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Spectra of Dilute Solutions of Bismuth Metal in Molten Bismuth Trihalides. III. The Bismuth–Bismuth Tribromide System[1]

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Previous spectrophotometric studies[2,3] in this series indicated two subvalent bismuth species present in dilute solutions of Bi in $BiCl_3$. The equilibrium

$$4Bi^+ = (Bi_4)^{4+} \qquad (1)$$

has been proposed to explain these results; however, other equilibria are consistent with both spectrophotometric and electrochemical measurements[4,5] on this system. The uncertainty results from the fact that Bi(III) as the solvent cation is present in large excess, and, therefore, the extent to which it participates in such equilibria cannot be readily determined. Thus, the data cannot distinguish between eq 1 and an equilibrium such as

$$4Bi^+ = Bi_3^+ + Bi^{3+} \qquad (2)$$

proposed by Corbett.[6] However, it is now generally assumed that the Bi^+ ion does exist in very dilute solutions in these melts and is in equilibrium with a lower valent polymeric species. Evidence reported here tends to confirm this view.

Recent measurements[7,8] in acidic solvents such as $AlCl_3$–NaCl eutectic showed the presence of Bi^+ and $(Bi_5)^{3+}$ in dilute solutions and $(Bi_8)^{2+}$ at higher concentrations. In these solvents the Bi(III) concentration is now variable and its role can be clearly established. In very dilute solutions in haloaluminate solvents, for example, the equilibrium

$$6Bi^+ = Bi_5^{3+} + Bi^{3+} \qquad (3)$$

was observed[7] and the absorption spectrum of Bi^+ was determined.

The purpose of this work is, first, to show that the spectrum of Bi^+ in $NaX–AlX_3$ melts is similar to the spectrum of dilute solutions of bismuth metal in BiX_3 lending support to the presumption that Bi^+ is present in both media, second, to show that the tendency for Bi^+ formation is greater in $BiBr_3$ than $BiCl_3$, and, finally, to point out an apparent example of intervalence-transfer absorption.

Methods of measurement and preparation of materials were similar to those reported in a Bi–$BiCl_3$ study.[2]

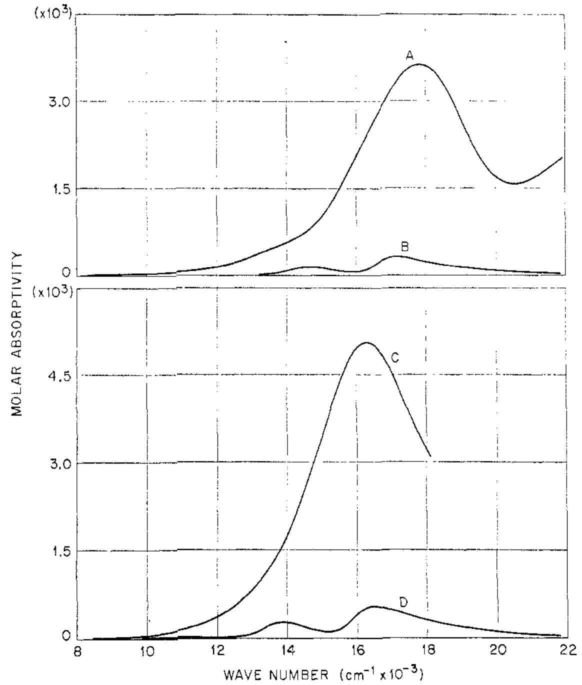

Figure 1.—Spectra of Bi^+ in: (A) molten $BiCl_3$ at 253°; (B) molten $AlCl_3$–NaCl eutectic at 310° (from ref 7); (C) molten $BiBr_3$ at 240°; (D) molten $AlBr_3$–NaBr eutectic at 250° (from ref 11).

Analysis of $BiBr_3$ gave 53.40% Br (theoretical, 53.43% Br). The formal concentration of solute bismuth, M_f, in moles per liter was calculated from the density data of Keneshea and Cubicciotti.[9] The formal molar absorptivity was calculated from the relation $\epsilon_f = A/bM_f$, where A is the absorbance of the solution and b is the path length in centimeters. Path lengths from about 20 to 500 μ were used.

Absorption spectra of Bi–$BiBr_3$ solutions were measured at concentrations from 0.00238 to 0.895 M_f and at 240, 350, and 410°. Bismuth tribromide absorbs strongly at wavelengths shorter than about 500 mμ, depending on the path length and the temperature, and obliterates the spectra of solutions in that region. Figure 1 (curve C) shows a typical Bi–$BiBr_3$ spectrum for solute concentrations below 0.15 M_f. The molar absorptivity, ϵ, used in this plot was calculated for Bi^+ as the absorbing species using the relation $\epsilon = {}^2/_3\,\epsilon_f$.

The influence of concentration on the band maximum at 240° is illustrated by Figure 2. At low concentrations Beer's law was obeyed and the slope of the straight line in Figure 2 is 7.5×10^3. At concentrations above about 0.15 M_f the spectra show large deviations from Beer's law. A concentration of about 0.9 M_f was the highest that could be studied at available path lengths because of the intense absorption. This concentration was too low to permit estimation of the spectrum of the species that predominates at high concentrations. Hence, specific models of a solute equilibrium could not be tested with any useful accuracy. However, the large deviations from Beer's law for the bromide system are clear evidence that more than one solute species occurs.

