The Electronic Spectra of the Mixed Mercury Dihalides. Part 1. Computational Procedures for calculating Spectra, for a New Route to Equilibrium and Formation Constants, and the Resolved Spectra

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Three possible methods for computing the spectra of the mixed mercury dihalides, HgClI, HgBrI, and HgBrCl, free from contributions of other species, are described and discussed as to their general applicability. The spectra studied are either those of equimolar mixtures of HgX_2 and HgY_2, or of HgX_2 with added halide Y^-. A new procedure is described for computing the formation constants of these species and the spectra have been resolved into their component bands. Each species is shown to contain three bands, even though this is not always apparent from inspection of the calculated spectra. Peak maxima have been found at 37 800, 46 600, and 53 400 for HgClI, 37 800, 43 200, and 51 210 for HgBrI, and 43 500, 47 400, and 57 200 cm^{-1} for HgBrCl. The other parameters of the resolved bands are given.

THE halide complexes of mercury(II) have been extensively studied by many workers using a variety of techniques. Several reviews have been written, that of Deacon [1] being the most comprehensive, but now rather out-of-date. Other reviewers have discussed the halogenomercurates as part of the general chemistry of mercury [2,3] or of the halogens,[4] or certain particular aspects, for example, the mixed halides.[5] This last includes complexes of the type HgXY, $[HgX_2Y_2]^{2-}$, and $[HgX_3Y]^{2-}$, where X is one halogen atom and Y is another (but neither is fluorine). The neutral mixed halides have been investigated by Delwaulle [6,7] who detected new lines in the Raman spectrum of an equimolar mixture of HgX_2 and HgY_2 and attributed them to HgXY. The formation constants of all the uncharged species have been measured in water [8,9] and a few other solvents.[10-12] However, the values for HgBrCl and HgClI agree in benzene [8] and in a mixture of phenyls,[12] but that for HgBrI is reportedly seven times greater in the polyphenyl mixture.[12] No explanation has been advanced.

The electronic spectra of the mixed mercury dihalides in water have been calculated by Spiro and Hume.[9] Recent work in our laboratory has involved the direct digitizing of absorption spectra and its subsequent processing in a computer to yield, for example, the spectra of species which are impossible to measure experimentally free from the contributions of other absorbing species, their formation constants, and, from temperature-dependent equilibria, thermodynamic data.[13-17] We have therefore sought to apply these techniques to the mixed mercury dihalides, to obtain more definitive spectra, and hence formation constants. As a result of our studies we now conclude that the previous data [9] are inaccurate and we therefore in this first paper discuss the various new computing approaches we employed.

EXPERIMENTAL

Digitizing of Spectra.—Spectra were recorded on an Applied Physics Cary 14 H spectrophotometer, modified to yield spectra in digitized form on paper tape. Details of the system have been published.[14,15,17]

Smoothing of Spectra.—Calculated spectra are normally very noisy because the absorbances increased by extrapolation contain the original noise contribution enhanced by the same factor. In all our earlier papers we used the original ' raw ' data in order to justify the technique unambiguously: now we smooth our original data. Where possible the spectra were recorded several times, usually five, and averaged in the computer; otherwise we smoothed the data mathematically, using the procedure of Savitsky and Golay [18] (as corrected by Steinier *et al.*[19]). The spectra in this study were digitized at 1 nm intervals and smoothed using a five-point convolution. This reduced the noise but did not degrade the broad charge-transfer bands observed. The subsequently calculated spectra were more noisy than recorded spectra and thus larger convoluting arrays were used to smooth them. Figure 1 shows the effect of a 15-point smoothing convolution on the calculated spectrum of HgClI in water.

Calculation of the Spectra of Mixed Mercury Dihalides.—The mixed neutral halides of mercury(II), HgBrI, HgClI, and HgBrCl, may be formed in two ways [equations (i) and (ii)], where Y^- is the more strongly co-ordinating, and

$$HgX_2 + HgY_2 \longrightarrow 2HgXY \qquad \text{(i)}$$

$$HgX_2 + Y^- \longrightarrow HgXY + X^- \qquad \text{(ii)}$$

electronegative, ligand. Here, three methods have been derived to calculate the spectrum of HgXY from both the above systems, and we therefore also discuss their various merits.

