k_{ij}	binary interaction parameter in Soave's equation of state
k_{aij}^0, k_{aij}^1, k_{bij}^0, k_{bij}^1	binary interaction parameters in Mathias' equation of state
k_{ij}^*, k_{ij}'	binary interaction parameters in Skjold-Jorgensen equation of state
K	$=y/x$
n	number of experimental data
Q	objective function
R_i	response coefficient to component i
R_{ij}	ratio of chromatographic response coefficients, R_i/R_j
P	pressure, MPa
T	temperature, K
x	liquid mole fraction
y	vapor mole fraction
z	total composition

Subscripts

exptl	experimental property
calcd	calculated property
i, j	components i and j

Greek Letters

α_{ij}	binary interaction parameter in Skjold-Jorgensen equation of state
δ_{ij}	binary interaction parameter in Peng-Robinson equation of state
σ	standard deviation

Literature Cited

(1) Tsonopoulos, C.; Heidman, J. L. *Fluid Phase Equilib.* **1985**, *24*, 1.
(2) Legret, D.; Richon, D.; Renon, H. *Fluid Phase Equilib.* **1984**, *17*, 443.
(3) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.
(4) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
(5) Mathias, P. M. *Ind. Eng. Chem. Process Des. Dev.* **1983**, *22*, 385.
(6) Huron, M. J.; Vidal, J. *Fluid Phase Equilib.* **1979**, *3*, 255.
(7) Skjold-Jorgensen, S. *Fluid Phase Equilib.* **1984**, *16*, 317.
(8) Laugier, S.; Richon, D. *Rev. Sci. Instrum.* **1986**, *57*, 469.
(9) Figuière, P.; Hom, J. F.; Laugier, S.; Renon, H.; Richon, D.; Szwarc, H. *AIChE J.* **1980**, *26*, 872.
(10) Fontalba, F.; Richon, D.; Renon, H. *Rev. Sci. Instrum.* **1984**, *55*, 944.
(11) Valtz, A.; Laugier, S.; Richon, D. *Int. J. Refrig.* **1986**, *9*, 283.
(12) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. R. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1977.
(13) Ambrose, D. N.P.L. Report Chem/07 1980.

Received for review June 16, 1986. Accepted February 9, 1987.

Thermodynamic Acid Dissociation Constant of the Protonated Form of Tris(hydroxymethyl)aminomethane in Water + 50 Mass % 2-Methoxyethanol Solvent from 278.15 to 318.15 K

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Electromotive force methods and cells without liquid junction have been utilized to determine the acidic dissociation constant of protonated tris(hydroxymethyl)aminomethane (Tris) [2-amino-2-(hydroxymethyl)-1,3-propanediol] in water + 50 mass % 2-methoxyethanol at nine temperatures from 278.15 to 318.15 K. The change of the dissociation constant with temperature has been used to calculate the changes of enthalpy and entropy when the dissociation takes place in the standard state. Comparisons with earlier measurements in water + 0 mass % 2-methoxyethanol and in water + 80 mass % 2-methoxyethanol are presented. The thermodynamic quantities for the transfer from water to water + 50 mass % 2-methoxyethanol are derived. The dissociation process is isoelectric, and the solvent dielectric constant is relatively high (ϵ = 51.5 at 298.15 K); consequently, electrostatic charging effects are expected to be minimal, and the change in dissociation constant depends primarily on solute-solvent interactions. Equations showing the acidic dissociation constant as a function of temperature and solvent composition are presented.

Introduction

Tris(hydroxymethyl)aminomethane (Tris) is widely used in biochemical research for the preparation of buffers because of its low toxicity and pK near 8, which make it useful for pH control in the clinical range (*1*), biological systems (*2*), and seawater (*3*, *4*). Accurate measurements of the protonated Tris dissociation constant over a wide temperature range are desirable. The solvent effect on the acidic dissociation of $TrisH^+$ has been studied in aqueous mixtures of several organic constituents such as methanol (*5*, *6*), methanol–propylene glycol mixtures (*7*), 2-propanol (*8*), and N-methylacetamide (*9*), to mention some.

