(2) Aminabhavi, T. M.; Manjeshwar, L. S.; Balundgi, R. H.; Halligudi, S. B. *Indian J. Chem.* **1988**, *27A*, 303.
(3) Aminabhavi, T. M.; Manjeshwar, L. S.; Halligudi, S. B.; Balundgi, R. H. *Indian J. Chem.* **1989**, *28A*, 217.
(4) McAllister, R. A. *AIChE J.* **1960**, *6*, 427.
(5) Heric, E. L. *J. Chem. Eng. Data* **1966**, *11*, 66.
(6) Heric, E. L.; Brewer, J. G. *J. Chem. Eng. Data* **1967**, *12*, 574.
(7) Auslaender, G. *Br. Chem. Eng.* **1964**, *9*, 610.
(8) Riddick, J. A.; Bunger, W. B. *Organic Solvents*, 3rd ed.; Techniques in Chemistry, Vol. II; Wiley-Interscience: New York, 1970.
(9) Gokavi, G. S.; Raju, J. R.; Aminabhavi, T. M.; Balundgi, R. H.; Muddapur, M. V. *J. Chem. Eng. Data* **1986**, *31*, 15.
(10) Aminabhavi, T. M. *J. Chem. Eng. Data* **1987**, *32*, 406.
(11) Aminabhavi, T. M.; Munk, P. *Macromolecules* **1979**, *12*, 1186.
(12) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941.

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Thermodynamics of the Dissociation of Boric Acid in Potassium Chloride Solutions from 273.15 to 318.15 K

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Electromotive force measurements have been made with the cell Pt|H_2(g, 101.325 kPa)|KCl (m_1),borax (m_2) |AgCl;Ag over the temperature range 273.15–318.15 K and at five ionic strengths from 0.1 to 1.5 mol·kg^{-1}. The results have been used to calculate the stoichiometric (ionic medium) dissociation constant for boric acid in potassium chloride media.

Introduction

A recent study by Felmy and Weare (*1*) has shown that the chemistry of boron in naturally occurring aqueous electrolyte solutions can be represented by a combination of chemical equilibria and ionic interactions. In the course of this work, Felmy and Weare identified the need for measurements that could be used to obtain parameters for the interaction of potassium ion with orthoborate ion.

The best technique available to characterize the extent of this interaction uses the cell

$$\mathrm{Pt|H_2(g,\ 101.325\ kPa)|KCl}\ (m_1),\mathrm{borax}\ (m_2)\mathrm{|AgCl;Ag} \qquad \text{(A)}$$

to make measurements at various concentrations of potassium chloride and of borax. This cell is similar to that used by Owen and King (*2*) to measure the dissociation constant of boric acid in sodium chloride media. I report here measurements on cell A over a range of ionic strengths and temperatures and at three values of m_2. In addition, these values have been used to calculate the ionic medium (stoichiometric) dissociation constants of boric acid in potassium chloride media. The interpretation of these results in terms of ionic interactions—Pitzer coefficients (*3*)—has been performed for the electromotive forces (emfs) at 298.15 K and reported elsewhere (*1*); further work extending the modeling of aqueous boron systems to a range of temperatures is currently in progress.

Experimental Section

The chemicals used in this work were of high purity. The borax was recrystallized from water, taking care to keep the temperature below 328 K (*4*). It was stored in a hygrostat (over a saturated solution of sucrose and sodium chloride) for a number of weeks to ensure the correct extent of hydration ($Na_2B_4O_7\cdot10H_2O$) and then assayed by titration with hydrochloric acid, which in turn had been assayed as silver chloride (*5*). The potassium chloride (reagent grade) was recrystallized from water and dried at 575 K. All dilutions were carried out with ultrafiltered, deionized water (Milli-Q); all apparent masses were corrected to mass. The details of electrode preparation and cell design have been given elsewhere, together with a description of relevant experimental procedures (*6*). All emfs reported have been corrected to a hydrogen fugacity of 101.325 kPa (see footnote to Table I) and have been adjusted so that the values of E° correspond to those published by Bates and Bower (*7*). This was achieved by subtracting the difference

$$\Delta E^\circ/\mathrm{V} = [E^\circ(298.15\ \mathrm{K})/\mathrm{V}] - 0.22240 \qquad (1)$$

from each emf reading. E°(298.15 K) was measured with cells containing hydrochloric acid at 0.01 mol·kg^{-1} (*6*, *8*, *9*). Typically ΔE° amounted to 0.000 02 V.

