Conductance study of association in aqueous CaCl 2, Ca(CH 3COO) 2, and Ca(CH 3COO) 2·nCH 3COOH from 348 to 523 K at 10 MPa

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Conductance Study of Association in Aqueous CaCl$_2$, Ca(CH$_3$COO)$_2$, and Ca(CH$_3$COO)$_2$·nCH$_3$COOH from 348 to 523 K at 10 MPa

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The conductances of aqueous CaCl$_2$, Ca(CH$_3$COO)$_2$, and Ca(CH$_3$COO)$_2$·nCH$_3$COOH were measured from 348 to 523 K at pressures near 10 MPa using a flow conductometric technique. The first association constant for calcium chloride and the first and second association constants for calcium acetate in water, were derived from a least-squares fit of the measurements to a conductance model in which activity coefficients were calculated using the mean spherical approximation (MSA) and the conductance was modeled by the Turq, Blum, Bernard, and Kunz (TBBK) equation, plus a mixture model.

Introduction

The vast majority of natural resources that are generated by geochemical processes owe their existence to aqueous solutions. Thermodynamic modeling of aqueous solutions and fluid/rock/organic reactions has provided enormous insight into the processes that lead to the formation, migration, and accumulation of petroleum hydrocarbons, as well as the study of the processes which govern the transport and deposition of metals and other inorganic species in sedimentary basins and in hydrothermal systems. In particular, the complexing of calcium ion by chloride and acetate ions plays an important role in modifying the transport of ore-forming metals because calcium ion reduces the amount of chloride and acetate ions that are available to form soluble complexes with ore-forming metals.

In natural environments, chloride and acetate ions are two of the most important complexing anions, but there is insufficient information in the literature on their complexes with calcium to accurately model natural brines containing these ions. Chloride ion is present in almost all brines while acetate ion is one of the most abundant organic ions in many oil field brines, and hydrothermal vent fluids.[1]

This paper is part of a series developing and exploiting the conductometric method of predicting association constants in aqueous solutions.[2−7] In this paper we present the conductometric study of the association in aqueous CaCl$_2$, Ca(CH$_3$COO)$_2$, and Ca(CH$_3$COO)$_2$·nCH$_3$COOH, from 348 to 523 K. Measurements were made on a wide range of concentrations (from 10^{-4} to 0.1 mol kg^{-1} for calcium chloride solutions and from 7×10^{-5} to 0.27 mol kg^{-1} for calcium acetate). The conductometric technique allowed the calculation of the first association constant for calcium chloride and the first and second association constants for calcium acetate. The use of modern conductance equations, activity coefficient models, and a mixing rule gave us the possibility of studying the association equilibrium of calcium and acetate by adding acetic acid to the solutions and consequently avoiding the hydrolysis of calcium and precipitation of portlandite.

Experimental Section

Materials. Calcium chloride stock solutions were prepared from solid CaCl$_2$·2H$_2$O (Alfa ACS, maximum impurities Na 0.02% and Sr 0.1%) and deionized water obtained by a water purification system. Calcium acetate stock solutions were made from Alfa solid calcium acetate (Ca(CH$_3$COO)$_2$·xH$_2$O) 97% and deionized water.

The concentration of the stock solutions was obtained by making conductance measurements at 298 K on diluted (by weight) stock solutions (concentration between 5×10^{-3} and 3×10^{-2} mol kg^{-1})

In the case of calcium chloride the conductance measurements of Shedlovsky and Brown[8] were used to calculate the concentration of our solutions. Knowing the dilution factor of the solutions, the concentration of the stock solutions was obtained.

In the case of calcium acetate, the concentration was found by making conductivity measurements at 298 K and comparing the values obtained with those predicted by the TBBK equation using the known limiting equivalent conductivities[9] of the ions.

Acetic acid was added to some of the calcium acetate solutions at temperatures higher than 500 K to avoid hydrolysis and precipitation of calcium hydroxide. The solution added was Aldrich acetic acid volumetric standard 1 N solution in water. The amount of acetic acid added was such that its concentration was close to the concentration of acetate in the solution, so that the pH of the solution was close to the pK_a of acetic acid.

Solutions were prepared by mass from concentrated stock solutions. The molality of the calcium chloride solutions varied between 10^{-4} and 0.1 mol kg^{-1} while that of calcium acetate varied between 3×10^{-5} and 0.27 mol kg^{-1}.

The constant of the conductance cell was determined at 298 K, both before the experiments took place and after replacing a cracked sapphire. A series of KCl solutions of molalities between 5×10^{-4} and 10^{-2} mol kg^{-1} were used. The solutions of KCl were prepared by weight from certified ACS grade KCl that had been dried at 473 K for at least 2 days. Buoyancy corrections were made when necessary. The equations of Juhász and Marsh[10] and Barthel et al.[11] were used to calculate the cell constant. The cell constants were determined to be 0.0484 ±

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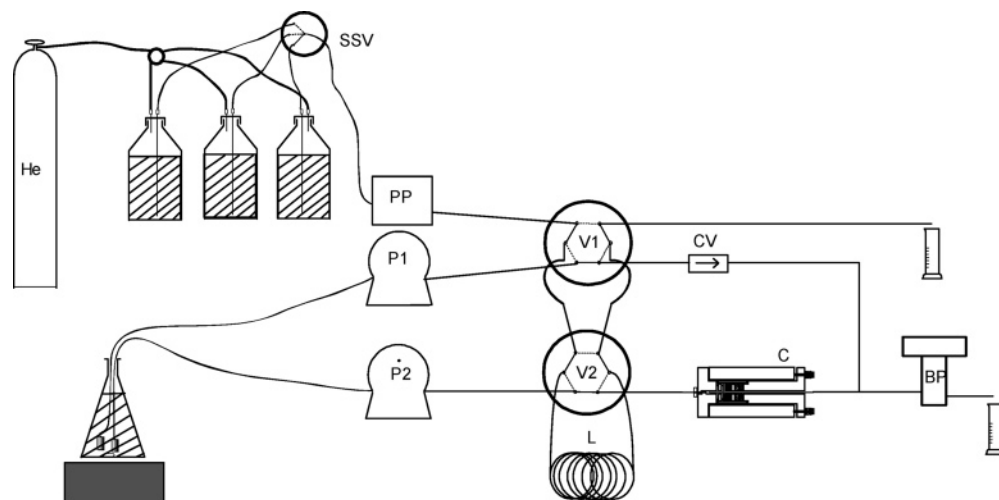† E-mail: rwood@udel.edu.

