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Ion Exchange in Molten Salts. IV. Complex Formation in Molten Salts. The Cadmium(II)–Chloro Complexes in the (Na,K)NO_3 Eutectic

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The distribution of cadmium between the eutectic (Na,K)NO_3 mixture and the synthetic zeolite "Linde 4A" was measured at 230°. The cadmium concentration varied from 6×10^{-5} to 4×10^{-3} mol/kg of solvent, and the chloride concentration varied from 2×10^{-3} to 3×10^{-2} mol/kg of solvent. In this range of concentration the exchange of cadmium at constant chloride concentration followed the relation $\log \bar{C}_{Cd^{2+}} = \log a_i + b \log C_{Cd^{2+}}$, where $\bar{C}$ and C are the molalities in the solid and liquid phase, respectively. The slope b was invariant with the chloride concentration, while the intercept a_i followed the relation $a_i = a_0 - \lambda C_{Cl^-}$. The association constants for Cl^- with Cd^{2+} were shown to be $\beta_1 = 32.1 \pm 1.5$, $\beta_2 = 610 \pm 320$, and $\beta_3 = (2.9 \pm 1.2) \times 10^4$ in (mol/kg of solvent)$^{-1}$ units.

1. Introduction

Complex ion formation in aqueous solution has been studied extensively and various types of measurements have been used to obtain the association constants of the complex ions. The increasing interest in high-temperature chemistry has promoted comprehensive investigations of molten salt properties and ion complexation therein. Distribution methods have proven to be useful and versatile in the determination of the association constants in aqueous as well as ionic media; so far only solvent extraction[1,2] and absorption chromatography[3,4] have been used. We decided to try ion exchange in molten salts to investigate complex formation in this medium using the synthetic zeolite "Linde Molecular Sieve 4A" as a cation exchanger, the (Na,K)NO_3 eutectic as the liquid phase, and Cd^{2+} and Cl^- as complexing species. The ion-exchange properties of NaA have been previously investigated.[5–7] The association constant β_1 (see eq 1 for the definition) of the cadmium–chloro complex $CdCl^+$ in the (Na,K)NO_3 eutectic at around 230° has been determined by many authors[8–14] although with rather conflicting results. Indeed, while Duke and Iverson[8] claim a value of 20 (mol/kg of solvent)$^{-1}$ for β_1, Delimarskii and Grishenko[9] found the value to be 38, Sinistri[10] 53, Inman, Regan, and Girling[11] and Inman[12] 79, Delimarskii and Grishenko[13] 90, and Inman and Bockris[14] 100 (mol/kg of solvent)$^{-1}$. The variations in β_2 are rather large, 100 ± 50,[8] 700 ± 350,[14] and 1900 ± 170;[12] the agreement for β_3 is somewhat better, $(2.45 \pm 1.48) \times 10^4$ [14] compared to $(1.8 \pm 0.1) \times 10^4$ [12] (mol/kg of solvent)$^{-1}$.

2. Experimental Section

a. **Materials.**—The powdered zeolite was obtained from Linde Air Products Ltd. Twenty grams of NaA was stirred with 250 ml of water, poured into a 250-ml cylinder, and allowed to stand for 2–3 hr. The deposit was practically free of gel and fines and was collected, washed with deionized water, and dried at 110°. The product was kept open to the air to ensure equilibrium with the atmosphere and therefore constant weight. The water content was determined by weight loss on heating to 900°.[6]

Reagent grade sodium nitrate, potassium nitrate, sodium chloride, and potassium chloride were used without further purification beyond drying at 100° for at least 24 hr. Anhydrous cadmium nitrate was prepared[15] from the ground tetrahydrate by dehydration under vacuum, raising the temperature gradually from room temperature to 120°. Due to the very small quantities of cadmium and chloride ions used, stock solutions of these ions in the (Na,K)NO_3 eutectic were prepared. The chloride solution was made by adding NaCl and KCl to the (Na,K)NO_3 eutectic in such quantities that the Na:K ratio remains at 1:1. Both mixtures were stored in an evacuated desiccator over P_2O_5.

