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MEDIUM COMPOSITION DEPENDENCE OF LEAD(II) COMPLEXATION BY CHLORIDE ION

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ABSTRACT. Determinations of the stepwise formation constants of $PbCl^+$, $PbCl^\circ_2$, and $PbCl^-_3$ in aqueous HCl–$HClO_4$, $NaCl$–$NaClO_4$, $MgCl_2$, and $CaCl_2$ media exhibit systematic medium composition effects at constant ionic strength. Our results indicate that the cationic composition of our test media influences the affinity of chloride ions for trace metals in a quantitatively predictable manner. Medium composition effects for both Pb(II) and Cu(II) complexation can be described in terms of chloride activity coefficient variation at constant ionic strength. Our lead chloride formation constant results at ionic strengths up to one molar are quantitatively examined in terms of the chloride ion pairing model of Johnson and Pytkowicz (1978).

INTRODUCTION

During investigations of lead and copper complexation in various chloride media, we found it necessary to consider the influence of medium on lead(II) and copper(II) complexation constants. Various lines of evidence (Näsänen and Lumme, 1951; Johnson and Pytkowicz, 1978; Sipos and others, 1980; Byrne, Young, and Miller, 1981) suggest that chloride complexation constants are strongly influenced, not only by ionic strength, but also by cationic medium composition. In this work we describe the effect of medium composition on three stepwise lead chloride formation constants:

$$Pb^{2+} + Cl^- \rightleftharpoons PbCl^+ ,\ K_1 = \frac{[PbCl^+]}{[Pb^{2+}]\,[Cl^-]} \tag{1}$$

$$PbCl^+ + Cl^- \rightleftharpoons PbCl^\circ_2 ,\ K_2 = \frac{[PbCl^\circ_2]}{[PbCl^+]\,[Cl^-]} \tag{2}$$

$$PbCl^\circ_2 + Cl^- \rightleftharpoons PbCl^-_3 ,\ K_3 = \frac{[PbCl^-_3]}{[PbCl^\circ_2]\,[Cl^-]} \tag{3}$$

We have examined the ionic strength dependence of these constants in aqueous HCl–$HClO_4$, $NaCl$–$NaClO_4$, $MgCl_2$, and $CaCl_2$ media at 25°C and 1 atm total pressure.

The medium composition effects we report are similar to those observed by Näsänen and Lumme (1951) in an investigation of the equilibrium

$$Cu^{2+} + Cl^- \rightleftharpoons CuCl^+ ,\ K_1(CuCl^+) = \frac{[CuCl^+]}{[Cu^{2+}]\,[Cl^-]} \tag{4}$$

At constant ionic strength, $K_1(CuCl^+)$ varies substantially between the media $HClO_4$, $NaClO_4$, and $Ca(ClO_4)_2$ (Näsänen and Lumme, 1951). The observed medium composition dependence of $K_1(CuCl^+)$ was attributed to the sum effects of Cu^{2+}, $CuCl^+$, and Cl^- activity coefficient variations.

Examinations of K_1, K_2, and K_3 in $HCl–HClO_4$, $NaCl–NaClO_4$, $MgCl_2$, and $CaCl_2$ suggest that the observed medium composition dependencies may be due dominantly to variations in chloride ion activity coefficients at constant ionic strength. Quantitative predictions of chloride ion activity coefficient variations in our test media are provided by the chloride ion pairing model of Johnson and Pytkowicz (1978). In this work our lead complexation data and the copper complexation data of Näsänen and Lumme (1951) are quantitatively compared with the predictions of the Johnson and Pytkowicz (1978) model.

EXPERIMENTAL SECTION

The complexation of lead by chloride ions was monitored using UV absorbance spectroscopy. Solutions were housed in 1 cm pathlength quartz cuvettes thermostated at 25.0 ± 0.1°C. Experiments were conducted by measuring the UV absorbance of 2×10^{-4} molar Pb(II) in various chloride media at 5 nm intervals over the 210 to 300 nm wavelength range.

Our twelve $CaCl_2$ and ten $MgCl_2$ experimental media were formed by mixing 0.01 molar HCl with either 0.33 molar $CaCl_2$ + 0.01 molar HCl or 0.33 molar $MgCl_2$ + 0.01 M HCl. The eleven NaCl media examined contained 0.01 M HCl and NaCl in concentrations not greater than 0.99 molar. Thirteen of our experimental media were solutions of HCl at total concentrations between 1.0 and 0.01 molar. Our five $NaCl–NaClO_4$ media were 0.01 molar in HCl and $\cong$ 0.305 molar in total chloride. Our five $HCl–HClO_4$ media were 0.296 molar in HCl. The total ionic strength of our test media varied between 0.010 and 1.00 molar.

