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Solubility of Oxygen in Aqueous Solutions of KCl, K_2SO_4, and $CaCl_2$ as a Function of Concentration and Temperature

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The solubility of oxygen in equilibrium with air has been measured in aqueous solutions of KCl, K_2SO_4, and $CaCl_2$ from 5 to 45 °C with molalities from 0.1 mol·kg^{-1} to saturation. The solubilities have been fitted to a Setschenow type equation. The adjustable parameters of the Setschenow equation were determined by a least-squares fit of the data over the temperature range measured. The standard errors of the fits of the molality of O_2 are less than ±1.7 μmol·kg^{-1} for all the salts. The limiting values of the salting coefficient, k_S, for the solutions have been determined from the fits. The results were also examined using the Pitzer equation. The coefficients determined for K^+, Ca^{2+}, Cl^-, and SO_4^{2-} are in reasonable agreement with the tabulations of Clegg and Brimblecombe.

Introduction

In recent papers,[4−6] we have examined the solubility of oxygen in a number of salts that are the major components of natural waters at 25 °C and between 5 °C and 45 °C. These measurements have been examined using the Setschenow[1] equation

$$\ln\{m^0_{O_2}/m_{O_2}\} = \ln \gamma = k_S(m/\text{mol·kg}^{-1}) \qquad (1)$$

where $m^0_{O_2}$ and m_{O_2} are the solubilities in water and solution, respectively, γ is the activity coefficient of O_2, k_S is the molal salting coefficient, and m is the molality, mol·kg^{-1}, of the salt. For concentrated solutions, a second-degree function of m is needed to fit experimental measurements.[2−6] The activity coefficients of oxygen in various salt solutions have been examined using the Pitzer[7] equation

$$\ln \gamma_{O_2} = 2\sum\nolimits_c \lambda_{O_2c}(m_c/\text{mol·kg}^{-1}) + 2\sum\nolimits_a \lambda_{O_2a}(m_a/\text{mol·kg}^{-1}) + \sum\nolimits_c \sum\nolimits_a (m_c m_a/\text{mol}^2\text{·kg}^{-2})\zeta_{O_2ca} \qquad (2)$$

where λ_{O_2i} is a parameter that accounts for the interaction of O_2 with cations (c) and anions (a) and ζ_{O_2ca} accounts for interactions for O_2 with the cation and anion (c−a). In this paper, we present the measurement of the solubility of oxygen equilibrated with air in aqueous solutions of KCl, K_2SO_4, and $CaCl_2$ as a function of temperature (5 °C, 15 °C, 35 °C, and 45 °C) from 0.1 m to saturation.

Experimental Section

The salts used were reagent grade and used without further purification. The concentrations of the solutions were determined from density measurements made at 25 °C with a Mettler densimeter. The density equations were taken from the work of Pierrot and Millero.[8] The densimeter was calibrated using ion-exchanged water and seawater solutions of known salinity.[9] The densities of water and seawater were taken from the equation of state of seawater.[9]

The solubility of oxygen in the solutions was determined by equilibrating the solutions with air in a 2-L water-jacketed vessel controlled at a given temperature with a Neslabs constant-temperature bath. The solutions were stirred vigorously with a magnetic bar stirrer for 4 to 24 h from 15 to 45 °C and over 40 h for the 5 °C runs. At least two measurements were made at a given temperature. The solubilities have been corrected to 0.101 mPa from the pressures measured with a Setra pressure gauge to ±0.001 mPa. The concentrations of oxygen in the solutions were determined using the Winkler technique as modified by Carpenter.[10] The samples were collected in biological oxygen demand bottles of known volume. The oxygen in the sample was fixed by the addition of a basic solution of KI and $MnCl_2$. The $Mn(OH)_2$ formed a complex that stabilized the O_2. The concentration of O_2 in the sample was determined by titrating the sample with a standard solution of $Na_2S_2O_3$ after acidification. The end point was determined from a spectroscopic end point technique using a Metrohm Dosimat titrator controlled by a computer.[11] The temperatures were set and measured to ±0.01 with a Guiline Pt thermometer.