Tracer ^{109}Cd (453-day half-life) was supplied as an aqueous cadmium nitrate solution by New England Nuclear Co.

b. **Methods.**—Due to the high hygroscopicity of the cadmium nitrate, the experiments were devised to minimize its handling. Batches (275 g) of eutectic were prepared, weighed amounts of cadmium nitrate stock solution and ^{109}Cd tracer were added, and the mixture was heated to 230° and homogenized by occasional stirring. Samples of the melt were withdrawn for radioactivity assay; the whole batch was divided into 30-g portions by pouring the melt into preweighed 50-ml round-bottom centrifuge tubes. The tubes were immediately transferred into a desiccator containing P_2O_5 and the whole assembly evacuated. After cooling and weighing, predetermined amounts of the chloride stock solution and approximately 0.1 g of air-dried NaA were added. The tubes were introduced into the oven at 230° and kept there without stirring for 20 hr. After equilibration, the tubes were transferred into a preheated aluminum block, in which holes had been drilled to accommodate the tubes, and two samples of each melt were taken by suction through a fine-fritted glass filter. The samples were weighed and dissolved in 3.0 ml of distilled water, and the activity was determined by γ-ray counting with a well-type NaI(Tl) counter and a single-channel analyzer. At least two measurements, of 10^4 counts or more each, were recorded for each sample. The equilibrium concentration in the solution $C_{Cd^{2+}}$ was calculated from the concentration and radioactivity assay of the original batch and the

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TABLE I

EXPERIMENTAL RESULTS OF THE DISTRIBUTION OF CADMIUM BETWEEN NaA AND A $(Na,K)NO_3$ EUTECTIC AS A FUNCTION OF CADMIUM AND CHLORIDE CONCENTRATION AT 230°

$10^3C_{Cd}^{initial}$	10^3C_{Cl}	C_{Cd}	10^4C_{Cd}	10^3D
1.07	0.00	0.37	0.58	6.29
	2.12	0.38	0.68	5.64
	4.22	0.40	0.72	5.56
	6.26	0.36	0.71	5.10
	8.30	0.37	0.92	4.04
	10.62	0.37	0.87	4.28
	19.77	0.34	1.06	3.20
	28.59	0.32	1.23	2.63
21.4	0.00	0.70	2.75	2.53
	2.13	0.70	2.81	2.48
	4.22	0.74	2.67	2.76
	6.26	0.70	2.61	2.69
	8.38	0.67	2.96	2.25
	10.63	0.69	3.35	2.05
	19.78	0.62	4.29	1.44
	28.59	0.53	5.76	0.92
3.23	0.00	0.99	4.82	2.06
	2.12	1.05	5.28	1.98
	4.22	1.01	5.89	1.72
	6.26	0.97	5.33	1.82
	8.29	0.96	5.62	1.71
	10.63	0.96	6.29	1.53
	19.78	0.83	7.54	1.10
	28.59	0.84	8.57	0.98
5.35	0.00	1.47	13.59	1.08
	2.12	1.50	13.86	1.08
	4.21	1.39	14.71	0.94
	6.27	1.38	13.03	1.06
	8.29	1.38	15.91	0.87
	10.63	1.38	14.94	0.92
	19.77	1.13	16.99	0.67
	28.59	1.08	19.36	0.56
8.55	0.00	2.00	31.20	0.64
	2.12	1.96	35.85	0.55
	4.22	1.83	33.95	0.54
	6.27	1.85	34.73	0.53
	8.30	1.86	35.36	0.53
	10.63	1.71	34.18	0.50
	19.78	1.58	36.15	0.44
	28.59	1.42	38.18	0.37

number of counts after equilibration. The equilibrium concentration in the zeolite $\bar{C}_{Cd^{2+}}$ was calculated from the difference between the initial and equilibrium concentration of the melt. Concentrations are expressed as molalities (mol/kg of solvent). No significant change in the distribution as a function of time was found over a period of 19–196 hr.

3. Results

Preliminary experiments showed that at tracer and near-tracer cadmium concentrations, the distribution coefficients are extremely high, of the order of 10^5–10^6. A higher concentration range was therefore chosen by compromising between the need to keep the solution sufficiently diluted in cadmium while maintaining an easily measurable range of distribution coefficients. Table I gives a synopsis of the results obtained. The ion-exchange capacity of the occluded zeolite was estimated to be 8 mol equiv/kg of occluded zeolite, assuming that all of the cations are exchangeable.