Figure 1. Scheme of the equipment. Key: SSV, stream selector valve; PP, peristaltic pump; P1, pump 1; P2, pump 2; V1, six-port valve 1; V2, six-port valve 2; CV, check valve; L, sample loop; C, conductivity cell; BP, backpressure regulator. For clarity only three bottles are represented

0.0003 and 0.0479 ± 0.0002 m^{-1}, respectively. The temperature dependence of the cell constant as calculated from the temperature dependence of the expansivity of sapphire and platinum is negligible in the present study.

Conductivity Measurements. A platinum−rhodium flow conductance apparatus described elsewhere[7] was used to make the measurements except that the procedure of injection of solutions into the cell was automated in a way similar to that described by Hnedkovsky and Cibulka.[12] Enough solutions to make measurements at all temperatures of interest were prepared and stored in 2 L Pyrex glass bottles under a helium atmosphere. Figure 1 is a diagram of the setup. A stream selector valve (SSV) connected to the bottles was used to select the solution to be loaded in the sample loop. Two six port valves were used in the procedure for filling the sample loop with the solution, pressurizing it and then injecting the sample. An HPLC pump (P2) operated at a constant flow of 0.5 mL min^{-1} was used to circulate either pure water or the solutions through the cell. The pure water reservoir was heated close to boiling point so it would be deaerated. To fill the sample loop with the desired solution, the stream selector valve is moved to the appropriate position. Then the valves V1 and V2 are set to connect the peristaltic pump (PP) with the sample loop (as the scheme shows), and the PP is turned on. Around 150 mL of solution are pumped through the sample loop (three times its volume). Larger volumes did not change the measured conductivities. Then the PP is turned off, the position of V1 is switched, connecting pump 1 (P1) to the sample loop, and P1 is turned on for 2 min at a flow of 0.5 mL min^{-1} in order to set the pressure in the sample loop to the same value as it is in the cell. With this method, the sample loop is connected to the same backpressure regulator as the cell unlike Hnedkovsky and Cibulka's method. A check valve (CV) is used to ensure that the flow of solution goes in the right way. Finally the position of valve V2 is switched, injecting the contents of the sample loop into the flow stream. After 15 min a stable measurement is obtained and impedance measurements are started. The whole procedure is monitored by a personal computer (PC) that controls the valves (V1, V2, SSV) and can switch on and off the pumps (P1, P2, PP), as well as store real and imaginary impedance, temperature, and pressure as a function of time.

Impedances (real + imaginary parts) were measured at frequencies from 100 Hz to 10 kHz using a RCL meter (Fluke Co, model PM6304c). All measured impedances were corrected for lead resistance (0.039 ohm). Around 100 impedance

measurements for each frequency, as well as the same number of measurements of temperature and pressure were made. The mean value and standard deviation of these values were calculated to estimate the best value and random error of a measurement.

Hnedkovsky et al.[7] showed that more accurate values of the conductivity of the solution could be obtained by considering the frequency dependence of both the real and the imaginary parts of the ac impedance of the cell. More recently Balashov[13] derived an equivalent circuit model that does not require the somewhat arbitrary choices in Hnedkovsky's method. We used Balashov's model, but essentially the same results are obtained by Hnedkovsky's method.

The experimental electrolytic conductivities of the solutions (κ_{soln}^{obs}) were corrected for the electrolyte conductivities of the impurities in the solvent accordingly to:[6]

$$\kappa_{soln}^{corr} = \kappa_{soln}^{obs} - \kappa_w^{obs} + \kappa_w \qquad (1)$$

where κ_w is the calculated conductivity of pure water. This correction is based on the assumption that the solvent electrolytic conductivity above that corresponding to H$^+$ and OH$^-$ is due to impurities present in solutions. The concentration of these impurities was always below 10^{-6} mol kg^{-1}.

Stoichiometric equivalent conductivities were calculated by dividing the conductivity of the solutions by the stoichiometric normality of the salt:

$$\Lambda = \kappa/N \qquad (2)$$

where

$$N = \sum_c c_c z_c = \sum_a c_a |z_a| \qquad (3)$$

The temperature of the experiments was determined with a platinum resistance thermometer (Hart Scientific, model 5612) with a stated calibration accuracy better than 0.033 K. The pressure was measured by means of a Digiquartz pressure transducer (ParoScientific, model 760−6K) with an accuracy of 0.01 MPa. The temperature and pressure fluctuations in a single measurement (that took approximately 1 h) were small (around 0.1 K for temperature and 0.05 MPa for pressure).

To check for proper thermal equilibrium of samples at every state point, a duplicate experiment, except with a lower flow rate, was made at every temperature, and compared to the

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measurements done at regular flow rate. They differed by at most 1%. The maximum temperature of these experiments was 523 K because at higher temperatures appreciable decomposition of acetate was observed.

Data Analysis

Conductance Model. The TBBK conductance model[14] was used to calculate the equivalent conductivity of solutions of a single salt. According to Sharygin et al.,[6] a simple mixture rule can be used to calculate the conductance of a mixture of aqueous electrolytes from the conductance of the single salts solutions with an accuracy of about 1% at molalities below about 0.1 mol kg^{-1}:

$$k[I\Gamma] = N\sum_c\sum_a x_c x_a \Lambda_{ca}[I\Gamma] \tag{4}$$

where Λ_{ca} represent the calculated conductivity of a single salt at the molar ionic strength of the solution I, and Γ is the MSA shielding parameter of the mixture. The sums are over all cations c and anions a. In this equation the equivalent fraction of ion i, x_i, is given by

$$x_i = \frac{c_i|z_i|}{N} \tag{5}$$

where c represents the concentration (mol/dm^3), z the charge of the ion, and the subscript i denotes the ion in solution.