Results

Table I contains values for the corrected emfs of cell A from 273.15 to 318.15 K at potassium chloride concentrations of approximately 0.1, 0.3, 0.5, 1.0, and 1.5 mol·kg^{-1} and at borax molalities of 0.005, 0.01, and 0.015 mol·kg^{-1}. The exact values of m_1 and m_2 corresponding to these nominal values are given in the table.

When the salt borax is dissolved in water, it yields an equimolal mixture comprised of boric acid and sodium orthoborate:

$$\mathrm{Na_2B_4O_7\cdot10H_2O = 2B(OH)_3 + 2Na^+ + 2B(OH)_4^- + 5H_2O} \qquad (2)$$

The charge-balance expression for the solution is thus

$$m(\mathrm{K^+}) + m(\mathrm{Na^+}) + m(\mathrm{H^+}) = m(\mathrm{Cl^-}) + m(\mathrm{B(OH)_4^-}) + m(\mathrm{OH^-}) \qquad (3)$$

and hence

$$m(\mathrm{B(OH)_4^-}) = 2m_2 - m(\mathrm{OH^-}) + m(\mathrm{H^+}) \qquad (4)$$

where m_2 is the molality of borax. The mass balance equation for boron is

$$4m_2 = m(\mathrm{B(OH)_3}) + m(\mathrm{B(OH)_4^-}) \qquad (5)$$

Substituting in eq 4 gives

$$m(\mathrm{B(OH)_3}) = 2m_2 + m(\mathrm{OH^-}) - m(\mathrm{H^+}) \qquad (6)$$

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Table I. Emfs of Cell A in Volts, Corrected to $p°$ = 101.325 kPa and $E°$(298.15 K) = 0.222 40 V^{a,b}