Plotting the concentration of cadmium in the zeolite against the concentration in the solution, at constant chloride concentration, on a log–log scale, gave a series of parallel lines. The results of a least-squares fit of the equations $\log \bar{C}_{Cd^{2+}} = \log a_i + b \log (10^3C_{Cd^{2+}})$, where i designates the level of ligand concentrations, are given in Table II. The reason $10^3C_{Cd^{2+}}$ was used instead of $C_{Cd^{2+}}$ was to move the intercept into the actual experimental range thus avoiding the error due to long extrapolations. The regression coefficients were calculated by Ergun's method.[16] Essentially this procedure consists of calculating the simultaneous regression of a family of linear expressions having a common slope. The use of all the data leads to better estimates of the common slope and individual intercepts than those obtained by separate regression of individual lines. The intercept a_i is a linear function of the chloride ion concentration (Figure 1). A weighted least-squares calculation of the line $a_i = a_0 - \lambda C_{Cl}$ shows that the slope is $\lambda = 17.12 \pm 0.46$ while the intercept a_0 at zero chloride concentration is 1.270 ± 0.009.

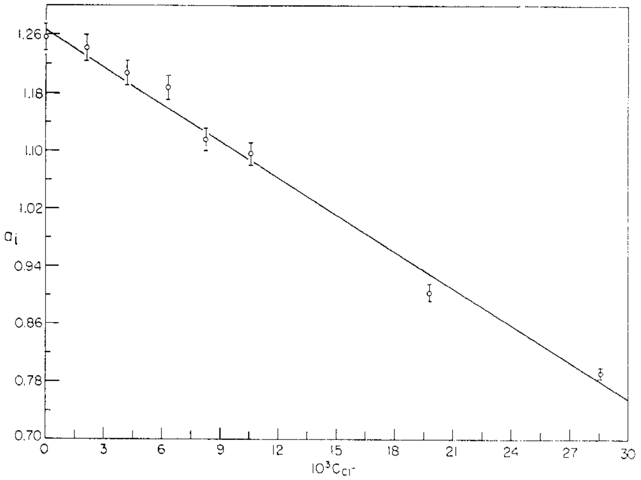

Figure 1.—The variation of the intercept a_i of the exchange isotherm with the ligand concentration C_{Cl^-}.

TABLE II

RESULTS OF THE LEAST-SQUARES CALCULATIONS OF THE EQUATION

$$\log \bar{C}_{Cd^{2+}} = \log a_i + b \log (10^3C_{Cd^{2+}})$$

AT CONSTANT LIGAND CONCENTRATION[a]

i[b]	10^3C_{Cl}, M	Log a_i[b]	i[b]	10^3C_{Cl}, M	Log a_i[b]
0	0.00	0.0993 ± 0.0063	4	8.30	0.0477 ± 0.0059
1	2.12	0.0940 ± 0.0062	5	10.63	0.0401 ± 0.0059
2	4.22	0.0825 ± 0.0061	6	19.78	−0.0445 ± 0.0055
3	6.26	0.0743 ± 0.0062	7	28.59	−0.1017 ± 0.0050

[a] $b = 0.427 \pm 0.008$. [b] i designates the ligand level concentration.

Discussion

The common slope and its independence of chloride concentration suggests that there is no exchange or absorption of cadmium–chloro complexes by the zeolite; furthermore, the independence of the intercept a_i from the cadmium concentration shows that no dinuclear species are present.

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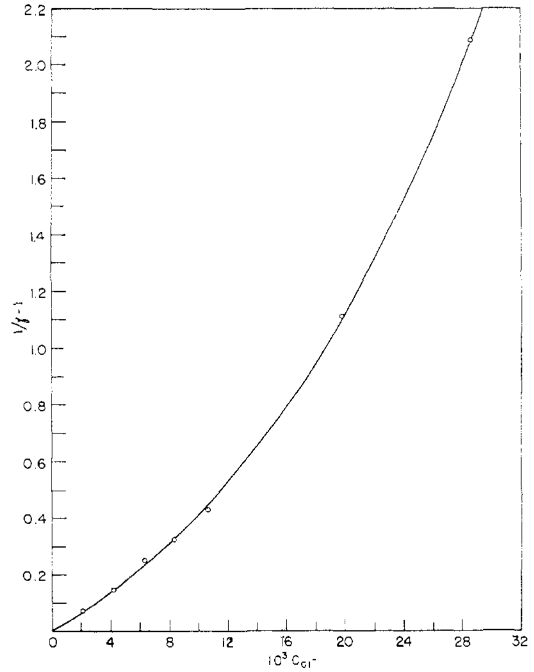

Figure 2.—$(1/\gamma_M - 1)$ as a function of the ligand concentration C_{Cl^-}. The points are experimental, while the line is the result of a least-squares fit. The goodness of fit is given by χ^2/(degrees of freedom) = 2.8563/3 = 0.952.