The reliability of the system has been demonstrated in our earlier studies[4,5] on water, seawater, and NaCl from 5 to 45 °C. The solubilities of O_2 in water and seawater were taken from the experimental measurements of Benson and Krause[12,13] as fitted by Garcia and Gordon[14] as follows:

$$\begin{aligned}\ln\{m_{O_2}/m^0\} = {} & 5.80871 + 3.20291\tau + 4.17887\tau^2 + 5.10006\tau^3 - (9.86643 \times 10^{-2})\tau^4 + 3.80369\tau^5 + \\ & S[-7.01577 \times 10^{-3} - (7.70028 \times 10^{-3})\tau - (1.13864 \times 10^{-2})\tau^2 - (9.51519 \times 10^{-3})\tau^3] - \\ & (2.75915 \times 10^{-7})S^2 \end{aligned} \qquad (3)$$

$\tau = (298.15 - t/°\text{C})/(273.15 - t/°\text{C})$, and S is the salinity in parts per thousand. The measured solubilities are thought to be reliable to ±3 μmol·kg^{-1}.

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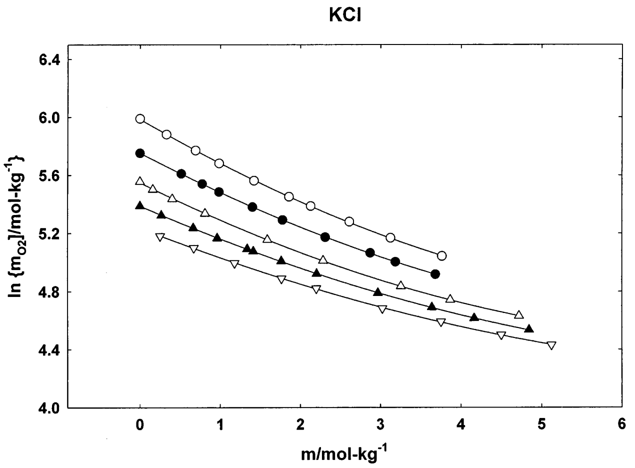

Figure 1. Values of $\ln\{m_{O_2}/\mathrm{mol{\cdot}kg^{-1}}\}$ as a function of molality in KCl at different temperatures. The lines are calculated from the least-squares fit of the measurements (eq 4).

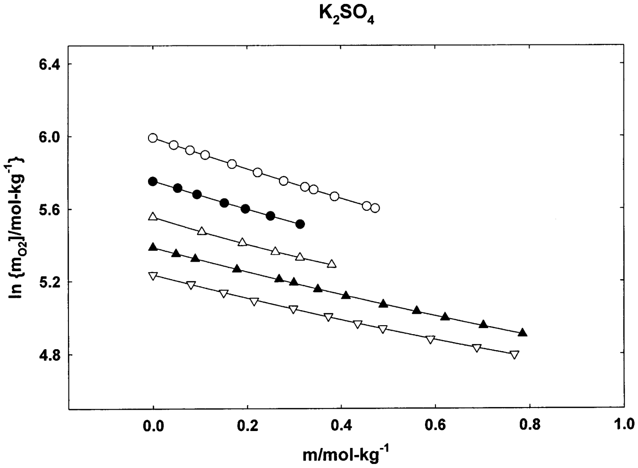

Figure 2. Values of $\ln\{m_{O_2}/\mathrm{mol{\cdot}kg^{-1}}\}$ as a function of molality in K_2SO_4 at different temperatures. The lines are calculated from the least-squares fit of the measurements (eq 4).

