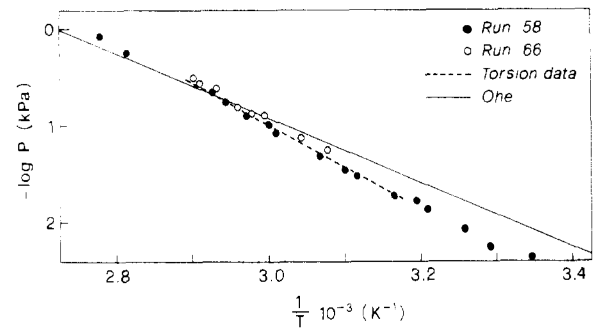

Figure 4. Vapor pressure of *p*-chloroaniline.

discussed in previous section. In the same table the results obtained by the conventional torsion apparatus and the derived enthalpy and entropy changes associated to the vaporization process are also reported. The associated errors are only standard deviations.

From the results, the following pooled equations were selected

o-chloroaniline

$$\log P\,(\mathrm{kPa}) = (8.63 \pm 0.16) - (3006 \pm 56)/T$$

m-chloroaniline

$$\log P\,(\mathrm{kPa}) = (8.86 \pm 0.10) - (3180 \pm 40)/T$$

p-chloroaniline

$$\log P\,(\mathrm{kPa}) = (11.20 \pm 0.20) - (4170 \pm 60)/T$$

where the values reported for each compound are the weighed ($1/\sigma$) averages of the data for each individual experimental run. The overall errors are estimated.

A comparison of our results with those reported in literature (see Figures 2, 3, and 4) shows a substantial agreement among the absolute vapor pressures in the covered temperature range but a disagreement as concerns the vaporization enthalpy values of *m*- and *p*-chloroaniline. In particular, our enthalpy value of *m*-chloroaniline is lower by about 30 kJ mol^{-1} than that selected by Ohe, while the value obtained for the *p*-chloroaniline is higher by about 20 kJ mol^{-1}. The agreement between the results obtained by two different methods leads to the conclusion that our vapor pressure values are more reliable than the very few data found in literature, and, therefore, we believe that the vaporization enthalpies of *o*-, *m*-, and *p*-chloroaniline, $\Delta H°_{298}$ = 57.5, 60.9, and 79.0 kJ mol^{-1}, respectively, are most reliable and that the associated overall uncertainties in all cases should not exceed 5 kJ mol^{-1}. It is surprising that *p*-chloroaniline shows a vaporization enthalpy value higher than those of *m*- and *o*-chloroaniline while the corresponding ΔH values (in kJ mol^{-1}, referred to *o*-, *m*-, *p*- structures respectively) of similar chloro compounds reported in literature, as chlorophenol (46, 53, 57) (*1*), chlorotoluene (38, 46, 44) (*1*), chlorobenzoyl chloride (53, 50, 52) (*15*), and chloroethylbenzene (46, 45, 44) (*15*) resemble very closely.

Registry No. *o*-Chloroaniline, 95-51-2; *m*-chloroaniline, 108-42-9; *p*-chloroaniline, 106-47-8.

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Thermodynamics of the Dissociation of Protonated Tris(hydroxymethyl)aminomethane in 25 and 50 wt % 2-Propanol from 5 to 45 °C

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The dissociation constants of the isoelectric dissociation of the protonated base tris(hydroxymethyl)aminomethane (TrisH$^+$) has been measured in 25 and 50 wt % 2-propanol as a function of temperature. The usual associated thermodynamic functions are calculated from the results. The effect of the added solvent (2-propanol) on the thermodynamics of this dissociation is compared to that of other alcohols for which comparable data is available. In this work the pK_a of TrisH$^+$ in the two solvent systems studied could be fitted to the following equations: 25 wt %(2-propanol), pK_a = 2546.3/T − 0.16244 − 0.0019578T; 50 wt %(2-propanol), pK_a = 3346.0/T − 6.7042 + 0.010640T with a standard deviation of fit to the line of 0.002 at the temperatures used.

