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Raman Spectral Study of the Coordination of Cadmium(II) with Chloride and Bromide Ions in Molten Sodium Nitrate–Potassium Nitrate

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Raman spectra were determined for solutions of cadmium nitrate with either potassium chloride or potassium bromide in molten equimolar sodium nitrate–potassium nitrate. From the variation with composition of the intensities of (a) bands due to CdCl and CdBr band stretching vibrations and (b) the characteristic ν_4 band of NO_3^- ions solvated to Cd^{2+} ions, it is shown that the predominant complex ions present in these systems are $CdCl_3^-$ and $CdBr_4^{2-}$, respectively. Evidence is presented for the stepwise formation of small relative concentrations of $CdBr^+$ and $CdBr_2$ in the cadmium(II)–bromide system. No other chloro complexes besides $CdCl_3^-$ were detected in the cadmium(II)–chloride system. Comparisons are made with the corresponding aqueous systems.

Introduction

The coordination of cadmium with halide ions in molten alkali metal nitrate solvents has been the subject of considerable investigation.[1-3] Although the results of potentiometric measurements[1] clearly indicate a high stability for the complex ions $CdCl^+$ and $CdBr^+$, estimates of the stability of higher complexes were not obtained. However, other electrochemical measurements[2] and some recent ion-exchange studies[3] indicate a high stability for ions such as $CdCl_3^-$ in these solvents. This Raman spectral study was initiated in order to obtain more direct evidence for the complexes formed by Cd^{2+} with chloride and with bromide ions in alkali metal nitrate solvents, preliminary to a study of Cd^{2+} in molten halide media.

Solutions of cadmium nitrate and either potassium chloride or potassium bromide produce well-defined Raman bands (at 264 ± 3 cm^{-1} and 164 ± 3 cm^{-1}, respectively) which, similar to the case of aqueous solutions,[4-6] are assigned, from their polarized character, to the symmetric stretching modes of cadmium chloride or bromide complexes. The frequencies and spectral shapes of these bands are remarkably insensitive to the ratio of halide to cadmium ions and these observations lead us to suspect that only one complex is predominant in each system. Using the proportionality relation between Raman intensity and concentration we have sought to determine the stoichiometry of these complexes by applying standard analytical methods.[7,8] In the Job method of continuous variations[7] measurements are made on solutions for which the total concentration of ligand plus metal ions is constant but the ratio between the total individual concentrations, R, is varied. The maximum concentration of the complex (or maximum in Raman intensity) is predicted to occur at a value of R corresponding to the stoichiometry of the complex. In an alternative method due to Yoe and Jones,[9] the Raman intensity per mole of metal ions is plotted against R. In this case the stoichiometry is indicated by the value of R at which the limiting and the initial slopes of the curve intersect. The theory and limitations of these methods and their use in conjunction with Raman intensity measurements are discussed thoroughly elsewhere:[7,8] it is assumed that a single complex is dominant in the system and that the formation quotient is constant over the concentration range studied.

It is clear from our own and other Raman studies[4,5] that the procedure of deciding on the structure of a complex from the observed pattern of vibrational bands is not successful with cadmium halide complexes since a complete spectrum of vibrations almost certainly is not observed. Asymmetric stretching modes, typically broad in molten salts systems,[10] are so broad and/or so weak in the Raman effect so as to be indistinguishable from background scattering for cadmium halide systems. Bands due to bending vibrations are similarly ill defined. The exact geometry of the complexes could, therefore, not be deduced.

Experimental Section

A stock equimolar mixture of sodium nitrate and potassium nitrate was made up from dried reagent grade components. Anhydrous samples containing 40 mol % of cadmium nitrate in the solvent mixture were prepared in the glassy form by standard methods.[11] These solutions were mixed and melted with dried potassium halide and further solvent mixture to give a range of samples of various cadmium to halide ratios but all containing a total of 40 mol % of cadmium nitrate plus potassium chloride or potassium bromide. All the samples gave clear, stable, and colorless melts which were filtered into the Raman cell in an atmosphere of dry nitrogen.

The furnace used to contain samples for spectral measurements is described elsewhere.[12] The temperature of a molten sample at *ca.* 400° is maintained constant to ±3°. Spectra were obtained with a Spex 1401 double monochromator and using the 514.5-nm exciting line of an argon ion laser (Spectra-Physics Model 140). The spectral slit width was 2 cm^{-1} for the chloride solutions and 4 cm^{-1} for the bromide solutions.