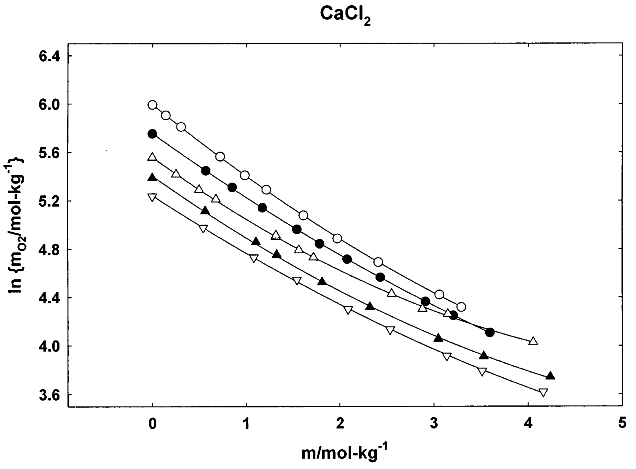

Figure 3. Values of $\ln\{m_{O_2}/\mathrm{mol{\cdot}kg^{-1}}\}$ as a function of molality in $CaCl_2$ at different temperatures. The lines are calculated from the least-squares fit of the measurements (eq 4).

Table 1. Solubility of Oxygen in KCl Solutions as a Function of Temperature and Molality

t/°C	m/mol·kg^{-1}	m_{O_2}/μmol·kg^{-1}	t/°C	m/mol·kg^{-1}	m_{O_2}/μmol·kg^{-1}
5.006	0.0000	399.9	35.006	0.0000	218.8
5.002	0.3292	358.4	35.003	0.2658	205.0
5.004	0.6919	321.1	34.997	0.6627	188.1
4.994	0.9859	293.5	35.001	0.9626	175.3
4.996	1.4214	260.5	34.999	1.3366	162.7
4.996	1.8580	233.1	34.998	1.4126	160.1
5.004	2.1298	218.6	34.998	1.7621	149.7
4.996	2.6128	196.4	35.007	2.2039	137.2
5.002	3.1264	175.7	34.994	2.9696	120.3
4.994	3.7671	154.9	34.999	3.6425	108.9
			35.003	4.1663	101.0
			35.002	4.8451	93.2
15.006	0.0000	315.1	45.003	0.0000	187.9
14.998	0.5139	273.2	44.991	0.2512	178.0
14.996	0.7748	254.7	45.001	0.6712	164.1
15.002	0.9828	241.1	45.000	1.1787	147.7
15.004	1.4013	217.3	44.999	1.7655	132.9
14.998	1.7768	198.7	45.006	2.2007	124.1
14.994	2.3113	176.6	45.005	3.0263	108.2
14.994	2.8731	158.4	45.004	3.7548	98.7
14.998	3.1875	149.0	45.001	4.5019	90.2
14.996	3.6849	136.7	44.997	5.1236	84.0

Table 2. Solubility of Oxygen in K_2SO_4 Solutions as a Function of Temperature and Molality

t/°C	m/mol·kg^{-1}	m_{O_2}/μmol·kg^{-1}	t/°C	m/mol·kg^{-1}	m_{O_2}/μmol·kg^{-1}
5.006	0.0000	399.9	35.006	0.0000	218.8
4.999	0.0445	384.3	35.004	0.0490	211.1
4.993	0.0791	373.6	34.996	0.0897	205.3
4.995	0.1113	363.8	34.992	0.1785	193.6
4.999	0.1684	346.0	34.998	0.2683	183.2
4.997	0.2230	330.1	34.998	0.2997	179.9
5.000	0.2786	315.0	34.994	0.3509	173.3
4.998	0.3238	304.9	35.001	0.4106	166.7
4.995	0.3425	300.5	35.002	0.4901	159.1
4.997	0.3870	289.1	34.996	0.5612	153.5
5.003	0.4554	274.2	34.996	0.6212	148.0
4.995	0.4733	270.9	35.002	0.7022	141.7
			34.998	0.7848	135.3
15.006	0.0000	315.1	45.003	0.0000	187.9
15.002	0.0529	303.5	44.996	0.0806	178.4
14.994	0.0940	293.0	45.003	0.1503	170.4
15.006	0.1520	279.5	44.995	0.2151	162.9
15.006	0.1967	270.5	44.997	0.2986	155.8
15.006	0.2503	260.0	44.997	0.3733	149.3
15.004	0.3134	248.4	45.004	0.4356	143.5
15.000	0.3558	241.4	44.992	0.4891	139.6
15.002	0.4089	232.0	45.003	0.5901	131.8
15.009	0.4903	219.1	45.001	0.6882	125.6
15.008	0.5320	213.5	45.005	0.7676	121.0
14.998	0.5661	209.5			

