CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

A Spectrophotometric Study of the Saturated Mixed Complexes of Mercury(II)–Bromide–Iodide

BY THOMAS G. SPIRO AND DAVID N. HUME

Received August 10, 1962

The replacement of bromide in $HgBr_4^{-2}$ by iodide has been investigated spectrophotometrically. The logarithms of the over-all equilibrium constants for the replacement of i bromides by iodides (at 23 ± 1° in a 1 M aqueous sodium bromide medium) are 3.20 ± 0.30, 5.49 ± 0.08, 7.40 ± 0.09, and 8.76 ± 0.09 for i = 1, 2, 3, and 4, respectively. The values for the three mixed complexes are greater than those expected on statistical grounds.

Although interest in equilibrium studies on mixed ligand complexes is relatively recent, a number of investigations have demonstrated the applicability of a variety of experimental methods long used on binary (single ligand) systems to cases where ternary (mixed ligand) complexes are formed. As examples one may cite the polarographic studies of ethylenediamine–oxalate complexes with copper(II) and cadmium(II),[1] spectrophotometric investigations of the chloride–bromide complexes of bismuth(III),[2] radiometric examination of the chloride–bromide platinum(II) complexes,[3] the solvent-extraction approach to the bromide–iodide system with mercury(II),[4] and the use of potentiometry in the ethylenediamine–oxalate–nickel(II) system.[5] An extensive theoretical discussion has been given by Rossotti and Rossotti.[6]

The present report concerns the mixed complexes formed when iodide successively replaces bromide in the saturated (maximum coördination level) complex, $HgBr_4^{-2}$. The equilibria were studied spectrophotometrically by an extension of the corresponding solutions method, developed previously for binary complexes.[7–9] The results are shown to be in substantial agreement with those of Marcus,[4] who used an entirely different method, and the mixed complexes are shown to be more stable than one would predict from the stabilities of the binary complexes together with expected statistical effects.

Mercury(II) binds bromide ion tightly and iodide ion even more so. From the formation constants reported by Marcus[10] one can calculate that mercuric ion is 98.5% converted to the saturated tetrabromide complex in a 1 M sodium bromide medium, and since the resulting ionic strength is twice as high as in Marcus' study, the fraction should be even higher. The essentially quantitative saturation of mercury(II) in this medium was confirmed spectrophotometrically, as described below. Consequently replacement of bromide by iodide in $HgBr_4^{-2}$ can be studied by substituting iodide for bromide in the medium; a maximum substitution of 20% is sufficient for the determination of all four successive replacement constants. Since the change in the medium is small, and since the sodium ion concentration is kept constant, it can reasonably be assumed that activity coefficients of the negatively charged species involved in the replacement reactions remain constant (*cf.* Sillén and Biedermann[11]).

List of Symbols

(Charges are omitted for simplicity)

M = central atom (mercury(II))
A = first ligand (bromide)
B = second (replacing) ligand (iodide)
C_M, C_A, C_B = total concentration in all species of M, A, and B
( ) = equilibrium concentration of the enclosed species
a, b = equilibrium concentrations of A and B
r = b/a
n = total number of ligands (A + B) bound in a given complex
i = number of ligands B bound in a given complex
$\bar{i}$ = $\frac{\Sigma i(MA_{n-i}B_i)}{\Sigma(MA_{n-i}B_i)}$ average number of B's replacing A's per MA_n complex
β_n = $\frac{(MA_n)}{(M)a^n}$ over-all formation constant
γ_i = $\frac{(MA_{n-i}B_i)}{(MA_n)r^i}$ over-all replacement constant
E = optical absorbance per cm. of path length
ϵ_i = molar absorptivity of $MA_{n-i}B_i$
ϵ_a, ϵ_b = molar absorptivity of A and B
E_M = $(E - \epsilon_a a - \epsilon_b b)/C_M$
E_M' = $(E = \epsilon_a C_A - \epsilon_b C_B)/C_M$
f = activity coefficient, molar basis

Method

The replacement reactions can be followed spectrophotometrically as substitution of iodide for bromide results in an appreciable shift of the intense ultraviolet absorption of $HgBr_4^{-2}$ to longer wave lengths. Because iodide competes effectively with bromide for coördination sites on mercury(II), a replacement function[6] (analogous to the formation function of binary systems) can be determined by a variation of the corresponding solution method.

---

[1] W. B. Schaap and D. L. McMasters, *J. Am. Chem. Soc.*, **83**, 4699 (1961).
[2] L. Newman and D. N. Hume, *ibid.*, **79**, 4581 (1957).
[3] W. W. Dunning and D. S. Martin, *ibid.*, **81**, 5566 (1959).
[4] Y. Marcus, *Acta Chem. Scand.*, **11**, 811 (1957).
[5] J. I. Watters and R. DeWitt, *J. Am. Chem. Soc.*, **82**, 1333 (1960).
[6] F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., New York, N. Y., 1961, Chapter 18.
[7] Reference 6, pp. 42, 282.
[8] J. Bjerrum, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.*, **21**, no. 4 (1944).
[9] S. Fronaeus, *Acta Chem. Scand.*, **5**, 139 (1951).
[10] Y. Marcus, *ibid.*, **11**, 599 (1957).
[11] L. G. Sillén and G. Biedermann, *Arkiv Kemi*, **5**, 425 (1953).