Introduction

Studies of acid-base behavior in mixed solvents generally include several acids which are easy to purify and work with and which represent fundamental acid or base "types". One of these is the protonated form of tris(hydroxymethyl)aminomethane which is readily available in a highly pure crystalline form and whose pK_a (near 8 at 25 °C) makes it a useful buffer for medical and marine chemical studies.

The effects of water and organic solvent mixtures on the dissociation of trisH$^+$ are of even greater interest because of the presence of three hydroxyl groups, which give the base a potentially high degree of hydrogen bonding.

The dissociation of TrisH$^+$ has been studied in a number of solvent/water mixtures (*1*-*8*). The pK_a of TrisH$^+$ is always

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observed to decrease on addition of a second component to water. In those cases where the organic solvent is less acidic (i.e., more basic) than water this decrease in pK_a of TrisH$^+$ is expected. Alcohols, however, are more acidic than water and on this basis an increase in pK_a would be expected. The measured pK_a of TrisH$^+$ in 50 mass % methanol/water is 7.84 (*3*).

In this work we will show that addition of 25 and 50 wt % 2-propanol leads to a lowering of pK_a of TrisH$^+$ of 0.29 and 0.39. The dissociation of TrisH$^+$ must therefore be ascribed to forces other than the acidity or basicity of the solvent.

In the hope of shedding some light on the interactions involved we have calculated the thermodynamic functions for the transfer of the TrisH$^+$ dissociation from water to the mixed solvents 25 and 50 wt % 2-propanol. These functions are related by

$$\Delta G^\circ(\text{diss}) = (RT \ln 10)(\text{p}_\text{s}K_\text{a} - \text{p}_\text{w}K_\text{a}) = \Delta G_\text{t}^\circ(\text{Tris}) + \Delta G_\text{t}^\circ(\text{HCl}) - \Delta G_\text{t}^\circ(\text{TrisH}^+)$$

where ΔG_t°(i) is the standard Gibbs energy change in the transfer process i(H_2O) → i(s).

Experimental Section

Hydrochloric acid stock solutions were prepared from reagent grade concentrated HCl diluted to 50% and distilled twice (keeping only the middle third of the distillate). Dilution of this acid solution produced other stock solutions, whose concentrations were verified by titration with NaOH solution, which had been standardized with potassium hydrogen phthalate (primary standard grade).

The water used for all solutions was distilled twice, deionized, and freed of carbon dioxide by boiling followed by cooling and storage in a carbon dioxide free atmosphere. The conductivity of the water was always less than 1 μS.

2-Propanol was obtained from Aldrich (99% pure, Spectrograde) and distilled once in glass, collecting the middle fraction.

Tris used was obtained from Sigma Chemical Co. (99–99.5% Sigma 7-9) or U.S. Biochemical Corp. (buffer grade). The commercial product was recrystallized twice from 75–80% methanol/water.

Potassium hydrogen phthalate used to standardize the NaOH solutions was primary standard grade (100.01% pure) obtained from Thorn Smith and used as received.

Silver oxide for the Ag/AgCl electrodes was prepared by mixing sodium hydroxide solution with a silver nitrate solution as described by Bates (*9*). Hydrogen electrodes used were of platinum foil freshly covered with platinum black from a solution of chloroplatinic acid containing lead (*9*). Silver chloride electrodes were the thermoelectrolytic type again prepared by the method described by Bates.

Solutions were prepared by dissolving a weighed amount of Tris in water, adding HCl solution to equal one-half the moles of Tris, and then adding the amount of 2-propanol to make a solution with the desired 2-propanol/water weight percent.

The cells used were all glass without any liquid junction of the type originally described by Gary, Bates, and Robinson (*10*). The solutions were purged of oxygen and the cells rinsed and filled as described previously (*11*). The cells were placed in a water bath whose temperature was monitored with a Digitec series HT5810 quartz thermometer (to ∓0.01 °C). Cell potentials were measured with a Fluke Model 8800A digital voltmeter.

