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Thermodynamics of the hydrolysis of TRISH $^+$ in (water +10 or +20 mass per cent of acetonitrile) from 263.15 to 298.15 K

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The standard potentials of $(AgCl + \frac{1}{2}H_2 = Ag + HCl)$ in (water +10 or +20 mass per cent of acetonitrile) were used to determine the acidity constants of protonated tris(hydroxymethyl)-aminomethane (TRISH⁺). Measurements were made at eight temperatures ranging from 263.15 to 298.15 K at 5 K intervals in cells without liquid junction. The molalities of TRISH⁺ ranged from 0.1 to 0.005 mol·kg⁻¹. The standard molar Gibbs free energy change $\Delta_r G_m^{\circ}$ of the reaction was calculated. From the values obtained in the literature for water and our values for the mixed solvents, the standard molar Gibbs free energy change of transfer $\Delta_t G_m^{\circ}$ was also estimated. It was found that the hydrolysis of TRISH⁺ is less favored in the mixtures than in pure water.

1. Introduction

Little work has been carried out on the thermodynamics of the hydrohalic acids in (water + acetonitrile). Most of it has been done in anhydrous acetonitrile by conductometric⁽¹⁾ or spectrophotometric^(2,3) methods. A very important contribution to this field by Mussini, Longhi, and Giammario⁽³⁾ was the determination of the e.m.f.s of the cell:

 $Pt|H_2(g, p = 101.325 \text{ kPa})|HCl in (water + 5, +10, or +15 mass per cent of acetonitrile)|AgCl|Ag.$

They determined the standard potential E° over the range of temperatures from 288.15 to 308.15 K. Recently E° was determined in our laboratory with the same cell as that used by Mussini *et al.* but this time in (water +10, +20, or +30 mass per cent of acetonitrile).⁽⁴⁾ The standard potential of the electrode together with potential measurements of cells without liquid junction were utilized to determine the acidity constant of protonated tris(hydroxymethyl)aminomethane {or 2-amino-2-(hydroxymethyl)-1,3-propanediol} in (water +10 or +20 mass per cent of acetonitrile) at eight temperatures from 263.15 to 298.15 K. The acidity constant of this acid of charge type A⁺B⁰, namely the acid conjugate of the weak uncharged base 2-amino-2-(hydroxymethyl)aminomethane, has been studied. The changes of

the acidity constant with composition were used to calculate the changes of standard Gibbs free energy.

The studies of this weak electrolyte (protonated TRIS), a cationic acid, in the acetonitrile mixtures were done by measurements of the e.m.f. of the cell:

$$Pt|H_2(g, p = 101.325 \text{ kPa})|Buffer + Cl^-, D|AgCl|Ag,$$
 (1)

in which D represents (water + acetonitrile), from 263.15 to 298.15 K. The buffer solutions were composed of TRIS \cdot HCl and TRIS, each at the same molality. Values of the acidity constant K° for the acid and related quantities were calculated by assuming complete ionization of TRIS \cdot HCl.

2. Experimental

The acetonitrile was obtained commercially and distilled twice. De-ionized water was distilled in an all-glass still. TRIS buffers were prepared from TRIS base and the standard solution of HCl. The cells, the preparation of the electrodes, and other details of the measurements have been described in our earlier paper,⁽⁴⁾ where the properties of (water + acetonitrile) will be found.

The reaction of TRISH⁺ can be represented by

$$\operatorname{TRISH}^{+} + \operatorname{H}_2 \operatorname{O} = \operatorname{TRIS} + \operatorname{H}_3 \operatorname{O}^{+}, \qquad (2)$$

and the acidity constant K° is given by:

$$K^{\circ} = a(H_{3}O^{+})m(\text{TRIS})\gamma(\text{TRIS})/m(\text{TRIS}H^{+})\gamma(\text{TRIS}H^{+}), \qquad (3)$$

where γ denotes an activity coefficient. Combination of equation (3) with the Nernst equation for the cell gives:

$$pK^{\circ} = (E - E^{\circ})/k + \log_{10}\{m(\text{TRISH}^{+})m(\text{Cl}^{-})/m(\text{TRIS})m^{\circ}\} + \log_{10}\{\gamma(\text{TRISH}^{+})\gamma(\text{Cl}^{-})/\gamma(\text{TRIS})\}, \quad (4)$$

where k is written for $(RT/F)\ln 10$, and $m^{\circ} = 1 \mod kg^{-1}$. If TRISH⁺ can be considered to be a strong electrolyte in (water + acetonitrile) and activity coefficients are represented by the extended Debye-Hückel equation, with ion-size parameter a, one has for the "apparent" pK[°], represented by pK':

$$pK' = (E - E^{\circ})/k + \log_{10}(m/m^{\circ}) - (2AI^{1/2})(1 + BaI^{1/2}),$$
(5)

since, for these solutions, the buffer ratio always remained close to 1. In equation (5), A and B are constants of the Debye-Hückel theory for (water + acetonitrile) and I is the ionic strength of the solutions. The $pK^{\circ}s$ are obtained by extrapolating values of pK' obtained by equation (5) to I = 0. The intercept is influenced to some extent by the choice of a; hence, the value of the ion-size parameter leading to the smallest standard deviation of regression from a straight line was selected (0.43 nm). For all the systems studied, solvolysis was negligible; thus $m(TRISH^+)$ and m(TRIS) were considered to be equal to the stoichiometric molalities.