Displaced equilibrium. If a large excess of HgX_2 is used in the reaction between HgX_2 and HgY_2, all the HgY_2 will be converted into HgXY and the solution will contain only HgX_2 and HgXY, *i.e.* the final concentrations will be $(a - b)$ and $2b$, respectively, where a and b are the initial concentrations of HgX_2 and HgY_2, respectively. If ε_a and ε_{ab} are the molar absorbances of HgX_2 and HgXY, then we obtain equation (1) where A is the observed absorbance.

$$\varepsilon_{ab} = [A - (a - b)\varepsilon_a]/2b \qquad (1)$$

Thus, from the known molar absorbance of HgX_2 and a sample spectrum of a solution containing a large excess of HgX_2, the molar absorbance of HgXY may be found at any wavelength. A simple computer program was written to implement this method over the complete wavelength range used.

The method has two disadvantages. First, if a very large excess of a given mercury halide is used, only part of the desired spectrum is observable, the remainder being hidden under the absorbance of the species in excess. Thus, low concentrations of HgY_2 must be used, and the halide in excess must be the one that absorbs at lowest wavelength, *e.g.*, excess of $HgCl_2$ for the determination of HgClI and HgBrCl spectra. Secondly, as a consequence of low HgY_2 concentrations, the contribution of HgXY to the observed spectrum is small, and any noise is magnified in the calculation, by fluctuations in the low values of 2*b* [equation (1)]. The calculated spectrum of HgXY thus required smoothing (see Figure 1).

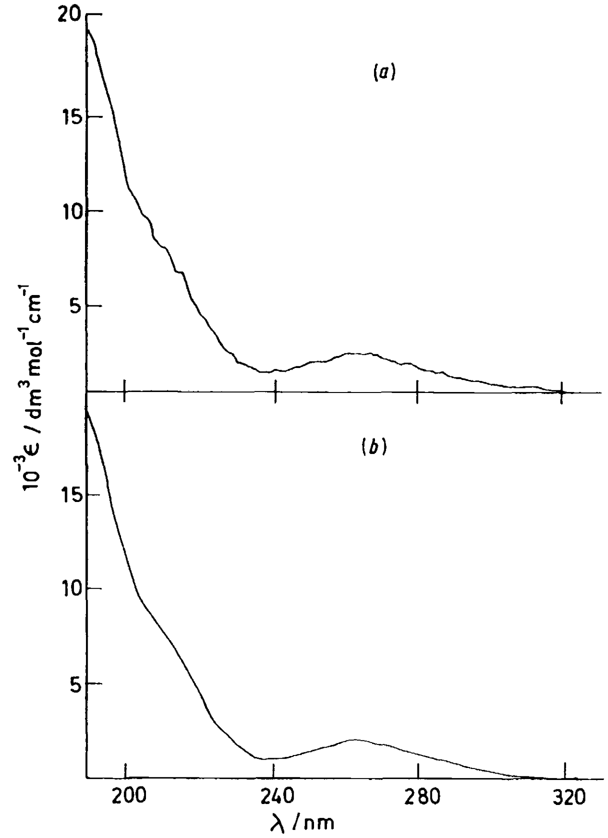

FIGURE 1 Effect of smoothing the calculated spectrum of HgClI in water: (*a*), calculated spectrum before smoothing; (*b*), after smoothing with a 15-point convolution

Reference-point method. (*a*) For a system containing three absorbing species in solution, the molar absorbance is given by equation (2), where x is the mol fraction and

$$\varepsilon = x_a\varepsilon_a + x_b\varepsilon_b + x_{ab}\varepsilon_{ab} \quad (2)$$

$x_a + x_b + x_{ab} = 1$. If the mol fractions of HgX_2 and HgY_2 are equal then equation (2) becomes (3). If data are

$$\varepsilon = x_a(\varepsilon_a + \varepsilon_b) + (1 - 2x_a)\varepsilon_{ab} \quad (3)$$

obtained for solutions containing different mol fractions, ε_{ab} can be evaluated as in (4). ε_{a+b} is the reference spectrum, and is the mean of the molar absorbances of HgX_2 and HgY_2, and equation (4) only holds for a sample solution containing equal quantities of HgX_2 and HgY_2; ε_{a+b} was therefore calculated from the known spectra of HgX_2 and HgY_2.