The ultraviolet absorbance of Pb(II) in our experimental media can be expressed as the summation of absorbance contributions from unassociated Pb^{2+} and its chloride complexes (Byrne, Young, and Miller, 1981);

$$A = {}_\lambda\epsilon_0[Pb^{2+}] + {}_\lambda\epsilon_1[PbCl^+] + {}_\lambda\epsilon_2[PbCl^\circ_2] + {}_\lambda\epsilon_3[PbCl^-_3] \qquad (5)$$

where ${}_\lambda A$ is the total absorbance of Pb(II) at wavelength λ, ${}_\lambda\epsilon_0$ and ${}_\lambda\epsilon_i$ are the molar absorptivities of Pb^{2+} and $PbCl_i$ at wavelength λ, and brackets denote the molar concentration of each chemical species. Using (A) eq (5), (B) the known molar absorptivity characteristics of Pb^{2+}, $PbCl^+$, $PbCl^\circ_2$, and $PbCl^-_3$ (Byrne, Young, and Miller, 1981), and (C) absorbance data at 19 wavelengths, the four unknown lead concentrations in eq (5) can be determined by least squares analysis (Byrne, Young, and Miller, 1981; Byrne and Kester, 1978). Formation constants for each lead chloride complex can then be determined using the known chloride ion concentration in each of our experimental media. All formation constants and ionic strengths reported in this work are expressed in terms of molar concentrations. Further experimental and analytical details follow the methods used by Byrne, Young, and Miller (1981) in determinations of the molar absorptivity characteristics of Pb^{2+} and $PbCl_i$ and application of eq (5) in examinations of lead speciation in a small number of aqueous $MgCl_2$ and HCl media.

RESULTS

The results of our determinations of the concentration of Pb^{2+}, $PbCl^+$, $PbCl^\circ_2$, and $PbCl^-_3$ in each of our test media are given in table 1. The results of our determinations of the stepwise lead chloride formation constants, K_1, K_2, and K_3 are shown in figures 1, 2, and 3. Formation constants are shown versus total ionic strength. With the exception of our K_1 determinations in HCl–$HClO_4$ and NaCl–$NaClO_4$ mixtures, the only anion used in our experiments was chloride. Use of perchlorate ion in our determinations of K_1 was necessitated by large uncertainties of K_1 values derived from experiments in HCl and NaCl at high chloride concentrations. Due to the relatively large uncertainties of $[Pb^{2+}]$ and K_1 in our HCl and NaCl media at high chloride concentrations, K_1 results obtained in pure HCl and NaCl at total ionic strengths greater than or equal to 0.60 M are not shown in figure 1 and were not used in our analyses. For ionic strengths greater than or equal to 0.60 M, our K_1 analyses used data obtained in HCl–$HClO_4$ and NaCl–$NaClO_4$ mixtures at $[Cl^-] \cong 0.30$ M. This procedure results in larger and better defined concentrations of Pb^{2+} and $PbCl^+$ but smaller and more poorly defined concentrations of $PbCl^\circ_2$ and $PbCl^-_3$. The data obtained in our Cl^-–ClO^-_4 mixtures were therefore used only in our determinations of K_1.

The curves shown in figures 1 through 3 were obtained by least squares fits to our data using the equation

$$\log K_i = {}_iA + \frac{{}_iB\mu^{1/2}}{1 + {}_iC\mu^{1/2}} + {}_iD_\mu \qquad (6)$$

Using eq (6), the best fit parameters in table 2 provide a quantitative summary of our formation constant determinations.

DISCUSSION

Figures 1 through 3 exhibit the substantial influence of medium on stepwise lead chloride formation constants. The effects of medium on the overall formation constants, $\beta_2 = K_1 \cdot K_2$ and $\beta_3 = K_1 \cdot K_2 \cdot K_3$, are, of course, larger and cause β_3 (HCl) and β_3 ($CaCl_2$) to differ by a factor of 0.64 at one molar total ionic strength.

A quantitative description of the observed medium effects can be sought using either a specific interaction approach (Brönsted, 1922; Whitfield, 1975; Harvie and Weare, 1980; Thurmond and Millero, 1982) or an ion pairing formalism (Bjerrum, 1927; Garrels and Thompson, 1962; Johnson and Pytkowicz, 1978; Sipos and others, 1980). In the following discussion we have described our results assuming the existence of chloride ion pairs: HCl°, $NaCl^\circ$, $MgCl^+$, and $CaCl^+$. The existence of such entities has been suggested in a variety of experimental and theoretical studies (Chiu and Fuoss, 1968; Paterson, Jalota, and Dunsmore, 1971; Nakayama, 1971; Elgquist and Wedborg, 1975; Kester and Pytkowicz, 1975; Fisher and Fox, 1977; Johnson and Pytkowicz, 1978).