Solution densities were measured using a 25-mL Guy-Lussac pycnometer. Solvent dielectric constants were measured with a Balsbaugh Model 2TN50 conductivity cell having a cell constant of approximately 0.001. A Janz-McIntyre ac bridge (*12*) was used. These measurements were carried out by S. David Klein (*13*).

Methods and Results

The solutions of TrisH$^+$ and Tris in the 2-propanol solvents were used to construct a cell which can be represented as

$$\text{Pt;H}_2\text{(g,1 atm)}\|\text{TrisHCl}(m),\text{Tris}(m) \text{ in } 50\% \text{ (or } 25\%) \text{ 2-propanol}\|\text{AgCl;Ag} \quad (\text{I})$$

If the potential of this cell is measured at a series of solution ionic strengths (i.e., (m)) then the results can be treated according to the procedure of Harned and Ehlers (*14*) to give a series of apparent p$K_a{}'$ values as a function of ionic strength

$$\text{p}K_\text{a}{}' = \frac{(E - E^\circ)F}{(RT \ln 10)} + \log m - \frac{2AI^{1/2}}{(1 + Ba^\circ I^{1/2})} \qquad (1)$$

where E is the cell emf, A and B are the Debye–Hückel constants for the solvent used, and a is an adjustable ion-size parameter.

Other authors have found (*15*) that as long as I is kept less than 0.1 mol/kg one can usually find a linear function relating p$K_a{}'$ to I by choosing the proper value for a^0. The proper value of a^0 is considered to be that which gives the minimum standard deviation for linear regression.

The pK_a values derived in this way were fitted to the equation

$$\text{p}K_\text{a} = A/T + B + CT \qquad (2)$$

and the thermodynamic functions ΔG°, ΔH°, ΔS°, and ΔCp calculated from the normal thermodynamic relationships for the dissociation process TrisH$^+$ ↔ Tris + H$^+$.

The values of E° for the Ag/AgCl electrode in the solvent mixtures, the values for density, and the Debye–Hückel constants A and B have all been recently published by this laboratory (*16*). The emfs of cell I (corrected to 1 atm of H_2 gas) for both solvent mixtures as a function of temperature and TrisH$^+$ molality are given in Tables I and II, respectively. Table III lists the constants A, B, and C for eq 2 derived from the calculated values for pK(TrisH$^+$) at 25 and 50 wt % 2-propanol as a function of temperature. The values of the coefficients for the same equation fitted to the data of Bates and Hetzer (*17*) for pK(TrisH$^+$) in pure water are also shown for the sake of comparison.

The constants in Table III were used to calculate values for ΔG°, ΔH°, and ΔS° for the dissociation TrisH$^+$ ↔ Tris + H$^+$ from the usual thermodynamic relationships.

Discussion

Values of pK_a obtained for different compositions of mixed water/alcohol solvents show that at 50% composition the methoxyethanol solvents have the same effect on the dissociation of TrisH$^+$ as pure water, indicating that the mixed solvents have more or less the same basic nature. The 2-propanol solvent in a 50% mixture produced a more basic character than pure water. Mixtures of 50% methanol and 25% 1-propanol (with water) show the same effect for the dissociation of TrisH$^+$, both having a more basic nature than pure water (see Table IV).

Adding the first amount of a new molecule to water changes the highly ordered solvent structure and causes a large change of enthalpy for the dissociation process. Increasing the percentage of the alcohol in the mixture does not lead to a major change in the enthalpy of the dissociation process (see Table V). The transfer thermodynamic functions listed in Table VI show that at 25 wt % of propanol there is an increase in energy. This increase indicates that it requires less energy to