The conductivity of a single salt in water, Λ_{ca} was calculated according to the TBBK[14] model:

$$\Lambda_{ca} = \lambda_a + \lambda_c \tag{6}$$

where the conductance of the ith ion is

$$\lambda_i = \lambda_i^0\left(1 + \frac{\delta v_i^{el}}{v_i^o}\right) + \left(1 + \frac{\delta X}{X}\right) \tag{7}$$

with λ_i^0, the conductance at infinite dilution, $\delta v_{el}^i/v_i^0$ is the free ion electrophoretic velocity effect, $\delta X/X$ the free ion relaxation force correction, and v_i^0 the ion velocity at infinite dilution.

Taking into account that the solutions were prepared by weight, it was necessary to know the density of each solution in the measurement conditions in order to calculate the concentration of the ions. For solutes k of molal concentration m_k the concentration is given by

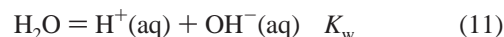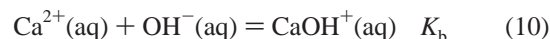$$c_i = \frac{m_i\rho_0}{1 + \rho_0\sum_k m_k V_k(I)} \tag{8}$$

where ρ_0 is the density of water,[15] M_k is the molar mass of solute k, m_k its molality, and V_k its partial molar volume. The values of V_k for the solutes were taken to be equal to their partial molar volume at infinite dilution. The partial molar volumes of solutes in experimental conditions were taken from Oakes et al.[16] for calcium chloride, from Ballerat-Busserolles et al.[17] for acetic acid and sodium acetate up to 393 K, from Rogers and Pitzer[18] for sodium chloride, and from correlation algorithms given by Shock et al.[19,20] whenever experimental information was not available. Setting all V_k in eq 8 to zero changed the concentration less than 1% for solutions up to 0.1 mol kg^{-1} and less than 4.5% for solutions between 0.1 and 0.3 mol kg^{-1}.

TABLE 1: Auxiliary Parameters Used for Fitting the Data. Calcium Chloride Experiments

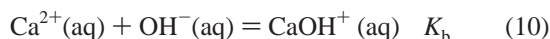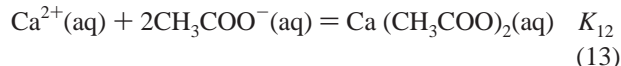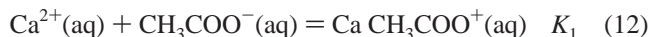| temp (K)	pressure (MPa)	pK_w	pK_b	λ^0 (cm^2 S mol^{-1})				
				H$^+$	Cl$^-$	OH$^-$	CaCl$^+$	CaOH$^+$
348.0	8.45	12.7	1.7	553.7	174.0	321.1	174.0	174.0
398.7	9.37	11.9	2.2	662.6	250.2	485.2	250.2	250.2
473.7	9.38	11.2	2.8	819.6	389.8	692.2	389.8	389.8
522.5	9.40	11.1	3.1	870.2	479.8	770.8	479.8	479.8

^{a} r_{H^+} = 0.14 nm, r_{Cl^-} = 0.183 nm, r_{OH^-} = 0.14 nm.

Equilibria in Solution. *Calcium Chloride Solutions.* In the calcium chloride solutions the following equilibria were taken into account:

$$Ca^{2+}(aq) + Cl^-(aq) = CaCl^+(aq) \quad K_{CaCl^+} \tag{9}$$

$$Ca^{2+}(aq) + OH^-(aq) = CaOH^+(aq) \quad K_b \tag{10}$$

$$H_2O = H^+(aq) + OH^-(aq) \quad K_w \tag{11}$$

The solutions were mainly neutral, so only very small concentrations of CaOH$^+$ and H$^+$ were present.

Calcium Acetate Solutions. To analyze the conductance data and calculate the association constants of calcium(II) and acetate, it was necessary to decide which equilibria took place in solution. A first approximation would include the first and second association of calcium(II) and acetate, the ionization of acetic acid, the association of Ca^{2+} with OH$^-$, and the autoprotolysis of water. That is

$$Ca^{2+}(aq) + CH_3COO^-(aq) = Ca\,CH_3COO^+(aq) \quad K_1 \tag{12}$$

$$Ca^{2+}(aq) + 2CH_3COO^-(aq) = Ca\,(CH_3COO)_2(aq) \quad K_{12} \tag{13}$$

$$CH_3COOH(aq) = CH_3COO^-(aq) + H^+(aq) \quad K_a \tag{14}$$

$$Ca^{2+}(aq) + OH^-(aq) = CaOH^+\,(aq) \quad K_b \tag{10}$$

$$H_2O = H^+(aq) + OH^-(aq) \quad K_w \tag{11}$$
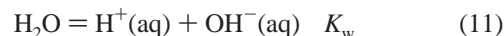
It was necessary to include both the first and second association of calcium(II) and acetate (K_1 and K_{12}). Preliminary attempts were made to fit the data only considering the formation of CaCH$_3$COO$^+$ (K_1), but the results clearly indicated that this model was not adequate.

Fitting Model. The present results allowed the determination of the association constants of calcium with chloride ion (K_{CaCl^+}) and acetate ion (K_1 and K_{12}). Also the limiting equivalent conductivities of Ca^{2+} could be determined from the CaCl$_2$ results. Thus, in fitting the data to our model it was necessary to fix values for many other parameters (auxiliary parameters) using literature results or estimation techniques. The values used for these parameters are given in Tables 1 and 2. The uncertainties caused by the uncertainties in these parameters were small and are described in detail below.