The reactions under consideration are

$$\mathrm{MA_4} + i\mathrm{B} = \mathrm{MA}_{4-i}\mathrm{B}_i + i\mathrm{A}$$

with replacement constants

$$\gamma_i = \frac{(\mathrm{MA}_{4-i}\mathrm{B}_i)}{(\mathrm{MA_4})r^i}$$

for which one may write a replacement function

$$\bar{\imath} = \frac{\Sigma i \gamma_i r^i}{\Sigma \gamma_i r^i} \qquad (1)$$

Experimentally

$$\bar{\imath} = (C_\mathrm{B} - b)/C_\mathrm{M}$$

or

$$C_\mathrm{B} = b + \bar{\imath} C_\mathrm{M}$$

When A is present in sufficient excess over M to make C_A equal to a (as in the present study)

$$C_\mathrm{B}/C_\mathrm{A} = r + \bar{\imath} C_\mathrm{M}/C_\mathrm{A} \qquad (2)$$

At a given wave length, the optical absorbance per centimeter path length of a solution containing the above species is given by

$$E = \Sigma \epsilon_i(\mathrm{MA}_{4-i}\mathrm{B}_i) + \epsilon_\mathrm{a} a + \epsilon_\mathrm{b} b \qquad (3)$$

Since

$$C_\mathrm{A} = a + \Sigma(4 - i)(\mathrm{MA}_{4-i}\mathrm{B}_i)$$

and

$$C_\mathrm{B} = b + \Sigma i(\mathrm{MA}_{4-i}\mathrm{B}_i)$$

then

$$[E - \epsilon_\mathrm{a} C_\mathrm{A} - \epsilon_\mathrm{b} C_\mathrm{B}]/C_\mathrm{M} = \frac{\Sigma[\epsilon_i - (4 - i)\epsilon_\mathrm{a} - i\epsilon_\mathrm{b}]\gamma_i r^i}{\Sigma \gamma_i r^i} = E_\mathrm{M}$$

or

$$\Sigma[\epsilon_i - (4 - i)\epsilon_\mathrm{a} - i\epsilon_\mathrm{b} - E_\mathrm{M}']\gamma_i r^i = 0 \qquad (4)$$

The coefficients of r^i in eq. 4 contain only E' as a variable. Therefore solutions having the same value of E_M' (corresponding solutions) must have the same value of r. They also will have the same value of $\bar{\imath}$, which is a function only of r (eq. 1). For corresponding solutions a plot of $C_\mathrm{B}/C_\mathrm{A}$ against $C_\mathrm{M}/C_\mathrm{A}$ (eq. 2) should give a straight line whose slope is $\bar{\imath}$ and whose intercept is r. From a series of such plots one can determine the replacement function for the system, which then can be treated by standard methods (those used for treating the formation functions of binary systems) to extract the successive replacement constants.

Corresponding solutions are best obtained (*cf.* Fronaeus[9]) by plotting E_M' as a function of $C_\mathrm{B}/C_\mathrm{A}$ for titrations with B of three or more solutions containing different amounts of M. Over the range of the titration, sets of points at constant E' are read from the plots, and the values of $C_\mathrm{M}/C_\mathrm{A}$ determined from the degree of titration.

The only limitation of the above method is that, for accurate determination of the $\bar{\imath}$, r values, the fraction of B bound by M must approach neither unity nor zero.[7] As C_B is increased to obtain higher values of $\bar{\imath}$, C_M must be raised accordingly. In this study, however, C_M is limited by the intensity of the ultraviolet absorption. It was found impractical to extend the replacement function beyond $\bar{\imath} > 2.5$. Consequently, only the first three replacement constants could be determined from $\bar{\imath}$ (r) data.