Table I. Corrected Emf Values for the Cell Pt;H_2(g,1 atm)||TrisHCl(*m*1), Tris(*m*2) in 25 wt % 2-Propanol/H_2O||AgCl;Ag[a]

	temp, °C								
*m*1, *m*2	5	10	15	20	25	30	35	40	45
0.912 2104, 0.912 123	0.7540	0.7523	0.7504	0.7480	0.7446	0.7411	0.7392	0.7362	0.7331
0.818 373, 0.818 373	0.7559	0.7542	0.7524	0.7501	0.7468	0.7427	0.7405	0.7379	0.7350
0.734 145, 0.733 998	0.7577	0.7501	0.7543	0.7513	0.7473	0.7432	0.7419	0.7401	0.7369
0.628 296, 0.628 170	0.7603	0.7587	0.7570	0.7541	0.7406	0.7469	0.7445	0.7415	0.7380
0.539 9719, 0.539 988	0.7627	0.7611	0.7593	0.7574	0.7545	0.7509	0.7484	0.7457	0.7428
0.507 1465, 0.507 239	0.7642	0.7628	0.7611	0.7591	0.7562	0.7525	0.7498	0.7470	0.7458
0.450 026, 0.450 193	0.7659	0.7644	0.7627	0.7608	0.7589	0.7543	0.7508	0.7478	0.7442
0.359 0664, 0.359 164	0.7704	0.7689	0.7670	0.7649	0.7611	0.7580	0.7550	0.7523	0.7489
0.270 6370, 0.270 703	0.7753	0.7740	0.7724	0.7705	0.7658	0.7629	0.7603	0.7587	0.7559
0.172 0496, 0.172 080	0.7844	0.7834	0.7823	0.7805	0.7775	0.7756	0.7734	0.7709	0.7679

[a] Emf values in volts. All potentials have an experimental uncertainty of +0.0002 V.

Table II. Corrected Emf Values for the Cell Pt;H_2(g,1 atm)||TrisHCl(*m*1), Tris(*m*2) in 50 wt % 2-Propanol/H_2O||AgCl;Ag[a]

	temp, °C								
*m*1, *m*2	5	10	15	20	25	30	35	40	45
0.019 235, 0.019 240	0.758 37	0.756 14	0.753 60	0.751 80	0.749 00	0.746 32	0.742 46	0.739 04	0.735 68
0.024 112, 0.024 113	0.754 27	0.752 04	0.749 50	0.747 58	0.744 74	0.742 02	0.738 16	0.734 64	0.731 28
0.033 764, 0.033 782	0.748 35	0.746 18	0.743 43	0.741 39	0.738 56	0.735 77	0.731 76	0.728 41	0.725 02
0.038 624, 0.038 678	0.746 05	0.743 81	0.741 15	0.739 05	0.736 22	0.733 43	0.729 24	0.726 08	0.722 61
0.043 394, 0.043 420	0.744 10	0.741 91	0.739 30	0.737 05	0.734 26	0.731 44	0.729 23	0.723 78	0.720 21
0.048 316, 0.048 348	0.743 28	0.740 19	0.737 47	0.735 18	0.732 36	0.729 52	0.725 29	0.721 79	0.718 50
0.060 215, 0.060 211	0.738 65	0.736 36	0.733 86	0.731 41	0.728 62	0.725 69	0.721 38	0.717 84	0.714 38
0.070 293, 0.070 294	0.736 35	0.734 00	0.731 36	0.728 87	0.726 02	0.722 99	0.718 78	0.715 24	0.711 68
0.080 410, 0.080 412	0.733 95	0.732 06	0.729 26	0.727 71	0.723 82	0.720 69	0.716 58	0.713 04	0.709 58
0.090 526, 0.090 522	0.732 15	0.730 10	0.727 36	0.724 81	0.721 82	0.718 79	0.714 58	0.710 94	0.707 68

[a] Emf values in volts. All potentials have an experimental uncertainty of +0.00005 V.

Table III. Values of the Coefficients *A*, *B*, and *C* of the Equation $pK_a = A/T + B + CT$ for $TrisH^+$ as a Function of Weight Percent of 2-Propanol

wt % 2-propanol	*A*	*B*	*C*
0[a]	2835.1	-2.6225	0.003 976
25	2546.3	-0.162436	-0.001 95778
50	3346	-6.7042	0.010 64

[a] Bates and Hetzer (*17*).