In 1938, Ruehle (*10*) recommended the use of 2-methoxyethanol (2-met) as an excellent solvent for potentiometric titrations. Later the apparent dissociation constants of a considerable number of weak acid systems were determined in the solvent mixture water + 80 mass % 2-methoxyethanol (*11*). This solvent medium was chosen to permit adequate solubility of a wide variety of organic compounds without encountering the appreciable ion association that occurs at very low dielectric constants. In 1970, Thun, Staples, and Bates (*12*) reported a determination of the standard emf ($E°$) of the cell without liquid junction

$$\mathrm{Pt/H_2(g,}\ P\mathrm{=101.325\ kPa)/HCl(}m\mathrm{)\ in\ water\ +\ 80\ mass\ \%\ 2\text{-}met/AgCl/Ag} \quad \text{(A)}$$

where m is molality, over the temperature range 283.15–325.15 K. Using these $E°$ values, Shanbhag, Vega, and Bates (*13*) determined the dissociation constants of acetic acid and $TrisH^+$ in the 80 mass % mixtures at the same range of temperature. The water + 80 mass % 2-methoxyethanol can be relatively volatile, especially for those experiments re-

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Table I. Standard Potential ($E°$) for the AgCl/Ag Electrode in the Cell Pt/H_2(g, P = 101.325 kPa)/HCl(m) in Water +80 Mass % 2-Methoxyethanol/AgCl, Debye–Hückel Constants A and B, Density (d), and Dielectric Constant (ϵ)

temp, K	$E°$, V	σ,[a] V × 10^{-3}	density, g mL^{-1}	ϵ	Debye–Hückel[b] A, $mol^{-1/2}$ $kg^{1/2}$	 B, cm^{-1} $mol^{-1/2}$ $kg^{1/2}$
278.15	0.2011	0.15	1.0206	57.42	0.91339	0.40199
283.15	0.1969	0.16	1.0166	55.97	0.92274	0.40276
288.15	0.1922	0.21	1.0130	54.52	0.93286	0.40384
293.15	0.1877	0.22	1.0106	53.07	0.94548	0.40533
298.15	0.1831	0.25	1.0058	51.61	0.95889	0.40659
303.15	0.1778	0.28	1.0036	50.16	0.97504	0.40856
308.15	0.1724	0.34	0.9991	48.71	0.99192	0.41027
313.15	0.1669	0.38	0.9946	47.26	1.01093	0.41227
318.15	0.1606	0.34	0.9927	45.81	1.03339	0.41502

[a] Standard deviation to the intercept ($E°$). [b] From eq 4 and 5.

quiring measurements over a long period of time. We report here the dissociation of $TrisH^+$ in water + 50 mass % 2-methoxyethanol mixture, in an effort to resolve that inconvenience.

Method

As in our previous study (*8*), a cell without liquid junction containing the hydrogen-gas electrode and a silver–silver chloride electrode

$$\mathrm{Pt/H_2(g,}P\mathrm{{=}101.325\ kPa)/Tris{\cdot}HCl(}m_1\mathrm{),Tris(}m_2\mathrm{)\ in\ water\ +\ 50\ mass\ \%\ 2\text{-}met/AgCl/Ag} \quad \mathrm{(B)}$$

where m is molality, was used. The standard emf ($E°$) of cell A has already been determined (*14*) from measurement of the emf of cells containing solutions of hydrochloric acid instead of Tris·HCl buffers.

Taking cell B as reversible to hydrogen and chloride ions, and the activity of the former in a given Tris·HCl buffer solution controlled by the equilibrium constant K_a for the dissociation process

$$\mathrm{TrisH^+} \leftrightarrow \mathrm{Tris} + \mathrm{H^+} \quad (1)$$

the emf E can be related to pK_a. The expression to calculate pK_a was

$$\mathrm{p}K_a = \frac{(E - E°)F}{RT \ln 10} + \log \frac{m_1^2\, \gamma_{\mathrm{TrisH^+}}\gamma_{\mathrm{Cl^-}}}{m_2\, \gamma_{\mathrm{Tris}}} \quad (2)$$

The activity coefficient term can be estimated by the Debye–Hückel formula. Taking $\log \gamma_{\mathrm{Tris}}$ as a linear function of ionic strength ($I = m_1$), eq 2 becomes

$$\mathrm{p}K_a' = \mathrm{p}K_a + \beta m_1 = \frac{(E - E°)F}{RT \ln 10} + \log \frac{m_1^2}{m_2} - \frac{2Am_1^{1/2}}{1 + Bam_1^{1/2}} \quad (3)$$

