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## Experimental determination of the complexation of strontium and cesium with acetate in high-temperature aqueous solutions

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**Abstract**—Radionuclides are present in contaminated surficial waters, but their behavior in the presence of natural organic acids is poorly known. Dissociation constants for the strontium acetate ( $\text{SrCH}_3\text{COO}^+$ ) and cesium acetate ( $\text{CsCH}_3\text{COO}^0$ ) ion pair were determined by potentiometry at temperatures from 25 to 175°C at the saturation pressure of water. Logarithms of measured dissociation constants ( $\log K$ ) decrease with increasing temperature, showing that Sr and Cs complexing increases as temperature rises.  $\log K$  for  $\text{SrCH}_3\text{COO}^+$  decreases from  $-1.38$  at 25°C to  $-2.10$  at 175°C, whereas  $\log K$  for  $\text{CsCH}_3\text{COO}^0$  decreases from 0.00 at 25°C to  $-0.85$  at 175°C. Species distribution calculations performed by means of the experimentally determined dissociation constants in this study suggest that acetate complexes do not dominate either aqueous Sr or Cs speciation in most natural fluids; Cs acetate complexes likely never account for more than a few percent of the total Cs in solution. Although Sr-acetate complexing is more important, it may only dominate in extreme conditions. Copyright © 2001 Elsevier Science Ltd

### 1. INTRODUCTION

$^{137}\text{Cs}^+$  (half-life, 30 yr) and  $^{90}\text{Sr}^{2+}$  (half-life, 28 yr) are the most abundant radionuclides in radioactive waste and contamination associated with nuclear accidents and nuclear waste (e.g., Tamura, 1967; Brookins, 1984; Vakulovsky et al., 1994). The “reference transuranic waste,” generated at the Rocky Flats plant in Colorado, derives 93% of its initial radioactivity from  $^{90}\text{Sr}$  (Brookins, 1984) and 90% after 100 yr, although by 1000 yr, its activity and that of  $^{137}\text{Cs}$  will be negligible. The geohazard index is a unit for comparison of relative hazards of radionuclides on the basis of their toxicity, persistence, and quality of material. For a theoretical high-level waste repository inventory resulting from the production of 1000 GW of power, the total geohazard index calculated by Brookins (1984) was  $4.4 \times 10^{13}$ ; more than 99% of this was due to  $^{90}\text{Sr}$ .

$^{137}\text{Cs}$ , and to a lesser extent  $^{90}\text{Sr}$ , are radionuclides that affect areas contaminated by Chernobyl fallout (e.g., Brittain et al., 1992; Tikhomirov and Shcheglov, 1994; WHO, 1996); they are continuously released into the surface environment in the Chernobyl area of the Ukraine and the Mayak region of the Ural Mountains (Vakulovsky et al., 1994; Edwards, 1996, 1997; Matsunaga et al., 1998). A multitude of studies, therefore, have been undertaken to evaluate Sr and Cs mobility in surficial environments (e.g., Ivanushkina and Ryabtseva, 1991; Ryabtseva et al., 1991; Brittain et al., 1992; Tikhomirov and Shcheglov, 1994; Vakulovsky et al., 1994), plant uptake (e.g., Yoneda et al., 1993; Entry et al., 1994; Gray et al., 1995; Riesen and Brunner, 1996), animals (e.g., Peters and Brisbin, 1996), animal foodstuffs (e.g., Kennamer et al., 1993; Tveten, 1994; Howard et al., 1997), bioavailability (e.g., Avery, 1996), bioaccumulation (e.g., Amiardtriet et al., 1993), the evaluation of population exposure (e.g., Henrich and Steinhauser,

1993; WHO, 1996; Balanov, 1997), and possible decontamination methods for Sr and Cs radionuclides (e.g., Apak et al., 1996; Lumetta et al., 1996). Because of its similarity with calcium,  $^{90}\text{Sr}$  consumed by ingestion of drinking water or fodder accumulates in the hydroxyapatite of teeth and bones and is leukemogenic (Romanyukha et al., 1996).  $^{137}\text{Cs}$ , on the other hand, behaves in a similar fashion to Na in the body and is found all over the body (WHO, 1996). It is therefore of vital importance to understand the transport mechanism of these radionuclides in natural environments.

In aqueous environments,  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  are highly mobile at low and intermediate pHs; they are weakly attenuated by prospective waste repository backfill materials (e.g., some clays and majority of natural zeolites; Brookins, 1984). However, recently, it has been shown that bentonite clays exhibit capacity for irreversible Cs uptake, and such clays would be optimal for constructing artificial reactive barriers (Krumhansl et al., 2001). At  $\text{pH} > 10$ , Sr can be attenuated by inner-sphere sorption to goethite (Collins et al., 1998). Acetate is a common simple acid found in natural waters, basinal brines, and hydrothermal solutions (e.g., Giordano, 1985; Drummond and Palmer, 1986; Helgeson et al., 1993; Giordano and Kharaka, 1994). The formation of strontium and cesium–organic complexes could thus significantly affect the transport of Sr and Cs and consequently the results of Sr and Cs species distribution calculations. This is indicated by the observation that  $^{137}\text{Cs}$  is more mobile in organic rich soils than in mineral-rich soils (Comans et al., 1998) and that Sr is more mobile in the summer than in the winter (Brittain et al., 1992).

A large number of experimental studies have been performed over the past two decades to better quantify the interactions among metals and organic ligands in natural solutions. The bulk of these studies have been aimed at metal–acetate and metal–oxalate aqueous complex formation. This work includes studies generating dissociation constants of sodium–acetate

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complexes (Fournier et al., 1998), aluminum–acetate complexes (Fein, 1991a; Bénézeth et al., 1994; Palmer and Bell, 1994), iron–acetate complexes (Palmer and Drummond, 1988), magnesium–acetate complexes (Semmler et al., 1990; Fein, 1991a), lead–acetate complexes (Giordano, 1989; Fournier et al., 1997), cadmium–acetate complexes (Bénézeth and Palmer, 2000), aluminum–oxalate complexes (Couturier et al., 1984; Sjöberg and Öhman, 1985; Fein, 1991b; Thyne et al., 1992), lanthanum–, gadolinium–, and ytterbium–acetate complexes (Deberdt et al., 1998, 2000), and europium–acetate complexes (Zotov, pers. comm.). The use of these dissociation constants in species distribution calculations suggest that aqueous metal–organic complex formation can substantially increase mineral solubility and chemical mass transport in natural systems (Bénézeth et al., 1994; Fein, 1994; Fournier et al., 1998). To assess the effect of organics on Sr and Cs species distribution, dissociation constants of strontium–acetate and cesium–acetate complexes ( $\text{SrCH}_3\text{COO}^+$  and  $\text{CsCH}_3\text{COO}^0$ ) were measured by potentiometry. The purpose of this article is to present the results of this experimental study and to apply them to assess the role of  $\text{SrCH}_3\text{COO}^+$  and  $\text{CsCH}_3\text{COO}^0$  in natural processes.

