Standard Electromotive Force of Silver–Silver Chloride Electrode and Related Thermodynamic Quantities in *tert*-Butyl Alcohol–Water Mixtures (2, 6, and 8 Wt %) between 5–45°C

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The electromotive force measurements of the cell Pt, H_2 (1 atm) | HCl (*m*) in H_2O || HCl (*m*), Bu^{t}OH (*x*), H_2O (*y*) | AgCl, Ag at nine temperatures in the range 5–45°C were used to derive the standard potential of the cell, the activity coefficient of HCl for molalities in the range 0.002–0.1, and the thermodynamic functions, $\Delta G°$, $\Delta H°$, and $\Delta S°$, for the transfer of HCl from water to the respective *tert*-butyl alcohol–water mixtures. The standard potential was calculated by a theoretically justified polynomial curve-fitting program and varied with temperature, *t*, °C, according to the equations

$${}^sE_m{}^0(x = 2) = 0.2154 - 7.528 \times 10^{-4}(t - 25) - 2.839 \times 10^{-6}(t - 25)^2$$

$${}^sE_m{}^0(x = 6) = 0.2128 - 7.676 \times 10^{-4}(t - 25) - 6.826 \times 10^{-6}(t - 25)^2$$

$${}^sE_m{}^0(x = 8) = 0.2103 - 7.571 \times 10^{-4}(t - 25) - 1.858 \times 10^{-6}(t - 25)^2$$

The molality of the acid ranged from 0.005–0.2 mol kg^{-1}.

The thermodynamic behavior and acid-base properties of electrolytes in amphiprotic mixed solvents are of considerable interest (*3, 10*). Such interest in alcohol–water mixtures stems, in part, from the investigations of glycerol–water (*17*) and isopropyl alcohol–water mixtures (*11, 15*), which involved ion-solvation and led to a partial understanding of acid-base reactions.

In a previous paper (*14*), we reported the results of potentiometric studies in 10, 20, 40, and 70 wt % *tert*-butyl alcohol. In the present work, an aqueous mixture of *tert*-butyl alcohol, x = 2, 6, and 8 wt %, was chosen for study. These media are used for studies of the acid-base properties (*3*) and involve structural alterations of the mixed solvent (*5, 6*).

Electromotive force measurements of the cell of the type

$$\text{Pt, H}_2\text{ (1 atm) | HCl } (m) \text{ in H}_2\text{O || HCl } (m)\text{, Bu}^t\text{OH } (x)\text{, H}_2\text{O } (y) \text{ | AgCl, Ag}$$

have been made at nine temperatures ranging from 5–45°C. The acid concentrations ranged from 0.005–0.2 mol kg^{-1}. The standard potentials of the cell, the mean activity coefficients of HCl, and the related thermodynamic quantities for the transfer of 1 mole of the acid from the aqueous standard state to the standard states of the mixed solvents have been computed.

EXPERIMENTAL

tert-Butyl alcohol was purified by refluxing over CaO for 24 hr and subsequent fractionation (*1*). It had bp 82.2–82.3°C/1 atm, d^{20} = 0.8756 g ml^{-1}, $n^{20}{}_D$ = 1.3838. The gas chromatographic analysis showed the water content in the solvent to be less than 0.02%.

An aqueous stock solution of hydrochloric acid was prepared from a twice-distilled sample of the acid and was analyzed gravimetrically by weighing silver chloride. No significant change, less than 0.05%, was detected in the molality of HCl for three separate gravimetric determinations. The distilled water having a specific conductance of 0.7 × $10^{-6}\Omega^{-1}$cm^{-1} was used. The mixed solvent was prepared by weighing distilled water and *tert*-butyl alcohol. The composition of the alcohol solution is accurate to within 0.02%. For deaeration, a rapid stream of hydrogen was forced into the saturators and the cell containing the solutions. The saturators were filled with a solution of identical composition as that present in the cell.

The silver–silver chloride electrodes were of the thermal-electrolytic type (*2*) and had bias potentials of ±0.05 mV. The hydrogen electrodes (*2*) were prepared from a Sargent half-cell platinum electrode having a length of approximately 12 cm and thickness of about 0.125 mm. The electrodes were replatinized as soon as the system showed any kind of instability. The electromotive forces (emf's) were measured by means of a Type K-3 Leeds & Northrup potentiometer having a mirror-type galvanometer with a sensitivity of ±0.02 mV per division. The temperature of the cell was thermostatically regulated to ±0.01°C by means of a Sargent thermonitor controlled water bath (*12*).