The association constants β_n for the formation of associated species are defined

$$\beta_1 = \frac{C_{ML}}{C_m C_l} \tag{1}$$

$$\beta_2 = \frac{C_{ML_2}}{C_m C_l^2} \tag{2}$$

$$\beta_3 = \frac{C_{ML_3}}{C_m C_l^3} \tag{3}$$

where C_{ML_n} is the concentration of the complex ML_n, C_m is the equilibrium concentration of the unbound metal ion, C_l is the unbound ligand concentration, and n is the ligand number.

From the mass balance equations and for concentrations low enough that all solute ions and associated species obey Henry's law, it can be shown that eq 4

$$1/\gamma_M - 1 = \beta_1 C_L + \beta_2 C_L^2 + \beta_3 C_L^3 + \ldots \tag{4}$$

holds, where C_M and C_L are the stoichiometric metal ion and ligand ion concentrations, respectively. The activity coefficient γ_M is, by definition, equal to

$$\gamma_M = \frac{C_m}{C_M} \tag{5}$$

At constant loading of the zeolite, the equilibrium concentration of the metal ion in the presence of a ligand has to be the same as that without a ligand. The ratio C_m/C_M can therefore be calculated from the equations

$$\log \bar{C}_M = \log a_0 + b \log C_m \tag{6}$$

$$\log \bar{C}_M = \log a_i + b \log C_M \tag{7}$$

which represent the exchange in the absence and presence of ligand, respectively; $\bar{C}_M$ is the concentration of cation M in the zeolite. From these two equations $-\log \gamma_M$ is obtained, as in

$$-\log \gamma_M = \log \frac{C_M}{C_m} = \frac{1}{b} \log (a_0/a_i) \tag{8}$$

Introducing a_0/a_n from

$$\frac{a_0}{a_n} = 1 - \frac{\lambda C_L}{a_i} \tag{9}$$

into eq 8 yields

$$-\log \gamma_M = \frac{1}{b} \log \left(1 + \frac{\lambda}{a_n} C_L\right) \tag{10}$$

$1/\gamma_M$ as a function of C_L (Figure 2) could therefore be calculated from data with known error. Relation 10 rather than (8) was preferred because the latter gives undue weight to one point, namely, a_0. A computer program was used to calculate, by a weighted least-squares fit, the coefficient of the polynomial

$$(y - 1) = ax + bx^2 + cx^3 \tag{11}$$

Equating eq 11 with eq 4, the following values for the association constants of cadmium–chloro complexes were found: $\beta_1 = 32.1 \pm 1.5$, $\beta_2 = 610 \pm 320$, and $\beta_3 = (2.9 \pm 1.2) \times 10^4$ in (mol/kg of solvent)$^{-1}$ units. This method of treatment of data has some interesting features.

(a) By using the fact that at constant $\bar{C}_M$ the equilibrium concentration, C_m, is independent of the presence or absence of the ligand, the need for tracer concentration is eliminated, provided that the concentration of the metal ion in the solution is sufficiently low so that eq 7 can be extrapolated to infinite dilution; in other words b can be considered as a limiting slope.

(b) The association constant is evaluated from limiting slopes of the metal ion and the ligand ion and is therefore a thermodynamic association constant.

(c) Constant probable error in $1/\gamma_M$ is obtained by the least-squares fitting of the experimental functions used for the evaluation of the association constants.

Table III compares the first association constant of the chloro complex of Cd^{2+} with that of the respective bromo complex and shows the effect of substituting lithium nitrate for sodium nitrate in the melt. As expected, the bromo complexes are more stable than the chloro complexes. From the data published so far on the halogeno complexes of Ag^+,[17,18]

TABLE III

ASSOCIATION CONSTANTS β_1 (MOL/KG OF SOLVENT)$^{-1}$ OF $CdCl^+$ AND $CdBr^+$ IN EQUIMOLAR MIXTURES OF $(Na,K)NO_3$ AND $(Li,K)NO_3$ AT 230°

	$CdBr^+$	$CdCl^+$	Ratio $\beta_1^{Br}/\beta_1^{Cl}$
$(Li,K)NO_3$	365[a]	92[b]	4.0
$(Na,K)NO_3$	134[c]	32[d]	4.2

[a] Interpolated value from ref 15 and from J. Braunstein and A. S. Minano, *Inorg. Chem.*, **5**, 942 (1966). [b] Interpolated from ref 15. [c] Interpolated from ref 19. [d] Present work.