To date, only few data exist on the stability of aqueous strontium acetate complexes.  $\text{SrCH}_3\text{COO}^+$  dissociation constants ( $K_{\text{SrAc}}$ ) at 25°C were deduced from solubility measurements by Coleman-Porter and Monk (1952) and measured by potentiometry by Nancollas (1956) and Archer and Monk (1964). No high-temperature  $K_{\text{SrAc}}$  values have been reported. Experimentally determined  $\text{CsCH}_3\text{COO}^0$  dissociation constants ( $K_{\text{CsAc}}$ ) are not available in the literature. To overcome the dearth of experimental data, Shock and Koretsky (1993) estimated standard partial molal thermodynamic data for Cs–acetate and proposed algorithms to predict  $\text{SrCH}_3\text{COO}^+$  and  $\text{CsCH}_3\text{COO}^0$  dissociation constants as a function of temperature and pressure. Their algorithm closely reproduce the 25°C Sr–acetate dissociation constants reported by Nancollas (1956) and Archer and Monk (1964), upon which their algorithm was based, but differ significantly from those reported by Coleman-Porter and Monk (1952).

## 2. EXPERIMENTAL METHODS

Potentiometric measurements were performed on solutions prepared with deionized/demineralized  $\text{H}_2\text{O}$  plus Prolabo Normapur reagent-grade  $\text{CH}_3\text{COOH}$ , NaOH, and either CsCl or  $\text{Sr}(\text{NO}_3)_2$ . Potentiometric titrations were conducted by creating a single 0.01 mol/kg NaOH/0.02 mol/kg  $\text{CH}_3\text{COOH}$  solution. Part of this solution was added to the potentiometric cell at the onset of the titration; the other part was spiked with either CsCl or  $\text{Sr}(\text{NO}_3)_2$  and used as a titrant. The total concentration of aqueous NaOH and  $\text{CH}_3\text{COOH}$  in the potentiometric cell therefore remained constant during each titration. Compositions of experimental solutions investigated during this study are provided in Table 1. All raw potentiometric data are tabulated in the Appendix.

Potentiometric measurements at temperatures of 25, 55, and 80°C were performed in a 60-cm<sup>3</sup> double-walled thermostated glass cell fitted to a PTFE lid to avoid evaporation. Temperature in this cell is regulated by flowing water through the exterior of the cell to within  $\pm 1^\circ\text{C}$ . Measurements were conducted with a Schott H62 combination electrode with a Philips PW9422 digital pH meter. Electrode calibration was performed with NBS phthalate and borate buffer solutions and the original titrant solution at each temperature. After a stable potential was obtained for each solution (typically within  $\pm 0.2$  mV), additional titrant was added to increase Cs or Sr concentration. Titrant was injected through a thin hole at the top of the potentiometric cell with a 10-mL syringe. When not injecting titrant, this hole was closed with a

Table 1. Solutions analyzed by potentiometry in the present study.

Solution	[HAc] (mol/kg)	[NaOH] (mol/kg)	[CsCl] (mol/kg)	[ $\text{Sr}(\text{NO}_3)_2$ ] (mol/kg)	Temperature (°C)
1	0.02002	0.01008	0–0.1663		25
2	0.02002	0.01008	0–0.1704		55
3	0.02002	0.01008	0–0.1968		80
4	0.02002	0.01008	0–0.1146		120
5	0.02006	0.010067	0–0.2050		160
6	0.0213	0.01008	0–0.2211		175
7	0.0213	0.01008		0–0.2236	25
8	0.0213	0.01008		0–0.2470	55
9	0.0213	0.01008		0–0.2342	80
10	0.0211	0.0100		0–0.2326	120
11	0.0211	0.0100		0–0.1830	160
12	0.0211	0.0100		0–0.1303	175

Teflon screw cap. The amount of injected solution was assessed by weighing the syringe before and after each injection. Eight to 19 injections were made for each initial solution such that Cs or Sr concentration ranged from 0 to 0.25 mol/kg.

At 120, 160, and 175°C, potentiometric measurements were performed in the  $\sim 300\text{-cm}^3$  titanium reactor shown in Figure 1. Solution potential of CsCl-bearing solutions were measured by means of three distinct pH electrodes, whereas those of  $\text{Sr}(\text{NO}_3)_2$ -bearing solutions were measured with a single pH electrode. The glass pH electrodes used for these high-temperature measurements were obtained from Potential and were connected to a Tacussel 2000 pH meter. Further details of the cell and electrode are provided by Pokrovski et al. (1996). An external AgCl/Ag, 3.2 M KCl electrode was used as a reference (Krukov et al., 1966). Electrodes were calibrated by measuring the potential of a 0.0107 mol/kg HCl solution, a 0.160 mol/kg  $\text{H}_3\text{BO}_3$ -0.0160 mol/kg NaOH solution, and the initial titrant solution at the temperature and pressure of interest. In all cases, the obtained electrode slope matched closely the theoretical Nernst slope. This reactor was placed into a temperature-regulated ( $\pm 1^\circ\text{C}$ ) oven, and approximately 200 cm<sup>3</sup> of initial solution was placed into the reactor. This solution

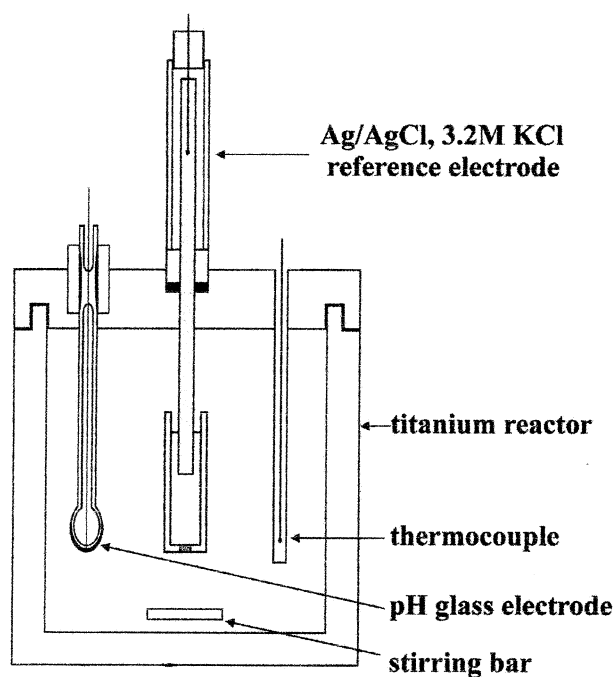


Fig. 1. Schematic illustration of the high-temperature potentiometric cell used in the present study.