All measurements were made with two Ag–AgCl electrodes and two hydrogen electrodes for each solution. The emf readings were taken after appropriate intervals of equilibration when the emf's remained constant with ±0.08 mV for a period of 1 hr. The equilibrium was reached in 3 to 4 hr after the initiation of hydrogen bubbling. The readings for 25°C were taken at the start, middle, and end of the run. These three values agreed within ±0.08 mV.

To correct the emf's to 1 atm hydrogen pressure, vapor pressures for the mixed solvents over the temperature range 5–45°C were assumed to obey Raoult's law and were so calculated.

RESULTS

The measured values of emf, corrected to 1 atm of the hydrogen gas, are recorded in Table I. Each entry is the average value from four replicate cells prepared for each molality of hydrochloric acid. The standard deviation of a single value of emf from the mean of the results from four replicate cells is 0.09 mV.

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Table I. Electromotive Force of Cell Pt, H_2 (1 atm) | HCl (*m*) in H_2O || HCl (*m*), Bu^tOH (*x*), H_2O (*y*) | AgCl, Ag at Different Temperatures

m_{HCl}	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C
					E (in volts)				
					x = 2 Wt % *tert*-Butyl Alcohol				
0.19400	0.3223	0.3208	0.3200	0.3196	0.3188	0.3167	0.3149	0.3131	0.3116
0.15015	0.3339	0.3333	0.3325	0.3317	0.3307	0.3290	0.3277	0.3261	0.3255
0.09215	0.3558	0.3559	0.3557	0.3551	0.3546	0.3527	0.3518	0.3506	0.3493
0.08111	0.3618	0.3616	0.3614	0.3610	0.3608	0.3592	0.3584	0.3573	0.3564
0.04004	0.3937	0.3942	0.3948	0.3949	0.3949	0.3934	0.3937	0.3917	0.3922
0.03003	0.4073	0.4079	0.4086	0.4090	0.4093	0.4072	0.4086	0.4062	0.4070
0.01001	0.4552	0.4572	0.4587	0.4597	0.4618	0.4598	0.4603	0.4602	0.4605
0.005006	0.4880	0.4900	0.4918	0.4935	0.4949	0.4948	0.4959	0.4967	0.4973
					x = 6 Wt % *tert*-Butyl Alcohol				
0.15015	0.3310	0.3306	0.3299	0.3292	0.3280	0.3264	0.3233	0.3226	0.3212
0.09215	0.3516	0.3513	0.3511	0.3510	0.3497	0.3487	0.3467	0.3457	0.3438
0.08111	0.3575	0.3574	0.3570	0.3585	0.3561	0.3534	0.3529	0.3511	0.3466
0.06006	0.3709	0.3716	0.3725	0.3724	0.3719	0.3705	0.3684	0.3668	0.3647
0.04004	0.3892	0.3898	0.3903	0.3906	0.3906	0.3879	0.3882	0.3860	0.3858
0.03003	0.4025	0.4033	0.4039	0.4045	0.4045	0.4043	0.4031	0.4009	0.3993
0.01001	0.4522	0.4535	0.4551	0.4561	0.4577	0.4572	0.4570	0.4563	0.4560
0.005006	0.4845	0.4865	0.4887	0.4901	0.4913	0.4917	0.4920	0.4918	0.4926
					x = 8 Wt % *tert*-Butyl Alcohol				
0.15015	0.3270	0.3259	0.3241	0.3225	0.3200	0.3170	0.3160	0.3131	0.3107
0.08111	0.3562	0.3561	0.3543	0.3535	0.3521	0.3497	0.3484	0.3456	0.3428
0.06006	0.3684	0.3688	0.3673	0.3673	0.3653	0.3640	0.3625	0.3606	0.3577
0.04755	0.3791	0.3792	0.3793	0.3789	0.3779	0.3767	0.3752	0.3666	0.3700
0.04004	0.3863	0.3866	0.3873	0.3871	0.3859	0.3855	0.3834	0.3817	0.3789
0.03003	0.4003	0.3999	0.4005	0.4001	0.4009	0.3998	0.3977	0.3962	0.3933
0.01001	0.4496	0.4502	0.4516	0.4521	0.4524	0.4519	0.4519	0.4519	0.4497
0.005006	0.4816	0.4833	0.4850	0.4862	0.4918	0.4877	0.4885	0.4881	0.4870

Table II. Standard Electromotive Force of Cell Pt, H_2 (1 atm) | HCl (*m*) in H_2O || HCl (*m*), Bu^tOH (*x*), H_2O (*y*) | AgCl, Ag at Different Temperatures