Results and Calculations

The solubilities of oxygen in aqueous solutions of KCl, K_2SO_4, and $CaCl_2$ as a function of the molality are given in Figures 1−3 and Tables 1−3. The measured values of $\ln\{m^0_{O_2}/m_{O_2}\}$ at each temperature were first fit to the equations of the form (m)

$$\ln\{m^0_{O_2}/m_{O_2}\} = \ln\gamma = A(m/\mathrm{mol{\cdot}kg^{-1}}) + B(m^2/\mathrm{mol^2{\cdot}kg^{-2}}) \quad (4)$$

where A and B are adjustable parameters given in Table 4 (along with the results at 25 °C).[4] The standard errors of all the fits are less than ±1.5 μmol·kg^{-1} over the entire temperature range. The limiting values of salting coefficient $k_S = A$ can be determined at various temperatures from the parameters given in Table 4. As shown in Table 5, our values of k_S are in reasonable agreement with the literature values determined from

$$k_S(M\nu_M X\nu_X) = 2\nu_M\lambda_{O_2M} + 2\nu_X\lambda_{O_2X} \quad (5)$$

Table 3. Solubility of Oxygen in $CaCl_2$ Solutions as a Function of Temperature and Molality

t / °C	m / mol·kg^{-1}	m_{O_2} / μmol·kg^{-1}	t / °C	m / mol·kg^{-1}	m_{O_2} / μmol·kg^{-1}
5.006	0.0000	399.9	35.006	0.0000	218.8
4.992	0.1428	366.5	35.002	0.5638	166.4
4.999	0.3046	333.3	35.005	1.1053	128.9
4.997	0.7219	260.8	35.001	1.3269	116.1
5.000	0.9862	223.4	34.998	1.8105	92.3
4.999	1.2154	198.4	34.998	2.3196	75.1
5.001	1.6116	160.4	34.998	3.0491	57.8
4.999	1.9738	132.5	34.996	3.5289	50.0
4.999	2.4106	109.0	35.003	4.2346	42.2
4.997	3.0598	83.2			
4.997	3.2931	75.1			
15.006	0.0000	315.1	45.003	0.0000	187.9
15.002	0.5700	232.0	44.995	0.5428	145.1
14.991	0.8517	202.2	44.997	1.0831	113.4
14.996	1.1727	171.0	44.993	1.5431	94.3
14.999	1.5426	143.0	44.993	2.0883	73.8
14.996	1.7838	126.9	44.997	2.5356	62.4
15.002	2.0790	111.7	44.998	3.1386	50.2
15.003	2.4315	96.1	45.000	3.5126	44.3
14.992	2.9117	78.7	45.002	4.1587	37.3
14.998	3.2081	70.1			
14.998	3.5955	60.8			

Table 4. Coefficients for Equation 4 at Various Temperatures for KCl, K_2SO_4, and $CaCl_2$ Solutions[a]

	t/°C	A	B	σ/μmol·kg^{-1}	m(max)/mol·kg^{-1}
KCl	5	0.3271	−0.020 43	0.82	3.8
	15	0.2900	−0.017 18	0.23	3.7
	25	0.2816	−0.018 28	1.16	4.7
	35	0.2387	−0.012 93	0.29	4.8
	45	0.2117	−0.010 89	0.54	5.1
K_2SO_4	5	0.8645	−0.090 70	0.55	0.47
	15	0.8064	−0.140 34	0.47	0.57
	25	0.8022	−0.251 47	0.57	0.76
	35	0.6939	−0.107 19	0.36	0.78
	45	0.6494	−0.103 61	0.46	0.77
$CaCl_2$	5	0.6221	−0.035 07	0.97	3.3
	15	0.5540	−0.026 61	0.58	3.6
	25	0.5537	−0.043 54	0.96	4.1
	35	0.5319	−0.033 02	1.47	4.2
	45	0.4935	−0.024 64	0.79	4.2

[a] These are nominal temperatures of the measurements. The results at 25 °C are taken from Millero et al. (ref 4).