Table IV. pK_a ($TrisH^+$) as a Function of Solvent Composition and Temperature

T, °C	H_2O[a]	25% 2-propanol[b]	50% 2-propanol[b]	50% methanol[c]	50% 2-methoxyethanol[d]
5	8.6774	8.45 (0.005)[e]	8.297 (0.003)		8.53
10	8.5164	8.28 (0.002)	8.123 (0.006)	8.273	8.39
15	8.3616	8.12 (0.013)	7.969 (0.006)	8.113	8.24
20	8.2138	7.96 (0.001)	7.811 (0.003)	7.962	8.11
25	8.0746	7.80 (0.019)	7.712 (0.003)	7.818	7.97
30	7.9344	7.65 (0.001)	7.575 (0.002)	7.681	7.84
35	7.8031	7.50 (0.020)	7.430 (0.002)	7.550	7.73
40	7.6772	7.37 (0.003)	7.314 (0.002)	7.426	7.60
45	7.5543	7.22 (0.010)	7.198 (0.002)		7.48

[a] Bates and Hetzer (*17*). [b] This work. [c] Reference 6. [d] Reference 18. [e] Numbers in parentheses are standard deviations of the extrapolated p*K* values.

Table V. Values of Standard Thermodynamic Functions for the Dissociation $TrisH^+ \leftrightarrow Tris + H^+$ in 2-Propanol/Water Mixtures (at 25 °C) Derived from the Coefficients in Table III

wt % 2-propanol	$\Delta G°$(diss)	$\Delta H°$(diss)	$\Delta S°$(diss)
0[a]	11.012	11.355	1.151
25	10.630	12.447	6.082
50	10.495	10.984	1.638

[a] From data of Bates and Hetzer (*17*); units are kcal/mol ($\Delta G°$ and $\Delta H°$) and kcal/(mol K) ($\Delta S°$).

Table VI. Values[a] of the Standard Thermodynamic Functions for the Transfer of TrisHCl from Pure Water to 2-Propanol/Water Mixtures (at 25 °C)

wt % 2-propanol	$\Delta G_t°$	$\Delta H_t°$	$\Delta S_t°$
25	0.38	1.85	5
50	-0.517	-0.371	0.487

[a] Units are kcal/mol ($\Delta G_t°$ and $\Delta H_t°$) and kcal/(mol K) ($\Delta S_t°$).

dissociate $TrisH^+$ in the mixed solvent than it does in pure water, once again indicating the stronger basic character of the propanol/water mixture in comparison to water. As the composition of the propanol increases to 50%, the values of the enthalpy of transfer changes to a negative value (-0.371 kcal/mol).

In general, small amounts of alcohols when mixed with water do not cause drastic changes in the dissociation patterns of $TrisH^+$. The alcohol/water mixtures are well-behaved for potentiometric studies using Pt;H_2 electrodes in that they do not increase the solubility of the Ag/AgCl electrode. Because of this, these electrodes show quite stable potentials in solutions of these solvents.

Registry No. Tris, 77-86-1.

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Isobaric Vapor–Liquid Equilibria for Systems Consisting of 2,4-Dimethylpentane, Cyclohexane, and *tert*-Butyl Alcohol

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Vapor–liquid equilibrium data for 2,4-dimethylpentane–cyclohexane binary and 2,4-dimethylpentane–cyclohexane–*tert*-butyl alcohol ternary systems are measured at 760 mmHg pressure. The binary data are correlated by the Wilson equation. The ternary experimental vapor-phase compositions have been compared with those calculated from the binary constants determined for 2,4-dimethylpentane–cyclohexane system and reported earlier for 2,4-dimethylpentane–*tert*-butyl alcohol and cyclohexane–*tert*-butyl alcohol systems. The agreement between the two sets of data shows the ability of the Wilson equation to predict the ternary compositions from binary data alone for this system.