273.15 K	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
I = 0.100 mol·kg^{-1}									
m_1 = 0.090 02 mol·kg^{-1}						m_2 = 0.005 00 mol·kg^{-1}			
0.808 31	0.812 67	0.817 08	0.821 54	0.826 04	0.830 56	0.835 09	0.839 61	0.844 13	0.848 62
0.808 30	0.812 66	0.817 08	0.821 56	0.826 07	0.830 60	0.835 13	0.839 65	0.844 18	0.848 68
0.808 36	0.812 73	0.817 13	0.821 69	0.826 07	0.830 59	0.835 10	0.839 60	0.844 13	0.848 61
m_1 = 0.080 40 mol·kg^{-1}						m_2 = 0.010 01 mol·kg^{-1}			
0.811 63	0.815 97	0.820 39	0.824 87	0.829 39	0.833 85	0.838 52	0.843 10	0.847 68	0.852 25
0.811 63	0.815 98	0.820 39	0.824 87	0.829 39	0.833 94	0.838 51	0.843 08	0.847 66	0.852 22
0.811 64	0.815 98	0.820 40	0.824 89	0.829 41	0.833 97	0.838 54	0.843 11	0.847 68	0.852 24
m_1 = 0.070 05 mol·kg^{-1}						m_2 = 0.015 01 mol·kg^{-1}			
0.815 46	0.819 78	0.824 19	0.828 68	0.833 22	0.837 79	0.842 40	0.847 00	0.851 61	0.856 21
0.815 50	0.819 81	0.824 23	0.828 72	0.833 26	0.837 83	0.842 44	0.847 03	0.851 65	0.856 28
0.815 49	0.819 81	0.824 22	0.828 72	0.833 25	0.837 83	0.842 43	0.847 03	0.851 65	0.856 27
I = 0.300 mol·kg^{-1}									
m_1 = 0.290 08 mol·kg^{-1}						m_2 = 0.005 00 mol·kg^{-1}			
0.780 20	0.784 09	0.788 03	0.792 01	0.796 02	0.800 06	0.804 09	0.808 09	0.812 07	
0.780 20	0.784 09	0.788 01	0.791 99	0.795 99	0.800 03	0.804 06	0.808 07	0.812 07	0.816 03
0.780 20	0.784 09	0.788 03	0.792 01	0.796 02	0.800 07	0.804 10	0.808 13	0.812 13	0.816 12
m_1 = 0.280 15 mol·kg^{-1}						m_2 = 0.010 01 mol·kg^{-1}			
0.781 67	0.785 51	0.789 41	0.793 37	0.797 36	0.801 40	0.805 44	0.809 48	0.813 51	0.817 52
0.781 67	0.785 51	0.789 42	0.793 38	0.797 38	0.801 42	0.805 47	0.809 50	0.813 54	0.817 56
0.781 67	0.785 50	0.789 41	0.793 38	0.797 38	0.801 42	0.805 47	0.809 50	0.813 54	0.817 57
m_1 = 0.270 22 mol·kg^{-1}						m_2 = 0.015 01 mol·kg^{-1}			
0.783 14	0.786 94	0.790 80	0.794 73	0.798 70	0.802 72	0.806 75	0.810 77	0.814 83	0.818 87
0.783 24	0.787 03	0.790 89	0.794 81	0.798 78	0.802 80	0.806 84	0.810 85	0.814 89	0.818 92
0.783 24	0.787 03	0.790 89	0.794 82	0.798 79	0.802 81	0.806 84	0.810 87	0.814 92	0.818 94
I = 0.500 mol·kg^{-1}									
m_1 = 0.490 12 mol·kg^{-1}						m_2 = 0.005 00 mol·kg^{-1}			
0.767 33	0.771 01	0.774 75	0.778 53	0.782 32	0.786 13	0.789 93	0.793 72	0.797 50	0.801 25
0.767 38	0.771 05	0.774 80	0.778 58	0.782 38	0.786 18	0.789 98	0.793 78	0.797 55	0.801 29
0.767 33	0.771 02	0.774 77	0.778 55	0.782 35	0.786 16	0.789 96	0.793 75	0.797 54	0.801 29
m_1 = 0.480 25 mol·kg^{-1}						m_2 = 0.010 01 mol·kg^{-1}			
0.768 67	0.772 29	0.775 98	0.779 71	0.783 46	0.787 25	0.791 06	0.794 84	0.798 63	0.802 42
0.768 59	0.772 21	0.775 91	0.779 64	0.783 41	0.787 21	0.791 02	0.794 81	0.798 61	0.802 40
0.768 61	0.772 22	0.775 92	0.779 65	0.783 42	0.787 23	0.791 04	0.794 83	0.798 62	0.802 40
m_1 = 0.470 36 mol·kg^{-1}						m_2 = 0.015 01 mol·kg^{-1}			
0.769 84	0.773 39	0.777 04	0.780 73	0.784 47	0.788 24	0.792 04	0.795 80	0.799 58	0.803 35
0.769 85	0.773 40	0.777 04	0.780 73	0.784 47	0.788 24	0.792 03	0.795 80	0.799 59	0.803 38
0.769 89	0.773 45	0.777 09	0.780 78	0.784 52	0.788 28	0.792 06	0.795 83	0.799 62	0.803 40
I = 1.000 mol·kg^{-1}									
m_1 = 0.990 21 mol·kg^{-1}						m_2 = 0.005 00 mol·kg^{-1}			
0.750 29	0.753 72	0.757 16	0.760 64	0.764 14	0.767 63	0.771 12	0.774 57	0.778 02	0.781 44
0.750 29	0.753 71	0.757 16	0.760 63	0.764 13	0.767 61	0.771 07	0.774 50	0.777 92	0.781 27
0.750 33	0.753 75	0.757 19	0.760 66	0.764 16	0.767 64	0.771 14	0.774 59	0.778 05	0.781 47
m_1 = 0.980 85 mol·kg^{-1}						m_2 = 0.010 01 mol·kg^{-1}			
0.750 93	0.754 34	0.757 74	0.761 16	0.764 65	0.768 10	0.771 57	0.775 03	0.778 51	0.781 96
0.750 86	0.754 25	0.757 66	0.761 10	0.764 58	0.768 05	0.771 51	0.774 97	0.778 43	0.781 86
0.750 97	0.754 34	0.757 73	0.761 18	0.764 66	0.768 13	0.771 59	0.775 04	0.778 50	0.781 93
m_1 = 0.970 79 mol·kg^{-1}						m_2 = 0.015 01 mol·kg^{-1}			
0.751 93	0.755 23	0.758 59	0.761 97	0.765 39	0.768 84	0.772 28	0.775 74	0.779 18	0.782 60
0.751 95	0.755 24	0.758 60	0.761 98	0.765 41	0.768 85	0.772 29	0.775 75	0.779 19	0.782 61
0.751 89	0.755 18	0.758 55	0.761 94	0.765 36	0.768 80	0.772 24	0.775 69	0.779 13	0.782 55
I = 1.500 mol·kg^{-1}									
m_1 = 1.490 37 mol·kg^{-1}						m_2 = 0.005 00 mol·kg^{-1}			
0.739 76	0.743 03	0.746 29	0.749 55	0.752 80	0.756 04	0.759 26	0.762 50	0.765 72	
0.739 86	0.743 11	0.746 37	0.749 64	0.752 92	0.756 18	0.759 43	0.762 66	0.765 87	0.769 03
0.739 76	0.743 28	0.746 54	0.749 82	0.753 09	0.756 37	0.759 62	0.762 86	0.766 09	0.769 24
m_1 = 1.493 58 mol·kg^{-1}						m_2 = 0.005 01 mol·kg^{-1}			
0.740 01	0.743 24	0.746 49	0.749 76	0.753 03	0.756 30	0.759 54	0.762 78	0.765 97	0.769 13
0.740 00	0.743 21	0.746 44	0.749 68	0.752 92	0.756 17	0.759 35	0.762 55	0.765 73	0.768 79
m_1 = 1.480 75 mol·kg^{-1}						m_2 = 0.010 00 mol·kg^{-1}			
0.740 70	0.743 89	0.747 09	0.750 32	0.753 55	0.756 78	0.760 00	0.763 20	0.766 40	0.769 54
0.740 77	0.743 96	0.747 17	0.750 41	0.753 66	0.756 91	0.760 15	0.763 39	0.766 62	0.769 83