The Debye–Hückel constants A and B (molality scale) were derived from the measured density (d) and the estimated dielectric constants (ϵ) of the water + 50 mass % 2-methoxyethanol solvent by using the equations

$$A = (1.8246 \times 10^6) d^{1/2} (\epsilon T)^{-3/2} \quad (4)$$

$$B = 50.29 d^{1/2} (\epsilon T)^{-1/2} \quad (5)$$

where T is the thermodynamic temperature in kelvin. They are listed in Table I along with the values of $E°$, the density, and the dielectric constant of the solvent for the nine temperatures. A value of 0.43 nm for a (the ion size parameter) was chosen in order to minimize the curvature of the plots of pK_a as a function of m_1 for the linear regression analysis of the data. The true value of pK_a is the intercept at $m_1 = 0$.

Experimental Section

Details of the purification of the 2-methoxyethanol solvent and $TrisH^+$ buffers and the preparation of the platinized platinum electrodes and the silver–silver chloride electrodes of the thermal type have been given in our earlier papers (*8*, *14*). The cells were of all-glass construction and incorporated a saturator for the purified hydrogen gas before it entered the hydrogen electrode compartment. The cells were placed in a water bath whose temperatures was monitored with a Digitec series H-T5810 quartz thermometer (to ±0.01 K). Cell potentials were measured at the beginning, middle, and end of the series of temperatures with a Fluke Model 8800A digital voltmeter. On the average, the initial and final values at 298.15 K differed by 0.1 mV, confirming the stability of the cells.

Results

The emf data, corrected to 101.325 kPa partial pressure of hydrogen gas, are summarized in Table II for 19 $TrisH^+$ buffer solutions in water + 50 mass % 2-methoxyethanol at nine temperatures from 278.15 to 323.15 K. Values of pK_a' were calculated by using eq 3, and the method of least squares was used to determine the intercept pK_a and slope β for the best straight line relating pK_a' with m_1. The extrapolated values of pK_a', the standard deviation of the intercept σ, together with the calculated values of the pK_a from the equation preferred by Harned and Robinson (*15*)

$$\mathrm{p}K_a = A/T + B + CT \quad (6)$$

are listed in Table III.

The constants A, B, and C are obtained after fitting the experimental pK_a as a function of temperature with a computer program.

The change of pK_a of $TrisH^+$ with thermodynamic temperature T is expressed by the following equations:

for water from ref *1*

$$\mathrm{p}K_a = 0.298759 \times 10^4/T - 3.63116 + 0.564267 \times 10^{-2}T \quad (7)$$

for water + 50 mass % 2-methoxyethanol (this work)

$$\mathrm{p}K_a = 0.236223 \times 10^4/T - 0.0900411 + 0.473822 \times 10^{-3}T \quad (8)$$

for water + 80 mass % 2-methoxyethanol from ref *13*

$$\mathrm{p}K_a = 0.284951 \times 10^4/T - 14.8311 + 2.38076 \ln T \quad (9)$$

Figure 1 shows plots of pK_a in water +0, +50, and +80 mass % 2-methoxyethanol as a function of T. Figure 2 shows a plot of pK_a as a function of mass % 2-methoxyethanol at 283.15, 298.15, and 318.15 K.

The dissociation of $TrisH^+$ is an isoelectric process affected much less by the change in the dielectric constant of the solvent

Table II. Emf of the Cell Pt/H_2(g, P = 101.325 kPa)/$TrisH^+$(m) in Water + 50 Mass % 2-Methoxyethanol/AgCl/Ag