	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C	45°C
					x = 2 Wt % *tert*-Butyl Alcohol ($\bar{M}$ = 18.29 G Mol^{-1})				
${}^sE_m^0$, V	0.2292	0.2258	0.2223	0.2191	0.2154	0.2113	0.2078	0.2035	0.1991
${}^sE_N^0$, V	0.0374	0.0306	0.0236	0.0169	0.0097	0.0022	−0.0047	−0.0124	−0.0203
					x = 4 Wt % *tert*-Butyl Alcohol ($\bar{M}$ = 18.87 G Mol^{-1})				
${}^sE_m^0$, V	0.2254	0.2225	0.2197	0.2164	0.2128	0.2087	0.2045	0.1998	0.1948
${}^sE_N^0$, V	0.0353	0.0288	0.0225	0.0158	0.0088	0.0013	−0.0063	−0.0144	−0.0228
					x = 8 Wt % *tert*-Butyl Alcohol ($\bar{M}$ = 19.18 G Mol^{-1})				
${}^sE_m^0$, V	0.2247	0.2212	0.2175	0.2141	0.2103	0.20652	0.2026	0.1986	0.1944
${}^sE_N^0$, V	0.0352	0.0283	0.0212	0.0143	0.0072	−0.00004	−0.0073	−0.0148	−0.0224

STANDARD EMF OF CELL

Sen et al. (*18*) and our more recent papers (*14*, *15*, *17*) have clearly shown that an equation of the type

$$E + (2\,RT/F)\ln m = E^0 + A_1 m^{1/2} + A_2 m + A_3 m^{3/2} + \ldots \quad (1)$$

is theoretically justified and precisely expresses the value of the standard potential. Equation 1 is analogous (*18*) to the Gronwall et al. equation of the Debye-Hückel theory (*9*). Furthermore, the activity coefficient can be represented as a power series in $m^{1/2}$ (*18*)

$$\ln \gamma_{\pm} = A_1' m^{1/2} + A_2' m + A_3' m^{3/2} + \ldots \quad (2)$$

in which the constants A_1', A_2', etc., as well as the constants A_1, A_2, etc., in Equation 1, are not arbitrarily adjustable parameters. Equation 1 can thus be written as a polynomial of the form

$$y = A_0 + A_1 x + A_2 x^2 + \ldots \quad (3)$$

The algebraic form of Equations 1 and 2 has been further shown to be consistent with the theory (*7*). It is evident from Equation 3 that the first approximation is of linear form, $y = A_0 + A_1 x$. The third degree equation was used in the present investigation. The values of ${}^sE_m^0$, the standard electrode potential on the molal scale, for various solvent compositions at different temperatures can be expressed as a function of temperature by the equations

$${}^sE_m^0\ (x = 2) = 0.2154 - 7.528 \times 10^{-4}\,(t - 25) - 2.839 \times 10^{-6}\,(t - 25)^2 \quad (4)$$

$${}^sE_m^0\ (x = 6) = 0.2128 - 7.676 \times 10^{-4}\,(t - 25) - 6.826 \times 10^{-6}\,(t - 25)^2 \quad (5)$$

$${}^sE_m^0\ (x = 8) = 0.2103 - 7.571 \times 10^{-4}\,(t - 25) - 1.858 \times 10^{-6}\,(t - 25)^2 \quad (6)$$

The values of E_N^0 have been calculated with the aid of the equation

$${}^sE_N^0 = {}^sE_m^0 - 2\,k \log (1000/\bar{M}) \quad (7)$$

where $k = 2.3026\,RT/F$ and $\bar{M}$, the mean molecular weight of the solvent. The values of these quantities are entered in Table II.

Table III. Mean Activity Coefficients of Hydrochloric Acid in 2, 6, and 8 Wt % *tert*-Butyl Alcohol at 25°C

m_{HCl}	$x = 2$	$x = 6$	$x = 8$
0.002	0.944	0.943	0.940
0.005	0.922	0.922	0.920
0.01	0.896	0.894	0.890
0.02	0.851	0.850	0.847
0.05	0.814	0.812	0.806
0.1	0.780	0.775	0.770

Table IV. Thermodynamic Functions[a] (Molal Scale) for Transfer of HCl from Water to 2, 6, and 8 Wt % *tert*-Butyl Alcohol–Water at 5°, 15°, 25°, 35°, and 45°C

x = Wt % *tert*-Butyl Alcohol

t,	$x = 2$			$x = 6$			$x = 8$		
°C	$\Delta G_t°$	$\Delta H_t°$	$\Delta S_t°$	$\Delta G_t°$	$\Delta H_t°$	$\Delta S_t°$	$\Delta G_t°$	$\Delta H_t°$	$\Delta S_t°$
5	114	−665	−2.8	201	−550	−2.7	222	−529	−2.7
15	145	−629	−2.7	205	−544	−2.6	255	−494	−2.6
25	160	−615	−2.6	220	−495	−2.4	277	−438	−2.4
35	181	−558	−2.4	257	−452	−2.3	301	−408	−2.3
45	213	−487	−2.2	312	−356	−2.1	321	−347	−2.1

[a] $\Delta G_t°$ and $\Delta H_t°$ are in cal mol^{-1}; $\Delta S_t°$ is in cal °K^{-1} mol^{-1}.

