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KSO_4^-, $NaSO_4^-$, and $MgCl^+$ Ion Pairs in Aqueous Solutions up to 2000 atm[1]

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Electrical conductance data at 25°C for K_2SO_4, Na_2SO_4, and $MgCl_2$ solutions are reported at concentrations up to 0.01 eq-liter^{-1} and as a function of pressure up to 2000 atm. The molal dissociation constants are as follows:

$$KSO_4^-: \log K_m = (-1.02 + 1.6 \times 10^{-4}P - 2.5 \times 10^{-8}P^2) \pm 0.03$$
$$NaSO_4^-: \log K_m = (-1.02 + 9.6 \times 10^{-5}P - 4.3 \times 10^{-9}P^2) \pm 0.03$$
$$MgCl^+: \log K_m = (-0.64 + 1.1 \times 10^{-4}P - 1.7 \times 10^{-8}P^2) \pm 0.04$$

with P in atmospheres. These values cannot be chosen solely on the basis of minimizing errors in fitting conductance data to theoretical equations. For the values cited above, the Bjerrum distances for 1–2 (or 2–1) and 1–1 salts were used. However, the conductance fits for KSO_4^- and $NaSO_4^-$ were equally good for half-Bjerrum distances and resulted in higher dissociation constants. Ultrasonic data are used to argue in favor of the lower dissociation values derived by using Bjerrum distances. Our results for $MgCl^+$ disagree with those of Havel and Högfeldt.

KEY WORDS: K_2SO_4; Na_2SO_4; $MgCl_2$; aqueous solutions; pressure dependence; electrical conductance; sound absorption.

1. INTRODUCTION

Although the concentration of potassium in seawater is only about 2% that of sodium, it is considered one of the main constituents of sea water.(1,2) The dissociation constant of KSO_4^- and its pressure dependence are needed to determine the concentration of the various ions and ion pairs in seawater.(3) Inasmuch as our recent conductance work on the $NaSO_4^-$ ion pair(4) resulted in a lower dissociation constant than is usually cited in the literature, we

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decided to investigate the electrical conductance of aqueous solutions of K_2SO_4 over the same pressure and concentration range as we did for Na_2SO_4 solutions.

For K_2SO_4 we have analyzed the data at elevated pressures over a lower concentration region (10^{-4} to 10^{-2} eq-liter^{-1}) using a different procedure from that which we used for Na_2SO_4. For this reason we include a similar treatment of our earlier Na_2SO_4 data. The reexamination of the Na_2SO_4 work produced some changes from the earlier results. For Na_2SO_4 we obtain $K_m = 0.094$ at 1 atm, slightly higher than the 0.080 we reported earlier, and still well below the Jenkins and Monk(5) value of 0.19. For K_2SO_4 we obtain $K_m = 0.096$, in good agreement with the value of 0.11 obtained by Jenkins and Monk.

As in the earlier Na_2SO_4 work we use the Davies, Otter, and Prue(6) conductance equation and the Bjerrum distances for the 1–2 (or 2–1) and 1–1 ion pairs required in the mixed-salt treatment. In fitting the conductance data for K_2SO_4 and Na_2SO_4 to the conductance equation we find that the fit is as good for half-Bjerrum distances as for the full Bjerrum distance. Beronius(7) and others(8) have discussed the fact that equally good fits to conductance data can be obtained with substantially different distance parameters.

The nonuniqueness of the distance parameter for obtaining a best fit to conductance data with various conductance equations suggests that independent evidence for ion pairing needs to be incorporated for making decisions about the extent of association of various ions. The use of ultrasonic data in $MgSO_4$–NaCl mixtures was suggested in an earlier paper(9) to arrive at a value for the dissociation constant for $NaSO_4^-$. However, even with errors from neglecting ionic strength effects and $MgCl^+$ ion pairing, a value was obtained for K_m for $NaSO_4$ in rough agreement with the conductance data. Ion pairing in $MgCl^+$, for example, has not been considered in seawater up to 1974.(2) Havel and Högfeldt(10) recently reported evidence for possible formation of $MgCl^+$ ion pairs.

Kurtze and Tamm(11) showed that the addition of NaCl to $MgSO_4$ solutions reduced sound absorption. Since the absorption is proportional to the concentration of the $MgSO_4{}^\circ$ ion pairs, a reduction in absorption upon adding NaCl implies formation of other ion pairs, aside from the reduction due to increasing ionic strength.