TABLE 1

HCl, HCl–HClO$_4$ media

μ_{Total}	$[ClO_4^-]_{Total}$	$[H^+]_{Total}$	$[Cl^-]$	$\%Pb^{2+}$	$\%PbCl^+$	$\%PbCl_2^0$	$\%PbCl_3^-$
0.011	0.0	0.0100	0.0104	84.98±0.60	15.01±0.34	0.0±0.0	0.0±0.0
0.113	0.0	0.1127	0.1131	37.91±0.26	49.16±0.15	11.93±0.14	1.01±0.13
0.254	0.0	0.2537	0.2541	20.47±0.17	49.07±0.10	25.53±0.09	4.93±0.08
0.451	0.0	0.4500	0.4504	10.99±0.22	41.25±0.12	35.68±0.12	12.08±0.11
0.558	0.0	0.5570	0.5574	7.90±0.18	36.46±0.10	38.90±0.10	16.74±0.09
0.596	0.299	0.5951	0.2960	19.77±0.15	46.93±0.09	26.98±0.08	6.32±0.07
0.696	0.399	0.6951	0.2961	19.75±0.13	46.71±0.07	26.97±0.07	6.56±0.06
0.796	0.499	0.7950	0.2960	19.68±0.12	46.41±0.07	27.01±0.06	6.91±0.06
0.896	0.599	0.8951	0.2961	19.59±0.11	46.13±0.06	27.32±0.06	6.95±0.05
0.996	0.699	0.9952	0.2962	19.12±0.25	46.09±0.14	27.52±0.13	7.26±0.12
0.694	0.0	0.6933	0.6937	5.19±0.09	30.78±0.05	41.01±0.05	23.03±0.04
0.736	0.0	0.7357	0.7361	4.43±0.06	29.20±0.03	41.38±0.03	25.00±0.03
0.789	0.0	0.7884	0.7888	4.02±0.11	27.20±0.06	41.36±0.06	27.41±0.05
0.829	0.0	0.8282	0.8286	4.18±0.19	25.45±0.11	41.16±0.10	29.20±0.09
0.829	0.0	0.8282	0.8286	3.45±0.23	25.78±0.13	41.25±0.12	29.51±0.11
0.921	0.0	0.9208	0.9212	3.06±0.42	22.84±0.24	40.76±0.22	33.33±0.20
0.968	0.0	0.9670	0.9674	2.87±0.49	21.41±0.28	40.44±0.26	35.28±0.24
0.987	0.0	0.9860	0.9864	2.75±0.56	20.78±0.32	40.14±0.30	36.32±0.27

NaCl, $NaClO_4$ media

μ_{Total}	$[ClO_4^-]_{Total}$	$[Na^+]_{Total}$	$[Cl^-]$	% Pb^{2+}	% $PbCl^+$	% $PbCl_2^o$	% $PbCl_3^-$
0.112	0.0	0.1010	0.1114	37.96±0.27	48.97±0.16	11.96±0.14	1.10±0.13
0.155	0.0	0.1441	0.1545	30.95±0.18	50.54±0.10	16.50±0.10	2.00±0.09
0.229	0.0	0.2188	0.2292	22.91±0.19	49.97±0.11	23.14±0.10	3.98±0.09
0.369	0.0	0.3580	0.3684	14.33±0.27	44.97±0.15	31.97±0.14	8.73±0.13
0.369	0.0	0.3580	0.3684	14.23±0.27	44.88±0.15	31.91±0.14	8.98±0.13
0.465	0.0	0.4543	0.4647	10.72±0.27	40.79±0.16	36.06±0.15	12.43±0.13
0.603	0.299	0.5923	0.3033	19.62±0.15	46.98±0.09	27.07±0.08	6.33±0.08
0.704	0.399	0.6932	0.3042	19.54±0.15	46.92±0.09	27.15±0.08	6.39±0.07
0.805	0.499	0.7943	0.3053	19.82±0.14	46.37±0.09	27.21±0.07	6.59±0.07
0.906	0.599	0.8954	0.3064	19.56±0.13	46.23±0.08	27.44±0.07	6.77±0.07
1.006	0.699	0.9952	0.3064	19.24±0.10	45.94±0.06	27.78±0.05	7.03±0.05
0.541	0.0	0.5301	0.5405	8.45±0.23	37.53±0.13	38.25±0.12	15.77±0.11
0.637	0.0	0.6264	0.6368	6.33±0.19	33.56±0.11	40.23±0.10	19.87±0.09
0.776	0.0	0.7656	0.7760	4.27±0.13	28.36±0.08	41.51±0.07	25.86±0.06
0.894	0.0	0.8834	0.8938	2.96±0.28	24.54±0.16	41.53±0.15	30.97±0.13
0.995	0.0	0.9844	0.9948	2.88±0.64	21.47±0.36	40.56±0.34	35.10±0.31

Table 1 (continued)

CaCl$_2$ media

μ_{Total}	$[Ca^{2+}]_{Total}$	$[Cl^-]$	% Pb^{2+}	% $PbCl^+$	% $PbCl_2^o$	% $PbCl_3^-$
0.117	0.0356	0.0816	47.17±0.38	44.75±0.22	7.62±0.20	0.46±0.18
0.223	0.0709	0.1522	33.84±0.19	49.71±0.11	14.82±0.10	1.64±0.09
0.359	0.1161	0.2425	24.33±0.16	49.56±0.09	22.25±0.09	3.86±0.08
0.453	0.1473	0.3050	19.99±0.20	47.91±0.12	26.38±0.11	5.72±0.10
0.526	0.1719	0.3541	17.30±0.23	46.25±0.13	29.07±0.12	7.38±0.11
0.620	0.2031	0.4165	14.41±0.25	43.88±0.14	32.06±0.13	9.65±0.12
0.755	0.2482	0.5068	11.24±0.25	40.24±0.14	35.41±0.13	13.11±0.12
0.826	0.2718	0.5540	9.79±0.24	38.25±0.14	36.83±0.13	15.13±0.12
0.876	0.2884	0.5871	8.87±0.19	36.96±0.11	37.56±0.10	16.61±0.09
0.925	0.3048	0.6200	8.26±0.20	35.63±0.11	38.16±0.11	17.95±0.10
0.968	0.3191	0.6486	7.89±0.21	34.51±0.12	38.68±0.11	18.92±0.10
0.968	0.3191	0.6486	7.24±0.25	34.67±0.14	38.63±0.13	19.46±0.12