The adjustable parameters were determined by a nonlinear, least-squares technique (Levenberg–Marquardt). In this calculation, for every set of trial values of the adjustable parameters, the equilibrium concentrations of all species in solution (eqs 9–11 for CaCl$_2$ solutions and eqs 10–14 in Ca(CH$_3$COO)$_2$ solutions) were calculated using MSA activity coefficients. Then the conductance of the solution was calculated with the TBBK equation and our mixture rule (eq 4). The adjustable parameters were varied to find a minimum in the weighted sum of the

TABLE 2: Auxiliary Parameters Used for Fitting the Data for Calcium Acetate Experiments[a]

					λ^0 (cm² S mol⁻¹)					
temp (K)	pressure (MPa)	pK_w	pK_a	pK_b	H⁺	Ca²⁺	Ac⁻	OH⁻	CaAc⁺	CaOH⁺
348.0	8.45	12.7	4.9	1.7	497.5	121.4	101.7	321.1	101.7	174.0
398.7	9.38	11.9	5.1	2.2	662.8	234	149.9	485.5	149.9	250.0
473.7	9.38	11.2	5.5	2.8	819.6	422	262.1	692.2	262.1	389.8
522.6	9.39	11.1	5.9	3.1	870.2	467	324.3	771.0	324.3	480.0

[a] r_{H+} = 0.14 nm, $r_{Ca^{2+}}$ = 0.115 nm, r_{CH3COO^-} = 0.159 nm, $r_{CH3COOH}$ = 0.14 nm r_{OH^-} = 0.14 nm.

squares of the errors. The weights in the least-squares fit were estimated from statistical uncertainties of the experimental impedance measurements.

Neither the MSA nor TBBK model use adjustable parameters. The radii of the ions, necessary in both the MSA and TBBK models, were taken from Marcus,[21] except for that of calcium-(II) that was calculated by fitting Sheldovsky's calcium chloride conductivity measurements at 298 K[8] to the TBBK model, using the radius of calcium as the only adjustable parameter. The radius obtained, 0.115 nm, was slightly greater than the crystallographic radius of the ion (0.104 nm). As before, the radii of the ion pairs were estimated as[7]

$$r_{MX} = \sqrt[3]{r_M^3 + r_X^3}$$

The limiting equivalent conductivities at the experimental conditions were taken from Marshall[22] for H⁺, OH⁻, and Cl⁻. The values for Ca²⁺ necessary for analyzing calcium acetate solutions were taken from experiments with calcium chloride performed in this study. The values for acetate ion necessary for the analysis of calcium acetate solutions were taken from Zimmermann and Wood.[3] For CaCl⁺ and CaOH⁺, the conductivity at infinite dilution was taken equal as that of Cl⁻. For CaCH₃COO⁺ it was estimated as equal as that of CH₃COO⁻.

The equilibrium constant for the ionization of acetic acid (Ka) under the experimental conditions was calculated from data from Lown et al.[23] using Read's description.[24] The equilibrium constant for the association of Ca²⁺ with OH⁻ (Kb) of Seewald and Seyfried,[25] and the equilibrium constant for the autoprotolysis of water (Kw) of Marshall and Frank[26] were used in our calculations. Neither the hydrolysis of calcium nor the autoprotolysis of water played an important role in the conditions of the experiments. The properties of water were taken from Wagner and Pruss[15] and the dielectric constants from Fernandez et al.[27]

When the pK's of the auxiliary equilibrium constants in Tables 1 and 2 were increased by 0.1 the fitted parameters changed by negligible amounts (less than 10% of the uncertainties from the least-squares fit). When the auxiliary limiting equivalent conductivities were increased by 10% there were negligible changes except for $\Lambda°$[CaCl⁺] and $\Lambda°$[CaCH₃COO⁺], where the changes were never more than twice the uncertainties from the least-squares fit.

When all of the activity coefficients were changed by 30% (increased and decreased) at the highest ionic strength with proportionally lower increases at lower ionic strengths, there were no significant changes in $\Lambda°$[Ca²⁺] or K_{CaCl^+}, but for K_1 and K_{12}, the changes were sometimes comparable to the uncertainties from the least-squares fit. The uncertainties reported in this paper are the sum of the uncertainties from the auxiliary parameters and from the least-squares fit.

Results

Calcium Chloride. Table 3 shows the experimental measurements and the deviations of our model from our results. We

TABLE 3: Equivalent Stoichiometric Conducitvity (Calculated Using the Stoichiometric Concentration of Salt) for Calcium Chloride Experiments

$10^3 m_{CaCl_2}$ (mol kg⁻¹)	Λ^{exp} (S mol⁻¹ dm³)	δ (%)[a]
T = 348.0 K; *p* = 8.45 MPa		
0.1066	284.9	−0.0
0.278	280.7	0.2
0.845	272.4	−0.2
4.500	249.8	−1.6
12.31	233.1	−1.4
29.98	218.5	0.3
90.21	193.6	0.5
T = 398.7 K; *p* = 9.37 MPa		
0.1066	457.2	1.0
0.278	441.6	−0.1
0.846	426.8	−0.3
4.500	393.0	0.5
12.31	366.2	1.3
29.98	331.1	0.5
90.21	286.7	−0.7
T = 473.7 K; *p* = 9.38 MPa		
0.845	615.6	−3.7
4.500	548.5	−0.8
12.31	491.8	0.3
29.98	437.8	−0.1
90.21	365.3	−5.1
T = 522.5 K; *p* = 9.40 MPa		
0.1066	751.2	−0.2
0.2782	721.9	0.2
0.845	673.7	0.8
4.500	582.5	2.2
12.31	510.3	1.9

[a] δ (%) = ($\Lambda^{calc} - \Lambda^{exp}$)/$\Lambda^{exp}$.

compared our equivalent conductivity measurements at 473 and 523 K with Marshall's data,[28] the only other published equivalent conductivity measurements of CaCl₂ at high temperatures. We found that our results were about a 10% lower than their results. We also found that Marshal's data at 298 K data did not agree with other published data[8,29] with errors as high as 5%. As an example of the quality of the fits, Figure 2 shows the fit obtained for the experimental data at 398.7 K and 9.37 MPa, Table 4 gives the values of λ[Ca²⁺] and K_{CaCl^+} obtained in this study.