$$\varepsilon_{ab} = \varepsilon + [x_a/(0.5 - x_a)](\varepsilon - \varepsilon_{a+b}) \quad (4)$$

A reference point is also needed to calculate the mixed mercury dihalide spectrum, and was obtained from the above displaced–equilibrium method [equation (1)]. The molar absorbance of the mixed species was determined at a wavelength where there was as low a slope in the spectrum as possible, and the difference between the calculated spectrum and the mean of the molar absorbances of the HgX_2 and HgY_2 spectra was greatest. The spectra calculated by this method were noisy and needed smoothing.

(*b*) For reaction (ii), with added halide ion, but insufficient to form $[HgX_2Y]^-$ or $[HgX_2Y_2]^{2-}$, a two-species system pertains, and based on the above system it is found that expression (5) is applicable. However, this assumes

$$\varepsilon_{ab} = \varepsilon + [x_a/x_{ab}(\varepsilon - \varepsilon_a)] \quad (5)$$

that the reference cell contains exactly the same amount of the added halide (Y^-) as there is, after reaction, in the sample cell, otherwise an absorbance imbalance will occur. The same concentration of Y^- was added to both sample and reference cells and the observed spectrum of the solution containing the mercury species HgY_2 and HgXY of reaction (ii) is thus altered by the absorbance of Y^- which has displaced X^-. If the absorbance of X^- is in the far u.v., and negligible over the wavelength range studied (as is the case for Cl^- and for most of the range with Br^-), then equation (1) may be used to determine the spectrum of HgXY, on applying a halide-imbalance correction, as follows.

Using first the measured spectrum, the spectrum of HgXY was calculated over the whole wavelength range employed. The concentration of HgXY was then calculated using this spectrum, from a knowledge of the total mercury content of the solution. The concentration of reacted halide was thus known and, from the known molar absorbance of free Y^- ions, the absorbance imbalance of the original sample spectrum was calculated, and a new corrected sample spectrum derived. This iterative process was repeated until the difference between successively amended spectra in the region where Y^- absorbed, usually below 250 nm, was less than a predetermined amount, normally set at 0.01%.

If the concentration of the added halide (Y^-) is less than that of HgX_2, and it is all used in displacing X^-, then the only absorbing species in solution would be HgX_2, HgXY, and X^-. If the spectrum of this solution is recorded using only solvent in the reference cell, the reference-point method (*a*) may be used without applying the halide-imbalance correction, so long as the additional absorbance of X^- is negligible, as is the case of Cl^- and Br^-. Unfortunately this method was found to be inapplicable as only a proportion of the added halide reacted with HgX_2 when the latter was in excess.

Calculation of Equilibrium and Formation Constants.— The term equilibrium constant is used to refer to reaction (i), and the term formation constant to reaction (ii). The constants are stoicheiometric constants since in this case activities cannot be measured, but the conditions are such that activity coefficients will be close to unity.

Potentiometric, polarographic, and radioactive tracer studies involving solvent extraction have all been applied to the mercury(II) halide system for the determination of equilibrium constants, as well as spectroscopic methods. Direct measurement of the concentration of individual species, and curve fitting for various equations, are among the methods used to yield equilibrium constants under various conditions of solvent type, ionic strength, and temperature.

If the molar absorbances of all the species in a solution are known, then the equilibrium (formation) constants may be calculated from a series of solutions of different ligand concentrations, but constant ionic strength, using equation (6) where K_{ab} is the equilibrium (formation) constant for

$$A/c_T = (\varepsilon_a + K_{ab}c_L\varepsilon_b)/(1 + K_{ab}c_L) \qquad (6)$$

HgXY, c_T is the total molar concentration of mercury, and c_L is the free ligand concentration.

In this study the mercury(II) halides in water at constant ionic strength did not yield reliable results on applying equation (6). It was found, as has been noted by others,[20,21] that equilibrium (formation) constants calculated in this way are very dependent on the values of the molar absorbance used. Instead, therefore, the *concentrations* of the individual species were calculated as follows.