$MgCl_2$ media

μ_{Total}	$[Mg^{2+}]_{Total}$	$[Cl^-]$	% Pb^{2+}	% $PbCl^+$	% $PbCl_2^o$	% $PbCl_3^-$
0.114	0.0346	0.0795	47.93±0.36	44.38±0.21	7.24±0.19	0.46±0.17
0.257	0.0823	0.1750	30.78±0.17	50.26±0.10	16.83±0.09	2.13±0.08
0.457	0.1487	0.3077	19.61±0.18	48.06±0.10	26.53±0.09	5.80±0.09
0.571	0.1868	0.3839	15.33±0.20	44.94±0.11	31.07±0.11	8.66±0.10
0.703	0.2308	0.4721	12.37±0.30	41.60±0.17	34.41±0.16	11.62±0.14
0.754	0.2478	0.5061	10.98±0.22	40.51±0.13	35.50±0.12	13.01±0.11
0.849	0.2794	0.5692	9.11±0.23	37.96±0.13	37.38±0.12	15.55±0.11
0.944	0.3111	0.6325	7.72±0.15	35.46±0.09	38.56±0.08	18.27±0.08
0.991	0.3269	0.6641	7.05±0.19	34.21±0.11	39.23±0.10	19.51±0.09
0.991	0.3269	0.6641	7.04±0.19	34.11±0.11	39.30±0.10	19.54±0.09

Distribution of Pb(II) among the species Pb^{2+}, $PbCl^+$, $PbCl^o_2$, and $PbCl^-_3$ in HCl, HCl-$HClO_4$, NaCl, NaCl-$NaClO_4$, $CaCl_2$, and $MgCl_2$ media.

Each of our experimental media contained Pb(II) at a total concentraiton of 2×10^{-4} M. Each of our NaCl, NaCl-$NaClO_4$, $MgCl_2$, and $CaCl_2$ media were 0.010 M in H^+. The total chloride concentration of each medium is given as $[Cl^-]$.

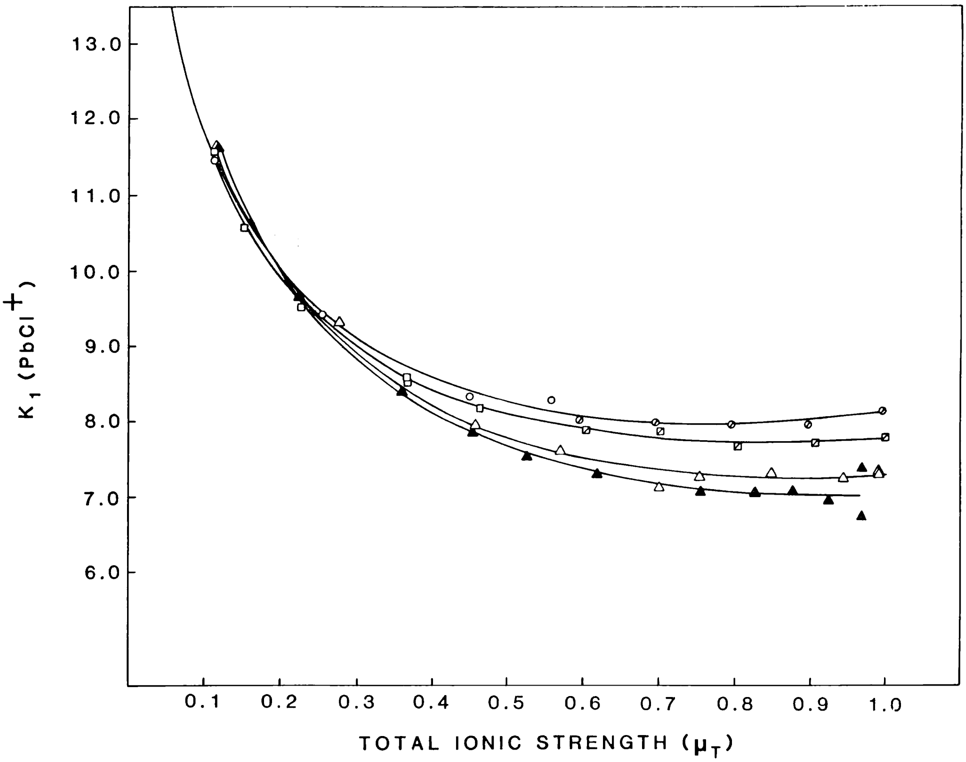

Fig. 1. The formation constant of $PbCl^+$ is shown versus total ionic strength. The curves shown in this figure correspond to K_1 values obtained using eq (6) and the parameters A, B, C, and D in column 3 of table 2. The media used in our experiments are depicted as follows: Circle, HCl; circle with line, $HCl-HClO_4$; square, NaCl; square with line, $NaCl-NaClO_4$; open triangle, $MgCl_2$; filled triangle, $CaCl_2$. One data point, obtained for 0.01 M HCl, is not shown in this figure.