Table I (Continued)

273.15 K	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K
m_1 = 1.484 18 mol·kg^{-1}					m_2 = 0.010 03 mol·kg^{-1}				
0.740 75	0.743 92	0.747 13	0.750 36	0.753 60	0.756 85	0.760 08	0.763 32	0.766 50	0.769 62
0.740 68	0.743 86	0.747 06	0.750 28	0.753 50	0.756 75	0.759 95	0.763 18	0.766 36	0.769 55
m_1 = 1.474 56 mol·kg^{-1}					m_2 = 0.015 05 mol·kg^{-1}				
0.741 61	0.744 73	0.747 89	0.751 08	0.754 29	0.757 51	0.760 72	0.763 95	0.767 15	0.770 33
0.741 73	0.744 85	0.748 00	0.751 19	0.754 39	0.757 62	0.760 83	0.764 07	0.767 28	0.770 48

[a] The emf readings were corrected to p° = 101.325 kPa: $E(p^\circ) = E(\text{observed}) - (RT/2F)\ln\{f(H_2, g)/p^\circ\}$. The fugacity of hydrogen was approximated by the partial pressure $f(H_2, g) \approx p\,(\text{atm}) + 0.4\rho gh - p(H_2O)$, where p (atm) is the barometric pressure at the time and place of the experiment, the term $0.4\rho gh$ is an empirical bubbler depth correction ($\approx$0.2 kPa) (*10*), and $p(H_2O)$ is the vapor pressure of water in the solution. $p(H_2O)$ is calculated from $p(H_2O) = p^*(H_2O)\exp(-0.018\phi\sum_B m_B/m^\circ)$, where $p^*(H_2O)$ is the vapor pressure of pure water (*11*), ϕ is the osmotic coefficient, $\sum_B m_B$ is the total concentration of dissolved species, and m° = 1 mol·kg^{-1}. [b] Gaps in the table indicate that values have been omitted because the cell potential was drifting unacceptably.

The buffer ratio is thus almost unity, requiring only a slight correction:

$$\frac{m(B(OH)_3)}{m(B(OH)_4^-)} = \frac{2m_2 + \{m(OH^-) - m(H^+)\}}{2m_2 - \{m(OH^-) - m(H^+)\}} \qquad (7)$$

$m(OH^-)$ was calculated from the relationship

$$m(OH^-) = K_W/m(H^+) \qquad (8)$$

where K_W is the ionization constant of water in the solution

$$K_W = m(H^+)\,m(OH^-) = K_W^\circ a(H_2O)/\gamma(H^+)\,\gamma(OH^-) \qquad (9)$$

Values of K_W and of the term $\gamma(H^+)\,\gamma(OH^-)/a(H_2O)$ were obtained by interpolating the relevant table from the monograph by Harned and Owen (*12*). An approximate value of $m(H^+)$, calculated from the cell emf

$$m(H^+) = \exp\left(\frac{E^\circ - E}{(RT/F)} - \ln\left\{\frac{m(Cl^-)}{m^\circ}\right\} - 2\ln\gamma_\pm^{tr}(HCl)\right) \qquad (10)$$

suffices to estimate the correction term $m(OH^-) - m(H^+)$ in eq 7. Values for $\gamma_\pm^{tr}(HCl)$, the "trace" activity coefficient of HCl in the solution, were estimated from the data of Macaskill et al. (*13*).