In the hope of shedding some light on the interactions involved we have calculated the standard molar Gibbs free energies for the transfer of the TRISH⁺

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from water to (water + acetonitrile). These functions are related by

$$\Delta_{\mathbf{t}} G_{\mathbf{m}}^{\circ} = (RT \ln 10)(\mathbf{p} K_{\mathbf{D}}^{\circ} - \mathbf{p} K_{\mathbf{W}}^{\circ}), \tag{6}$$

where $\Delta_t G_m^{\circ}$ is the standard molar Gibbs free energy change for the transfer from water to the mixed solvent.

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T/K	: 298.15	293.15	288.15	283.15	278.15	273.15	268.15	263.15
<i>m</i> /(mol·kg ⁻¹)			E(water	+ 10 mass j	per cent ace	tonitrile)/V		
0.09365	0.7593	0.7644	0.7688	0.77338	0.77657	0.77946	0.78192	
0.08465	0.7630	0.7670	0.7706	0.77385	0.77681	0.77960	0.78205	0.78400
0.07406	0.7673	0.7713	0.7748	0.77795	0.78073	0.78335	0.78560	0.7842
0.06772	0.7707	0.7748	0.77868	0.78143	0.78419	0.78547	0.78721	0.78836
0.04060	0.7814	0.7855	0.78899	0.79261	0.79458	0.79739	0.79935	0.80082
0.03234	0.7865	0.7913	0.79500	0.79826	0.80092	0.80316	0.80505	
0.03025	0.7910	0.7953	0.7987	0.8016	0.80369	0.80602	0.80761	
0.02021	0.7995	0.8047	0.8108	0.8140	0.81663	0.81876	0.82040	
			E(water +	20 mass pe	er cent of ac	etonitrile)/	v	
0.10769	0.7407	0.7425	0.74636	0.74498	0.75407	0.75676	0.75570	0.76326
0.07097	0.7556	0.7594	0.76335	0.76722	0.77090	0.77426	0.77712	0.77973
0.06375	0.7601	0.7640	0.76741	0.77080	0.77389	0.77645	0.77765	
0.02822	0.7788	0.7840	0.79160	0.79544	0.79833	0.80101	0.80296	0.80488
0.01904	0.7907	0.7948	0.80070	0.80408	0.80643	0.80865	0.81086	0.81214
0.01084	0.8073	0.8122	0.81770	0.82072	0.82301	0.82512	0.82664	0.82796

TABLE 1. Cell e.m.f.s E for (water + acetonitrile)

TABLE 2. Apparent acidity constants K' for TRISH⁺ in (water + acetonitrile)

m(TRISH ⁺)	m(TRIS)	T/K: 263.15	268.15	273.15	278.15	283.15	288.15	293.15	298.15
mol·kg ¹	$mol \cdot kg^{-1}$	pK'(water + 10 mass per cent acetonitrile)							
0.09365	0.09518		8.90	8.74	8.56	8.40	8.31	8.16	8.02
0.08465	0.08476	9.08	8.88	8.71	8.53	8.38	8.32	8.17	8.05
0.07406	0.07265	9.10	8.90	8.74	8.56	8.41	8.35	8.20	8.09
0.06772	0.07275	9.05	8.86	8.71	8.54	8.40	8.35	8.19	8.07
0.04060	0.04121	9.12	8.92	8.76	8.58	8.44	8.36	8.21	8.09
0.03234	0.03066		8.97	8.81	8.64	8.48	8.41	8.26	8.12
0.03025	0.02992		8.98	8.82	8.64	8.50	8.43	8.28	8.15
0.02021	0.01913		9.08	8.92	8.74	8.58	8.51	8.31	8.16
			p <i>K</i>	'(water +	20 mass	per cent	acetonit	rile)	
0.10769	0.10609	8.91	8.65	8.55	8.38	8.14	8.07	7.92	7.86
0.07097	0.07410	9.05	8.88	8.70	8.51	8.36	8.18	8.04	7.93
0.06375	0.06196		8.88	8.73	8.56	8.42	8.26	8.11	8.01
0.02822	0.02709	9.23	9.06	8.89	8.71	8.56	8.37	8.15	8.03
0.01904	0.01689	9.26	9.09	8.92	8.74	8.60	8.37	8.11	
0.01084	0.00972	9.33	9.16	9.00	8.82	8.67	8.50	8.30	8.17

3. Results

The molalities of the buffer solutions and the corresponding values of the e.m.f. are summarized in table 1 for the different solvent compositions as a function of temperature. The stabilities and accuracies of the cells were better at lower T. The e.m.f.s corrected to $p(H_2) = 101.325$ kPa were used to calculate pK' by equation (5). These values are listed in table 2. The extrapolation of pK' to I = 0 was performed by linear regression and the intercepts pK° are given in table 3, together with corresponding results for pK° in water obtained from reference 5.