m, mol kg^{-1}		temp, K						
$TrisH^+$	Tris	278.15	283.15	288.15	293.15	298.15	303.15	308.15
0.004 72	0.004 61	0.8110	0.8090	0.8067	0.8044	0.8019	0.7991	0.7964
0.009 50	0.009 49	0.7935	0.7911	0.7887	0.7861	0.7834	0.7811	0.7782
0.014 64	0.014 91	0.7943	0.7811	0.7785	0.7760	0.7732	0.7695	0.7664
0.019 05	0.019 10	0.7801	0.7781	0.7754	0.7726	0.7697	0.7665	0.7637
0.022 61	0.022 66	0.7766	0.7739	0.7712	0.7634	0.7654		
0.024 13	0.024 11	0.7755	0.7732	0.7702	0.7674	0.7645	0.7611	
0.029 70	0.029 70	0.7728	0.7701	0.7673	0.7644	0.7615	0.7588	
0.032 83	0.032 96	0.7710	0.7684	0.7658	0.7629	0.7601	0.7571	0.7539
0.34 36	0.034 37	0.7679	0.7651		0.7601	0.7571	0.7531	0.7498
0.038 14	0.038 12	0.7665	0.7637	0.7607	0.7579	0.7548	0.7518	0.7480
0.046 24	0.046 25	0.7650	0.7621	0.7592	0.7560	0.7529	0.7498	0.7468
0.048 42	0.048 42	0.7629	0.7601	0.7572	0.7540	0.7511	0.7481	0.7448
0.054 57	0.054 52	0.7615	0.7584	0.7554	0.7524	0.7493	0.7465	0.7433
0.056 45	0.057 07				0.7506	0.7477	0.7437	
0.059 21	0.059 20	0.7591	0.7558	0.7530	0.7499	0.7469	0.7437	
0.066 90	0.067 09	0.7573	0.7543	0.7512	0.7481	0.7450	0.7415	0.7380
0.077 63	0.078 90	0.7560	0.7530	0.7502	0.7471	0.7439		
0.097 73	0.097 85	0.7514	0.7483	0.7453	0.7421	0.7388	0.7390	0.7324

Table III. Acid Dissociation Constants (pK_a) of $TrisH^+$ in Water + 50 Mass % 2-Methoxyethanol

temp, K	exptl pK_a	σ^a	calcd pK_a
278.15	8.53	0.01	8.53
283.15	8.39	0.01	8.39
288.15	8.24	0.01	8.24
293.15	8.11	0.01	8.11
298.15	7.97	0.01	7.97
303.15	7.84	0.01	7.85
308.15	7.73	0.01	7.72
313.15	7.60	0.01	7.60
318.15	7.48	0.01	7.48

[a] Standard deviation to the intercept (pK_a).

and more by the hydrogen-bonding capacity of the solvent. In water + 50 mass % 2-methoxyethanol at 298.15 K, the pK_a is 0.10 units lower than in water (8.08), but when the organic constituent of the solvent increases to +80 mass %, pK_a is 0.21 units higher.

Thermodynamic Properties of the Acidic Dissociation of $TrisH^+$

The relative partial molal enthalpy and entropy for the acidic dissociation of $TrisH^+$ are calculated by

$$\Delta G° = 2.303R(A + BT + CT^2) \qquad (10)$$

since

$$\Delta S° = -(\partial G°/\partial T)_p \qquad (11)$$

$$\Delta S° = -2.303R(B + 2CT) \qquad (12)$$

using

$$\Delta H° = \Delta G° + T\Delta S° \qquad (13)$$

and substituting eq 10 and 12 in eq 13

$$\Delta H° = 2.303R(A - CT^2) \qquad (14)$$

Values obtained from eq 10, 12, and 14 are listed in Table IV.

The difference $\Delta pK_a = p(_DK_a) - p(_WK_a)$ between the pK_a in water + 2-methoxyethanol (designated D) and in water (designated W) is a measure of the change in standard molar Gibbs energy $\Delta G°_t$(diss) for the transfer process

$$TrisH^+(D) + Tris(W) + H^+(W) = TrisH^+(W) + Tris(D) + H^+(D) \qquad (15)$$

The relationship is

$$\Delta G°_t(\text{diss}) = (RT \ln 10)\Delta pK_a \qquad (16)$$

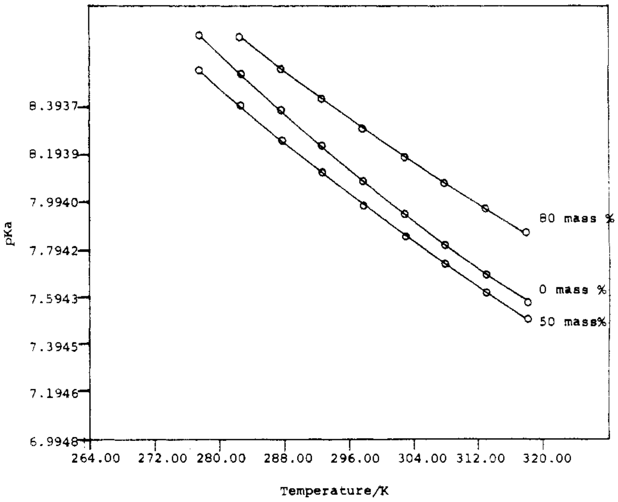

Figure 1. Thermodynamic dissociation constants of $TrisH^+$ as $F(T)$.