Table 5. A Comparison of k_S, the Salting Coefficients, for KCl, K_2SO_4, and $CaCl_2$ Determined in This Study to Literature Values, k_S(lit)[a]

t/°C	salt	k_S	k_S(lit)	$k_S - k_S$(lit)
5	KCl	0.33	0.40	−0.07
15		0.29	0.35	−0.06
25		0.28	0.30	−0.02
35		0.24	0.26	−0.02
45		0.21	0.22	−0.01
5	K_2SO_4	0.86	0.84	0.02
15		0.81	0.812	0.00
25		0.79	0.78	0.01
35		0.69	0.76	−0.06
45		0.65	0.73	−0.08
5	$CaCl_2$	0.62		
15		0.55		
25		0.52	0.50	0.02
35		0.53		
45		0.49		

[a] The literature values were determined from eq 5 from the tabulations of Clegg and Brimblecombe (ref 3). The measured results at 25 °C are taken from Millero et al. (ref 4).

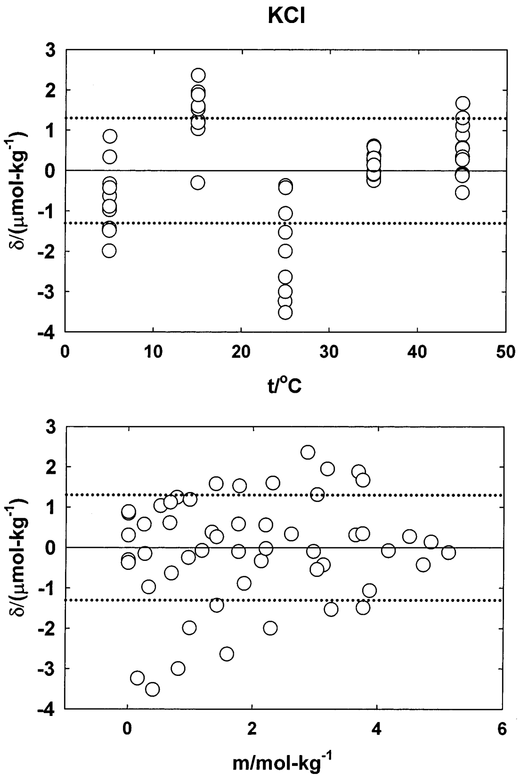

Figure 4. Differences between the measured and calculated (eqs 4, 6, and 7) values of oxygen in KCl solutions as a function of temperature and molality. The dotted lines represent the standard error of the fit.

Table 6. Coefficients for the Fit of the Oxygen Solubilities (μm) to Equations 4, 6, and 7

coefficients	KCl	K_2SO_4	$CaCl_2$
a_0	5.8981	51.4847	−19.675
a_1	−38.7309	−1786.11	1112.33
a_2	−0.9654	−7.8486	2.8941
b_0	0.3186	−213.952	−25.959
b_1	−32.0769	9331.976	1139.68
b_2	−0.0397	32.0235	3.87888
m(max)/mol·kg^{-1}	5.1	0.78	4.2
σ/μmol·kg^{-1}	1.31	0.89	1.68
number of measurements	51	60	52

where cations (M) and anions (X) have a charge of ν_M and ν_X, respectively. The Pitzer[7] parameters λ_{O_2M} and λ_{O_2X} determined from eq 5 are in good agreement with the results of Clegg and Brimblecombe.[3] These tabulations are based on assuming $\lambda_{O_2Cl} = 0$. The values of k_S for KCl, K_2SO_4, and $CaCl_2$ at 25 °C are in reasonable agreement (±0.02) with the literature values.[3] At present, data for the effect of temperature on the values of λ_{O_2Ca} are not available. The effect of temperature on the k_S of KCl is in reasonable agreement at high temperatures, while the values of k_S of K_2SO_4 are in agreement at low temperatures.