The fourth constant was obtained by manipulating absorbance data at higher values of r in a manner similar to the treatments of Newman and Hume,[2] and Rossotti and Rossotti.[12]

Rearranging eq. 3 and dividing by C_M, one obtains

$$[E - \epsilon_\mathrm{a} a + \epsilon_\mathrm{b} b]/C_\mathrm{M} = \sum_0^4 \epsilon_i \gamma_i r^i \Big/ \sum_0^4 \gamma_i r^i = E_\mathrm{M}$$

$$(a = C_\mathrm{A}, \text{ and when } r \gg C_\mathrm{M}/C_\mathrm{A},\ b = C_\mathrm{B})$$

$$\sum_0^4 (E_\mathrm{M} - \epsilon_i)\gamma_i r^i = 0$$

which, on expansion and rearrangement gives

$$E_\mathrm{M} = \epsilon_3 + \frac{\gamma_4}{\gamma_3}(\epsilon_4 - E_\mathrm{M})r + \Sigma(\epsilon_i - E_\mathrm{M})\frac{\gamma_i}{\gamma_3} r^{i-3} \qquad (5)$$

If r is sufficiently high so that only $\mathrm{MB_4}$ and $\mathrm{MAB_3}$ are present in appreciable quantities, then the summation term in eq. 5 can be neglected, and a plot of E_M against $(\epsilon_4 - E_\mathrm{M})r$ should produce a straight line with an intercept of ϵ_3 and a slope of γ_4/γ_3. (ϵ_4, the absorptivity of $\mathrm{MB_4}$, can be determined in the absence of A.) Since the first three replacement constants already have been determined, γ_4 can be calculated.

Experimental

(A) Materials.—Stock solutions were prepared with distilled water as follows. Mercuric perchlorate: Mercuric oxide (Fisher reagent) was dissolved in a slight excess of perchloric acid. The solution was analyzed for mercury by titration with potassium thiocyanate which was standardized against a solution made by dissolving triply distilled mercury in dilute nitric acid. Sodium halides: Reagent grade sodium bromide and sodium iodide (Mallinckrodt) were used directly. The concentrations were determined by Volhard titration. Air oxidation of sodium iodide, even in neutral solution, is a serious problem for spectrophotometry because of the intense ultraviolet absorption of the triiodide ion. However, the reaction apparently is very slow in the absence of light, and the iodide stock could be kept indefinitely (several weeks) without significant increase in its ultraviolet absorption, if kept in a brown bottle.

Spectra were recorded on a Cary Model 11 spectrophotometer, which was kept in an air-conditioned room, thermostated at 23 ± 1°.

The saturation of mercury(II) in 1 M sodium bromide was checked spectrophotometrically. With increasing concentration of bromide a mercury(II) solution develops an absorption peak at 249 mμ. The absorbance at this wave length was found to level off and remain essentially constant between 0.5 and 1 M sodium bromide.

(B) Corresponding Solutions.—The experimental technique was to mix two solutions, one containing 1 M sodium bromide and x M mercuric perchlorate ($x << 1$), the other containing y M sodium iodide and $(1 - y)$ M sodium bromide. This procedure had the advantage that the iodide was kept free from acid (which enhances oxidation by air) until immediately before measurements were made. In order to measure E as a function of $C_\mathrm{B}/C_\mathrm{A}$ in the same range of total absorbance, the path length, d, was varied to maintain xd constant from one series of measurements to another. Three cells were used, of path length 1, 5, and 10 cm.

---

[12] Reference 6, pp. 280, 398.

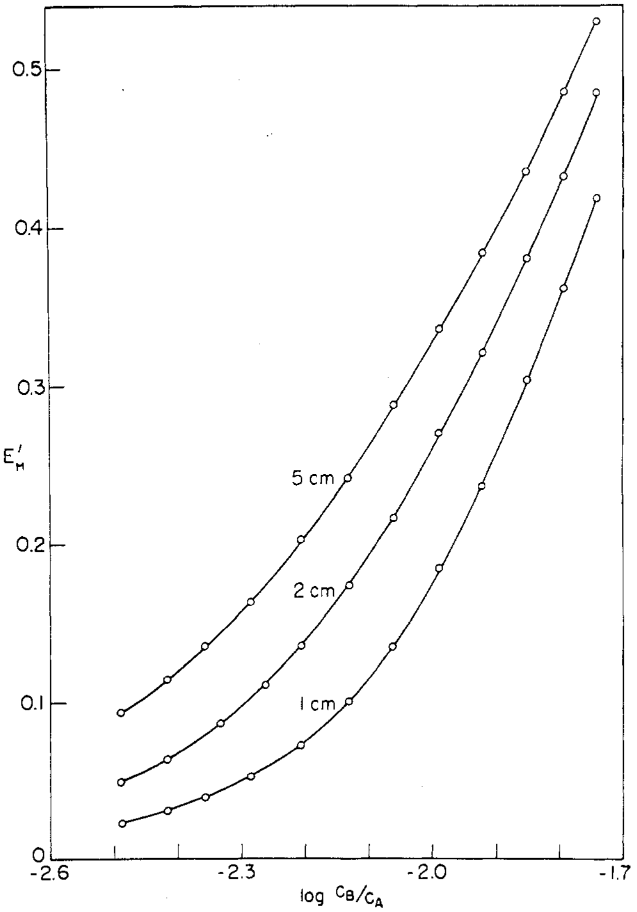

Fig. 1.—Corresponding solutions plots for three path lengths used: xd = 5 mM-cm.; λ = 364 mμ.