At any given wavelength, the absorbance A of a solution will be given by (7) where c_i and ε_i are the molar concen-

$$A = \Sigma c_i\varepsilon_i \qquad (7)$$

tration and molar absorption coefficient, respectively, of the ith species in solution. This equation holds true for all wavelengths, and hence if A is measured for n different wavelengths, then n linear equations of i unknowns may be derived. For $n \gg i$ these equations may be accurately solved for c_i by means of multiple linear regression analysis. A library computer program was amended to perform this.

The output of the program consisted of the required concentrations, with their standard error, and various parameters indicating the accuracy of the main computation and the precision of the fitted data. These were the residual and the regression sum of squares, F ratio, multiple correlation coefficient, and degrees of freedom of the F ratio. A table of residuals and standardized residuals was also output. Equilibrium (formation) constants, with their standard error, were computed from the regression coefficients.

This method has the advantage that conditions of constant ionic strength were not necessary and hence the variation of equilibrium (formation) constant with ionic strength could be studied. Another advantage was the use of complete spectra in the calculation. Equation (7) is wavelength independent and hence so should be the calculated equilibrium (formation) constants. If they are not, in a certain wavelength region, it may be assumed that one of the reference spectra is inaccurate over part of the spectrum. For example, in reference-point method (*b*), the use of the spectrum of HgXY, calculated without allowing for halide imbalance below 250 nm, gives formation constants in the 250—300 nm range that are significantly different from those calculated in the 200—250 nm range. No such difference was found after corrections for halide imbalance. The use of a correct spectrum is also reflected in the accuracy of the computation, as indicated by the improvement in the correlation coefficient and the standard errors.

These properties were also utilized when comparing the spectrum of a species calculated by different methods, or using different data, in order to determine the best spectrum possible, particularly when the computation required an accurate reference-point absorbance, since this was sometimes difficult to obtain.

An additional independent check on this method of calculating formation constants is that the total metal concentration may be computed, and must be the same as, within experimental error, the known experimental quantity of metal in the sample solution.

All three methods gave essentially identical calculated spectra.

Resolution of the Calculated Spectra of the Mixed Mercury Dihalides.—The calculated spectra of the neutral mixed dihalide species in water were analyzed for their component bands. It is first necessary to determine the number of bands under a profile, and this may be obtained definitively by careful second and fourth differentiation of the spectra.[16,22] The presence or absence of a high-energy tail is not evidenced in this way but unless the spectrum exhibits zero absorbance at both wavelength extrema its presence must normally be included in subsequent curve fitting.

Derivative analysis. In this study the earlier procedures [16,22] were not suitable because of the magnitude of the residual noise in the smoothed calculated spectra. A higher-order differentiating procedure [18,19] was therefore employed. Several second and fourth differentiations were performed on each calculated spectrum, with various size sets of convoluting space elements, since the use of too large sets may result in a loss of resolution of closely overlapping bands, and small sets may not enable unambiguous identification of peak maxima from noise. This procedure allowed the authoritative conclusion that all the spectra contained hidden bands not always obvious on visual inspection.

Band shape. For resolving a spectrum the conventional least-squares method of fitting a set of component bands requires an assumption concerning the type of band distribution involved. The usual functions considered are Gaussian, Cauchy (Lorentzian), or the product or sum functions of both.[23] Charge-transfer-to-solvent (c.t.t.s.) spectra require the latter combination for proper resolution; [24] for the intramolecular c.t. transitions described here the commonly employed Gaussian function was found most suitable. The program was based on the least-squares minimization procedure of Fletcher and Powell,[25] and included matrix inversion [26] to increase the rate of convergence of fit.