To compare the data with literature results, all experimental results were corrected to the same pressure, 17.6 MPa, using (ln $K/\partial p)_T = \Delta V°/RT$). The partial molar volumes were estimated using correlation algorithms from Shock et al.[20,30,31] This correction was always below 0.12 units of log K at temperatures below 525 K, so it is quite small (cf. Table 5). When necessary the results were corrected to infinite dilution. Figure 3 is a plot of log K_{CaCl^+} at 17.6 MPa vs 1/*T*, which compares the present results with published data obtained by different experimental methods such as solubility measurements,[32] calorimetry,[33,34] potentiometry,[35] and ion selective electrode measurements.[36] In general, the agreement is satisfactory. Our uncertainties are larger at 473 K where the measurements at the two lowest concentrations were not consistent with the other results so only
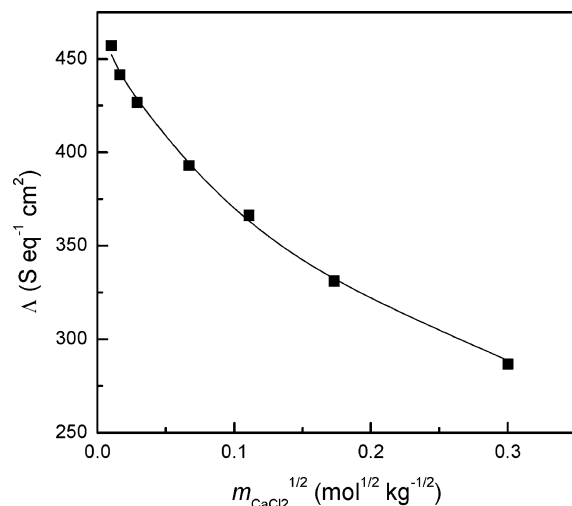
Figure 2. Equivalent stoichiometric conducitvity ($\kappa/N = \kappa/(2c)$) of calcium chloride solutions vs square root of the molality of calcium chloride in the solution, measured at 398.7 K and 9.37 MPa. The line represents the best fit using the procedure described in the text.

TABLE 4: Calculated Infinite Dilution Conductivity of Calcium Ion and Association Constants of Calcium(II) and Chloride in Water

temp (K)	pressure (MPa)	density (kg m^{-3})	λ^0(Ca^{2+})^a (cm^2 S)	$K_{CaCl^+}{}^a$
348.0	8.45	979	121.4 ± 0.6	7 ± 4
398.7	9.37	943	234 ± 4	12 ± 4
473.7	9.38	870	442 ± 97	71 ± 60
522.5	9.40	806	467 ± 5	114 ± 24

^{a} The uncertainties reported for K_{CaCl^+} and λ^0(Ca^{2+}) correspond to the 95% confidence level estimate in the least-squares fit plus the uncertainties due to our choice of auxiliary parameters.

TABLE 5: Literature Results for the Association of Calcium Chloride. Experimental Values and Values Corrected to 17.6 MPa

temp (K)	pressure (MPa)	logK_{CaCl^+}	logK_{CaCl^+} (17.6 MPa)
	This Study		
348.0	8.45	0.85	0.89
398.7	9.37	1.08	1.10
473.7	9.38	1.85	1.83
522.5	9.40	2.06	1.95
	Majer et al.[41]		
288.15	0.10	0.72	0.77
298.15	0.10	0.82	0.87
318.15	0.10	0.81	0.86
338.15	0.10	0.94	0.99
358.15	0.10	1.05	1.08
	Johnson and Pytkowicz[35]		
298.15	0.10	0.60	0.71
	Oscarson et al.[34]		
573.15	11.00	2.02	1.59
598.15	14.80	2.47	2.54
623.15	17.60	3.10	3.10
	Gillespie et al.[33]		
523.15	10.30	1.85	1.76
548.15	11.00	2.24	2.17
573.15	11.00	2.67	2.24
598.15	13.20	3.15	3.25
	William-Jones and Seward[32]		
423.15	0.48	−0.07	−0.04

five concentrations were available for the analysis. A thunderstorm may have changed the calibration of our Fluke impedance meter. To compare the potentiometric concentration quotients
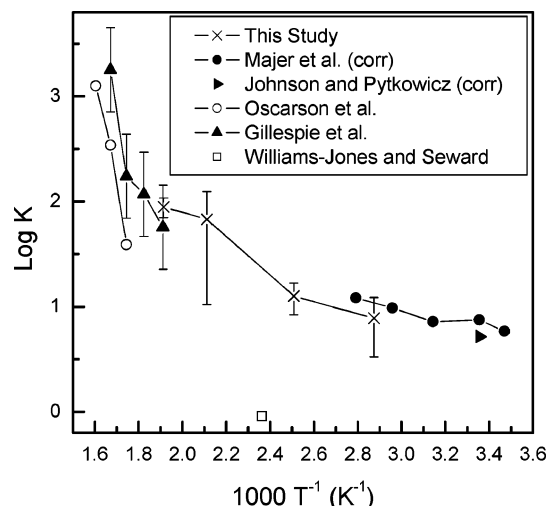

Figure 3. Log of K_{CaCl^+} vs $1/T$ at 17.6 MPa.

of Johnson and Pytkowicz[35] at ionic strengths between 0.3 and 1 mol kg^{-1} with our equilibrium constants, we calculated activity quotients using an extended Debye−Hückel model and then linearly extrapolated the activity quotients to infinite dilution. In the case of Majer and Stulík's[36] results, we used the Pitzer interaction model to correct the concentration quotients using a β_0 and β_1 for Ca^{2+}, NO$_3^-$; Na$^+$, Cl$^-$; and Na$^+$, NO$_3^-$ interactions from Pitzer.[37] The low-temperature results of both Majer and Stulík and Johnson and Pytkowicz are in good agreement with our results.

The equilibrium constant at 423 K of Williams-Jones and Seward[32] is too low, perhaps because they calculated first and second association constants from the same solubility experiment and the error bars are bigger than they estimated.