Introduction

2,4-Dimethylpentane (DMP) and cyclohexane (CH) are close-boiling components and form a minimum-boiling azeotrope (*1*) at 80.2 °C and therefore cannot be separated by ordinary distillation. Isobaric binary vapor–liquid equilibrium (VLE) data on these hydrocarbons and *tert*-butyl alcohol (TBA) have been reported earlier (*2*). With a view to try TBA as a suitable separating agent for these hydrocarbons, isobaric VLE have been determined for DMP–CH binary and DMP–CH–TBA ternary at 760 ± 1 mmHg. The binary data on DMP–CH have been correlated with a two-parameter Wilson equation. The binary Wilson parameters estimated for DMP–CH system and reported (*2*) earlier for the other two binaries have been used to calculate the ternary compositions by using a ternary form of the Wilson equation.

Experimental Section

***Materials*.** Both the hydrocarbons were of minimum 99% purity, procured from Phillips, U.S.A., and used as such without further purification. *tert*-Butyl alcohol obtained from BDH, India, was dried and purified by fractional distillation with high reflux ratio in an Oldershaw column. The heart cut was collected discarding the first 10% and last 15%. The physical properties reported (*2*) earlier correspond to 99% purity.

***Apparatus*.** The VLE studies for the binary and the ternary system were carried out in the modified Fowler–Norris (*3*) still with provision for liquid and vapor circulation. The reboiler, Cottrell pump, and the equilibrium chambers were thoroughly lagged to avoid condensation which facilitated proper separation of liquid and vapor in the equilibrium chamber. Equilibriated liquid and vapor samples were collected separately after 4 h and were analyzed by gas chromatography.

Table I. Isobaric VLE Data for 2,4-Dimethylpentane (1)–Cyclohexane (2) Systems

		Y_1		exptl		calcd	
temp, °C	X_1	exptl	calcd	γ_1	γ_2	γ_1	γ_2
80.67	0.040	0.046	0.042	1.144	0.992	1.047	1.000
80.60	0.095	0.105	0.099	1.102	0.993	1.041	1.000
80.50	0.157	0.168	0.162	1.070	0.994	1.034	1.001
80.38	0.254	0.266	0.260	1.051	0.995	1.026	1.004
80.31	0.331	0.340	0.336	1.033	0.999	1.020	1.006
80.25	0.398	0.404	0.401	1.022	1.004	1.016	1.008
80.22	0.430	0.435	0.432	1.020	1.006	1.014	1.010
80.20	0.471	0.471	0.472	1.009	1.016	1.012	1.011
80.22	0.581	0.577	0.580	1.001	1.025	1.007	1.016
80.27	0.685	0.679	0.683	0.998	1.033	1.004	1.022
80.35	0.797	0.791	0.795	0.997	1.042	1.001	1.029
80.42	0.895	0.888	0.893	0.995	1.077	1.000	1.035
80.46	0.950	0.945	0.949	0.996	1.109	1.000	1.039

Since the binary DMP–CH is a close-boiling system, the equilibrium boiling temperatures were repeatedly verified in an ebulliometer with the synthetic blends in the whole range of compositions by using a calibrated Beckmann thermometer. The temperatures were measured within ±0.01 °C. The accuracy of the chromatographic method used for analysis of the equilibrium phase was ±3.0%.

Results and Discussion

The VLE data on DMP–CH and DMP–CH–TBA are presented in Tables I and II, respectively. From these data the liquid-phase activity coefficients were calculated by using the following equation (*4*).

$$\gamma_i = \frac{PY_i}{P_i^0 X_i} Z_i \tag{1}$$

However, the values of vapor-phase imperfection, Z_i, were found to be almost equal to unity and as such was ignored in eq 1.

The pure component vapor pressures were calculated from the Antoine constants reported in the literature (*5–7*).

The values of activity coefficients calculated as above are presented in Table I. The data for binary DMP–CH system were tested for the thermodynamic consistency by Heringtons's (*8*) area method. The values of D and J for this system were 0.0364 and 1.010, respectively, which show that the data are consistent as the value of D is less than the value of J.