The integrated intensities of the 264- and 164-cm^{-1} bands from the chloride and bromide solutions, respectively, were measured relative to the integrated intensity of the 1047-cm^{-1} band due to the ν_1 vibration of NO_3^-. The procedure was to scan $\nu_1(NO_3^-)$ and the 264-cm^{-1} (or 164-cm^{-1}) band alternately on the spec-

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trometer. Spectra were accepted for measurement only if the intensity of $\nu_1(NO_3^-)$ was constant to ±3%. The reproducibility of relative intensity measurements was within ±5%. Both the 264-cm^{-1} band of the chloride solutions and the 164-cm^{-1} band of the bromide solutions were resolved easily from the strong background due to Rayleigh scattering and NO_3^- librational modes.[12,13] For each mixture the scattering level at 100 cm^{-1} was adjusted to the same intensity and a common background drawn by comparison with that observed for the pure sodium nitrate–potassium nitrate mixture at the same temperature. The resolved bands were all symmetric. In solutions of cadmium nitrate alone, a weak polarized band is observed at 236 cm^{-1} due to the Cd–ONO_2 stretching vibration.[12] However, the intensity is an order of magnitude less than that of the Cd–Cl stretching vibration at 264 cm^{-1} for the solution with $R = 1$ and the error involved is negligible.

This use of an internal intensity standard, besides being convenient, eliminates errors due to changing refractive index of solutions.[14] The disadvantage of using an internal standard is that changing molecular interactions (*e.g.*, due to interaction with Cd^{2+}) may affect its molar intensity. Indeed, the spectra indicate that free cadmium ions do interact with nitrate ions (see above). However, most of the mixtures contain only about 10% cadmium nitrate and nearly all of the cadmium is coordinated with halide ions. The Job mixtures for which the ratio of halide to cadmium is unity contained 12–15 mol % of solvated cadmium ions. However, the ν_1 vibration of the nitrate ions involved in this solvation is apparently little affected. No new bands are observed in this region of the spectrum and the intense and sharp 1047-cm^{-1} band is only slightly broader than in the case of the pure eutectic. Consequently we have assumed the molar intensity of $\nu_1(NO_3^-)$ to be constant. For comparison, in the case of pure molten silver nitrate, in which there is strong cation–anion interaction, the molar intensity of $\nu_1(NO_3^-)$ differs[12] by only about 10% from that of sodium nitrate or potassium nitrate for which the interaction is relatively weak.

Results

Details of some of the measurements for the cadmium(II)–chloride and cadmium(II)–bromide systems at 320° are contained in Tables I and II, respectively.

Table I

Raman Spectral Measurements for $Cd(NO_3)_2$–KCl Solutions in Molten Sodium Nitrate–Potassium Nitrate at 320°

Temp, °C	Mole fractions $Cd(NO_3)_2$	KCl	Raman band Freq, cm^{-1}	Half-width, cm^{-1}	Intens rel to $\nu_1(NO_3^-)$
320	0.200	0.200	264	66	0.135
320	0.100	0.100	264	52	0.067
320	0.160	0.240	265	54	0.205
320	0.133	0.267	261	50	0.203
320	0.110	0.290	264	49	0.257
320	0.100	0.300	263	47	0.263
320	0.080	0.320	264	40	0.243
320	0.067	0.333	264	40	0.222
320	0.057	0.343	262	38	0.202

Measurements were made for all solutions also at either 390 or 420°; apart from small Boltzmann correction factors, relative intensities were, within the limits of reperimental error, the same as at 320°.

For each set of solutions, relative intensities were corrected for the varying ion fraction of nitrate ions to give intensities I_R on a common scale. If N_c is the mole fraction of the complex, then for each mixture $N_c \propto I_R$. Similarly, if P is the proportion of Cd(II) in the form of the complex, then $P \propto I_R/N_m$ where N_m is the total mole fraction of cadmium nitrate.

Table II

Raman Spectral Measurements for $Cd(NO_3)_2$–KBr Solutions in Molten Sodium Nitrate–Potassium Nitrate at 320°

Temp, °C	Mole fractions $Cd(NO_3)_2$	KBr	Raman band Freq, cm^{-1}	Half-width, cm^{-1}	Intens rel to $\nu_1(NO_3^-)$
320	0.200	0.200	167	30	0.223
320	0.133	0.267	168	30	0.343
320	0.110	0.290	167	29	0.461
320	0.100	0.300	165	27	0.542
320	0.089	0.311	164	30	0.604
320	0.080	0.320	165	25	0.653
320	0.073	0.327	164	24	0.604
320	0.067	0.333	162	24	0.571
320	0.057	0.343	163	24	0.455
320	0.050	0.350	161	24	0.426

In the Job method, I_R is plotted against the function f, where $f = N_X/(N_m + N_X)$ (X = Cl or Br).[7] The results are shown in Figure 1. In accordance with the Yoe and Jones method of analysis, I_R/N_m is plotted against the ratio of halide to cadmium ions in Figure 2. This function achieves a maximum when all the Cd(II) is in the form of the complex (*i.e.*, when $P = 1$).