Table IV. Thermodynamic Functions for the Acid Dissociation of $TrisH^+$ in Water + 50 Mass % 2-Methoxyethanol

temp, K	$\Delta G°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} K^{-1}	$\Delta H°$, kcal mol^{-1}
278.15	10.86	−0.7942	10.64
283.15	10.87	−0.8159	10.64
288.15	10.87	−0.8376	10.63
293.15	10.88	−0.8593	10.62
298.15	10.88	−0.8810	10.62
303.15	10.88	−0.9027	10.61
308.15	10.89	−0.9244	10.60
313.15	10.89	−0.9460	10.60
318.15	10.90	−0.9677	10.59

Table V. Transfer Thermodynamic Functions for the Acid Dissociation Process of $TrisH^+$ in Water + 50 Mass % 2-Methoxyethanol

temp, K	$\Delta G°_t$, kcal mol^{-1}	$\Delta S°_t$, cal mol^{-1} K^{-1}	$\Delta H°_t$, cal mol^{-1}
278.15	−0.1844	−3.046	−1.0318
283.15	−0.1698	−2.810	−0.9654
288.15	−0.1563	−2.573	−0.8978
293.15	−0.1440	−2.337	−0.8291
298.15	−0.1329	−2.100	−0.7591
303.15	−0.1230	−1.864	−0.6880
308.15	−0.1143	−1.627	−0.6157
313.15	−0.1068	−1.391	−0.5423
318.15	−0.1004	−1.154	

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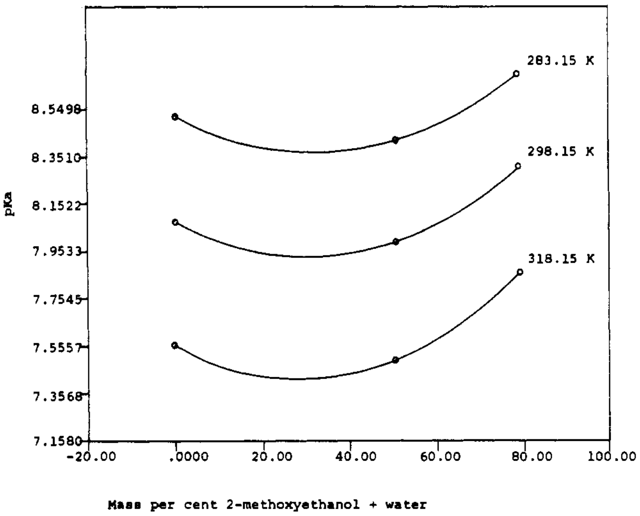

Figure 2. pK_a as a function of mass percent 2-methoxyethanol + water.

By use of the constants A, B, and C of the polynomials representing pK_a as a function of T, the standard molar thermodynamic quantities ($\Delta_t G^\circ{}_m$, $\Delta_t S^\circ{}_m$, $\Delta_t H^\circ{}_m$) for the transfer process

$$\mathrm{TrisH^+(W) = TrisH^+(D)} \tag{17}$$

were calculated and are listed in Table V.