Table 2. Values of dissociation constants used for data regression in the present study.

	Temperature (°C)					
	25	55	80	120	160	175
log $K_{\text{H}_2\text{O}}^{\text{a}}$	-13.995	-13.14	-12.61	-11.54	-11.54	-11.42
log $K_{\text{NaCl}}^{\text{b}}$	0.78	0.67	0.57	0.37	0.16	0.07
log $K_{\text{CsCl}}^{\text{a}}$	0.14	-0.02	-0.16	-0.36	-0.55	-0.63
log $K_{\text{SrCl}}^{\text{c}}$	0.24	0.08	-0.09	-0.43	-0.80	-0.95
log $K_{\text{HCl}}^{\text{d}}$	0.68	0.70	0.67	0.54	0.34	0.25
log $K_{\text{NaOH}}^{\text{e}}$	0.45	0.46	0.45	0.43	0.27	0.17
log $K_{\text{HAc}}^{\text{f}}$	-4.76	-4.80	-4.86	-5.02	-5.24	-5.34
log $K_{\text{NaAc}}^{\text{g}}$	0.11	0.07	-0.06	-0.25	-0.50	-0.60
log $K_{\text{SrNO}_3}^{\text{c}}$	-0.81	-0.66	-0.58	-0.52	-0.48	-0.48
log $K_{\text{SrOH}^+}^{\text{c}}$	13.28	12.30	11.61	10.72	9.99	9.75

<sup>a</sup> Johnson et al. (1992).<sup>b</sup> Shock et al. (1992).<sup>c</sup> Wolery (1979).<sup>d</sup> Ruaya and Seward (1987).<sup>e</sup> Pokrovskii and Helgeson (1995).<sup>f</sup> Shock (1995).<sup>g</sup> Shock and Koretsky (1993).

was stirred continuously and left overnight at 90°C so that the electrodes are not thermally shocked when heating the system to 120°C. Titrant was injected into this solution by putting a known quantity of titrant into a piston, which was subsequently injected into the cell by  $\text{N}_2(\text{g})$  pressure. Six to 10 injections were made to each initial solution such that the Cs or Sr concentration ranged from 0 to 0.23 mol/kg. After the injection of titrant, the cell potential stabilized in 2 to 4 min.

The pH of all solutions studied by potentiometry is related to the electromotive force of the potentiometric cell ( $E$ ) by means of

$$\text{pH} = \frac{(E - E^\circ - E_j)}{S}, \quad (1)$$

where  $E^\circ$  represents the sum of the standard glass electrode potential and the total reference electrode potential and  $E_j$  and  $S$  stand for the liquid junction potential and the electrode slope, respectively. Values of  $E^\circ$  and  $S$ , which depend only on temperature, were deduced from electrode calibration. Liquid junction potentials ( $E_j$ ) were estimated by the Henderson equation (Bates, 1973), together with limiting equivalent conductances for  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{OH}^-$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{Cl}^-$  computed by equations and parameters reported by Robinson and Stokes (1986) at 25°C. At higher temperatures, limiting equivalent conductances for all these species other than acetate anion were generated from equations and parameters reported by Oelkers and Helgeson (1989) at higher temperatures. Corresponding values for  $\text{CH}_3\text{COO}^-$  were assumed to be equal to 0.8 of the limiting equivalent conductance of  $\text{Na}^+$ . The contribution to  $E_j$  of other charged species is negligible. The variations of  $E_j$  between the initial  $\text{CH}_3\text{COOH-NaOH}$  solution and the final  $\text{CH}_3\text{COOH-NaOH-CsCl}$  solution are 1.5 mV at 25°C and 9 mV at 175°C. The corresponding values for  $\text{CH}_3\text{COOH-NaOH-Sr}(\text{NO}_3)_2$  solutions are 5 mV at 25°C and 11 mV at 175°C.

### 3. RETRIEVAL OF DISSOCIATION CONSTANTS

The standard state for aqueous species adopted in the present study is one of unit activity of the species in a hypothetical one molal solution referenced to infinite dilution at any temperature and pressure. The standard state adopted for  $\text{H}_2\text{O}$  corresponds to unit activity of the pure liquid at any temperature and pressure.

Equilibrium constants are obtained in the present study by the competition between  $\text{H}^+$  and either  $\text{Cs}^+$  or  $\text{Sr}^{2+}$  for association with acetate ions. The addition of either  $\text{Cs}^+$  or  $\text{Sr}^{2+}$  to an acetic acid bearing solution liberates protons through the formation of metal acetate complexes, thus lowering pH. The reaction dissociating an aqueous metal acetate complex can be written



for which the laws of mass action can be expressed as

$$K = \frac{a_{\text{CH}_3\text{COO}^-} a_{\text{M}^+}}{a_{\text{MCH}_3\text{COO}^0}} = \frac{c_{\text{CH}_3\text{COO}^-} c_{\text{M}^+}}{c_{\text{MCH}_3\text{COO}^0}} \frac{\gamma_{\text{CH}_3\text{COO}^-} \gamma_{\text{M}^+}}{\gamma_{\text{MCH}_3\text{COO}^0}}, \quad (3)$$

where  $K$  designates the dissociation constant,  $\text{M}^+$  and  $a_i$  refers to the activity of the subscripted aqueous species,  $C_i$  denotes the concentration of the subscripted species, and  $\text{M}$  refers the aqueous metal of interest. The equation adopted in the present study to compute the activity coefficients of charged species is given by (Helgeson et al., 1981)

$$\log \gamma_i = \frac{A_\gamma Z_i^2 \sqrt{I}}{1 + a B_\gamma \sqrt{I}} + \Gamma_\gamma + (\omega_i^{\text{abs}} b_{\text{NaCl}} + b_{\text{Na}^+\text{Cl}^-} - 0.19(|Z_i| - 1) \bar{I}), \quad (4)$$