The emf of cell A is given by

$$E = E^\circ - (RT/F)\ln\{m(H^+)\,m(Cl^-)/(m^\circ)^2\} - (2RT/F)\ln\gamma_\pm(HCl) \qquad (11)$$

where m° = 1 mol·kg^{-1} and $\gamma_\pm(HCl)$ is the activity coefficient of HCl in the solution. The molality product for the reaction

$$B(OH)_3 + H_2O = H^+ + B(OH)_4^- \qquad (12)$$

given by the expression

$$Q_m = \frac{m(H^+)\,m(B(OH)_4^-)}{m(B(OH)_3)} = K^\circ\frac{a(H_2O)\,\gamma(B(OH)_3)}{\gamma(H^+)\,\gamma(B(OH)_4^-)} \qquad (13)$$

where K° is the standard equilibrium constant for reaction 12 in pure water, is combined with eq 11:

$$\ln\left\{\frac{Q_m}{m^\circ}\right\} = \frac{E^\circ - E}{(RT/F)} - \ln\left\{\frac{m(Cl^-)}{m^\circ}\right\} - \ln\left\{\frac{m(B(OH)_3)}{m(B(OH)_4^-)}\right\} - 2\ln\gamma_\pm(HCl) \qquad (14)$$

Table II. Values of ln $\{K_m/m^\circ\}$, Measured at Various Temperatures and Ionic Strengths[a]

	I/(mol·kg^{-1})				
T/K	0.10	0.30	0.50	1.00	1.50
273.15	-21.377_2	-21.196_1	-21.118_8	-21.099_3	-21.123_2
278.15	-21.228_9	-21.049_8	-20.973_4	-20.956_5	-20.986_1
283.15	-21.094_7	-20.916_9	-20.843_1	-20.826_5	-20.854_1
288.15	-20.974_7	-20.794_7	-20.722_6	-20.706_6	-20.734_4
293.15	-20.861_8	-20.683_9	-20.612_5	-20.597_0	-20.622_1
298.15	-20.760_1	-20.583_3	-20.510_2	-20.491_7	-20.517_0
303.15	-20.669_1	-20.489_0	-20.416_0	-20.397_3	-20.418_5
308.15	-20.580_9	-20.401_6	-20.330_7	-20.309_6	-20.325_6
313.15	-20.507_1	-20.320_9	-20.248_5	-20.226_4	-20.242_4
318.15	-20.436_6	-20.248_8	-20.174_9	-20.148_7	-20.164_2

[a] The fourth decimal place (the subscripted digit) is retained to maintain the full precision of the data through subsequent arithmetical manipulations. It does not reflect the probable accuracy of the data.

Equation 14 can then be used to determine the limiting value of ln $\{Q_m/m^\circ\}$ at zero molality of borax, ln $\{K_m/m^\circ\}$:

$$\ln\left\{\frac{K_m}{m^\circ}\right\} = \lim_{m_2 \to 0\ \text{mol·kg}^{-1}}\left[\frac{E^\circ - E}{(RT/F)} - \ln\left\{\frac{m(Cl^-)}{m^\circ}\right\} - \ln\left\{\frac{m(B(OH)_3)}{m(B(OH)_4^-)}\right\}\right] \qquad (15)$$

A plot of the term in brackets against m_2 is linear in accordance with Harned's rule and has an intercept of ln $\{K_m/m^\circ\}$. On the whole the assumption of a linear plot is excellent (see Figure 1); however, the fits for the values at I = 1.0 mol·kg^{-1} and at I = 1.5 mol·kg^{-1} are somewhat worse than at other ionic strengths. The results obtained for ln $\{K_m/m^\circ\}$ at the various temperatures and ionic strengths are given in Table II.

These results for ln $\{K_m/m^\circ\}$, the ionic medium equilibrium constant for reaction 12, have been fitted to the following function, which is widely used to represent the temperature dependence of dissociation constants:

$$\ln\{K_m/m^\circ\} = (-8966.9 + 2502.0(I/m^\circ)^{1/2} + 350.0(I/m^\circ) - 181.0(I/m^\circ)^{3/2})(K/T) + (148.0248 - 59.009(I/m^\circ)^{1/2} - 3.077(I/m^\circ) + 1.138(I/m^\circ)^{3/2}) + (-24.4344 + 9.2609(I/m^\circ)^{1/2})\ln(T/K) \qquad (16)$$

This expression represents the results in Table II with an imprecision of ±0.004 in ln $\{K_m/m^\circ\}$. Deviations from this equation are plotted in Figure 2. The parameters at I = 0 mol·kg^{-1} were published in ref 16 and allow a smooth extrapolation to the infinite dilution data for K° (*14*, *15*).