The solubilities over the entire temperature and concentration range were fitted to a function of m and T/K where A and B are given by

$$A = a_0 + a_1(K/T) + a_2 \ln(T/K) \tag{6}$$

$$B = b_0 + b_1(K/T) + b_2 \ln(T/K) \tag{7}$$

where a_0, b_0, and so forth are adjustable parameters. The coefficients for the salts along with the standard error of the fits are given in Table 6. The numbers of parameters used to fit a given salt were determined using an F-test. The fits are quite good (σ within ±1.7 μmol·kg^{-1}) and indicate that the standard errors of the measurements on the three salts are similar to our precision of the measure-

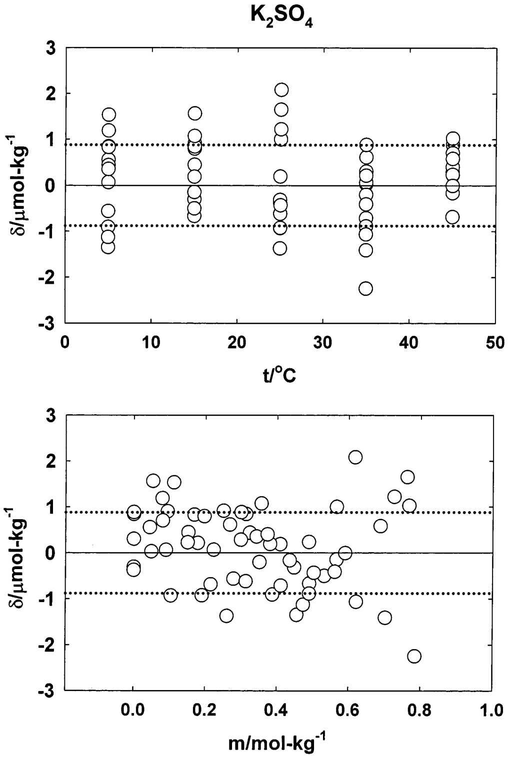

Figure 5. Differences between the measured and calculated (eqs 4, 6, and 7) values of oxygen in K_2SO_4 solutions as a function of temperature and molality. The dotted lines represent the standard error of the fit.

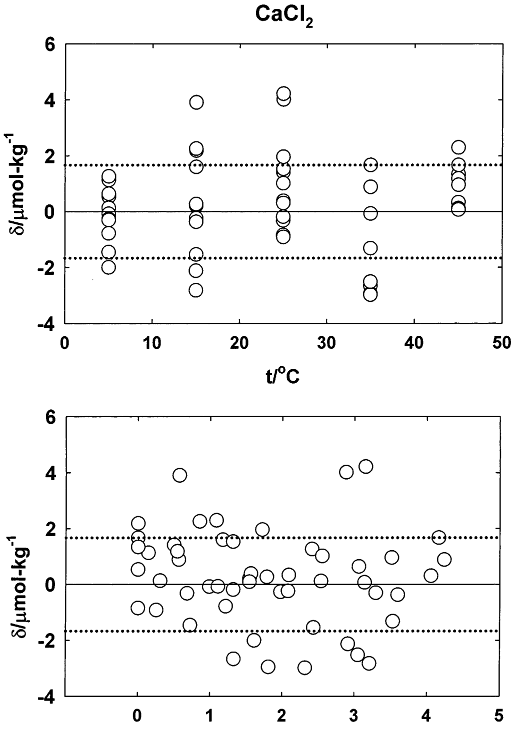

Figure 6. Differences between the measured and calculated (eqs 4, 6, and 7) values of oxygen in $CaCl_2$ solutions as a function of temperature and molality. The dotted lines represent the standard error of the fit.

Table 7. Ionic Values of the Pitzer Coefficients for Oxygen at 25 °C

parameter	our results	Clegg and Brimblecombe
$\lambda(O_2{-}Na)$	0.148	0.160
$\lambda(O_2{-}Ca)$	0.243	0.230
$\lambda(O_2{-}SO_4)^a$	0.124	0.088
$\zeta(O_2{-}K{-}Cl)$	−0.0099	−0.0092
$\zeta(O_2{-}K{-}SO_4)$	−0.0510	−0.046
$\zeta(O_2{-}Ca{-}Cl)$	−0.0460	−0.0057

[a] From Na_2SO_4.

ments at a given temperature (within ±1.5 μmol·kg^{-1}). Comparisons of the measured solubilities of O_2 in the salts to those calculated from eqs 4, 6, and 7 are shown in Figures 4−6 as a function of temperature and molality. Most of the differences are within the standard error of the fits and are independent of temperature and concentration. The solubilities measured at 25 °C for KCl at low concentrations appear to be higher than expected but are within 2 μmol·kg^{-1}.