Following the approach of Johnson and Pytkowicz, it is assumed that chloride ions in aqueous media are partitioned into free and complexed forms. In our experimental media this is expressed as:

$$[Cl^-] = [Cl^-]_f + [HCl^\circ] + [NaCl^\circ] + [MgCl^+] + [CaCl^+] \tag{7}$$

The formation constant of each chloride species is written as:

$$K_{HCl} = \frac{[HCl^\circ]}{[H^+]\,[Cl^-]_f} \tag{8}$$

$$K_{NaCl} = \frac{[NaCl^\circ]}{[Na^+]\,[Cl^-]_f} \tag{9}$$

$$K_{MgCl} = \frac{[MgCl^+]}{[Mg^{2+}]\,[Cl^-]_f} \tag{10}$$

$$K_{CaCl} = \frac{[CaCl^+]}{[Ca^{2+}][Cl^-]_f} \tag{11}$$

The ion pairing constants in eqs (8) through (11) are assumed to be dependent only on temperature, pressure, and effective ionic strength, μ_E, where in any of our experimental media

$$\mu_E = 1/2\,([ClO^-_4] + [Cl^-]_f + [H^+] + [Na^+] + 4[Mg^{2+}] + 4[Ca^{2+}] + [MgCl^+] + [CaCl^+]) \tag{12}$$

and

$$(ClO^-_4)_{total} = [ClO^-_4] \tag{13}$$

$$(H^+)_{total} = [H^+] + [HCl^\circ] \tag{14}$$

$$(Na^+)_{total} = [Na^+] + [NaCl^\circ] \tag{15}$$

$$(Mg^{2+})_{total} = [Mg^{2+}] + [MgCl^+] \tag{16}$$

$$(Ca^{2+})_{total} = [Ca^{2+}] + [CaCl^+] \tag{17}$$

Using these equations it is possible to calculate the ratio $[Cl^-]/[Cl^-]_f$ and convert lead chloride complexation constants, defined in terms of total chloride concentrations, to constants defined in terms of free chloride concentrations:

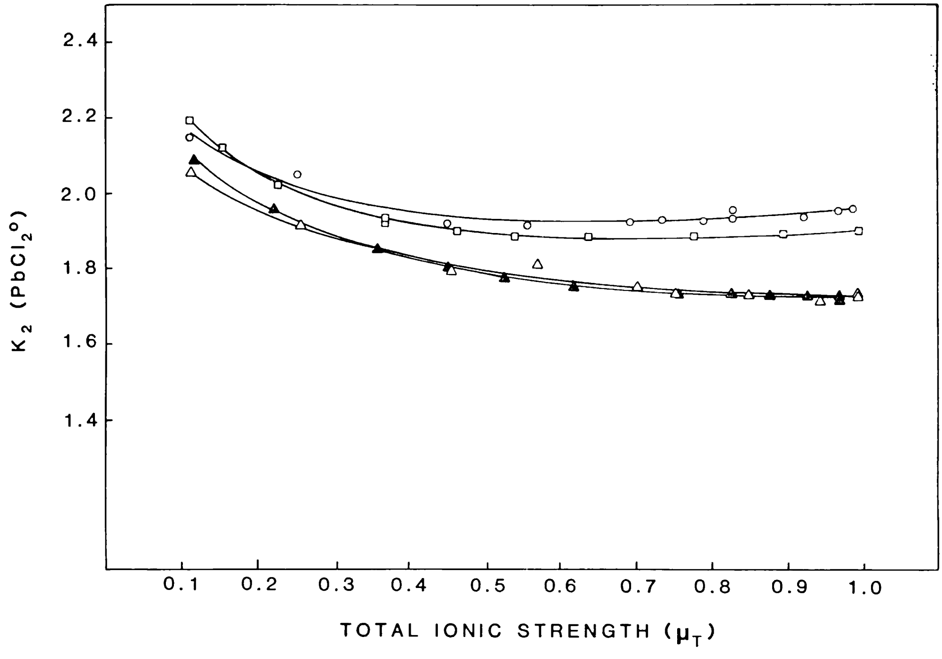

Fig. 2. The stepwise formation constant of $PbCl^\circ_2$ is shown versus total ionic strength. The curves shown in this figure correspond to K_2 values obtained using eq (6) and the parameters A, B, C, and D in column 4 of table 2. The media used in our experiments are depicted as follows: Circle, HCl; square, NaCl; triangle, $MgCl_2$; filled triangle, $CaCl_2$.