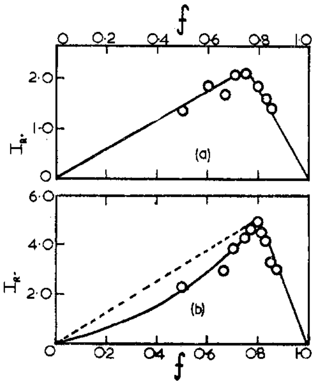

Figure 1.—Job plots for the intensity I_R of (a) the 264-cm^{-1} band of $Cd(NO_3)_2$–KCl solutions in molten sodium nitrate–potassium nitrate at 320° and (b) the 164-cm^{-1} band of $Cd(NO_3)_2$–KBr solutions at 320°. The total mole fraction of $Cd(NO_3)_2$ plus either KCl or KBr was 0.4 for all solutions.

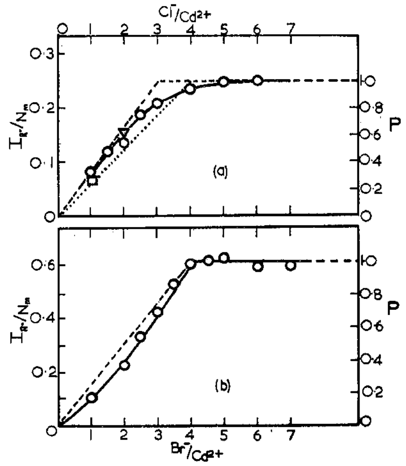

Figure 2.—Yoe and Jones plots for (a) the 264-cm^{-1} band of cadmium(II)–chloride solutions and (b) the 164-cm^{-1} band of cadmium(II)–bromide solutions in molten sodium nitrate–potassium nitrate at 320°: ○, solutions for which the mole fraction of $Cd(NO_3)_2$–KCl or –KBr is 0.4; □, 10 mol % $Cd(NO_3)_2$–10 mol % KCl; △, 39 mol % $CdCl_2$.

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Discussion

We consider first the results for the cadmium(II)–chloride system. The maximum in Raman intensity occurs at $f = 0.75$, corresponding to $R = 3$, on the Job plot (Figure 1a), indicating that the 264-cm^{-1} band originates from the complex $CdCl_3^-$. The shape of the plot approximates well to that expected for the formation of a single complex of high stability constant (two straight lines intersecting at the maximum).[7] These conclusions are confirmed by the Yoe and Jones plot (Figure 2a) where the intersection of the initial and limiting slopes occurs also at $R = 3$. The high stability of the complex is clearly evident in the Yoe and Jones presentation; at $R = 3$, over 80% of the cadmium present is in the form of the complex.

Before these results are accepted, however, we must consider whether the data can be fitted by assuming the formation of other complexes such as $CdCl^+$, $CdCl_2$, or $CdCl_4^{2-}$. (We have not considered polynuclear aggregates such as Cd_2Cl^{3+}.) Initially, the observed data could be fitted by supposing the stepwise formation of $CdCl^+$, $CdCl_2$, and $CdCl_3^-$ provided that we make two assumptions: (1) that all three complexes contribute to the measured Raman intensity and (2) that the molar intensities of the different species are *exactly* in proportion to the number of CdCl bonds. In fact, neither of these assumptions gains support from what is known of the behavior of cadmium–halo complexes. The characteristic symmetric vibration frequencies of $CdCl^+$ and $CdCl_2$ are significantly higher than that of $CdCl_3^-$ (280 cm^{-1} for $CdCl^{15}$). The instrumental resolution was sufficiently great so that their presence should have been indicated at least by some asymmetry of the observed Raman band. However, although it is slightly broader for the solutions for which $R < 2$, the band still retains essential symmetry. In regard to the second assumption, if a comparison with the corresponding bromide complexes[6] is valid, then the molar intensities of $CdCl^+$ and $CdCl_2$ are probably much lower than expected on the basis of simple bond additivity. As actually observed for the bromide solutions (see later) we would then expect the presence of these lower complexes to be indicated by much lower intensities than observed for solutions with $R < 3$. For similar reasons, it is not possible to account for the observed intensity data assuming the formation of $CdCl_4^{2-}$ with $CdCl^+$ or $CdCl_2$ but negligible quantities of $CdCl_3^-$. In this case, the limiting value of I_R/N_m for high Cl/Cd ratios on the Yoe and Jones plot would yield the molar intensity of $CdCl_4^{2-}$. With this assumption the maximum possible intermediate values of I_R/N_m are as indicated by the dotted line in Figure 2a. Finally, there is no indication of the initial stepwise formation of $CdCl_3^-$ and then $CdCl_4^{2-}$. The symmetric stretching frequencies of $CdCl_3^-$ and $CdCl_4^{2-}$ differ[15,16] by at least 5 cm^{-1}. This small difference is easily detectable with our instrumental resolution and it is seen from Table I that there is no such change in the peak frequency across the composition range. The results for the cadmium–chloride system are, therefore, best accounted for by assuming the dominant equilibrium

