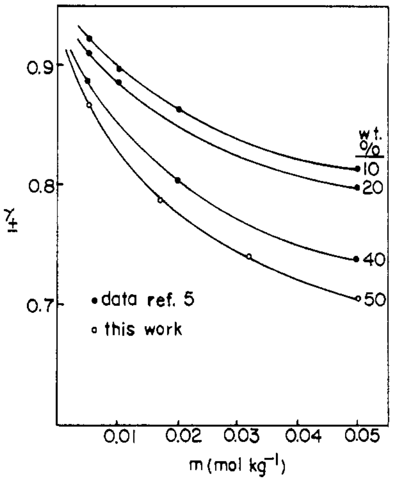

Figure 1. Mean activity coefficient of HCl vs molality in 10, 20, 40, and 50 wt % ethanol/water solvents at 25 °C.

The ion-size parameter, å, in eq 3 was treated as an adjustable term and allowed to vary successively until the function $E°'$ vs m yielded the best straight line. A value of å was chosen such that the standard deviation of regression was at a minimum. The $E°_m$ values obtained in this manner are listed in Table III, along with the values of å and the standard deviations (s) of the intercept. Also included in Table III for comparison is the value at 25 °C obtained by Harned and coworkers (*9*), who used å = 4.3 Å. Our value for $E°_m$ at 25 °C is in reasonable agreement with Harned's at the same temperature, although 0.38 mV lower. Over the temperature range studied, the å value leading to the best fit of the data averaged 4.1 Å and ranged from 3.5 to 4.8 Å. This is in accord with what has been found earlier in 40 wt % ethanol/water solvent (*5*) and in pure water (*13*).

*2. **Dissociation Constant of Tris-H$^+$***. The $E°$ values in Table III were used in the determination of pK values for Tris-H$^+$. Table IV lists the corrected emf values obtained from cell A containing equimolal Tris/Tris-HCl solutions spanning the molality range 0.1–0.01 m and from 25 to −10 °C. The pK values at each temperature were obtained by plotting the function, pK' vs m and extrapolating to m = 0

$$\mathrm{p}K' \equiv \mathrm{p}K - bm = \frac{(E - E°)}{k} + \log m - \frac{2Am^{1/2}}{1 + B\mathring{a}m^{1/2}} \tag{4}$$

where $k = RT$ ln 10/F and m is the molality of chloride ion (= m_{TrisHCl}). This function is derived from the Nernst equation

Table IV. Corrected EMF Values for the Cell Pt;H_2(g, 1 atm)|Tris–HCl(m),Tris(m) in 50 wt % C_2H_5OH/H_2O|AgCl;Ag from 25 to −10 °C

m	25 °C	20 °C	15 °C	10 °C	5 °C	0 °C	−5 °C	−10 °C
0.09892	0.72432	0.72700	0.72972	0.73215	0.73458	0.73692	0.73909	0.74134
0.07500	0.72898	0.73166	0.73442	0.73668	0.73903	0.74132	0.74346	0.74556
0.05000	0.73585	0.73847	0.74091	0.74328	0.74557	0.74779	0.74991	0.75177
0.02500	0.74862	0.75105	0.75336	0.75559	0.75770	0.75974	0.76166	0.76333
0.01000	0.76632	0.76857	0.77064	0.77269	0.77454	0.77632	0.77797	0.77941

Table V. p*K* of Tris-H$^+$ in 50 wt % Ethanol/Water from 25 to -10 °C

T, °C	p*K*	$s(\times 10^3)^a$	*T*, °C	p*K*	$s(\times 10^3)^a$
25	7.640	2.7	5	8.216	2.3
20	7.776	2.5	0	8.379	2.3
15	7.914	2.8	-5	8.549	2.6
10	8.063	2.2	-10	8.723	2.1

[a] Standard deviation of the intercept.