Absorption-band parameters for HgXY in water at 20 °C

	Observed peaks		Resolved bands				
Species	$E_{max.}$	ε_m	$E_{max.}$	ε_m	w	A	O.S.
HgClI	37.44	2 080	37.80	2 000	5.88	2.50	1.08
			46.60	4 700	5.00	5.01	2.16
			53.40	20 000	7.42	31.6	13.7
HgBrI	51.28	26 370	37.80	2 200	6.06	2.84	1.23
			43.20	2 550	5.25	2.86	1.24
			51.21	26 300	6.51	36.5	15.8
HgBrCl	46.95	3 400	43.50	2 100	6.51	2.91	1.26
			47.40	2 300	4.60	2.25	0.97
			57.20	35 000	7.42	55.4	23.9

ε_m = molar absorbance ($dm^3\ mol^{-1}\ cm^{-1}$); $E_{max.}$ = peak maximum ($10^3\ cm^{-1}$); w = band width at half-height ($10^3\ cm^{-1}$); A = band area ($cm^3\ mol^{-1}\ cm^{-1} \times 10^{-4}$); O.S. = oscillator strength.

RESULTS

The smoothed calculated spectra, and their resolutions, are given in Figure 2 and the computed band constants in the Table. (The experimental details and justification for the calculated spectra are given in the following paper.) The resolved peak maxima were close to those indicated by the derivative spectra. The difference plot given in Figure 2 also shows that a good fit to the data was obtained.

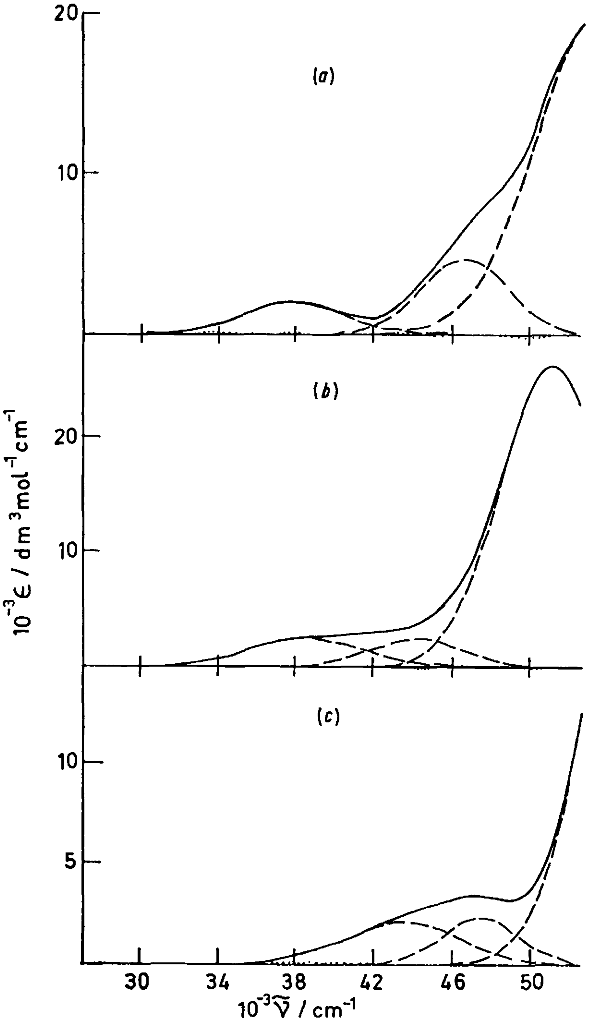

FIGURE 2 Gaussian analysis of the spectra of the mixed neutral halogenomercurates in water at 20 °C: (*a*) HgClI, (*b*) HgBrI, and (*c*) HgBrCl; (— — —), resolved bands; (· · · ·), difference between sum of resolved bands and HgXY profile

Conclusion.—The application of three different computational approaches to the problem of separating the spectra of HgXY from the ever-present spectral contributions of neutral dihalide and/or halide ion has been successful. Consequently, accurate equilibrium and formation constants may now be obtained, and the spectra have been resolved into their component bands. It is however recommended that for future similar applications more than one route to a calculated spectrum should be followed whenever possible.

We thank the S.R.C. for the provision of the Cary 14 H spectrophotometer. The digitizing attachment was purchased on Harwell Contract EMR 1913. We thank the University of Leeds Computing Service for assistance and R. A. A. acknowledges a postgraduate research grant from Leeds University. T. R. G. thanks the Royal Society for a travel grant and the Chemistry Department, Michigan State University, East Lansing, Michigan 48824, U.S.A. for hospitality and facilities during the preparation of this paper.

[8/1692 *Received, 25th September,* 1978]

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