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Cd^{2+}, and Pb^{2+},[15] it is apparent that the bromo complexes are about four times more stable than the respective chloro complexes, if other factors are equal. The destabilization of the halogen compounds upon substitution of sodium instead of lithium in the nitrate melt is apparently a polarization effect on NO_3^- by the small lithium ion, resulting in greater stability of the halogeno compound in lithium nitrate than in sodium or potassium nitrate.[19]

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Addition Compounds of Niobium(IV) Halides Formed with Monodentate Alkyl Sulfides. Synthesis, Spectra, and Magnetism[1]

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The reactions of $S(CH_3)_2$, $S(C_2H_5)_2$, and $S(CH_2)_4$ with NbX_4 (X = Cl, Br, or I) have been investigated. For the case of $S(CH_2)_4$ only paramagnetic diadducts were isolated. With $S(CH_3)_2$ paramagnetic diadducts as well as weakly paramagnetic monoadducts could be obtained. For the case of $S(C_2H_5)_2$ only weakly paramagnetic 1:1 (acceptor:donor) adducts were recoverable as stable solid phases. Infrared, far-infrared, and visible–near-infrared spectra of solid and solution phases of the compounds were recorded and the results are discussed relative to proposed molecular structures.

Introduction

While a number of adducts formed by niobium(IV) halides with nitrogen and oxygen donors have been described[2–6a] only two reports[6b,c] discuss adducts formed with different donors. The most frequently occurring ratio of acceptor to donor is 1:2 for monodentate donors and 1:1 for bidentate donors. The model expected to apply is that of an octahedral disposition of ligands about the central metal with the added possibility of *cis–trans* isomerism for monodentate ligands. Where molecular structure data have been reported[2b,6c,7] they tend to support predominance of the *cis* isomer.

Only two reports[6c,8] describe adducts in which the ratio of acceptor to donor is 1:1. The adducts are obtained *via* the direct reaction of $NbCl_4$ and triethylamine or methyl sulfide. In contrast to the known diadducts which are all paramagnetic, the triethylamine adduct is diamagnetic[8] and the methyl sulfide adduct is only weakly paramagnetic at room temperature.[6c] The magnetic behavior of $NbCl_4(N(C_2H_5)_3)$ together with other properties suggested its formulation as a dimer or higher polymer having bridging halides and niobium–niobium bonds similar to those of the anhydrous halides.[9,10] Steric effects arising from the bulky alkyl groups were thought to contribute to the destabilization of any diadduct. A similar model could be invoked to rationalize the behavior of the methyl sulfide compound, but the space requirements of a methyl group are not expected to be restrictive.

In order to more fully assess (1) the acceptor behavior of niobium(IV) halides with respect to sulfur donors and (2) the stereochemical consequences of sterically hindered ligands for the adducts formed, we chose the compounds methyl and ethyl sulfide as well as tetrahydrothiophene as potential ligands. We have also studied the electronic and vibrational spectra as well as the magnetic properties of solid and/or solution phases of the adducts.

Experimental Section

Materials.—The alkyl sulfides were purchased from commercial sources and dried prior to use by stirring them together with $LiAlH_4$ for 24 hr. After extensive outgassing *in vacuo* they were vacuum distilled onto $NbCl_5$ contained in dry, evacuated 50-ml round-bottom flasks and stored there until required.

Benzene, Spectrograde, was dried under reflux over sodium and stored *in vacuo* over anhydrous $NbCl_5$.

Niobium(IV) halides were prepared using established procedures[2a] and stored in screw-capped vials in an inert-atmosphere drybox.

Analytical Procedures.—Solid samples were hydrolyzed in the absence of air with concentrated ammonia and this mixture was heated to boiling. Heating was continued for *ca.* 1 hr and the mixture was then cooled to room temperature. This process was repeated three times to ensure complete hydrolysis and the

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