Literature Cited

(1) Durst, R. A.; Staples, B. R. *Clin. Chem.* **1972**, *18*, 206.
(2) Bates, R. G. *Ann. N.Y. Acad. Sci.* **1961**, *92*, 341.
(3) Smith, W. H.; Hood, D. W. In *Recent Researches in the Fields of Hydrosphere, Atmosphere, and Nuclear Geochemistry*; Maruzen: Tokyo, 1964; p 185.
(4) Hetzer, H. B.; Bates, R. G. *J. Phys. Chem.* **1962**, *66*, 308.
(5) Woodhead, M.; Paabo, M.; Robinson, R. A.; Bates, R. G. *J. Res. Natl. Bur. Stand.* **1965**, *69A*, 263.
(6) Schindler, P.; Robinson, R. A.; Bates, R. G. *J. Res. Natl. Bur. Stand.* **1968**, *72A*, 141.
(7) Kundu, K. K.; De, A. L.; Das, M. N. *J. Chem. Soc., Dalton. Trans.* **1972**, *3*, 386.
(8) Vega, C. A.; Butler, R. A.; Perez, B.; Torres, C. *J. Chem. Eng. Data* **1985**, *30*, 376.
(9) Butler, R. A.; Vega, C. A.; Bates, R. G. *J. Solution Chem.* **1980**, *9*(4), 293.
(10) Ruehle, A. E. *Ind. Eng. Chem. Anal. Ed.* **1938**, *10*, 130.
(11) Simon, W. *Uber die Mikrobestimmung Sheinbaren Dissociations-konstanten in Nechtwasserigen Medien*; Tesis E.T.H., Juris-Verlag, Zurich, 1956.
(12) Thun, H. P.; Staples, B. R.; Bates, R. G. *J. Res. Natl. Bur. Stand.* **1970**, *74A*, 641.
(13) Shanbhag, P. M.; Vega, C. A.; Bates, R. G. *Bull. Soc. Chim. Belg.* **1981**, *90*(1), 1.
(14) Vega, C. A.; Delgado, S. *J. Chem. Eng. Data* **1986**, *31*, 74.

Received for review June 16, 1986. Accepted January 27, 1987.

Electrical Conductance of Liquid and Supercritical Water Evaluated from 0 °C and 0.1 MPa to High Temperatures and Pressures. Reduced-State Relationships

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The electrical conductance of liquid and supercritical water to high temperatures and pressures is represented by an equation that incorporates some earlier observed trends and a newly discovered reduced-state relationship presented here. Calculations with the equation are believed to describe within ±1 to ±5% the specific conductance of liquid water at temperatures from 0 to 374 °C and at pressures from saturated vapor pressure to 1000 MPa (10 kbar). For supercritical water at fluid densities from about 0.3 to 1 g cm^{-3} and at temperatures from 374 to 1000 °C, the uncertainties probably will increase from 5% to perhaps 15% at the highest temperatures and pressures. Some general conclusions on conductance behavior are presented based on the observations.

1. Introduction

Reliable values of the electrical conductance of pure water at high temperatures are useful as background conditions for estimating ionic impurities by conductance measurements in steam cycles as well as for their fundamental value. However, there are only a few experimental measurements on the electrical conductance of water at high temperatures. It is very difficult to obtain and keep absolutely pure water in a containment system at high temperatures and pressures, with the result that most experimentally determined conductances (of water) generally include also the conductances of the unremoved (or introduced by corrosion of the containment vessel) electrolyte impurities. The earlier careful measurements that have been made are mostly at temperatures between 0 and 25 °C at saturated vapor pressures, and these are reviewed in detail by Bignold, Brewer, and Hearn (*1*) and by Light (*2*).

There are, however, two carefully determined sets of experimental measurements: those of Bignold et al. (*1*) up to 271 °C and, recently, of Light up to 70 °C (*2*). Although limited to liquid water under saturated vapor, these two sets provide essentially the only reasonably accurate, directly obtained values for comparing with calculated values at temperatures much above 25 °C by any equations that might be developed.

The best procedure to obtain the conductance of water is by an indirect method that applies (i) the extent of ionization of water as expressed by its ion product (K_w) and (ii) the limiting ionic conductances of the hydrogen ion [$\lambda_0(\mathrm{H^+})$] and the hydroxide ion [$\lambda_0(\mathrm{OH^-})$]. If these or their estimated values are available at a given temperature and pressure (or density), then the specific conductance of water can be calculated without assumptions. Its accuracy will depend upon the accuracy of the values of K_w, $\lambda_0(\mathrm{H^+})$, and $\lambda_0(\mathrm{OH^-})$ used in the calculation. An equation providing values of K_w as a function of temperature from 0 to 1000 °C and pressures up to 1000 MPa is available elsewhere as an International Association for the Properties of Steam (IAPS) standard (*3*). The problem then is to obtain

0021-9568/87/1732-0221$01.50/0