For this reason, we also include conductance measurements of $MgCl_2$ solutions, from which we find evidence for ion-pair formation. Together with the Na_2SO_4 data, we calculate what the reduction in sound absorption should be as NaCl is added to a $MgSO_4$ solution. We relate the reduction in sound absorption to the formation of $NaSO_4^-$ and $MgCl^+$ ion pairs, and the extent of ion pairing is consistent with the use of the full-Bjerrum distances in the conductance and activity-coefficient equations we use.

2. METHOD OF CALCULATION

The dissociation reaction of the various salts discussed in this paper is given by the following:

$$KSO_4^- \rightleftharpoons K^+ + SO_4^{2-} \tag{1}$$

$$NaSO_4^- \rightleftharpoons Na^+ + SO_4^{2-} \tag{2}$$

$$MgCl^+ \rightleftharpoons Mg^{2+} + Cl^- \tag{3}$$

and the dissociation constant is given by

$$K_m = m(2 - \alpha)(1 - \alpha)f_{12}f_{21}/\alpha f_{11} \tag{4}$$

where m is the pressure-independent concentration in moles per kilogram H_2O, the molal concentration. At atmospheric pressure, the difference between molal and molar units is ignored. The ionic strength is then $I = C(1.5 - \alpha)$, where C is the usual concentration in equivalents per liter and α is the degree of association. At elevated pressures, C (corrected for density) is used in all calculations of equivalent conductance and ionic strength.

The degree of association α is determined from conductance measurements in the same manner as Jenkins and Monk.(5) Applying the mixture rule to the equivalent conductance of the solution, Jenkins and Monk obtained

$$\Lambda = 0.5\alpha\Lambda_{11} + (1 - \alpha)\Lambda_{12} \tag{5}$$

However, we use the Davies, Otter, and Prue conductance equations(6)

$$\Lambda_{11} = \Lambda_{11}^\circ - \{[2.801 \times 10^6 q_{11}/(\varepsilon T)^{3/2}(1 + \sqrt{q_{11}})]\Lambda_{11}^\circ/1 + (B\mathring{a}\sqrt{I/2}) + 82.5/\eta(\varepsilon T)\}\sqrt{I}/(1 + B\mathring{a}\sqrt{I}) \tag{6}$$

for the uni-univalent salts with $\mathring{a} = 3.57$ Å at 1 atm and $q_{11} = 1/2$ with $\Lambda_{11}^\circ = 113.3$, 90.0, and 101.8, respectively, for $\Lambda^\circ(KSO_4^-)$, $\Lambda^\circ(NaSO_4^-)$, and $\Lambda^\circ(MgCl^+)$. We have set Λ° for the ion pair to be 0.5 that of the divalent ion.

For the unsymmetrical ion pair we use the conductance equation

$$\Lambda_{12} = \Lambda_{12}^\circ - \{[5.601 \times 10^6 q_{12}/(\varepsilon T)^{3/2}(1 + \sqrt{q_{12}})]\Lambda_{12}^\circ/(1 + B\mathring{a}\sqrt{I/2}) + 123.75/\eta(\varepsilon T)^{1/2}\}\sqrt{I}/(1 + B\mathring{a}\sqrt{I}) \tag{7}$$

with $\mathring{a} = 7.14$ Å at 1 atm and $q_{12} = 2\Lambda_{12}^\circ/3[\Lambda_{12}^\circ + \Lambda_1^\circ]$, where Λ_1° is the value for the univalent ion.

For the activity coefficient of species i paired with species j, we use the equation

$$-\log f_{ij} = \frac{AZ_i^2\sqrt{I}}{1 + B\mathring{a}_{ij}\sqrt{I}} \tag{8}$$

where the $\mathring{a}_{ij}$ is the Bjerrum value for the distance parameter for the ion pair formed by species i with species j.

The properties of water as a function of pressure were given in the earlier paper(4) and the A and B parameters are those given by Robinson and Stokes.(12)

The volume change upon dissociation is calculated from the pressure dependence of the molal dissociation constant K_m as follows:

$$\partial \ln K_m/\partial p = -\Delta \bar{V}^\circ/RT \tag{9}$$

where $\Delta \bar{V}^\circ$ is the difference in partial molal volumes between the products and reactants.