Activity Coefficient of HCl. The mean activity coefficients of hydrochloric acid in the experimental solvent compositions have been calculated from the following rearranged Nernst equation:

$$\ln \gamma_{\pm} = \frac{{}^{s}E_m{}^0 - [E + (2\,RT/F)\ln m]}{(2\,RT/F)} \tag{8}$$

where the values of ${}^{s}E_m{}^0$ are listed in Table II. The values of $\gamma_{\pm}$ were obtained by using the smoothed values of $[E + (2\,RT/F)\ln m]$ at rounded molalities from the constants of Equation 1. These values, $\gamma_{\pm}$, at 25°C are given in Table III.

THERMODYNAMIC QUANTITIES

The standard thermodynamic functions, $\Delta G_t°$, $\Delta S_t°$ and $\Delta H_t°$, for the transfer process HCl in $H_2O \rightarrow$ HCl in x wt % Bu^{t}OH were derived from the standard emf of the cell in water (*4*) and in x = 2, 6, and 8 wt % *tert*-butyl alcohol together with the variations of ${}^{s}E_m{}^0$ and ${}^{w}E_m{}^0$ (*4*) with temperature. The values of transfer Gibbs free energy, $\Delta G_t°$, transfer entropy, $\Delta S_t°$, and transfer enthalpy $\Delta H_t°$, were obtained by the application of the usual thermodynamic relationships.

$$\Delta G_t° = F({}^{w}E_m{}^0 - {}^{s}E_m{}^0) \tag{9}$$

$$\Delta S_t° = -d\Delta G_t°/dT \tag{10}$$

$$\Delta H_t° = \Delta G_t° + T\Delta S_t° \tag{11}$$

where t represents the transfer function and the superscripts w and s refer to water and the mixed solvent, respectively. The values of these quantities are shown in Table IV.

DISCUSSION

The values of ${}^{s}E_m{}^0$ given in Table II are estimated to be correct to within ±0.2 mV. Further data have been placed with the American Chemical Society Microfilm Depository Service. The general pattern of the results of $\gamma_{\pm}$ is in good agreement with those obtained in tetrahydrofuran-water (*13*) and glycerol–water mixtures (*16*). An error of ±0.1 mV in the measured emf value corresponds to an error of ±0.003 in the values of $\gamma_{\pm}$ (Table III).

Table IV shows that the transfer Gibbs free energy is positive, and the value increases with the increase in temperature. The positive value suggests that the transfer of HCl from water to the mixed solvent is not a spontaneous process, or, in other words, that water is a more basic component of the solvent mixture. The values of $\Delta G_t°$ are accurate to within ±8 cal.

Some insight in regard to the structural changes characteristic of alcohol–water mixtures (*8*) might be obtained from the values of $\Delta S_t°$ and $\Delta H_t°$. The negative values of these quantities suggest that the transfer of HCl from water to the mixed solvent is an exothermic process, and the changes of the structure of the mixed solvent are pronounced (*5*, *6*).

ACKNOWLEDGMENT

The authors thank Jorge Padron for providing the facility for this experimental work.

NOMENCLATURE

${}^{w}E_m{}^0$, ${}^{s}E_m{}^0$ = standard electrode potential (molal scale) in water and in a mixed solvent, respectively, volts
${}^{s}E_N{}^0$ = standard electrode potential (mole fraction scale) in a mixed solvent, volts
A_1, A_2 = constants of Equation 1 and 3
$\overline{M}$ = mean molecular weight of the solvent, g/mol
x = wt % organic solvent (*tert*-butyl alcohol) in a mixture with water
$\gamma_{\pm}$ = mean activity coefficients (molal scale) of hydrochloric acid
$\Delta G_t°$ = standard transfer Gibbs free energy, cal/mol
$\Delta H_t°$ = standard transfer enthalpy, cal/mol
$\Delta S_t°$ = standard transfer entropy, cal/mol-deg

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RECEIVED for review April 26, 1971. Accepted October 20, 1971. Further data in the form of 12 equations and two tables will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Business Operations Department, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036 by referring to author, title of article, volume, and page number. Remit by check or money order, $3.00 for photocopy or $2.00 for microfiche.