Table VI. Thermodynamic Functions for the Dissociation of Tris-H$^+$ in 50 wt % Ethanol/Water at 298.15 K

$\Delta G°$, kcal mol^{-1}	10.42
$\Delta S°$, cal mol^{-1} K^{-1}	1.2
$\Delta H°$, kcal mol^{-1}	10.77
A	3610.48
B	-28.4918
C	4.21610
s	0.0008

combined with the mass-action expression for the dissociation of Tris-H$^+$. The Debye-Hückel term is used to approximate the mean activity coefficient of Tris-HCl. The activity coefficient of neutral Tris is taken to be unity, referred to its standard state in the mixed solvent.

The value of å was varied until the best fit of the data was obtained. At all temperatures, the best value for å was zero, as has been found previously (*4*) for other weak acids of this charge type. The values for p*K* obtained are listed in Table V at each temperature, along with the standard deviations of fit, *s*.

Discussion

The values of the standard potential $E°_m$ (Table III), are given by the equation

$$E°_m = 0.20478 - (6.6211 \times 10^{-4})t - (4.3786 \times 10^{-6})t^2 \quad (5)$$

where *t* is in Celsius. The standard deviation of the polynomial is 0.02 mV. One can readily calculate the mean ionic activity coefficient of hydrochloric acid in the ethanol/water mixture at any molality within the range of the fitted data by rearrangement of the Nernst equation:

$$-\log \gamma_{\pm} = \frac{E - E°}{2k} + \log m \quad (6)$$

The variation in $\gamma_{\pm}$ with molality at 25 °C is shown graphically in Figure 1, along with results obtained in 10, 20, and 40 wt % ethanol/water (*5*) where comparison can be made.

The p*K* values summarized in Table V were fitted to the equation

$$\mathrm{p}K = A/T + B + C \ln T \quad (7)$$

where *T* is the thermodynamic temperature. The method of Ives and Moseley (*14*), coded for a microcomputer, was used. From the first and second derivatives of p*K* with respect to temperature, the changes in Gibbs free energy, enthalpy, and entropy for the dissociation process were obtained. Table VI lists the thermodynamic quantities at 298.15 K, along with the numerical values of *A*, *B*, and *C*, and the standard deviation fit.

Table VII. Conventional pa$_H$ Values of the Buffer Tris(0.05 *m*):Tris-HCl(0.05 *m*) in 50 wt % Ethanol/Water from 25 to -10 °C

T, °C	pa$_H$	*T*, °C	pa$_H$
25	7.845 (8.173)^a	5	8.411 (8.774)
20	7.977 (8.313)	0	8.571 (8.946)
15	8.114 (8.461)	-5	8.739
10	8.258 (8.614)	-10	8.912

[a] pa$_H$ values in water, ref *1*, are enclosed in parentheses.

The dissociation of Tris-H$^+$ is an isoelectric process and therefore the p*K* would not be expected to change dramatically with changes in the dielectric constant of solvent. The p*K* value at 298.15 K in the mixed solvent (7.640) is only about 0.4 units lower than the value in water (8.075), corresponding to a transfer free energy (ΔG_{tr}) of about -0.593 kcal/mol.

The activity pH (pa$_H$) can be estimated from p*K* at any of the molalities studied here through the relation

$$\mathrm{pa_H} = \frac{E - E°}{k} + \log m - \frac{Am^{1/2}}{1 + 4.57Bm^{1/2}} \quad (8)$$

where å = 4.57 Å was chosen for consistency with the Bates-Guggenheim convention for aqueous solutions (*15*). The other terms have their usual meaning. Table VII lists pa$_H$ values for 0.05 *m* Tris, Tris-HCl in 50 wt % ethanol/water, along with the corresponding values in water (*1*). The change in pH with temperature is not significantly different from that in water, $\delta\mathrm{pH}/\delta T = -0.030$, over the 25 to 0 °C range.

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Registry No. Tris-H$^+$, 19320-52-6; AgCl, 7783-90-6; HCl, 7647-01-0; Ag, 7440-22-4; ethanol, 64-17-5.

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