3. EXPERIMENTAL RESULTS

The experimental work was done using the same methods as reported earlier.(4) A set of measurements over the whole pressure range generally took 9 h to complete. Readings at 1 atm the following day were within +0.1% of the reading at 1 atm at the beginning of the run. Heise pressure gauges, accurate to ±2 atm, were used.

The measurements are made in several cells(4) having cell constants appropriate for the concentrations. Solvent corrections, derived from several solvent-only pressure runs in each cell, ranged from about 0.5% at the lowest concentration to about 0.005% at the highest concentration.

Plots of Λ vs. $\sqrt{C}$ were used to obtain initial values for the pressure dependence of Λ_{12}°; we assume the same pressure dependence for Λ_{11}°. A binary search for K_m was used to find a minimum in σ_Λ at each pressure Upon finding a minimum, Λ_{12}° was varied slightly to further minimize σ_Λ, where

$$\sigma_\Lambda = \left[\sum_N (\Lambda_{\text{exp}} - \Lambda_{\text{calc}})^2/(N-2)\right]^{1/2} \tag{10}$$

The final Λ_{12}° values were generally within 0.1 conductance units of the graphically obtained values. We did not adjust Λ_{12}° when we used the half-Bjerrum distances.

The experimental data for equivalent conductance for K_2SO_4, Na_2SO_4, and $MgCl_2$ solutions are shown in Tables I, II, and III. Results obtained for σ_Λ, K_m, and ΔV° are also included in these tables for both (A) full-Bjerrum and (B) half-Bjerrum distance. The quadratic fit for the pressure dependence of log K_m yielded a smaller error than a linear one; no significant improvement in the fit was obtained with a cubic equation.

Table I. KSO_4^- Ion Pairs in Aqueous Solutions at Pressures up to 2000 atm

C, eq-liter^{-1}	Λ at various values of P								
	1 atm	250 atm	500 atm	750 atm	1000 atm	1250 atm	1500 atm	1750 atm	2000 atm
0.0000	153.30	154.30	154.75	154.90	154.78	154.50	154.07	153.30	152.50
0.0001141	151.20	152.25	152.70	152.91	152.81	152.50	152.05	151.35	150.60
0.0002034	150.51	151.55	152.00	152.21	152.10	151.80	151.35	150.65	149.90
0.0004308	149.19	150.20	150.67	150.96	150.90	150.57	150.18	149.49	148.70
0.0006412	148.32	149.32	149.83	150.06	150.00	149.69	149.42	148.72	147.95
0.0007794	147.76	148.80	149.24	149.64	149.60	149.25	148.88	148.20	147.40
0.0011098	146.70	147.70	148.25	148.55	148.50	148.30	147.91	147.20	146.51
0.0019756	144.55	145.54	146.10	146.50	146.51	146.20	145.89	145.19	144.55
0.004102	140.56	141.65	142.39	142.75	142.85	142.52	142.22	141.75	141.10
0.01001	134.10	135.32	135.97	136.48	136.74	136.52	136.24	135.87	135.34
(A) σ_Λ	0.11	0.12	0.08	0.05	0.05	0.08	0.07	0.05	0.05
(B) σ_Λ	0.10	0.11	0.07	0.05	0.05	0.07	0.07	0.04	0.05
(A) K_m	0.096	0.103	0.111	0.124	0.135	0.134	0.138	0.150	0.158
(B) K_m	0.149	0.164	0.185	0.219	0.254	0.243	0.252	0.291	0.316
(A) $\Delta\bar{V}$	−8.8	−8.1	−7.3	−6.6	−5.9	−5.2	−4.5	−3.8	−3.1
(B) $\Delta\bar{V}$	−13.1	−12.1	−11.0	−9.9	−8.9	−7.8	−6.7	−5.7	−4.6

(A) $\log K_m = -1.019 + 1.6 \times 10^{-4}P - 2.5 \times 10^{-8}P^2$ Std. error of estimate = 0.030

(B) $\log K_m = -0.083 + 2.3 \times 10^{-4}P - 3.8 \times 10^{-8}P^2$ Std. error of estimate = 0.057