where  $A_\gamma$  and  $B_\gamma$  signify Debye-Hückel electrostatic parameters,  $Z_i$  denotes the charge of the subscripted aqueous species,  $a$  designates an ion size parameter taken to be 4 Å for all charged species other than  $\text{H}^+$  (for which  $a$  is set to 9 Å),  $\bar{I}$  stands for the effective ionic strength of the solution,  $\Gamma_\gamma$  refers to a mole fraction to molality conversion factor,  $\omega_i^{\text{abs}}$  represents the absolute Born coefficient for the subscripted species, and  $b_{\text{NaCl}}$  and  $b_{\text{Na}^+\text{Cl}^-}$  correspond to extended term parameters for the NaCl electrolyte. Parameters required to compute activity coefficients using Eqn. 4 were taken from Helgeson et al. (1981) and Shock et al. (1992). Activity coefficients of neutral solute species were taken to be unity. Dissociation constants in the present study were generated assuming the following species were present in solution:  $\text{CH}_3\text{COOH}^0$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{NaCH}_3\text{COO}^0$ ,  $\text{CsCH}_3\text{COO}^0$  or  $\text{SrCH}_3\text{COO}^+$ ,  $\text{Cs}^+$  or  $\text{Sr}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{NaOH}^0$ ,  $\text{NaCl}^0$ ,  $\text{HCl}^0$ ,  $\text{CsCl}^0$  or  $\text{SrCl}^+$ ,  $\text{OH}^-$ ,  $\text{H}^+$ , and  $\text{H}_2\text{O}$ . For the case of  $\text{CH}_3\text{COOH-NaOH-CsCl}$  solutions, the 14 equations required to define the activities of each of the 14 aqueous species assumed present in solution consist of five mass balance equations (one each for total  $\text{CH}_3\text{COOH}$ , Na, Cl, Cs, and H), eight mass action equations (one each for the dissociation of  $\text{CH}_3\text{COOH}^0$ ,  $\text{NaCH}_3\text{COO}^0$ ,  $\text{CsCH}_3\text{COO}^0$ ,  $\text{NaOH}^0$ ,  $\text{NaCl}^0$ ,  $\text{HCl}^0$ ,  $\text{CsCl}^0$ , and  $\text{H}_2\text{O}$ ), and the definition of  $\text{H}_2\text{O}$  activity prescribed by the adopted standard state. For the case of the  $\text{CH}_3\text{COOH-NaOH-Sr}(\text{NO}_3)_2$  solutions, two additional species were also considered:  $\text{NO}_3^-$  and  $\text{Sr}(\text{NO}_3)^+$ . Sixteen equations are thus required to define the activities of each of the 16 aqueous species assumed present in these solutions—specifically, six mass balance equations (one each for total  $\text{CH}_3\text{COOH}$ , Na, Cl, Sr,  $\text{NO}_3^-$ , and H), nine mass action equations (one each for the dissociation of  $\text{CH}_3\text{COOH}^0$ ,  $\text{NaCH}_3\text{COO}^0$ ,  $\text{SrCH}_3\text{COO}^+$ ,  $\text{Sr}(\text{NO}_3)^+$ ,  $\text{NaOH}^0$ ,  $\text{NaCl}^0$ ,  $\text{HCl}^0$ ,  $\text{SrCl}^+$ , and  $\text{H}_2\text{O}$ ), and the definition of  $\text{H}_2\text{O}$  activity prescribed by the adopted standard state. Equilibrium constants for  $\text{CH}_3\text{COOH}^0$ ,  $\text{NaCH}_3\text{COO}^0$ ,  $\text{NaOH}^0$ ,  $\text{NaCl}^0$ ,  $\text{HCl}^0$ ,  $\text{SrCl}^+$ ,  $\text{Sr}(\text{NO}_3)^+$ , and  $\text{H}_2\text{O}$  dissociation are listed in Table 2. The final dissociation constant for  $\text{CsCH}_3\text{COO}^0$  or  $\text{SrCH}_3\text{COO}^+$  was generated by fixing the hydrogen ion activity to that measured during each titration. This regression was performed with the aid of the Eqn. 3 computer code (Wolery, 1979) by adopting a provisional estimate for the  $\text{CsCH}_3\text{COO}^0$  or  $\text{SrCH}_3\text{COO}^+$  dissociation constant and calculating the solution pH as a function of Cs or Sr concentration. The resulting pH–composition curve was compared with the measured pH values. If the calculated pH differed from those measured, a new estimated dissociation constant was chosen and the process was repeated. The process was continued until the computed pH was equal to within uncertainty to that deduced from the potentiometric measurements.

### 4. RESULTS AND DISCUSSION

The degree to which the formation of aqueous metal complexes affected the measured pH of the aqueous  $\text{CH}_3\text{COOH-NaOH-CsCl}$  and  $\text{CH}_3\text{COOH-NaOH-Sr}(\text{NO}_3)_2$  solutions considered in this study can be assessed with the aid of Figures 2 and 3. The dashed curves in these figures represent pH computed assuming no formation of aqueous  $\text{CsCH}_3\text{COO}^0$  or  $\text{SrCH}_3\text{COO}^+$ . It can be seen in these figures that pH computed