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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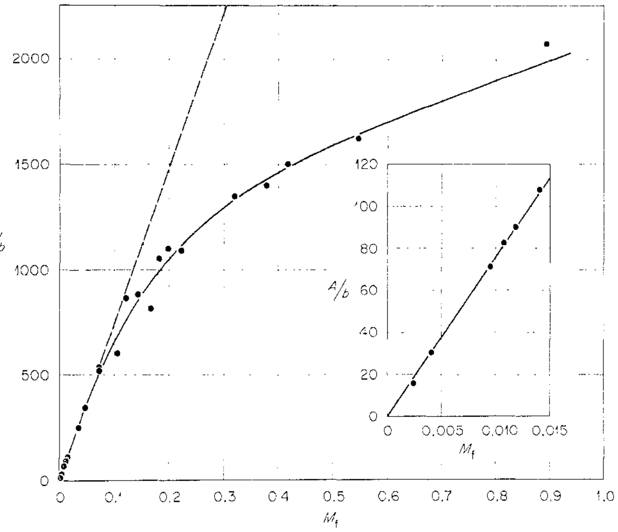

Figure 2.—Beer's law plot of A/b *vs.* M_f for values of A at the band maximum and at 240°. Inset shows the dilute, linear range and the dashed line represents limiting Beer's law behavior.

To compare this work with recent measurements of lower oxidation states of bismuth in NaX–AlX_3 for X = Cl or Br, it was necessary to extend the spectrum of the proposed Bi^+ ion in pure molten $BiCl_3$ into the near-infrared region as shown in Figure 1 (curve A). Also shown are spectra for Bi^+ in NaBr–$AlBr_3$[10] and NaCl–$AlCl_3$.[7] Similar changes in spectrum occur in both solvent systems as chloride is replaced by bromide. The bands shift to lower energies and become somewhat more intense. A comparison of the main band maxima for all four solvents is given in Table I, and the similarities are obvious. The most striking difference between solvent systems, as seen in Figure 1, is in the intensities which are 10 times greater in BiX_3 than in NaX–AlX_3 mixtures. This absorptivity intensification in BiX_3 solvents may arise from a Bi(I)–Bi(III) intervalence-transfer absorption similar to that observed in the Ti(III)–Ti(IV) system.[11] Such an effect has been suggested for these ions in molten NaCl–$AlCl_3$.[7] If one assumes this explanation for the large intensity differences, then the spectra are otherwise fairly similar, lending support to the presumption that Bi^+ exists in $BiCl_3$ and $BiBr_3$ melts and that curves A and C, respectively, represent its spectrum in these media.

TABLE I

ENERGIES (CM^{-1}) OF BAND MAXIMA IN AlX_3–NaX AND BiX_3 SOLVENTS

X	AlX_3–NaX	BiX_3
Br	16,400	16,300
	13,900	
Cl	18,200	17,900
	14,500–15,100	13,300

As pointed out earlier the exact equilibria occurring in BiX_3 melts cannot be specified. However, if one makes the reasonable assumption that Bi^+ is present in equilibrium with a polymeric species as in eq 1 and 2, constants for such equilibria can be calculated from the spectrophotometric data and a comparison of these constants for Bi–$BiCl_3$ and Bi–$BiBr_3$ will then show the relative tendency for Bi^+ formation in the two systems. Thus, the exact equilibrium need not be known as long as it is of the general type

$$n\mathrm{Bi}^{+} = \mathrm{Bi}_m^{(3m-2n)+} + (n - m)\mathrm{Bi}^{3+} \qquad (4)$$

Since a mass action constant for eq 1 has already been calculated for the chloride system, this same constant was calculated for Bi–$BiBr_3$ using the same procedures.[3] The value compared reasonably well with the equilibrium constant obtained by Topol and Osteryoung[5] from emf measurements on the Bi–$BiBr_3$ system. The mass action constant, K_M, based on molarity, was converted to K_N, based on mole fraction using the density data of Keneshea and Cubicciotti.[9] At 240°, $K_N = 1.16 \times 10^3 K_M$ so that the spectrophotometric K_N is 2.4×10^4. K_N, calculated from emf data at this temperature, is 1.9×10^4. In the chloride case K_N's of 3.8×10^6 and 2.7×10^6 were obtained at 264° by spectrophotometric[3] and emf[5] methods, respectively. The agreement between emf and spectrophotometric results in both systems is quite good considering the experimental uncertainty in determining these constants.

The equilibrium constant for reaction 1 is about 100 times larger for chloride than bromide indicating that the replacement of chloride by bromide favors the formation of Bi^+. Electrical conductivity measurements[12] indicate that the tendency for Bi^+ formation is even greater in BiI_3 so that the order of increasing stability of Bi^+ in BiX_3 melts appears to be X = Cl < Br < I.

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Studies of Boranes. XXVII. Boron-11 Nuclear Magnetic Resonance Spectrum of *n*-Nonaborane(15) at 64.16 MHz[1]

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We have recently had the opportunity to obtain the ^{11}B nmr spectra of a number of compounds at 64.16 MHz,[2] and since the published literature contains only

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[1] For paper XXVI of this series see R. Maruca, J. D. Odom, and R. Schaeffer, *Inorg. Chem.*, **7**, 412 (1968).

[2] The spectra were obtained with the cooperation of Mr. Eugene Pier, Varian Associates, Palo Alto, Calif.