(A) 7.14/3.57 Å spacing

(B) 3.57/1.79 Å spacing

Table II. $NaSO_4^-$ Ion Pairs in Aqueous Solutions at Pressures up to 2000 atm

	Λ at various values of *P*								
C, eq-liter^{-1}	1 atm	250 atm	500 atm	750 atm	1000 atm	1250 atm	1500 atm	1750 atm	2000 atm
0.0000	130.13	130.77	131.10	131.20	131.09	130.66	130.20	129.42	128.48
0.0002024	127.43	128.08	128.53	128.50	128.18	127.77	127.19	126.50	125.70
0.0004002	126.32	126.98	127.34	127.32	127.00	126.64	126.09	125.46	124.69
0.0006228	125.33	126.14	126.55	126.61	126.22	125.87	125.32	124.69	123.90
0.0008220	124.64	125.38	125.72	125.72	125.59	125.21	124.70	124.04	123.79
0.001018	124.04	124.78	125.21	125.28	125.12	124.78	124.28	123.64	122.89
0.002130	121.42	122.18	122.73	122.80	122.75	122.47	122.07	121.55	120.75
0.004038	118.31	119.02	119.62	119.75	119.73	119.60	119.10	118.64	117.91
0.01014	112.38	113.22	113.71	113.97	113.97	113.78	113.46	112.97	112.42
(A) σ_Λ	0.28	0.24	0.16	0.26	0.33	0.38	0.48	0.41	0.32
(B) σ_Λ	0.27	0.23	0.16	0.26	0.32	0.38	0.48	0.41	0.32
(A) K_m	0.094	0.101	0.111	0.114	0.120	0.125	0.125	0.135	0.149
(B) K_m	0.148	0.168	0.191	0.198	0.213	0.223	0.218	0.251	0.298
(A) $\Delta\bar{V}$	−5.4	−5.3	−5.2	−5.1	−5.0	−4.8	−4.7	−4.6	−4.5
(B) $\Delta\bar{V}$	−7.2	−7.2	−7.2	−7.2	−7.2	−7.2	−7.1	−7.1	−7.1

(A) $\log K_m = -1.017 + 9.6 \times 10^{-5}P - 4.3 \times 10^{-9}P^2$ Std. error of estimate = 0.030

(B) $\log K_m = -0.81 + 1.3 \times 10^{-4}P - 4.2 \times 10^{-10}P^2$ Std. error of estimate = 0.061

(A) 7.14/3.57 Å spacing

(B) 3.57/1.79 Å spacing

Table III. $MgCl^+$ Ion Pairs in Aqueous Solutions at Pressures up to 2000 atm

	Λ at various values of P								
C, eq-liter^{-1}	1 atm	250 atm	500 atm	750 atm	1000 atm	1250atm	1500 atm	1750 atm	2000 atm
0.0000	129.44	130.64	131.38	131.84	131.98	131.88	131.49	130.81	130.10
0.0002128	126.89	128.13	128.85	129.33	129.52	129.41	129.00	128.39	127.68
0.0005365	125.54	126.77	127.53	128.00	128.20	128.10	127.70	127.11	126.31
0.0008080	124.70	125.91	126.69	127.16	127.36	127.27	126.88	126.30	125.49
0.001006	124.15	125.35	126.13	126.62	126.80	126.72	126.35	125.77	124.99
0.001977	122.16	123.40	124.17	124.65	124.81	124.73	124.40	123.84	123.10
0.004021	119.22	120.46	121.24	121.73	121.90	121.82	121.53	121.01	120.47
0.009803	114.60	115.84	116.66	117.15	117.35	117.28	117.05	116.57	116.01
(A) σ_Λ	0.08	0.08	0.10	0.10	0.12	0.11	0.08	0.11	0.07
(B) σ_Λ	0.52	0.57	0.61	0.62	0.62	0.59	0.59	0.63	0.62
(A) K_m	0.220	0.242	0.264	0.273	0.280	0.274	0.286	0.314	0.320
(B) K_m	0.419	0.441	0.463	0.472	0.479	0.473	0.485	0.513	0.519
(A) $\Delta\bar{V}$	−5.9	−5.5	−5.0	−4.5	−4.0	−3.5	−3.1	−2.6	−2.1
(B) $\Delta\bar{V}$	−3.1	−2.9	−2.7	−2.5	−2.3	−2.1	−1.9	−1.7	−1.5

(A) $\log K_m = -0.64 + 1.05 \times 10^{-4}P - 1.70 \times 10^{-8}P^2$ Std. error of estimate = 0.039

(B) $\log K_m = -0.37 + 5.52 \times 10^{-5}P - 7.26 \times 10^{-9}P^2$ Std. error of estimate = 0.022

(A) 7.14/3.57 Å spacing

(B) 3.57/1.79 Å spacing

4. DISCUSSION OF RESULTS

We find the dissociation constants for KSO_4^- and $NaSO_4^-$ to be virtually the same, 0.096 and 0.094, respectively. The value for KSO_4^- agrees well with the Jenkins and Monk value of 0.11. However, when we treat the Jenkins and Monk data with our equations, we obtain a much lower value. Using Simpson's data(13) and our equations, we obtain essentially the same value as reported here.