The best wave length at which to measure absorbance is at a peak in the spectrum, where $dE/dn = 0$, since the error due to non-monochromaticity of the incident light is minimized at this point. Unfortunately such a wave length was not accessible to these measurements because of the very intense ($\epsilon \simeq 2 \times 10^4$) ultraviolet peaks of the mercuric halides, and the requirement for the corresponding solutions method that the mercury(II) be present in sufficient concentration to bind a significant fraction of the iodide. Instead, rising portions of the spectra had to be utilized, but the results appear to show that the errors introduced by this were not serious.

To maintain a reasonable balance between the mercury and iodide concentrations, two values of xd were used: 1.00 mM-cm. for C_B/C_A = 0–3 $\times 10^{-3}$ and 5.00 mM-cm. for C_B/C_A = 3–20 $\times 10^{-3}$. Spectra were recorded for each series of mixtures and the absorbances were read at 336 and 342 mμ for xd = 1 mM-cm. and at 364 and 368 mμ for xd = 5 mM-cm. E_M was calculated as a function of C_B/C_A, and plotted on large size (11 × 16.5 in.) graph paper, with a smooth curve then drawn through the points. Figure 1 shows such a plot for xd = 5 mM-cm. at 364 mμ. A log scale was used for C_B/C_A, in order to obtain a more even distribution of points throughout the range of E_M'. Values of C_B/C_A were read from the graphs at regular intervals of E', and the corresponding values of C_M/C_A were calculated, using the expression[13]

$$\frac{C_M}{C_A} = X\left(1 - \frac{1-y}{y}\right)\left(\frac{C_B}{C_A}\right)$$

The term C_B/C_A then was plotted against C_M/C_A and values of $\bar{\imath}$ and r were determined from the best straight lines drawn through each set of points. The replacement function, $\bar{\imath}$ (log r), measured in this way, is plotted in Fig. 2.

Replacement constants were calculated from the $\bar{\imath}$ (r) data by the successive extrapolation method of Rossotti and Rossotti[14] (with i, r, and γ_i substituted for $\bar{n}$, a, and β_n, respectively). The extrapolations were refined by including preliminary constants, as well as the γ_4/γ_3 value determined below, to correct for terms originally neglected. The refined functions were treated by the method of least squares. The constants and their uncertainties, so determined, are listed in Table I and the replacement function calculated from them is compared with the experimental points in Fig. 2.

Table I

Replacement Constants for $HgBr_4^{-2} + iI^- = HgBr_{4-i}^{-2} + iBr^-$

	Calculated from Marcus' results	This study		
i	log γ_i	log γ_i	log $\gamma_{i\text{-calcd}}$	Δ log γ_i
1	3.33 ± 0.11	3.20 ± 0.04	2.79	0.41 ± 0.04
2	6.29 ± 0.10	5.49 ± 0.08	5.16	.33 ± 0.08
3	7.69 ± 0.12	7.40 ± 0.09	7.17	.23 ± 0.09
4	8.96 ± 0.07	8.76 ± 0.09	8.76	...

(C) Evaluation of γ_4/γ_3.—Mercury(II) in iodide solution exhibits an absorption band with a peak at 323 mμ. With increasing iodide concentration the absorbance levels off to a constant value well below 0.9 M, showing that the mercury is quantitatively converted to HgI_4^{-2} at this concentration. The molar absorptivity, ϵ_4, of HgI_4^{-2} therefore could be determined from a plot of absorbance against mercury concentration in 0.9 M sodium iodide. The mercuric perchlorate stock solution could not be used for these measurements, however, because the concentrated iodide solution was found to oxidize very rapidly in the presence of even the small amount of acid introduced with the mercuric perchlorate. Instead a mercuric chloride stock solution was prepared by dissolving the analytical reagent (Mallinckrodt) in distilled water. The amount of chloride introduced by the use of this stock solution (0.2 mM) was insignificant compared to the amount of iodide present.

Spectra were taken of solutions containing 0.0997 mM mercuric chloride; and 1.000 M sodium halide with the ratio of iodide to bromide varying between 0.02 and 0.2. The concentration of mercury was sufficiently low that no significant fraction of either halide was consumed and, therefore, $r = C_B/C_A$. These spectra are shown in Fig. 3. From them, E_M was measured, after a small correction for absorbance due to the halides, as a function of r. The points determined in this way were used to construct plots of E_M against $(\epsilon_4 - E_M)r$, which are shown in Fig. 4. These plots should describe parallel lines since the equilibrium constant, γ_4/γ_3, is independent of the wave length used for the measurements. Actually, the slopes of the plots decrease with increasing wave length, converging toward a minimum value at 350 mμ. The reason for this behavior can be seen from the spectra in Fig. 3. Clearly there are more than two components in the system, since the spectra at the lower values of r fail to pass through an isosbestic point. Presumably some $HgBr_2I_2^{-2}$ is formed as r is decreased. Consequently, the summation term in eq. 5 cannot be neglected entirely. The influence of $HgBr_2I_2^{-2}$ on the plots in Fig. 4 depends on its stability, relative to $HgBrI_3^{-2}$, and also on its absorptivity. Since the spectra of the complexes shift to shorter wave lengths with increasing substitution of bromide for iodide, it seems reasonable that the absorptivity of $HgBr_2I_2^{-2}$, and therefore its influence on the E_M $vs.$ $(\epsilon_4 - E_M)r$ plots, should decrease with increasing wave length. In Fig. 5 the slopes of the plots in Fig. 4 are plotted