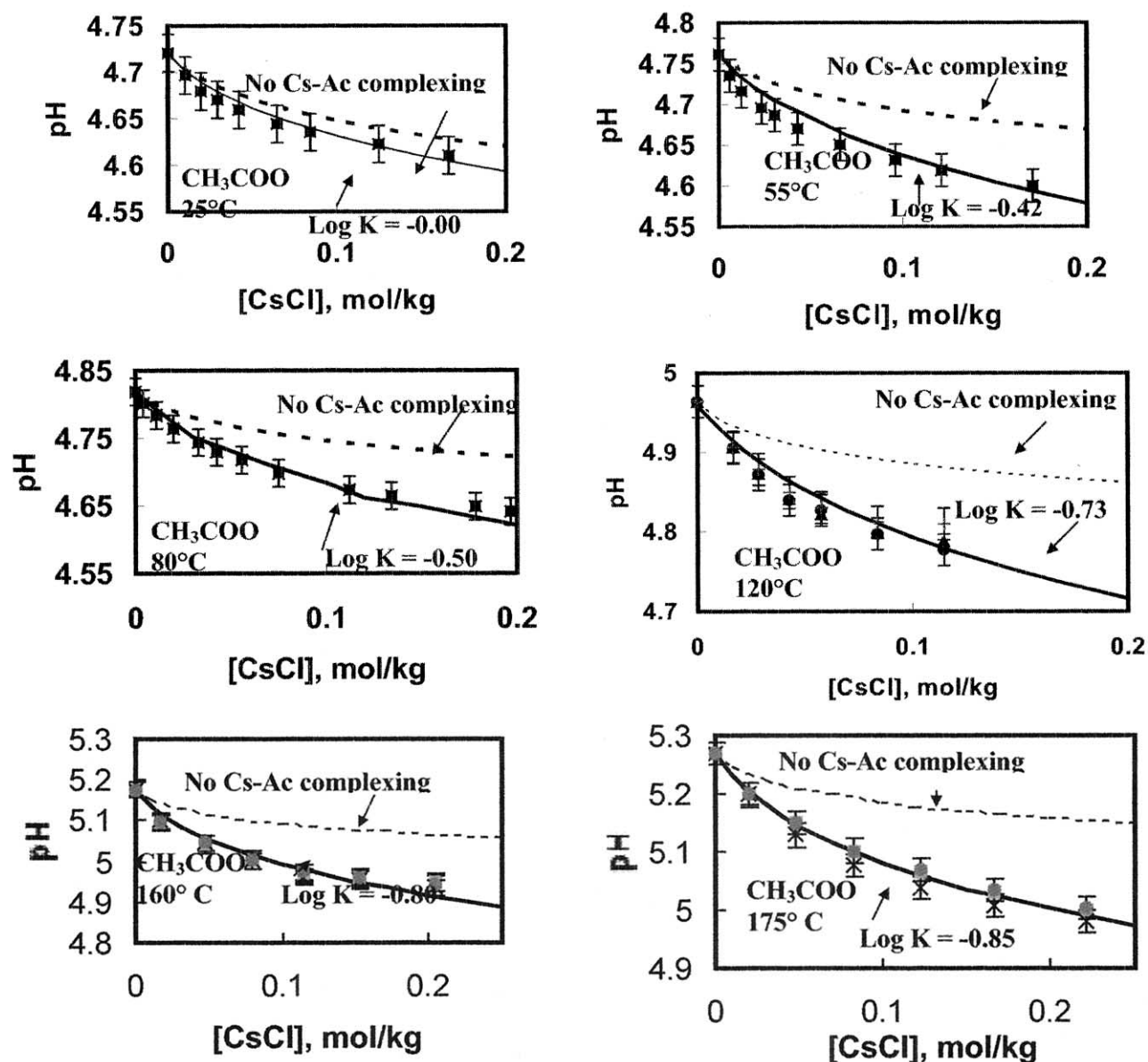


Fig. 2. Variation of measured pH as a function of aqueous Cs concentration measured during the potentiometric titrations performed at the indicated temperatures in the present study. The symbols represent measured pH values; the dashed and solid curves correspond to the results of regression calculations performed, assuming no Cs-Ac complexing and the presence of Cs-Ac complexes having the indicated dissociation constant, respectively.

assuming no aqueous  $\text{CsCH}_3\text{COO}^0$  or  $\text{SrCH}_3\text{COO}^+$  formation are significantly higher than those obtained from potentiometric measurements. This difference was resolved by assuming that aqueous  $\text{CsCH}_3\text{COO}^0$  or  $\text{SrCH}_3\text{COO}^+$  formed in accord with the dissociation constants given in these figures and Table 3. The dissociation constants given in these figures were obtained from the regression method described above; the solid curves illustrate the results of these regression calculations. Corresponding calculations performed assuming the existence of two aqueous Sr-acetate complexes ( $\text{SrCH}_3\text{COO}^+$  and  $\text{Sr}(\text{CH}_3\text{COO})_2^0$ ) or two Cs-acetate complexes ( $\text{CsCH}_3\text{COO}^0$  and  $\text{Cs}(\text{CH}_3\text{COO})_2^-$ ) did not improve the quality of these fits. This observation, and the fact that the computed pH values

accurately represent the shape of the experimentally measured pH values indicates that our data are consistent with the formation of only a single 1:1 metal acetate complex in both the Cs- and Sr-bearing solutions considered in this study. Moreover, pH-composition curves generated assuming the 1:2 metal acetate complex formed were inconsistent with measured pH values.

Resulting  $\text{CsCH}_3\text{COO}^0$  or  $\text{SrCH}_3\text{COO}^+$  dissociation constants are illustrated as a function of temperature in Figures 4 and 5, where they can be compared to previously measured dissociation constants as well as estimates reported by Shock and Koretsky (1993). The 25°C  $\text{SrCH}_3\text{COO}^+$  dissociation constant generated in the present study is approximately 0.2 log

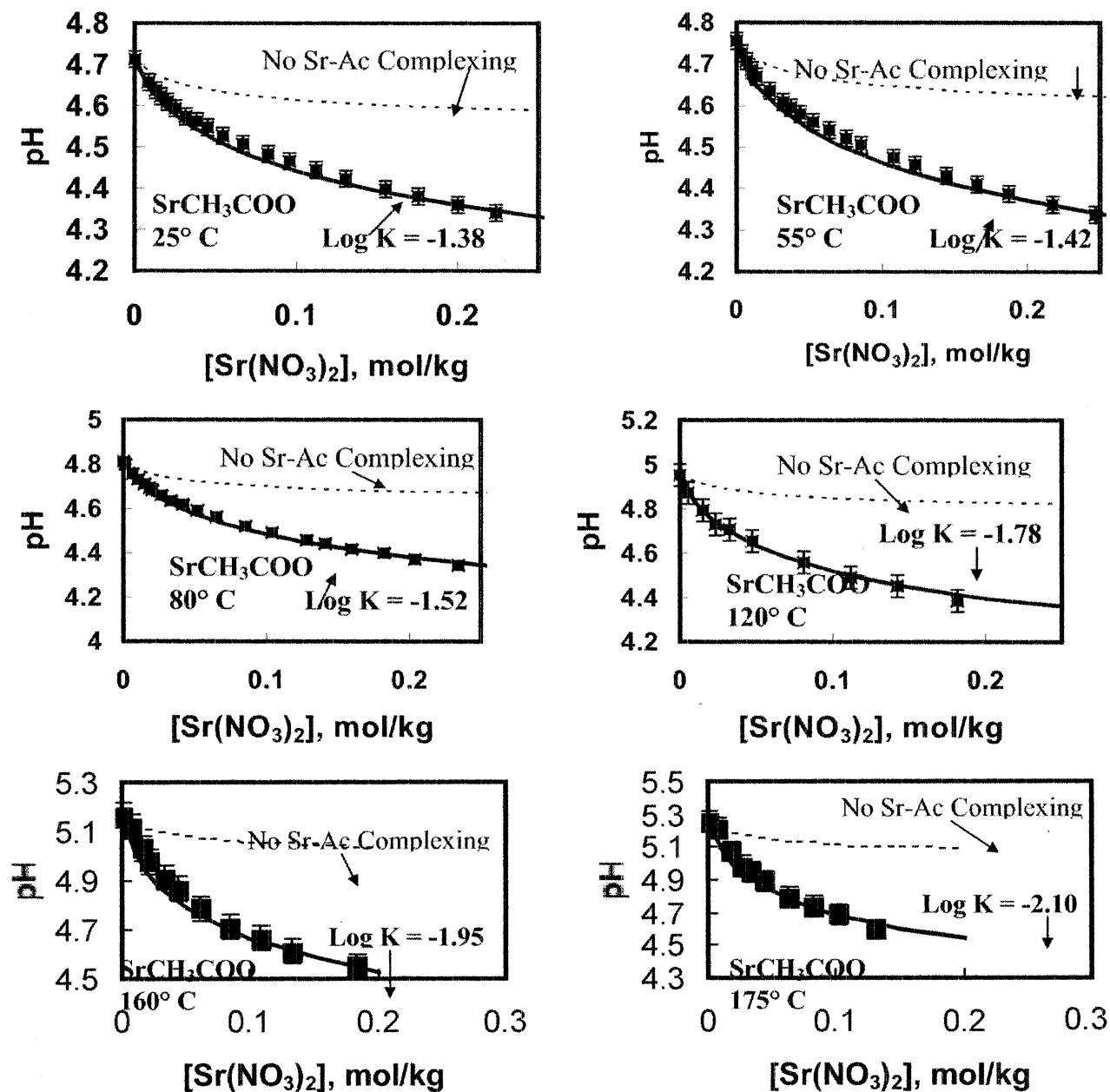


Fig. 3. Variation of measured pH as a function of aqueous Sr concentration measured during the potentiometric titrations performed at the indicated temperatures in the present study. The symbols represent measured pH values; the dashed and solid curves correspond to the results of regression calculations performed, assuming no Sr-Ac complexing and the presence of Sr-Ac complexes having the indicated dissociation constant, respectively.