Gillespie et al.[33] measured the enthalpy of dilution ($\Delta_{dil}H$) and calculated the equilibrium constants and the enthalpy of ion association (K_{CaCl^+} and $\Delta_r H$) assuming the Meissner model for activity coefficients. When comparing their CaCl$_2$ data with other published data, they stated that a difference of 0.3 log K "is near the uncertainty of our experimental method", so we used 0.3 as the uncertainty in Figure 3.

Oscarson at al.[34] measured $\Delta_{dil}H$ at 598 and 523 K and used Gillespie's results at 573 K data, but did not use Gillespie's 548 and 523 K results. They determined parameters for Pitzer's model for $\gamma\pm$ from the data. Meissner's activity coefficients were 20 to 30% lower than Pitzer's, giving as a result log K's that were 20 to 30% larger. No uncertainties were reported because they were "difficult to estimate" and there was a large covariance between the parameters determined by the least-squares fit. They reported that "A unique set of log K, $\Delta_r H°$, and γ values could not be determined using only $\Delta_{dil}H$ values". Considering these difficulties, their results are in good agreement with the present measurements since the largest difference in log K is 0.21 at 523 K. Oscarsons results are in reasonable agreement with Gillespie et al.'s results. It is surprising that K increases so rapidly at temperatures above 523 K. It would have been of great interest to make measurements at higher temperatures, but a lack of support for this project prevented this.

Frantz and Marshall calculated K_{CaCl^+} from 673 to 873 K, from conductance measurements, but as noted above their conductances at lower temperature do not agree with the present results and they reported K_{CaCl^+} only at temperatures much higher than the present results.

Calcium Acetate. Table 6 shows the experimental data obtained in the experiments on Ca(CH$_3$COO)$_2$, and Ca(CH$_3$-

TABLE 6: Equivalent Stoichiometric Conductivity (Calculated Using the Stoichiometric Concentration of Salt) for Calcium Acetate−Acetic Acid Experiments

$10^3 m_{CaAc_2}$ (mol kg^{-1})	$10^3 m_{HAc}$ (mol kg^{-1})	Λ^{exp} (S mol^{-1} dm^3)	δ (%)	$10^3 m_{CaAc_2}$ (mol kg^{-1})	$10^3 m_{HAc}$ (mol kg^{-1})	Λ^{exp} (S mol^{-1} dm^3)	δ (%)
$T = 348$ K; $p = 8.45$ MPa
0.0730	0.000	220.7	0.2	3.280	3.134	190.9	−0.3
0.270	0.000	216.9	1.3	40.28	0.000	134.8	−0.9
0.777	0.000	208.4	0.6	97.96	0.000	109.9	0.0
2.756	0.000	194.1	0.3	0.1400	0.000	215.1	−1.1
8.288	0.000	175.0	0.0	66.06	0.000	121.7	0.1
24.022	0.000	150.1	0.0	130.6	0.000	101.6	0.3
0.0750	0.000	219.9	−0.1	173.3	0.000	93.0	0.2
0.254	0.000	216.7	1.0	69.73	0.000	120.3	0.3
0.983	1.208	208.9	0.7	280.2	0.000	77.8	−1.4
$T = 398.7$ K; $p = 9.38$ MPa
0.073	0.000	371.2	0.9	3.291	0.000	294.6	−1.4
0.270	0.000	352.0	−0.0	11.81	0.000	248.3	−0.4
0.777	0.000	334.4	−0.3	40.28	0.000	191.7	−0.7
2.756	0.000	302.9	−0.4	97.96	0.000	150.4	−1.3
8.288	0.000	264.7	0.2	67.34	35.03	170.4	1.0
24.02	0.000	220.7	1.6	64.74	20.49	172.6	1.2
0.0750	0.000	379.3	3.1	124.01	51.80	142.6	0.8
0.254	0.000	354.5	0.4	167.87	31.80	129.0	0.1
0.984	0.000	330.6	−0.0				
$T = 473.7$ K; $p = 9.38$ MPa
0.2710	0.000	548.3	−3.6	0.983	1.208	463.5	−4.9
0.2710	0.853	541.5	−3.6	3.280	3.134	374.2	2.4
0.782	0.000	484.9	−2.3	11.69	10.01	279.8	2.7
0.780	2.019	480.0	−1.1	38.87	35.45	203.0	0.0
2.772	0.000	390.2	1.3	92.62	55.05	156.8	−5.2
2.754	6.392	388.0	1.2	0.0410	0.000	632.4	−3.5
8.203	16.02	305.1	1.5	0.1400	0.000	579.7	−5.7
23.22	39.38	234.0	−0.9	124.0	51.80	143.2	0.7
0.0750	0.000	606.3	−3.6	167.9	31.80	130.1	−1.0
0.254	0.000	551.7	−3.2	271.2	32.63	110.9	−6.1
0.984	0.000	468.9	−0.7	67.34	35.03	173.7	2.5
11.81	0.000	280.9	2.2				
$T = 522.6$ K; $p = 9.39$ MPa
0.0720	0.000	685.3	4.3	23.05	39.38	200.9	−1.0
0.2690	0.853	558.4	1.9	124.0	51.80	122.1	5.8
0.775	2.019	475.2	0.8	167.9	31.80	108.0	4.2
2.734	6.391	364.3	−0.3	271.2	32.63	87.1	0.0
8.14	16.02	273.7	−0.9	64.74	20.49	153.8	5.4

[a] δ (%) = $(\Lambda^{calc} - \Lambda^{exp})/\Lambda^{exp}$.

COO)$_2$·nCH$_3$COOH. Figure 4 shows the equivalent stoichiometric conductivities ($\kappa/N = \kappa/(2c)$) vs molality obtained at two different state points, and the fitting of these data using only K_1, only K_{12}, and $K_1 + K_{12}$. It is clear that both K_1 and K_{12} were needed to fit the experimental results. Table 7 and Figure 5 show the uncertainties in K_1 and K_{12}. The wide range of concentrations used during this study, added to the accuracy of the conductometric method, allowed the determination of both K_1 and K_{12}. This is the first measurement of K_{12}.