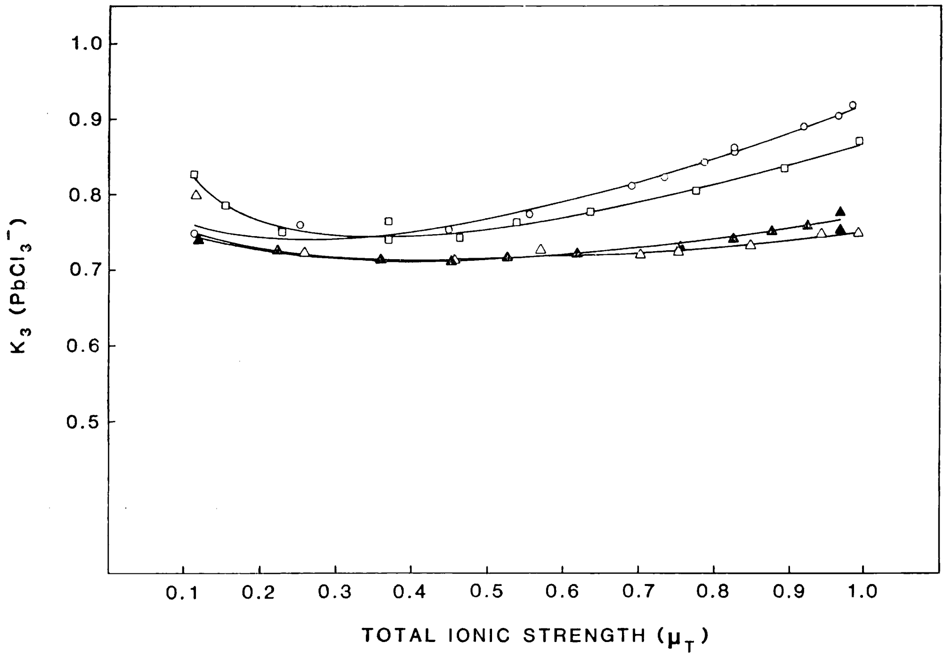

Fig. 3. The stepwise formation constant of $PbCl^-_3$ is shown versus total ionic strength. The lowest ionic strength data point obtained in $MgCl_2$ media was not included in the analysis (eq 6) used to describe our K_3 data. Inclusion of this point in our analysis produced a deterioration in the description (table 2) of our higher ionic strength data.

$$K'_1 = \frac{[PbCl^+]}{[Pb^{2+}][Cl^-]_f} \tag{18}$$

$$K'_2 = \frac{[PbCl^\circ_2]}{[PbCl^+][Cl^-]_f} \tag{19}$$

$$K'_3 = \frac{[PbCl^-_3]}{[PbCl^\circ_2][Cl^-]_f} \tag{20}$$

According to the Johnson and Pytkowicz model, the formation constants K'_1, K'_2, and K'_3 expressed as a function of effective ionic strength, μ_E, should not exhibit medium composition effects.

As a means of examining quantitatively the ability of chloride ion pairing to account for the medium composition effects shown in figures 1 through 3 we determined $NaCl^\circ$, $MgCl^+$, and $CaCl^+$ ion pairing constants that best explain the medium composition dependence of K_i in each of our test media.

We took as a starting point in our determinations the HCl° formation constants of Johnson and Pytkowicz (1978)

$$\ln K_{HCl} = -1.179 - 0.982\,\mu_E$$

$$0.1 \leqslant \mu_E \leqslant 1.0 \tag{21}$$

Using eqs (7), (8), (12), (13), (14), and (21), the ratio $[Cl^-]/[Cl^-]_f$ was determined for each of our HCl and $HCl–HClO_4$ experimental media. Our smoothed $K_i(HCl–HClO_4)$ data (table 2 plus eq 6) were multiplied by $[Cl^-]/[Cl^-]_f$ values appropriate to each of our HCl and $HCl–HClO_4$ experimental media. The results of this process are three sets of K'_i values which, when plotted against μ_E, are well described by the following equations:

$$K'_1 = \frac{1.314 - 1.114\mu^{1/2} + 1.196\mu}{1 - 0.212\mu^{1/2} + 0.667\mu} \tag{22}$$

$$K'_2 = \frac{0.349 - 0.995\mu^{1/2} + 0.763\mu}{1 - 2.835\mu^{1/2} + 2.182\mu} \tag{23}$$

$$K'_3 = \frac{-0.117 + 0.238\mu^{1/2} - 0.121\mu}{1 - 1.932\mu^{1/2} + 0.971\mu} \tag{24}$$

For each $K_i(\mu_T)$ datum obtained in NaCl, $NaCl–NaClO_4$, $MgCl_2$, and $CaCl_2$ media we then determined the $[Cl^-]/[Cl^-]_f$ value necessary to transform the (K_i, μ_T) datum to a point (K'_i, μ_E) on our K'_i (μ_E) curve defined by eqs (22) to (24). Finally, the $[Cl^-]/[Cl^-]_f$ values obtained for each medium were used, in conjunction with eqs (7) through (17) to determine (K_{NaCl}, μ_E), (K_{MgCl}, μ_E), and (K_{CaCl}, μ_E) values. The NaCl°,

TABLE 2

The parameters shown in this table were obtained by least squares fits to the data shown in figures 1 through 3. The data fit was obtained by using the equation

$$\log K_i = A + \frac{B\mu^{1/2}}{1 + C\mu^{1/2}} + D\mu .$$

This procedure was undertaken in order to provide a smoothed, concise representation of our data. No significance should be attached to individual values of parameters A, B, C, and D.

Medium		K_1	K_2	K_3
$HCl–HClO_4$	A	1.327	0.432	−0.036
	B	−1.009	−0.369	−0.378
	C	0.284	0.000	0.000
	D	0.368	0.229	0.376
$NaCl–NaClO_4$	A	1.537	0.541	0.505
	B	−2.574	−1.023	−6.175
	C	2.271	1.887	7.122
	D	0.149	0.093	0.193
$MgCl_2$	A	1.371	0.401	−0.057
	B	−1.093	−0.313	−0.027
	C	0.000	0.000	0.000
	D	0.585	0.148	0.198
$CaCl_2$	A	1.376	0.433	−0.057
	B	−1.098	−0.397	−0.290
	C	0.000	0.000	0.000
	D	0.570	0.201	0.233

MgCl+, and CaCl+ formation constants obtained through this procedure are compared in figures 4, 5, and 6 with the potentiometrically obtained formation constants of Johnson and Pytkowicz (1978).