The activity coefficients of oxygen in the solutions can be examined using the Pitzer[7] equation (eq 2), which account for the interactions of the ions in the solutions with oxygen. The values of λ_{O_2i} and ζ_{O_2ij} as a function of temperature can be determined from the coefficients in Table 6. The λ_{O_2i} coefficients for K^+, Ca^{2+}, and $SO_4{}^{2-}$ can be determined from

$$\lambda_{O_2K} = A_{KCl}/2 = 32.9374 - 1388.54(K/T) - 4.9417\ln(T/K) \quad (8)$$

$$\lambda_{O_2Ca} = A_{CaCl_2}/2 = 32.9374 - 1388.54(K/T) - 4.9417\ln(T/K) \quad (9)$$

$$\lambda_{O_2SO_4} = A_{K_2SO_4}/2 - 2\lambda_{O_2K} = 32.9374 - 1388.54(K/T) - 4.9417\ln(T/K) \quad (10)$$

The values of the binary interactions of KCl, K_2SO_4, and $CaCl_2$ with O_2 are given by

$$\zeta_{O_2KCl} = B_{KCl} = 5.7292 - 260.89(K/T) - 0.85431\ln(T/K) \quad (11)$$

$$\zeta_{O_2K_2SO_4} = B_{K_2SO_4}/2 = 18.8007 - 862.37(K/T) - 2.7987\ln(T/K) \quad (12)$$

$$\zeta_{O_2CaCl_2} = B_{CaC_2}/2 = 19.715 - 888.35(K/T) - 2.93893\ln(T/K) \quad (13)$$

As discussed elsewhere,[4] the Pitzer[7] coefficients determined at 25 °C from our results[4] are in good agreement with the values summarized by Clegg and Brimblecombe[3] (see Table 7). The effect of temperature on these coefficients cannot be determined with certainty since many of the measurements were made before the improvements in the Winkler titration method that was used to determine the solubility of oxygen in salt solutions. As shown in Figure 7, data for the effect of temperature on the Pitzer coefficients for K^+, Ca^{2+}, and $SO_4{}^{2-}$ from K_2SO_4 determined in this study are in reasonable agreement with the values for Na^+, Mg^{2+}, and $SO_4{}^{2-}$ from Na_2SO_4 determined in our earlier studies.[5] The values of $\lambda_{O_2SO_4}$ determined from K_2SO_4 are higher than the values determined from Na_2SO_4. As discussed elsewhere,[3,7] a value determined from a number of sulfates (Li^+, Na^+, K^+) would give a reasonable consensus value.

With our recent studies of all the major sea salts from 5 to 45 °C, it should be possible to make reliable estimates

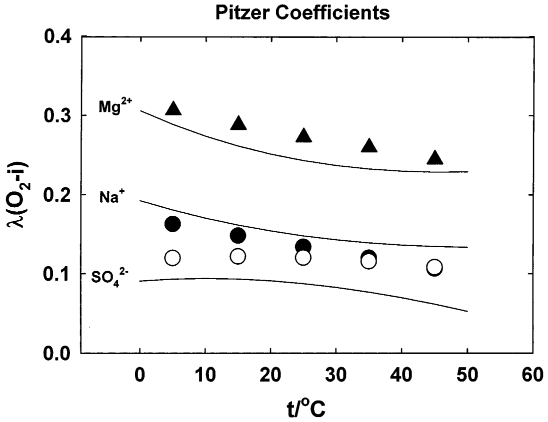

Figure 7. Comparisons of the λ_{O_2i} Pitzer coefficients for KCl (solid circle), K_2SO_4 (open circle), and $CaCl_2$ (solid triangle) with the results for NaCl, Na_2SO_4, and $MgCl_2$.

for the solubility of oxygen in natural waters over a temperature range of 0 to 50 °C and ionic strength of 0 to 6 m.

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