Table 2 shows the auxiliary parameters used to fit the data as described in the text above. Table 7 shows the association constants obtained in this study. Figure 5 is a plot of log K_1 and K_{12} vs T^{-1}.

To compare our results with previous measurements, all association constants were calculated at the same pressure, 50 MPa, using the partial molar volumes of the reactants and products estimated using the predictions of Shock et al.[20,30] This correction was always below 0.13 units of log K (see Table 8). The results obtained are shown in Figure 6. Smith and Martell[38] reviewed the earlier literature. Their value at 298 K is a little higher than a simple extrapolation of our results. The complex is weak at this temperature, so it is hard to measure.

It can be seen that there is some disagreement with the results of Sehata.[39] Sehata used a conductance technique to determine

K_1. No experimental conductivities and no uncertainties in K_1 or $\Lambda°$ are reported by Sehata. Only values of $\Lambda°$, K_1, and the distance of approach, d, were reported. Five parameters ($\lambda[^1/_2$-Ca^{2+}], $\lambda[$ CaCH$_3$COO$^+$], $\lambda[$CH$_3$COO$^-$], K_1, and d) were determined but $\lambda[$ CaCH$_3$COO$^+$], K_1 and d were strongly coupled so that they could not be determined accurately from the data. We found the same coupling at higher temperatures. In addition our results indicate that at 298 K Ca(CH$_3$COO)$_2$ will be almost as abundant as CaCH$_3$COO$^+$. Because of these problems, it seems probable that the agreement between the present results and those of Sehata is reasonable.

The agreement with the solubility measurements of Fein[40] at 350 K is very good. At higher temperatures the data in this work are in good agreement with the results of Seewald and Seyfried[25] for K_1. They determined K_1 from studies of portlandite (Ca(OH)$_2$) solubility in water and aqueous acetate solutions from 473 to 623 K at 50 MPa. Equilibrium was approached from supersaturation and undersaturation and ionic strengths were low (below 0.033 mol kg^{-1}), so uncertainties due to estimates of activity coefficients were low. Unfortunately, their sensitivity analysis showed that uncertainties in the literature values for the solubility product of portlandite could cause uncertainties in log K as large as 0.2 and 0.8 log units at 473
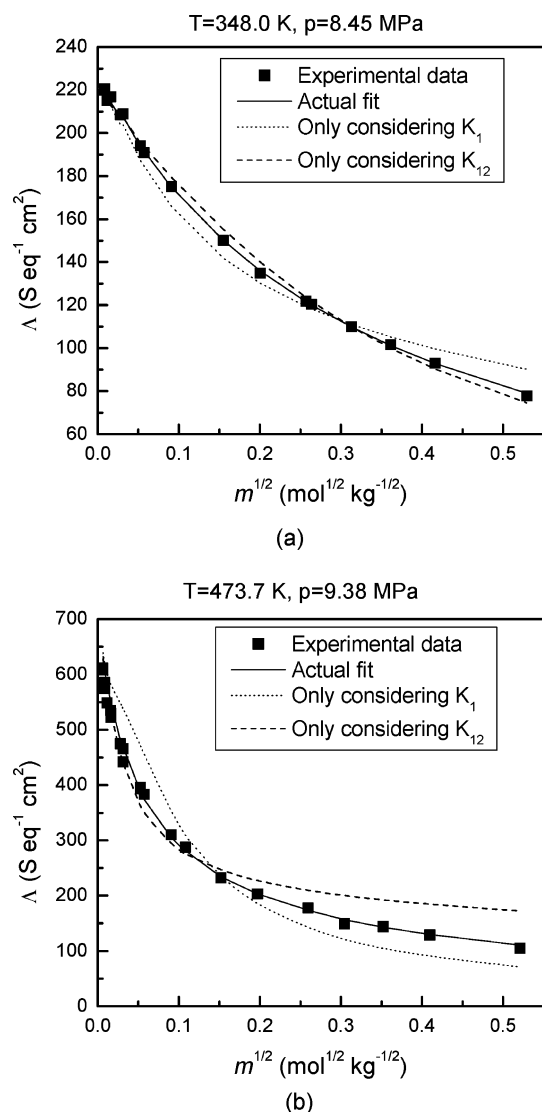
Conductance Study of Association

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(a)

(b)

Figure 4. Equivalent stoichiometric conducitvity ($\kappa/N = \kappa/(2c)$) of calcium acetate solutions vs square root of the molality of calcium acetate in the solution. The solid line represents the best fit obtained using the first and second association constants for calcium and acetate (K_1 and K_{12}), the dotted line represents the best fit using just the first association constant of calcium and chloride (K_1), and the dashed line represents the best fit using only the second association constant of calcium and chloride (K_{12}). Experimental conditions: (a) 348.0 K and 8.45 MPa; (b) 473.67 K and 9.38 MPa.

TABLE 7: Association Constants of Calcium(II) and Acetate in Water

temp (K)	pressure (MPa)	density (kg m^{-3})	$K_1{}^a$	$K_{12}{}^a$
348.0	8.45	979	12 ± 8	112 ± 67
398.7	9.38	943	35 ± 5	286 ± 110
473.7	9.38	870	290 ± 54	4647 ± 1500
522.6	9.39	806	561 ± 129	25,991 ± 6600

^{a} The uncertainties reported for K_1 and K_{12} correspond to the 95% confidence level estimate in the least-squares fit plus the uncertainties due to our choice of auxiliary parameters.

and 623 K respectively, so we have used these uncertainties in Figures 6 and 7. Our results agree with Seewald and Seyfried's results.