units lower than that reported by Archer and Monk (1964). This difference may be because these previous investigators did not account for the effect of liquid junction potentials when generating pH values from their measured potentials. This may also be the reason why Archer and Monk (1964) were unable to retrieve  $\text{CsCH}_3\text{COO}^0$  dissociation constants from their potentiometric measurements. Our measured dissociation constants are at most 0.2 log units different from those estimated by Shock and Koretsky (1993), although the slope of the measured

$\text{SrCH}_3\text{COO}^+$  dissociation constant vs. temperature differ significantly from the previously proposed estimates.

Uncertainties associated with the equilibrium constants obtained in the present study are difficult to assess quantitatively because of the large number of equilibrium constants and the limitations of the Henderson equation to computing liquid junction potentials. Consideration of these contributions and the  $\pm 0.02$  estimated uncertainty associated with the pH values generated from potentiometric measurements in the present

Table 3. Dissociation constants for metal acetate complexes obtained in the present study.

Temperature	CsCH <sub>3</sub> COO <sup>0</sup>	SrCH <sub>3</sub> COO <sup>+</sup>
25	0.00	-1.38
55	-0.42	-1.42
80	-0.50	-1.52
120	-0.73	-1.78
160	-0.08	-1.95
175	-0.85	-2.10

study suggest a reasonable estimate of the uncertainty associated with the log K values listed in Table 3 is on the order of  $\pm 0.2$  log units.

#### 4.1. SPECIES DISTRIBUTION CALCULATIONS

To assess the potential effect of aqueous strontium- and cesium-acetate complexes in natural systems, species distribution calculations were performed as a function of temperature on pH = 6 aqueous solutions containing 0.1 m NaCl, 1000 ppm total acetate, and 0.001 m CsCl or SrCl<sub>2</sub>. These calculations were performed by means of the Eqn. 3 computer code (Wolery, 1979) together with equilibrium constants listed in Table 2, and those for Sr-carbonate complexes generated from SUPCRT92 (Johnson et al., 1992) and the SLOP98 database (Shock et al., 1997; Sverjensky et al., 1997; Shock, 1998). The results of calculations performed in the presence of Cs are illustrated in Figure 6. The Cs in these solutions is dominated by the Cs<sup>+</sup> aqueous ion at all temperatures to at least 175°C. CsCH<sub>3</sub>COO<sup>0</sup> accounts for at most 3% of the Cs present in solution. Moreover, for these simple solutions, Cs-chloride complexation is far more important than acetate complexation; CsCl<sup>0</sup> concentrations are approximately four times greater than those of CsCH<sub>3</sub>COO<sup>0</sup> at all temperatures from 25 to 175°C.

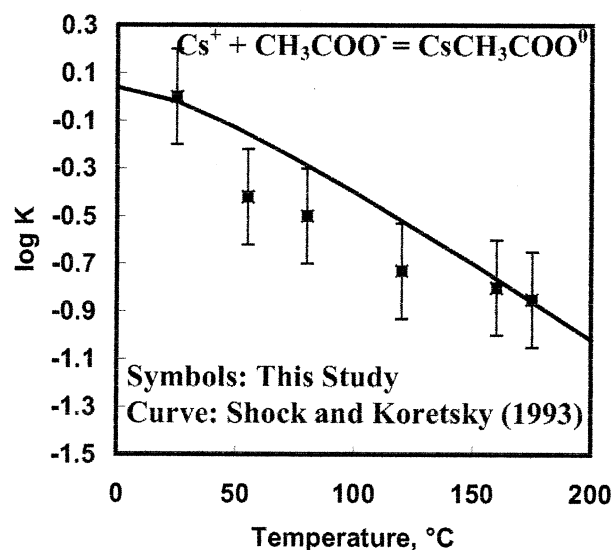


Fig. 4. Comparison of aqueous cesium acetate dissociation constants as a function of temperature. The symbols represent the logarithm of dissociation constants obtained from experimental measurements; the curve corresponds to correlations reported in the literature (see text).

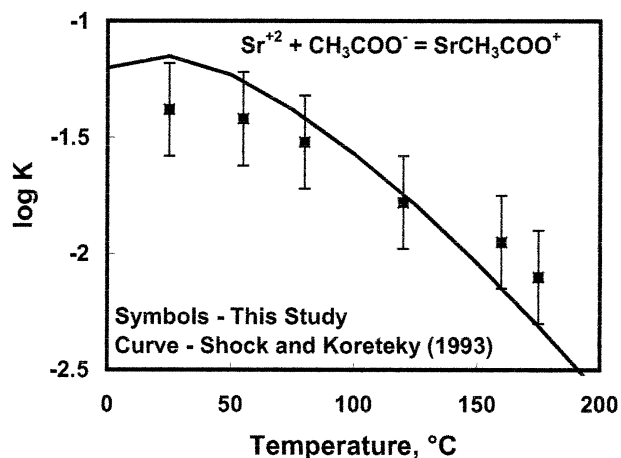


Fig. 5. Comparison of aqueous strontium acetate dissociation as a function of temperature. The symbols represent the logarithm of dissociation constants obtained from experimental measurements; the curve corresponds to theoretical extrapolations of 25° experimental data reported in the literature (see text).

Although increasing the concentration of this solution to an extreme case of 10,000 ppm acetate makes acetate complexation more important than chloride complexation, Cs<sup>+</sup> is still the dominant cesium-bearing aqueous species.