---

[13] This may be obtained by elimination of the volume terms from the mass balances: (1) $C_M V_T = XV_1$; (2) $C_A V_T = V_1 + (1 - y)V_2$; and (3) $C_B V_T = yV_2$, where V_1 is the volume of the solution containing mercury and bromide and V_2 is the volume of the solution containing bromide and iodide, and $V_1 + V_2 = V_T$. The third balance gives $V_2/V_T = C_B/y$. Substitution for V_2/V_T in the second balance leads to $V_1/V_T = C_A - ((1 - y)/y)C_B$, which by substitution for V_1/V_T in the first balance and division by C_A gives the desired expression.

[14] (a) Reference 6, p. 110; (b) F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, 9, 1166 (1955).

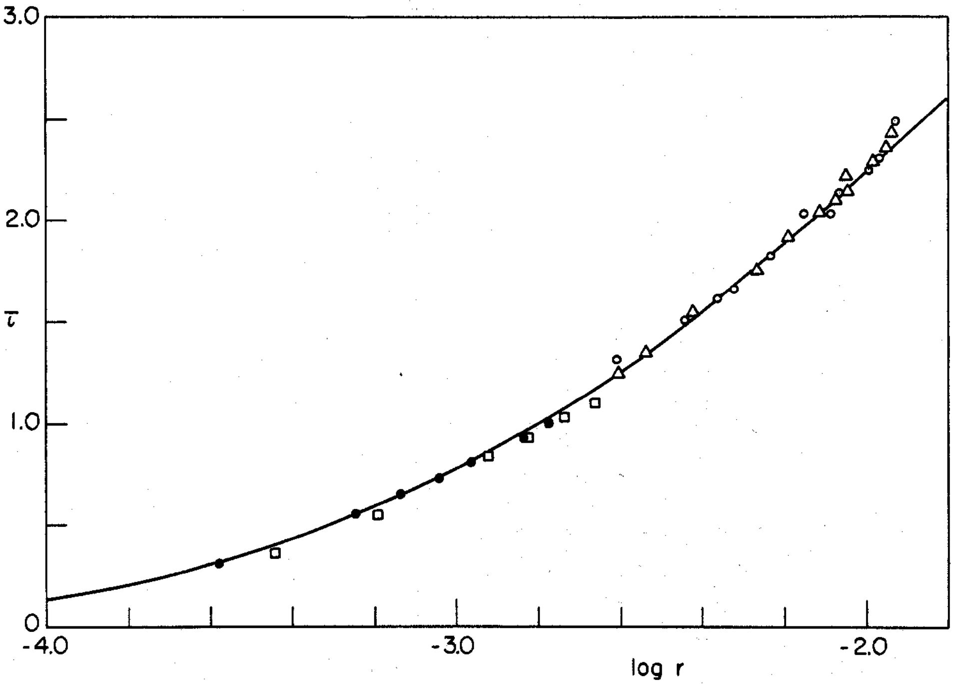

Fig. 2.—Replacement function determined from corresponding solutions at 1.00 mM-cm.: ● = 336 mμ, □ = 342 mμ; and at 5.000 mM-cm.: ○ = 364 mμ, △ = 368 mμ.

against wave length. Clearly the curve approaches a limiting value, which therefore should be the true equilibrium constant, whose value has, on this basis, been estimated as 23.0 ± 0.5.

Discussion

These results may be compared with those reported by Marcus[4] in his study of the ternary system mercury–bromide–iodide, although the ionic media were not the same in the two investigations. Essentially, Marcus used a 0.5 M sodium perchlorate medium, while a 1.0 M sodium bromide medium was used in the present study. However, replacement constants should be fairly insensitive to ionic strength because they involve concentration ratios of ionically similar species. One would not expect the activity coefficient ratio

$$\frac{f_{\mathrm{HgBr}_{4-i}\mathrm{I}_i^{-2}}\,f_{\mathrm{Br}^-}{}^{i}}{f_{\mathrm{HgBr}_4^{-2}}\,f_{\mathrm{I}^-}{}^{i}}$$

to vary widely with changing ionic strength. Nor would one expect specific interaction of either perchlorate or bromide with the saturated complexes.