Since the fit to the conductance data seems to be the same for KSO_4^- and $NaSO_4^-$ whether we use the full- or half-Bjerrum distance in our equations, we must support our choice of dissociation constants on other grounds.

As pointed out earlier, Kurtze and Tamm(11) showed that sound absorption A at 20°C in $MgSO_4$ solutions decreased upon addition of NaCl from an initial value A_0 as follows:

$$A/A_0 = [MgSO_4]/([MgSO_4] + f[NaCl]) \qquad (11)$$

From their work they found f to be 0.21 over a wide range of concentration ratios. The larger f is, the greater the reduction in $MgSO_4^\circ$ ion pairs due to formation of $NaSO_4^-$ and $MgCl^+$ ion pairs. Using the dissociation constants obtained with the full-Bjerrum distances, we find $f = 0.17$ at 25°C for the addition of 0.017 moles of NaCl to a 0.017 M $MgSO_4$ solution. The results are essentially the same whether we use 0.005 or 0.007 for the dissociation constant of $MgSO_4$. In these calculations for f, we use Eq. (8) to calculate the activity coefficients. For the half-Bjerrum distances we obtain a lower f value. The $MgSO_4$–NaCl sound absorption data, therefore, support the dissociation constants calculated with the full-Bjerrum distance and suggest even more association. Havel and Högfeldt find evidence for association of $MgCl^+$ in their work, but their $pK = -0.98$ for the molar association constant yields a value of 10 for the dissociation constant compared to our value of 0.22. We cannot account for such a large discrepancy. If the association were as low as Havel and Högfeldt indicate, $MgCl_2$ solutions would behave as nearly fully dissociated salts. The ratio of Λ_p to Λ_1 as a function of concentration would resemble that of NaCl and KCl, namely, that the ratio is independent of concentration.

Although the $MgSO_4$–NaCl sound absorption data yield an f value of 0.21, it should be mentioned that similar work in $MnSO_4$–NaCl solutions(11) yield $f = 0.08$, a substantial difference which bears further study. Both sets of acoustic experiments were performed at 20°C at a frequency of 100 kHz. At this frequency, sound absorption in $MnSO_4$ solution is a factor of 10 lower than in $MgSO_4$ solutions of the same concentration.

Reardon(14) chose $pK = 0.85$ for KSO_4^- and determined $pK = 0.82 \pm 0.05$ for $NaSO_4^-$. We agree with him in the sense that we obtain the same dissociation constant for the two salts. However, we would be in greater disagreement with the $MgSO_4$–NaCl acoustic data if our pK values were as low as his.

There may be deficiencies in our treatment of the data. However, the sound absorption work in $MgSO_4$–NaCl solutions suggests we are not in serious error.

To complement the Reardon work on monovalent sulfate ion pairs,(14) we are completing a conductimetric study of the same salts they measured. Since they conclude that there are substantial differences in pK values for the various salts, acoustic work with these salts would be especially worthwhile in evaluating results obtained by other techniques.

The $\Delta\bar{V}^\circ$ value we obtain here at 1 atm for Na_2SO_4 (-5.4 cm^3-mole^{-1}) is higher than the -8.3 cm^3-mole^{-1} value we obtained earlier(4) from higher concentration data only. This makes the disagreement with the data of Millero(15) and Kester and Pytkowicz(16) even greater than before.

One way to resolve the discrepancies in pressure effects (the different $\Delta\bar{V}^\circ$ values) would be to measure sound-absorption reduction due to addition of NaCl (or other alkali halides) at elevated pressures. The laser Raman spectroscopic technique used to study $MgSO_4$ ion pairing at elevated pressures(17) would be useful especially if it could be done at concentrations lower than 2 M.

In conclusion, we argue that our results for $NaSO_4^-$ and $MgCl^+$ ion pairing are supported by the work of Kurtze and Tamm. We feel that the nonuniqueness of the distance parameter in fitting conductance data to theory requires the use of independent techniques to determine ion pairing. The usefulness of the acoustic technique needs to be explored more fully.

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