$$Cd^{2+} + 3Cl^- \rightleftharpoons CdCl_3^- \qquad (1)$$

In addition to the measurements made on solutions satisfying the Job requirements, a few spectra were obtained for solutions with different *total* solute concentrations. For solutions with $R = 1$ and 2 in the cadmium(II)–chloride system, variation of the total cadmium concentration had no measurable effect either on the peak frequency of the CdCl stretching vibration or on the Raman intensity per mole of cadmium (see Figure 2a). The only consequence of increasing the total solute concentration was an increase in half-width (tending toward values observed for cadmium chloride–potassium chloride mixtures[16]). For solutions with $R < 2$ there is a substantial relative concentration of solvated cadmium ions and the half-width increases may reflect the increasing effect of intermolecular interactions. However, the essential identity of $CdCl_3^-$ appears to be unchanged.

Further evidence for the above conclusion was obtained from estimates of the concentration of solvated cadmium ions in the solutions. One consequence of the solvation of cadmium by nitrate ions is the appearance of a second ν_4 band, ν_4', in the Raman spectrum of the nitrate ions, a band which is not observed in the absence of cadmium.[17] In Figure 3, spectra in the ν_4 region are shown for various cadmium(II)–chloride solutions. It is seen that the perturbation of nitrate ions evident in solutions of cadmium nitrate alone progressively disappears on the addition of chloride. For solutions with $R > 3$ the perturbation is absent. We might expect that the intensity, I_R', of the resolved ν_4' component, measured relative to the intensity of $\nu_1(NO_3^-)$, should be proportional to the concentration of solvated cadmium ions. Indeed, this was shown to be the case (to within ±5%) for solutions of cadmium nitrate alone in the eutectic, with concentrations varying from 5 to 20 mol %. This relationship was used to determine the fraction, F, of cadmium ions solvated by nitrate ions, in the mixtures containing chloride. Similar to equations developed previously, then, F is proportional to I_R'/N_m.

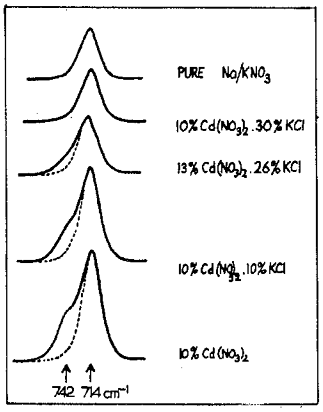

Figure 3.—Raman spectra of the ν_4 vibrations of nitrate ions for various solutions in molten sodium nitrate–potassium nitrate at 320°. Intensity scales for different solutions are not comparable. The band at 742 cm^{-1} is due to the ν_4' vibration of NO_3^- ions involved in solvation of Cd^{2+}. The band at 714 cm^{-1} is due to ν_4 of unperturbed NO_3^- ions.

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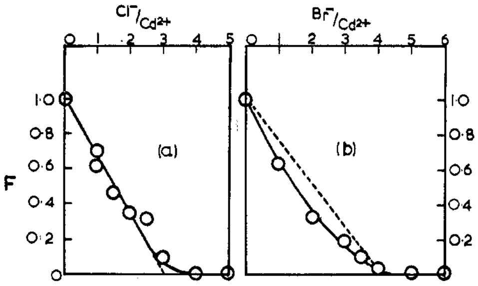

Figure 4.—Plots of the fraction, F, of total Cd(II) solvated with nitrate ions for solutions of $Cd(NO_3)_2$ with (a) KCl and (b) KBr in molten sodium nitrate–potassium nitrate at 320°. Values of F were determined from intensities of the 742-cm^{-1} band.