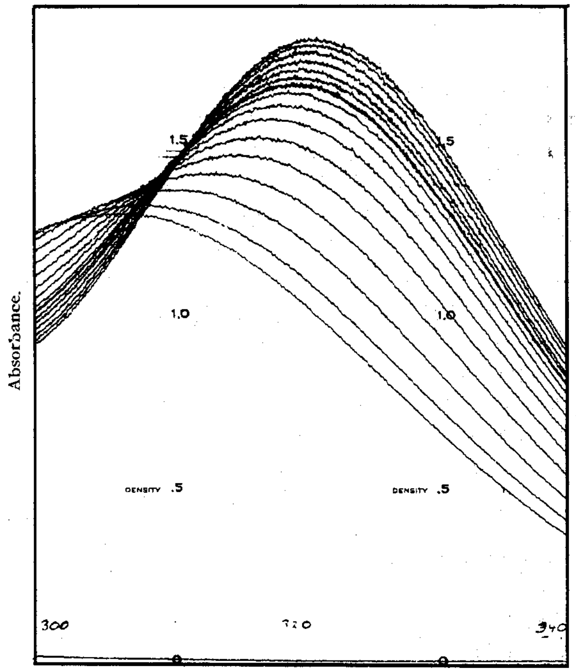

Fig. 3.—Spectra of 0.997 mM mercuric chloride in 1.000 M sodium halide with the iodide:bromide ratio varying between 0.02 (lowest curve) and 0.2 (highest).

Marcus did not determine replacement constants, but rather constants for the reactions: $MA_nB_i + B = MA_nB_{i+1}$. Since he was able to elucidate the entire ternary system, however, it is possible to calculate replacement constants for the saturated level by suitable combination of his constants. The results of these calculations are listed in Table I along with the present values for the same constants. For γ_1, γ_3, and γ_4 there is reasonably good agreement, the present values lying slightly lower than those calculated from Marcus' data. For γ_2 there is quite a significant difference, with Marcus' value lying considerably higher. The reason for this discrepancy is not clear.

For successive replacement reactions

$$MA_n + iB = MA_{n-i}B_i + iA$$

one can calculate equilibrium constants from the relative stabilities of the binary complexes on the assumption that the replacement proceeds statistically. One first divides the free energy for the total replacement reaction, $MA_n + nB = MB_n + nA$, equally among the successive replacement steps. Then one adds the contribution to the free energy of each step arising from the entropy due to the mixing of the ligands. The number