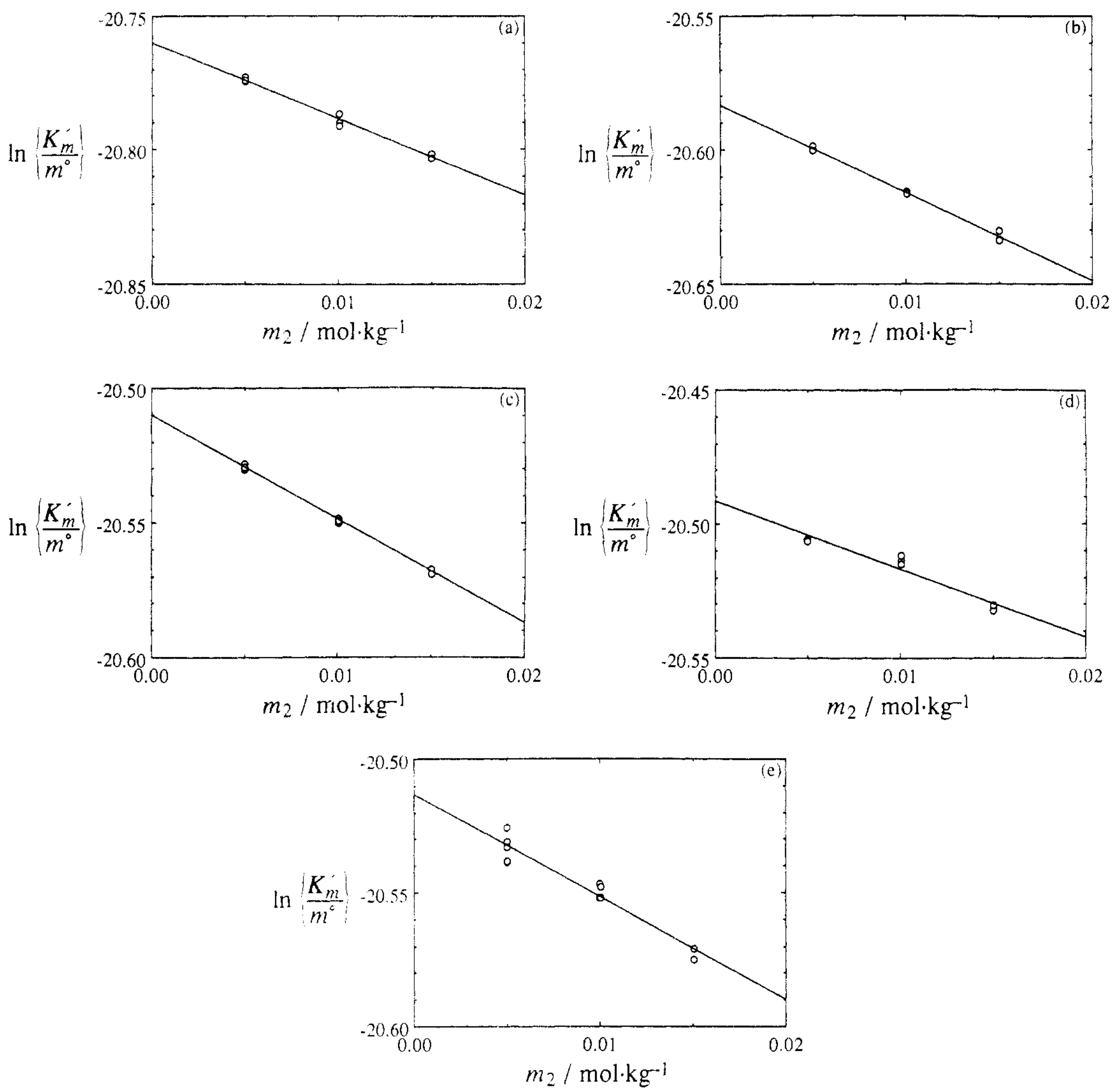

Figure 1. Plots of ln $\{K_m'/m^\circ\} = [(E^\circ - E)/(RT/F)] - \ln\{m(Cl^-)/m^\circ\} - \ln\{m(B(OH)_3)/m(B(OH)_4^-)\}$ against m_2, the molality of borax: (a) I = 0.100 mol·kg^{-1}; (b) I = 0.300 mol·kg^{-1}; (c) I = 0.500 mol·kg^{-1}; (d) I = 1.00 mol·kg^{-1}; (e) I = 1.50 mol·kg^{-1}.