In view of the substantial differences between our experimental methods and the very small formation constants determined, the agreement between the Johnson and Pytkowicz results and our own seems unusually good. Our K_{NaCl} results are generally 61 to 67 percent as large as the Johnson and Pytkowicz results, and our K_{MgCl} and K_{CaCl} results are 62 to 72 percent and 58 to 61 percent as large as the Johnson and Pytkowicz results. The solid lines shown in figures 4, 5, and 6 are best fit straight lines to our formation constant data:

$$K_{NaCl} = (0.33 \pm 0.02) - (0.19 \pm 0.03)\mu_E \qquad 0.2 \leqslant \mu_E \leqslant 0.96 \tag{25}$$

$$K_{MgCl} = (1.61 \pm 0.12) - (0.62 \pm 0.20)\mu_E \qquad 0.3 \leqslant \mu_E \leqslant 0.76 \tag{26}$$

$$K_{CaCl} = (1.80 \pm 0.16) - (0.79 \pm 0.27)\mu_E \qquad 0.3 \leqslant \mu_E \leqslant 0.76 \tag{27}$$

Among the fundamental characteristics of the Johnson and Pytkowicz model is the requirement that the medium composition dependencies of K_1, K_2, and K_3 should be identical. As a consequence of this predicted behavior, the chloride complexation constants K_{NaCl}, K_{MgCl}, and K_{CaCl} calculated according to our methods should be identical whether based on K_1, K_2, or K_3 data. Figure 4 shows that there are no easily observable differences in K_{NaCl} attributable to differences in the medium dependencies of K_1, K_2, and K_3. Our K_{MgCl} data, although somewhat scattered, also exhibit no obvious differences between the three K_i data sets. In contrast, our K_{CaCl} constants indicate that factors other than chloride ion complexation are in part responsible for the differences in K_i between HCl–HClO$_4$ mixtures and CaCl$_2$ media. The K_{CaCl} constants determined by our methods are largest when based on K_1 data and smallest when

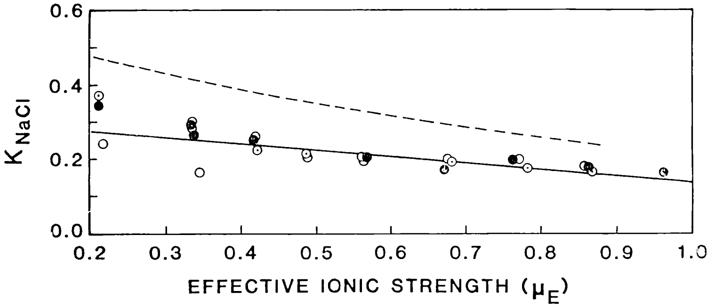

Fig. 4. Results of our determinations of K_{NaCl}. Results derived from K_1 data are given as filled circles. Results derived from K_2 data are given as circles with dot. Results derived from K_3 data are given as open circles. The solid line provides the best linear least squares fit to our data. The dashed line shows the K_{NaCl} results obtained by Johnson and Pytkowicz (1978).

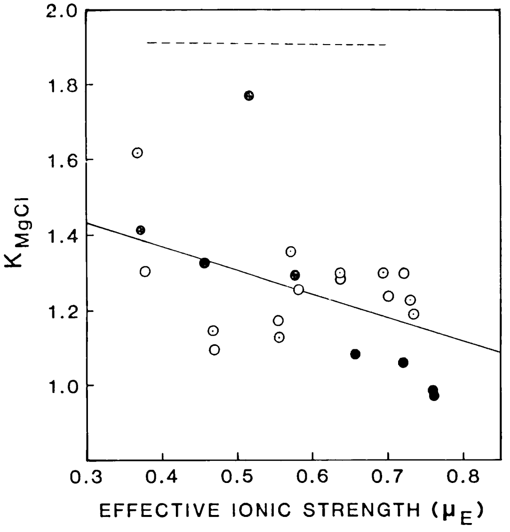

Fig. 5. Results of our determinations of K_{MgCl}. Results derived from K_1 data are given as filled circles. Results derived from K_2 data are given as circles with dot. Results derived from K_3 data are given as open circles. The solid line provides the best linear least squares fit to our results when the uppermost data point is deleted. Inclusion of this data point in the fit provides the result

$$K_{MgCl} = (1.69 \pm 0.15) - (0.72 \pm 0.25)\,\mu_E$$

This line has a slightly steeper slope than that shown in the figure.

based on K_3 data. Nevertheless, it is seen that for our data taken as a whole, and even for our K_{CaCl} data alone, the prediction that our observed K_i medium dependencies are solely attributable to chloride ion complexation is a good first order approximation.

It is interesting to note that the ionic strength dependencies of K_{NaCl}, K_{MgCl}, and K_{CaCl} are in reasonably good agreement with the predictions of the Johnson and Pytkowicz model. Our best fit K_{NaCl} versus μ_E slope is only slightly smaller (fig. 4) than that obtained by Johnson and Pytkowicz. The best fit slope we obtained for K_{CaCl} versus μ_E is in very good agreement with the strong dependence of K_{CaCl} on μ_E obtained by Johnson and Pytkowicz. Our K_{CaCl} data decrease substantially with μ_E, whether based on K_1, K_2, or K_3 data. The Johnson and Pytkowicz model predicts a weak dependence of K_{MgCl} on μ_E. Our K_{MgCl} results are in agreement with this conclusion to the extent that, in contrast to K_{CaCl}, there is no consistent K_{MgCl} versus μ_E dependence among K_1, K_2, and K_3 data sets.