TABLE 3. Acidity constants for TRISH⁺ in water (w), (water + 10 mass per cent of acetonitrile) (D1), and (water + 20 mass per cent of acetonitrile) (D2). Uncertainties are standard deviations of the intercept for water, and standard deviations of the intercept for the mixture

T/K	p <i>K</i> °(w)	<i>pK</i> °(D1)	p <i>K</i> °(D2)
263.15		9.15+0.03	9.35+0.02
268.15		9.06 ± 0.05	9.20 ± 0.02
273.15	8.8500 ± 0.0008	8.90 ± 0.04	9.02 ± 0.02
278.15	8.6774 ± 0.0008	8.72 ± 0.04	8.84 ± 0.02
283.15	8.5164 ± 0.0008	8.57 ± 0.03	8.72 ± 0.02
288.15	8.3616 ± 0.0008	8.50 + 0.03	8.49 + 0.04
293.15	8.2138 ± 0.0009	8.32 ± 0.02	8.30 ± 0.04
298.15	8.0746 + 0.0006	8.18 + 0.02	8.16 ± 0.04

4. Discussion

The variation of pK° with temperature is given by the equation:

$$pK^{\circ} = A + B(T/K) + C(T/K)^2.$$
 (7)

The constants A, B, and C, determined by a computer program, are given for (water + 10 mass per cent of acetonitrile) by

$$pK^{\circ} = 17.11 - 0.03207(T/K) + 7.116 \times 10^{-5} (T/K)^2, \qquad (8)$$

and for (water + 20 mass per cent of acetonitrile) by

$$pK^{\circ} = 16.61 - 0.02113(T/K) - 2.382 \times 10^{-5}(T/K)^{2}.$$
 (9)

The changes in standard molar Gibbs free energy calculated by

$$\Delta_{\rm r} G_{\rm m}^{\circ} = (RT \ln 10) \{ A + B(T/{\rm K}) + C(T/{\rm K})^2 \}, \tag{10}$$

are given in table 4, together with the standard molar Gibbs free energy of transfer of $TRISH^+$ from pure water to the (water +10 or +20 mass per cent of acetonitrile).

The effect of enriching the aqueous solvent with acetonitrile in altering the acidity of TRISH⁺ is evident since $\Delta p K^{\circ}$ at 298.15 K is $0.11pK^{\circ}$ when the first 10 mass per cent of acetonitrile is added, but there is no noticeable change when the next 10 mass per cent of acetonitrile is added, indicating that the alteration in the solvation pattern is considerable with the first amount of acetonitrile, but once altered, an

$\frac{T}{K}$	$\frac{\Delta_{r} G^{\circ}_{m}(w)}{k J \cdot mol^{-1}}$	$\frac{\Delta_{r}G^{\circ}_{m}(D1)}{kJ\cdotmol^{-1}}$	$\frac{\Delta_t G_m^{\circ}(\mathbf{w} \to \mathbf{D}1)}{\mathbf{k}\mathbf{J} \cdot \mathbf{mol}^{-1}}$	$\frac{\Delta_{\rm r} G^{\circ}_{\rm m}({\rm D2})}{{\rm kJ}\cdot{\rm mol}^{-1}}$	$\frac{\Delta_{t}G_{m}^{\circ}(w \rightarrow D2)}{kJ \cdot mol^{-1}}$
278.15	46.229	46.443	-0.214	47.082	-0.853
288.15	46.121	46.899	-0.789	46.678	-0.557
298.15	46.058	46.700	-0.642	46.642	-0.584

TABLE 4. Standard molar Gibbs free energies and standard molar Gibbs free energies of transfer for $TRISH^+ + H_2O = TRIS + H_3O^+$ at 278.15, 288.15, and 298.15 K

additional small amount of acetonitrile will not cause any significant change in the pK° value.

The precision of only three significant figures for the pK° values of TRISH⁺ in (water + acetonitrile) as compared with five for the same process in pure water has been attributed to the possibility of acetonitrile reacting at the Pt|H₂ electrode. Smith and Massart⁽⁶⁾ attribute the low stability to a reduction of acetonitrile to ethylamine. Alexander *et al.*⁽⁷⁾ studied this system and concluded that the Ag⁺ ions at the Ag|AgCl electrode were being complexed by acetonitrile at the electrode surface. Nevertheless the pK° values of TRISH⁺ reported here have three significant figures and can be of great use in buffering reactions taking place in the studied solvent mixtures.

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