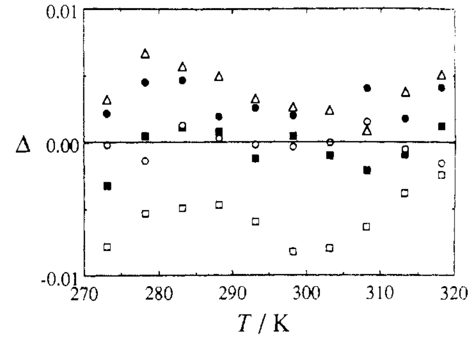

Figure 2. Deviations from eq 10 for the data of Table II plotted against temperature. $\Delta = \ln\{K_m^\circ/m^\circ\}_{exp} - \ln\{K_m^\circ/m^\circ\}_{eq\,10}$. Key: (●) I = 0.1 mol·kg^{-1}; (□) I = 0.3 mol·kg^{-1}; (△) I = 0.5 mol·kg^{-1}; (■) I = 1.0 mol·kg^{-1}; (○) I = 1.5 mol·kg^{-1}.

Although a limited number of measurements have been reported (*17*) by investigators using the cell

$$Pt|H_2(g,\ 101.325\ kPa)|KCl,B(OH)_3,KB(OH)_4|AgCl;Ag \qquad (B)$$

it is almost impossible to compare the two sets of measurements. The results reported here are much more extensive than those of ref 17 and seem to have a considerably higher precision. The overall accuracy of the results of Table II depends on a number of contributing factors such as the purity of salts, calibration of voltmeters, reproducibility of electrodes, etc. I believe the maximum inaccuracy of the various measurements to be of the order of ±0.15 mV (based on reproducibility between laboratories on other similar measurements), which is equivalent to an error of about ±0.006 in ln $\{K_m/m^\circ\}$. This is about 1.5 times the imprecision of the fit of eq 16 to the data.

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Literature Cited

(1) Felmy, A.; Weare, J. H. *Geochim. Cosmochim. Acta* **1986**, *86*, 2771.
(2) Owen, B. B.; King, E. J. *J. Am. Chem. Soc.* **1943**, *65*, 1612.
(3) Pitzer, K. S.; Kim, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 9701.
(4) Vogel, A. E. *A text book of quantitative inorganic analysis, including elementary instrumental analysis*, 3rd ed.; Longman: Birmingham, AL, 1961.
(5) Little, K. *Talanta* **1971**, *18*, 927.
(6) Dickson, A. G. *J. Chem. Thermodyn.* **1987**, *19*, 993.
(7) Bates, R. G.; Bower, V. E. *J. Res. Natl. Bur. Stand.* **1954**, *53*, 283.
(8) Bates, R. G.; Guggenheim, E. A.; Harned, H. S.; Ives, D. J. G.; Janz, G. J.; Monk, C. B.; Robinson, R. A.; Stokes, R. H.; Wynne-Jones, W. F. K. *J. Chem. Phys.* **1956**, *25*, 361.
(9) Bates, R. G.; Guggenheim, E. A.; Harned, H. S.; Ives, D. J. G.; Janz, G. J.; Monk, C. B.; Prue, J. E.; Robinson, R. A.; Stokes, R. H.; Wynne-Jones, W. F. K. *J. Chem. Phys.* **1957**, *26*, 222.
(10) Hills, G. J.; Ives, D. J. G. *J. Chem. Soc.* **1951**, 305.

J. Chem. Eng. Data 1990, 35, 257-260

(11) Ambrose, D.; Lawrenson, I. J. *J. Chem. Thermodyn.* **1972**, *4*, 755.
(12) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed.; Reinhold: New York, 1957.
(13) Macaskill, J. B.; Vega, C. A.; Bates, R. G. *J. Chem. Eng. Data* **1978**, *23*, 314.
(14) Owen, B. B. *J. Am. Chem. Soc.* **1934**, *56*, 1695.
(15) Manov, G. G.; DeLollis, N. J.; Acree, S. F. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1944**, *33*, 287.
(16) Millero, F. J. *Geochim. Cosmochim. Acta* **1979**, *43*, 1651.
(17) Simonson, J. M.; Roy, R. N.; Roy, L. N.; Johnson, D. A. *J. Solution Chem.* **1987**, *16*, 791.