The most notable difference between the Johnson and Pytkowicz model and our K_{NaCl}, K_{MgCl}, and K_{CaCl} results is the consistently smaller magnitude of chloride ion pairing constants in this study. As a further check on our observations, we examined the $K_1(CuCl^+)$ complexation data of Näsänen and Lumme (1951). As a starting point in our analysis we carefully digitized the graphically presented $K_1(CuCl^+)$ results of Näsänen and Lumme (1951) which were obtained in $HClO_4$, $NaClO_4$, and

$Ca(ClO_4)_2$. Since Cl^- was a very minor constituent in their experiments, effective and total ionic strength are identical in their media. Using the procedures outlined for our analyses based on K_i, we determined the K_{NaCl} and K_{CaCl} ion pairing constants that eliminated the pronounced dependence of $K_1(CuCl^+)$ upon medium composition. The results we obtained, based on $\ln K_{HCl} = -1.179 - 0.982\ \mu_E$ (Johnson and Pytkowicz, 1978) are:

$$K_{NaCl} = 0.21 \pm 0.02 \qquad 0.2 \leqslant \mu_E \leqslant 1.0$$

$$K_{CaCl} = 1.72 \pm 0.07 \qquad 0.3 \leqslant \mu_E \leqslant 1.0$$

where the uncertainties listed reflect the range of values obtained for each constant. These results are in better agreement with our determinations based on K_i data than the results of Johnson and Pytkowicz, particularly at lower effective ionic strengths. The constant $K_{NaCl} = 0.21$ is nearly equal to the average result (fig. 4) which we obtained between 0.2 and 1.0 M ionic strength, and the result $K_{CaCl} = 1.72$ is in fair agreement (fig. 6) with our K_{CaCl} results based on K_1 data. In contrast both to our results and the Johnson and Pytkowicz results, K_{NaCl} and K_{CaCl} based on $K_1(CuCl^+)$ exhibit no significant ionic strength dependence.

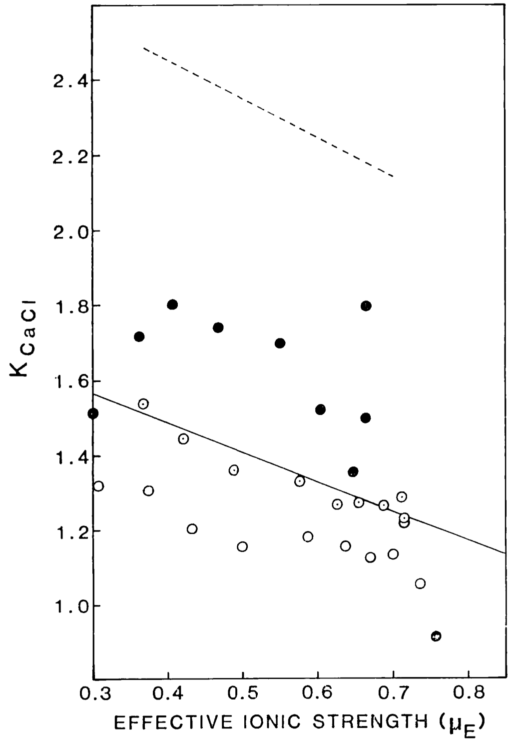

Fig. 6. Results of our determination of K_{CaCl}. The solid line provides the best least squares fit to our data. The dashed line shows the K_{CaCl} results obtained by Johnson and Pytkowicz (1978).

Our results, including ion pairing constants derived from Näsänen and Lumme (1951), differ numerically from the results of Johnson and Pytkowicz (1978). Nevertheless, our observations are consistent with their general model. Our calculations show that a chloride ion pairing model can substantially account for the medium effects in reactions (1) through (4) which have only one ion in common. Our results do not, of course, demonstrate the existence of the hypothesized HCl°, $NaCl^\circ$, $MgCl^+$, and $CaCl^+$ ion pairs. Although our results are consistent with their existence, it is possible to describe activity coefficient variations using an ion pairing model even if the hypothesized entities do not exist (Pytkowicz and Kester, 1969).

Our observations, and treatments such as Sipos and others, (1980), are important in modeling the behavior of trace metals in chloride media. Environmental solutions such as seawater, Red Sea brines, and oil field brines contain Cl^-, Na^+, Mg^{2+}, and Ca^{2+} at high concentrations (Garrels and Thompson, 1962; Tsai and Cooney, 1976; Carpenter, Trout, and Pickett, 1974). Chloride ion complexation strongly influences the behavior of ions such as Pb^{2+}, Cd^{2+}, and Hg^{2+} in such media. Quantitative predictions of trace metal complexation by chloride ions must consider both the cationic and anionic composition of the complexing medium. Chloride complexation constants determined in HCl–$HClO_4$ mixtures are not appropriate to solutions that contain significant concentrations of Na^+, Mg^{2+}, and Ca^{2+}. Conversely, chloride complexation constants determined in the presence of high magnesium concentrations (Libus, 1973) should be systematically smaller than complexation constants determined in HCl–$HClO_4$ mixtures (Näsänen and Lumme, 1951). Our results indicate that the presence of Na^+, Mg^{2+}, and Ca^{2+} in chloride media alters the affinity of chloride ions for trace metals in a quantitatively predictable manner.

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