Results for Sr-bearing solutions are illustrated in Figure 7. SrCH<sub>3</sub>COO<sup>+</sup> accounts for 11.6% of the Sr present in solution at 25°C; this percentage increases to 23.5% at 175°C. In contrast to the results discussed above for Cs acetate, Sr-chloride complexes appear to be less important than acetate complexes by a factor of 2 to 5, depending on the temperature. Nevertheless, the free Sr<sup>2+</sup> aqueous ion dominates these solutions at all temperatures up to 175°C. It is only in the extreme case of increasing the aqueous acetate concentration of these solutions to 10,000 ppm that acetate complexes could dominate Sr speciation in these solutions. Such high aqueous acetate concentrations are, however, uncommon in natural systems, and where present, such systems may also contain other aqueous acetate

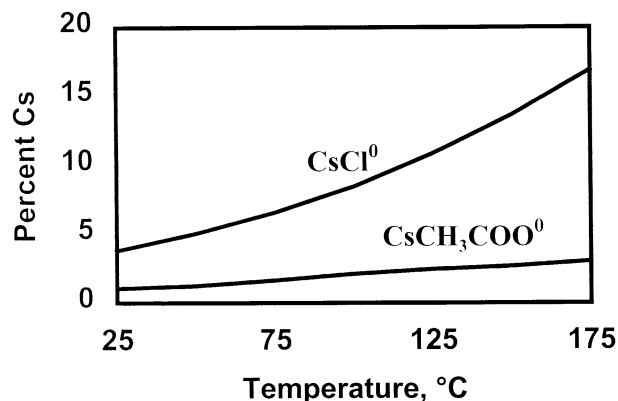


Fig. 6. Results of species distribution calculations performed on a pH 6 aqueous solution containing 0.1 m NaCl, 1000 ppm total acetate, and 0.001 m CsCl depicted as a function of temperature. The curves correspond to the percentage of the labeled species present in solution (see text).

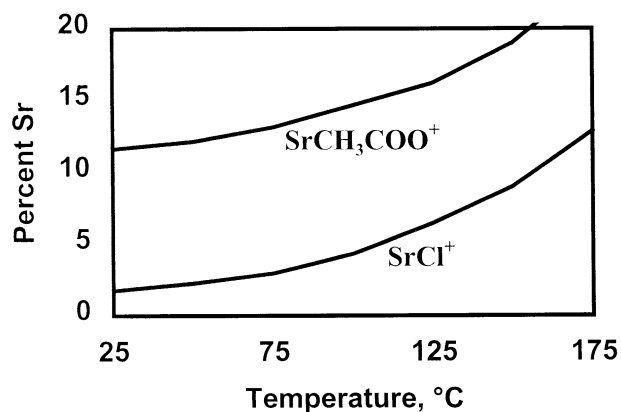


Fig. 7. Results of species distribution calculations performed on a pH 6 aqueous solution containing 0.1 m NaCl, 1000 ppm total acetate, and 0.001 m SrCl<sub>2</sub> depicted as a function of temperature. The curves correspond to the percentage of the labeled species present in solution (see text).

complexing metals such as Al and Fe, which would compete with Sr for the free acetate. Note that the presence of dissolved CO<sub>2</sub> has little effect on these results; if the dissolved CO<sub>2</sub> concentration of these Sr-bearing solutions were controlled by strontianite solubility, aqueous Sr-carbonate species would account for at most 5.5% of the Sr present in solution.

## 5. CONCLUSIONS

The application of aqueous Cs-acetate and Sr-acetate dissociation constants obtained in this study by potentiometry suggest that these complexes do not dominate Cs or Sr speciation in most natural fluids. It appears unlikely that aqueous Cs-acetate complexes ever account for more than a few percent of the total Cs present in natural solutions; Sr-acetate complexes can be more important but may only dominate aqueous Sr speciation in extreme conditions. It should nevertheless be emphasized in this regard that because other aqueous organic anions, such as oxalate, may be more effective Cs and Sr complexing agents than acetate, and because <sup>90</sup>Sr and <sup>137</sup>Cs bearing intermediate- and high-level nuclear waste repositories will initially contain high quantities of organic material (e.g., Savage, 1995), aqueous organic transport may be significant for the transport of these radionuclides from waste repositories.

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## APPENDIX

Summary of Solution Compositions, Measured Potentials, and Computed pH Obtained in the Present Study

**CsCl<sub>+</sub>NaOH<sub>+</sub>CH<sub>3</sub>COOH**

25°C Initial solution: 0.01008 m/kg NaOH + 0.02002 m CH<sub>3</sub>COOH

Titration	C <sub>CsCl</sub>	Potential (mV)	pH
0	0	139.7	4.721
1	0.010403	140.7	4.697
2	0.019623	141.5	4.680
3	0.029373	141.9	4.670
4	0.041986	142.4	4.659
5	0.064594	143.1	4.544
6	0.08731	143.5	4.636
7	0.124807	144.1	4.623
8	0.16630	144.7	4.610

55°C Initial solution: 0.01008 m/kg NaOH + 0.02002 m CH<sub>3</sub>COOH

Titration	C <sub>CsCl</sub>	Potential (mV)	pH
0	0	147.1	4.680
1	0.005927	148.3	4.660
2	0.012290	149.2	4.646
3	0.023158	150.1	4.631
4	0.030220	150.5	4.625
5	0.042652	151.3	4.612
6	0.65722	152.2	4.597
7	0.095938	153.1	4.582
8	0.120916	153.7	4.573
9	0.170452	154.6	4.558

80°C Initial solution: 0.01008 m/kg NaOH + 0.02002 m CH<sub>3</sub>COOH

Titration	C <sub>CsCl</sub>	Potential (mV)	pH
0	0	153.1	4.819
1	0.004242	153.8	4.802
2	0.01111	154.5	4.784
3	0.019942	155.4	4.764
4	0.033042	153.3	4.744
5	0.042598	157.0	4.730
6	0.055797	157.5	4.718
7	0.075083	158.5	4.698
8	0.112296	159.7	4.676
9	0.134289	160.1	4.665
10	0.178301	160.8	4.649
11	0.196788	161.2	4.641

120°C Initial solution: 0.01008 m/kg NaOH + 0.02002 m CH<sub>3</sub>COOH

Titration	C <sub>CsCl</sub>	Electrode 3/4		Electrode 4yct7		Electrode 5	
		Potential (mV)	pH	Potential (mV)	pH	Potential (mV)	pH
0	0	-643.2	4.964	-616.2	4.964	-642.8	4.964
1	0.01663	-640.7	4.906	-613.7	4.907	-640.2	4.905
2	0.02834	-638.1	4.873	-612.2	4.879	-638.3	4.872
3	0.04261	-636.9	4.841	-610.5	4.849	-636.4	4.840
4	0.05743	-635.4	4.822	-609.5	4.830	-633.2	4.827
5	0.08368	-634.8	4.799	-608.7	4.812	-634.2	4.797
6	0.11455	-634.5	4.788	-609.1	4.810	-633.2	4.777