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Distribution of a Complex Phenolic Mixture between Water and Supercritical Carbon Dioxide

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A complex phenolic mixture was successfully extracted from an aqueous solution by using near-critical and supercritical carbon dioxide, with and without entrainers. Experimental extractions were performed at 298 and 323 K at pressures up to 27.6 MPa to measure distribution coefficients. The Peng–Robinson equation of state with a recently published mixture combining rule quantitatively modeled the system and provided a qualitative prediction of the effect of adding a small amount of benzene as an entrainer.

Introduction

Recent attention has been given to supercritical extraction as a potential means of separating organic compounds from aqueous solutions. Phase equilibrium data and (to a limited extent) thermodynamic models have been reported in the literature for a variety of pure organic compounds distributed between water and a supercritical fluid. Many practical applications, however, involve processes for the extraction of multicomponent complex organic mixtures from water, such as applications in waste water treatment. Phase equilibrium behavior for such systems is quite complex, making experimental data and accurate thermodynamic models scarce. In addition, use of entrainers (or cosolvents) to increase the solvent power of supercritical fluids further complicates the phase behavior.

The objective of this study was to investigate the extraction of complex organic mixtures from water with supercritical fluids. This work is an extension of our study of the extraction of aqueous solutions of phenol, a model single-component compound. Therefore, as a model complex system, a multicomponent phenolic mixture (beechwood extract) was extracted from water by using near-critical and supercritical carbon dioxide (with and without entrainers). The fundamental thermodynamic parameter of interest for the extraction of organics from water is the distribution coefficient, defined as the ratio of the mole fraction of organic in the supercritical phase to the mole fraction of organic in the aqueous phase. We have measured the distribution coefficient of the phenolic mixture as a function of pressure and temperature. The Peng–Robinson equation of state (*1*) with a new mixing rule recently proposed by Panagiotopoulos and Reid (*2*) was used to model the pseudoternary system. In addition, the model was used to predict the effect of adding a small amount of an entrainer (benzene) to the system, and the predictions were verified experimentally.

The majority of the previous work in the area of high-pressure phase equilibria of supercritical fluids with aqueous solutions of organic compounds has focused on single-component oxygenated organic compounds in water. Kuk and Montagna (*3*) reported 2-propanol and ethanol extractions from water as a function of pressure and temperature using supercritical carbon dioxide. McHugh et al. (*4*) investigated the ethanol–water system but used ethane as the supercritical fluid for extraction. Paulaitis et al. (*5*) discussed some of the important phase equilibrium behavior of alcohol–water–supercritical fluid systems. Radosz (*6*) reports phase equilibrium data for the 2-propanol–water–carbon dioxide system. DeFillippi et al. (*7*) describes a process for removing ethanol from water, and Schultz and Randall (*8*) present a general correlation for the distribution coefficient of normal aliphatic alcohols as a function of carbon number. Systems other than alcohols, such as acetone (*9*) and aroma constituents of fruits and other foods (*8*), have also been investigated. In our previous work, we extracted phenol from water using near-critical and supercritical carbon dioxide and demonstrated the inadequacies of several cubic equations of state with conventional mixing rules (*10*). We also investigated the use of entrainers for aqueous systems and developed a method of qualitatively predicting a priori the effect of adding a small amount of cosolvent to our system (*11*). Benzene was found to be an appropriate entrainer for the extraction of phenol from water.

Table I. Composition and Estimated Properties of Phenolic Mixture

component	wt %	T_c,[a] K	P_c,[b] MPa	accentric
phenol	0.76	692.1	6.13	0.461
phenol, 2-methyl	10.1	692.4	5.03	0.480
phenol, 2-methoxy	77.5	700.2	4.91	0.566
phenol, 2,3-dimethyl	5.5	716.6	4.32	0.530
phenol, methoxy, methyl	5.08	708.7	4.06	0.598
unidentified	~1			
av mixture properties		700.3	4.85	0.556

[a] Joback's method (ref 2). [b] Lee–Kesler (ref 2).

Methods

An aqueous solution was prepared by vigorously mixing distilled water and a phenolic mixture (beechwood extract) purchased from Matheson, Coleman & Bell (lot no. 330, 344113). Table I contains the composition and estimated properties of the phenolic mixture. After the aqueous and organic phases separated, the saturated aqueous phase (8700 ppm total organic carbon) was isolated. Carbon dioxide was purchased from Conroe Welding Supplies with a purity of at least 99.8%. Standard benzene, purchased from Fisher Scientific Co. (lot no. 724430), and radioactively labeled ^{14}C benzene, from Sigma Chemical Co. (0.02 mCi/mmol), were added together to create

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