This fraction is plotted in Figure 4a as a function of R. (The proportionality constant has been chosen so that F is unity when the chloride concentration is zero.) As expected on the basis of equilibrium 1 a linear decline is observed—the inverse, in fact, of the Yoe and Jones plot of Figure 2a.

A comparison of the results obtained for the cadmium(II)–bromide system with those discussed above is remarkable in two respects. Firstly, the evidence is that $CdBr_4^{2-}$ and not $CdBr_3^-$ is the dominant complex—the maximum Raman intensity occurs at f = 0.8, or R = 4, on the Job plot, Figure 1b. Secondly, just those deviations from simple behavior are observed which might have been expected also in the cadmium(II)–chloride system; for solutions with $R < 4$, the Raman intensities are lower than would be expected if $CdBr_4^{2-}$ were the only complex present (the dashed lines on Figure 1b and Figure 2b), indicating the stepwise formation of species such as $CdBr^+$ and $CdBr_2$. The fraction F of solvated cadmium ions again was calculated for the various solutions from the nitrate ν_4' intensities and the results are shown in Figure 4b. Although substantial amounts of solvated cadmium ions appear to be present for solutions with $R < 4$, values of F are less than as predicted for the simple equilibrium $Cd^{2+} + 4Br^- \rightleftharpoons CdBr_4^{2-}$ (the dashed line in Figure 4b), strengthening the conclusion that there is some formation of lower complexes.

The symmetric stretching vibrations of $CdBr_2$ and $CdBr^+$ occur at 185 and 200 cm^{-1}, respectively.[6,15] However, the molar Raman intensities are so low[6] compared to that of $\nu_1(CdBr_4^{2-})$ that small amounts of the lower complexes could be present and yet remain undetected in our spectra. The formation of $CdBr_3^-$, however, cannot be accounted for in the results. The molar intensity of the symmetric stretching vibration is, in this case, slightly greater than that for $CdBr_4^{2-}$ and the presence of substantial amounts of $CdBr_3^-$ would result in much higher intensities than actually observed for $R \approx 3$. Assuming that the concentration of free bromide ions is negligible for solutions where $R < 4$, relative concentrations of $CdBr^+$, $CdBr_2$, and $CdBr_4^{2-}$ have been calculated from the experimental data in Figure 2b and Figure 4b and from the mass balance equations. (The data cannot be fitted by considering $CdBr_4^{2-}$ together with either $CdBr^+$ or $CdBr_2$ alone.) The distribution of cadmium between the various complexes is shown in Figure 5; no accuracy beyond ±20% is claimed for the relative concentrations of $CdBr^+$ and $CdBr_2$.

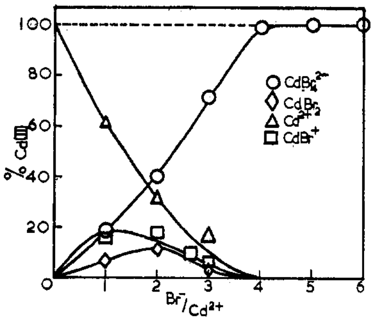

Figure 5.—The distribution of Cd(II) between various bromide complexes for solutions in molten sodium nitrate–potassium nitrate at 320°.

The formation quotient of $CdCl_3^-$, corresponding to equilibrium 1, was $(4 \pm 2) \times 10^4$ in mole fraction units at 320°, calculated for solutions with R values between 2 and 4. However, one should not expect to obtain accurate values of formation quotients since these values are most sensitive to the concentrations of free cadmium and chloride ions which are obtained by difference. For the bromide system the maximum value of P (Figure 2b) is achieved essentially *at* the value of R corresponding to the complex stoichiometry, indicating that $CdBr_4^{2-}$ is much more stable even than $CdCl_3^-$. Although no estimate of the stability quotient of $CdBr_4^{2-}$ could be obtained, this conclusion is qualitatively in agreement with potentiometric, etc., investigations,[2,3] in which the stabilities of complexes are computed from the measured metal or halide free-ion concentrations.

Various Raman spectral studies of cadmium(II)–bromide aqueous solutions have been reported.[4-6] For these solutions, Job plots[5] show very marked deviations from simple behavior. Furthermore, spectra[16] indicate that there is more than one band in the region of CdBr stretching vibrations (similar results are obtained in the corresponding chloride system[16]). The most important difference from the results obtained for sodium nitrate–potassium nitrate as solvent is the apparent predominance[6] of $CdBr_2$ (either monomeric or polymeric) in aqueous solutions where the ratio of bromide to cadmium ions is less than 4. It seems probable that the ionic molten salt solvent promotes the autoionization of the uncharged complex.

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