160°C Initial solution: 0.01006 m/kg NaOH + 0.020067 m/kg CH<sub>3</sub>COOH

Titration	C <sub>CsCl</sub>	Electrode 3/4		Electrode 4yct7		Electrode 5	
		Potential (mV)	pH	Potential (mV)	pH	Potential (mV)	pH
0	0	-673.3	5.176	-648.0	5.176	-673.2	5.176
1	0.01732	-669.3	5.095	-644.4	5.100	-669.4	5.098
2	0.04744	-666.9	5.042	-641.9	5.404	-667.1	5.046
3	0.07856	-664.9	5.004	-639.5	5.003	-664.6	5.002
4	0.1148	-663	4.970	-637.0	4.962	-663.1	4.973
5	0.1527	-662.9	4.960	-637.1	4.954	-662.7	4.960
6	0.2050	-662.7	4.949	-636.3	4.936	-662.2	4.645

175°C Initial solution: 0.01008 m/kg NaOH + 0.0213 m/kg CH<sub>3</sub>COOH

Titration	C <sub>CsCl</sub>	Electrode 3/4		Electrode 4yct7		Electrode 5	
		Potential (mV)	pH	Potential (mV)	pH	Potential (mV)	pH
0	0	-685.2	5.268	-662.2	5.268	-685.2	5.268
1	0.02012	-682.4	5.201	-659.2	5.198	-682.3	5.200
2	0.04853	-679.7	5.150	-655.0	5.129	-679.6	5.148
3	0.08307	-676.8	5.102	-651.7	5.077	-676.6	5.100
4	0.1220	-674.8	5.068	-649.3	5.039	-674.4	5.064
5	0.1660	-672.7	5.036	-647.4	5.009	-672.3	5.032
6	0.2211	-670.7	5.005	-645.6	4.980	-670.3	5.001

**Sr(NO<sub>3</sub>)<sub>2</sub> + NaOH + CH<sub>3</sub>COOH**25°C Initial solution: 0.01008 m/kg NaOH + 0.0213 m/kg CH<sub>3</sub>COOH

Titration	C <sub>Sr(NO<sub>3</sub>)<sub>2</sub></sub>	Potential (mV)	pH
0	0	139.6	4.713
1	0.00879	142.1	4.657
2	0.01307	143.0	4.637
3	0.01618	143.7	4.622
4	0.02032	144.3	4.609
5	0.02515	145.05	4.593
6	0.03153	146.0	4.574
7	0.03848	146.5	4.562
8	0.04499	147.2	4.547
9	0.05451	148.2	4.527
10	0.06698	149.1	4.507
11	0.08242	150.3	4.482
12	0.09581	151.1	4.465
13	0.1122	152.1	4.444
14	0.1305	153.1	4.423
15	0.1553	154.3	4.398
16	0.1756	155.1	4.380
17	0.2000	156.1	4.359
18	0.2236	157.0	4.340

55°C Initial solution: 0.01008 m/kg NaOH + 0.0213 m/kg CH<sub>3</sub>COOH

Titration	C <sub>Sr(NO<sub>3</sub>)<sub>2</sub></sub>	Potential (mV)	pH
0	0	148.5	4.756
1	0.00364	149.9	4.726
2	0.00681	150.8	4.707
3	0.01053	151.9	4.685
4	0.01362	152.7	4.670
5	0.02287	154.4	4.636
6	0.03204	155.8	4.609
7	0.03738	156.5	4.595
8	0.04370	157.3	4.580
9	0.05254	158.3	4.561
10	0.06372	159.3	4.541
11	0.07545	160.4	4.520
12	0.08563	161.2	4.505
13	0.1079	162.8	4.475
14	0.1225	163.7	4.457
15	0.1442	165.1	4.431
16	0.1653	166.2	4.410
17	0.1872	167.4	4.388
18	0.2175	168.8	4.362
19	0.2470	170.1	4.337

80°C Initial solution: 0.01008 m/kg NaOH + 0.0213 m/kg CH<sub>3</sub>COOH

Titration	C <sub>Sr(NO<sub>3</sub>)<sub>2</sub></sub>	Potential (mV)	pH
0	0	154.8	4.706
1	0.00159	155.2	4.700
2	0.00654	157.3	4.668
3	0.01029	158.6	4.648
4	0.01475	159.7	4.631
5	0.01837	160.6	4.617
6	0.02026	161.1	4.610
7	0.02665	162.4	4.590
8	0.03328	163.7	4.570
9	0.04165	164.4	4.559

80°C Initial solution: 0.01008 m/kg NaOH + 0.0213 m/kg CH<sub>3</sub>COOH

Titration	C <sub>Sr(NO<sub>3</sub>)<sub>2</sub></sub>	Potential (mV)	pH
10	0.05172	165.9	4.536
11	0.06492	167.5	4.512
12	0.08541	169.8	4.477
13	0.1039	171.4	4.452
14	0.1281	173.2	4.425
15	0.1411	174.1	4.411
16	0.1596	175.5	4.390
17	0.1821	176.4	4.376
18	0.2038	178.0	4.351
19	0.2342	179.5	4.329

120°C Initial solution: 0.01000 m/kg NaOH + 0.0211 m/kg CH<sub>3</sub>COOH

Titration	C <sub>Sr(NO<sub>3</sub>)<sub>2</sub></sub>	Potential (mV)	pH
0	0	-635.4	4.952
1	0.0536	-631.6	4.872
2	0.01510	-627.7	4.793
3	0.02333	-624.0	4.730
4	0.03261	-623.1	4.706
5	0.04732	-620.2	4.654
6	0.08098	-614.5	4.558
7	0.1117	-610.4	4.490
8	0.1422	-608.3	4.452
9	0.1816	-604.0	4.385
10	0.2326	-599.7	4.317

160°C Initial solution: 0.01000 m/kg NaOH + 0.0211 m/kg CH<sub>3</sub>COOH

Titration	C <sub>Sr(NO<sub>3</sub>)<sub>2</sub></sub>	Potential (mV)	pH
0	0	-674.1	5.164
1	0.00662	-673.2	5.123
2	0.01499	-667.3	5.033
3	0.02140	-663.7	4.981
4	0.03238	-659.0	4.912
5	0.04381	-656.0	4.867
6	0.06116	-650.3	4.788
7	0.08321	-644.8	4.712
8	0.1076	-641.8	4.667
9	0.1331	-638.0	4.613
10	0.1830	-633.8	4.551

175°C Initial solution: 0.01000 m/kg NaOH + 0.0211 m/kg CH<sub>3</sub>COOH

Titration	C <sub>Sr(NO<sub>3</sub>)<sub>2</sub></sub>	Potential (mV)	pH
0	0	-689.4	5.260
1	0.0622	-688.1	5.216
2	0.01676	-677.9	5.077
3	0.02546	-670.9	4.985
4	0.03344	-668.8	4.952
5	0.04428	-664.5	4.894
6	0.06259	-656.7	4.974
7	0.08151	-652.8	4.740
8	0.1004	-649.0	4.689
9	0.1303	-642.0	4.599