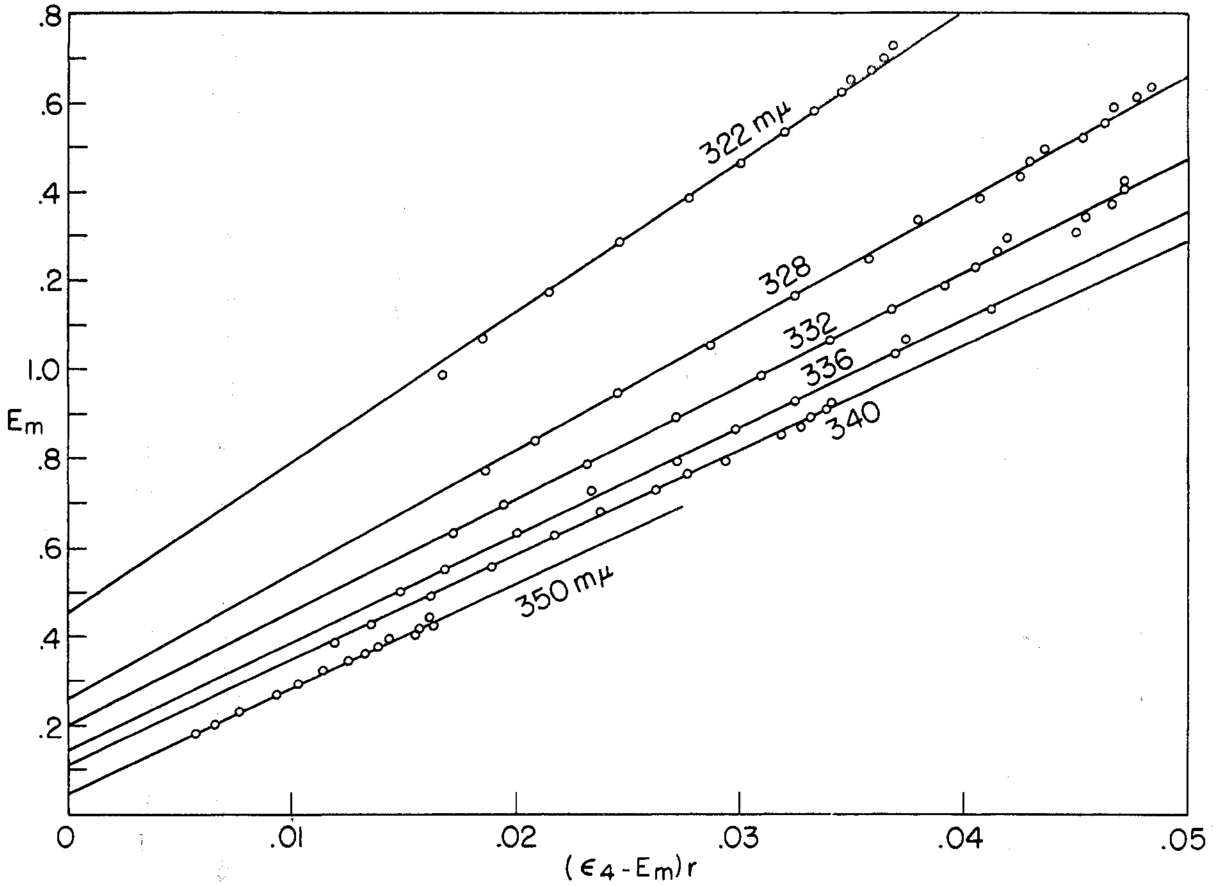

Fig. 4.—Plots to determine γ_4/γ_3.

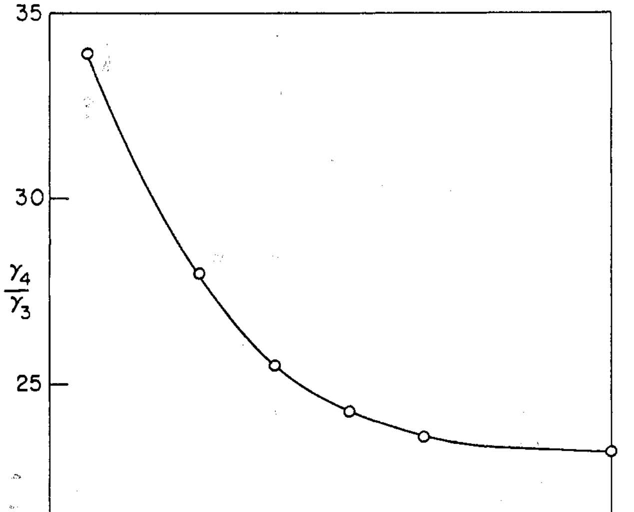

Fig. 5.—Apparent γ_4/γ_3 as a function of wave length.

of discernible arrangements of ligands on the ternary complex $MA_{n-i}B_i$ is $n!/(n - i)!i!$ (*cf.* Rossotti[15]). For the binary complex MA_n, this term is unity. The statistical part of the i^{th} replacement constant, is, therefore, given by log γ_i statistical = log $n!/(n - i)!i!$.

The same result can be obtained from considerations of reaction probabilities, similar to those of Bjerrum.[16] The statistically predicted replacement constants are consequently given by

$$\log \gamma_i = \frac{i}{n} \log \gamma_n + \log \frac{n!}{(n - 1)!i!}$$

The experimental and calculated constants are compared in Table I ($\Delta \log \gamma_i = \log \gamma_i - \log \gamma_{i \text{ calcd}}$). It turns out that the experimental values are all greater than the calculated ones by small but significant amounts, *i.e.*, the ternary complexes are all more stable than one would predict from the stabilities of the binary complexes together with statistical effects. Since the charges on the reacting species do not change during the replacement reactions under consideration, there can be no gross electrostatic contribution[16] to the equilibrium constants, but there may be a small effect due to differences in coulombic repulsion and polarization between the different ligands. As calculated by Marcus and Eliezer,[17] this effect is of the right order of magnitude to explain the extra stabilization of the ternary complexes. In this connection, it may be noted that our value of γ_2 gives an extra stabilization for $HgBr_2I_2^{-2}$ closer to the calculated electrostatic effect than does that determined from

---

[15] F. J. C. Rossotti in "Modern Coordination Chemistry," Lewis and Wilkins, Ed., Interscience, New York, N. Y., 1960, p. 36.

[16] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[17] Y. Marcus and I. Eliezer, Proc. 7 ICCC, p. 361; *J. Phys. Chem.*, in press. (1963).

Marcus' data. There exists also the posssibility of a solvent interaction, similar to that suggested previously[18] for the uncharged mixed mercuric halides, since the binary HgX_4^{-2} ions, being tetrahedral,[19] have a symmetric charge distribution, while the distribution of charge on the ternary complexes should be asymmetric.

Acknowledgments.—The authors are indebted to the American Cyanamid Company for the grant of a predoctoral fellowship to T. G. Spiro (1959–1960) and to the United States Atomic Energy Commission for partial support of the work under Contract AT-(30-1)-905.

[18] T. G. Spiro and D. N. Hume, *J. Am. Chem. Soc.*, **83**, 4305 (1961).

[19] C. L. van Panthaleon van Eck, H. B. M. Wolters, and W. J. M. Jaspers, *Rec. trav. chim.*, **75**, 802 (1956).

CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY,[1]
OAK RIDGE, TENNESSEE

Association Constants of Lead and Bromide Ions in Molten Sodium Nitrate–Potassium Nitrate Mixtures and their Comparison with the Quasi-Lattice Theory

BY D. L. MANNING,[2] M. BLANDER, AND J. BRAUNSTEIN

Received September 19, 1962

The association constants K_1 and K_2 for the formation of $PbBr^+$ and $PbBr_2$ were evaluated from electromotive force measurements in molten mixtures of $NaNO_3$ and KNO_3. The constants K_1 and K_2 in mole fraction units are, respectively, 250, 125 at 240°, 190, 85 at 280°, and 170, 70 at 300° when the solvent is equimolar $NaNO_3$ and KNO_3. A variation in the composition of the solvent changes the value of the association constants so as to give stronger binding as the proportion of KNO_3 increases. The temperature dependence of the association constants, within the experimental error, is predictable from calculations based on the quasi-lattice model.

Introduction

In this paper, the association constants for the formation of the species $PbBr^+$ and $PbBr_2$ in molten $NaNO_3$–KNO_3 mixtures are evaluated from electromotive force measurements. The values are compared with the equations

$$K_1 = Z(\beta_1 - 1) \tag{1}$$

$$K_1K_2 = \frac{Z(Z-1)}{2}(\beta_1\beta_2 - 2\beta_1 + 1) \tag{2}$$

which have been derived from the quasi-lattice model,[3–5] where K_1 and K_2 are the association constants for the formation of $PbBr^+$ and $PbBr_2$, respectively, Z is a coördination number, $\beta_i = \exp(-\Delta A_i/RT)$, and ΔA_i is the specific free energy of bond formation. In previous papers,[6] it was shown that for the association of monovalent ions, ΔA_i is independent of temperature for any given association in any system. Recently, it was demonstrated[7] that the equations also hold for the association of a divalent ion (cadmium) with Br^- and I^-. Since the quasi-lattice theory applies to monovalent ions only, this indicates that calculations based on the model, *i.e.*, eq. 1 and 2, are more general than is implied by the model.

The comparison of experimental measurements with eq. 1 and 2 in this paper was made to further test the applicability of these equations for predicting the temperature coefficient for associations involving a divalent ion. The influence of the solvent cation on the association constants also was measured by varying the composition of the $NaNO_3$–KNO_3 melt.

Experimental

Reagent grade NaBr was dried at 300° and stored in a desiccator. Reagent grade $Pb(NO_3)_2$ was dried in a vacuum oven at 150° and likewise stored in a desiccator. Otherwise the procedure, apparatus, and methods of calculation were essentially the same as described previously.[6,7]

Results and Discussion

It was demonstrated[7] that silver–solid silver halide electrodes are reversible to halide ions in molten nitrates and that the activity coefficient of the alkali halide, $\gamma_{(Na,K)X}$, may be evaluated from e.m.f. measurements of the cell

$$\mathrm{Ag}\left|\begin{array}{l}\mathrm{NaBr}\\ \mathrm{AgBr(s)}\\ \mathrm{(Na,K)NO_3}\end{array}\right\|\left.\begin{array}{l}\mathrm{Pb(NO_3)_2}\\ \mathrm{NaBr}\\ \mathrm{AgBr(s)}\\ \mathrm{(Na,K)NO_3}\end{array}\right|\mathrm{Ag}$$

and the equation

$$\Delta E = \frac{-RT}{F}\ln \gamma_{(Na,K)X} \tag{3}$$

From the change in e.m.f. (ΔE) occurring with the addi-

---

[1] Operated for the United States Atomic Energy Commission by Union Carbide Corporation.

[2] Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

[3] M. Blander, *J. Phys. Chem.*, **63**, 1262 (1959).

[4] M. Blander and J. Braunstein, *Ann. N.Y. Acad. Sci.*, **79**, 838 (1960).

[5] M. Blander, *J. Chem. Phys.*, **34**, 342 (1961).

[6] (a) M. Blander, F. F. Blankenship, and R. F. Newton, *J. Phys. Chem.*, **63**, 1259 (1959). (b) J. Braunstein and M. Blander, *ibid.*, **64**, 10 (1960). (c) D. G. Hill, J. Braunstein, and M. Blander, *ibid.*, **64**, 1038 (1960). (d) D. G. Hill and M. Blander, *ibid.*, **65**, 1866 (1961). (e) A. Alvarez-Funes, J. Braunstein, and M. Blander, *J. Am. Chem. Soc.*, **84**, 1538 (1962). (f) D. L. Manning, R. C. Bansal, J. Braunstein, and M. Blander, *ibid.*, **84**, 2028 (1962).

[7] J. Braunstein and R. M. Lindgren, *ibid.*, **84**, 1534 (1962).