Figure 6 illustrates the power and accuracy of the conductometric method. Our estimated error bars are much lower than those of Seewald and Seyfried and we were able to measure both K_1 and K_{12}. However our values of log K_1 are not on a
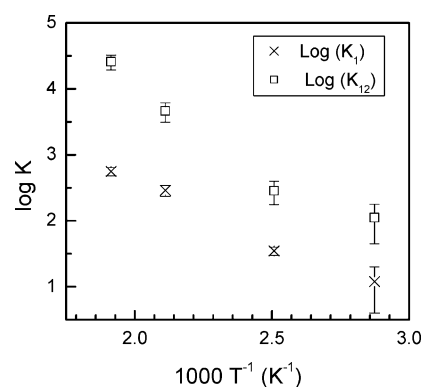

Figure 5. Logarithm of K at experimemtal pressure vs T^{-1}.

TABLE 8: Literature Results for the Association of Calcium Acetate^a

| temp (K)	pressure (MPa)	log K_1	log K_1 (50 MPa)	log K_{12}	log K_{12} (50 MPa)
		This Study			
347.95	8.45	1.08	1.14	2.02	1.96
398.74	9.38	1.52	1.54	2.41	2.33
473.67	9.38	2.42	2.34	3.55	3.41
522.60	9.39	2.76	2.52	4.44	4.17
		Smith and Martell[38]			
298.15	0.1		0.12		
		Fein[40]			
353	0.1	1.2	1.3		
		Sehata[39]			
298.15	0.1	1.71	1.83		
308.15	0.1	1.75	1.86		
318.15	0.1	1.79	1.89		
328.15	0.1	1.83	1.92		
		Seewald and Seyfried[25]			
473.15	50	2.53	2.53		
573.15	50	3.72	3.72		
623.15	50	4.59	4.59		

^{a} Experimental values and values corrected to 50 MPa.
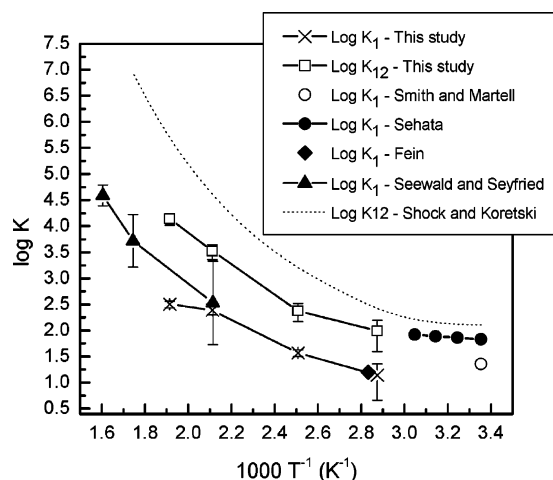
Figure 6. Logarithm of K for Ca(CH$_3$COO)$_2$ corrected to 50 MPa vs T^{-1}. The results of Sehata are not consistent with the present results.

smooth curve indicating that our estimated uncertainties may be a factor of 2 too low. The present results are the first measurements of K_{12}. Shock and Koretsky[20] have predicted values of K_{12} from correlation of K_1 and K_{12} for a variety of metal acetate complexes. The predicted K_{12} is plotted in Figure 6. The predicted values are 0.5 to 1.5 unit of log K higher than our measurements.
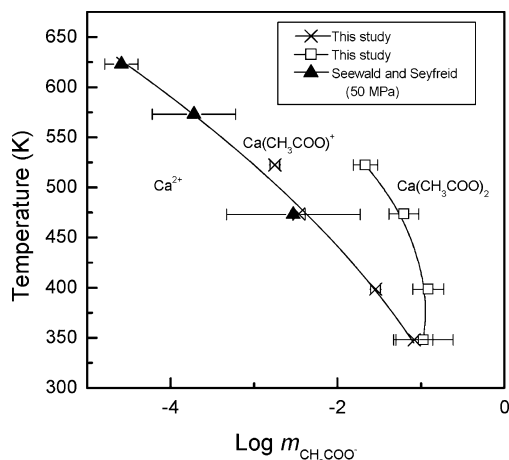
Figure 7. Speciation as a function of T and $m_{CH_3COO^-}$. The lines give the temperature and molalities where the predominant species changes: ($\times$) $m_{Ca^{2+}} = m_{Ca(CH_3COO)^+}$ according to this study; ($\square$) $m_{Ca(CH_3COO)^+} = m_{Ca(CH_3COO)_2}$, according to this study; ($\blacktriangle$) $m_{Ca^{2+}} = m_{Ca(CH_3COO)^+}$ at 50 MPa according to Seewald and Seyfried.[25]

Figure 7 shows the two boundaries between regions of temperature and acetate molality where the most abundant species is Ca^{2+}, $CaCH_3COO^+$, and $Ca(CH_3COO)_2$. The region of stability of $CaCH_3COO^+$ is fairly small at 525 K and decreases almost to extinction at 350 K. The results of Sehata and Smith and Martell at lower temperatures are probably inaccurate because of failure to include $Ca(CH_3COO)_2$ as a species so their data are not plotted.

Final Remarks

In this study, the first association constant of calcium chloride and first and second association constants for calcium acetate were calculated from conductivity measurements. The results are in agreement with published data where there is overlap. In the case of calcium chloride, a study of its association constant at higher temperatures would be helpful.

The error bars in Figures 3, 6, and 7 illustrate the accuracy of the present conductometric method of measuring association constants at high temperatures. Except at 473 K (where our result for K_{CaCl^+} has a large scatter for unknown reasons) our estimated uncertainties are much less than the uncertainties reported by Seewald and Seyfried. The one important advantage of our technique is that when association is strong we make measurements at very low ionic strengths (below 0.01 mol kg^{-1}) so that our uncertainties in the estimated activity coefficients are small. In the present case, higher concentrations were necessary to produce appreciable amounts of $Ca(CH_3COO)_2$, so, to measure K_{12} we had to make some measurements at higher ionic strengths (up to 0.7 mol kg^{-1}) with a corresponding decrease in accuracy. The authors believe that the present method and solubility measurements at low ionic strengths are the preferred methods whenever they are feasible. Of course the present technique cannot be used when association is so weak that it is only detectable in concentrated solutions. The TBBK equation together with the mixture rule allows the investigation of complex mixtures at ionic strengths to about 1 mol kg^{-1} with reasonable accuracy.

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