An Infrared Spectroscopic Determination of the Charge Distribution in Mercury (II) Chloride

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The infrared absorption intensity of the asymmetric stretching vibration of $HgCl_2$ has been measured in six different solvents (Table 1). The bond moment has been calculated from the value of the intensity in ethanol solutions where solute-solvent interactions were assumed to be least. Applying a fixed-charge model the "ionic character" of the Hg—Cl bond was found to be 0.52 ± 0.04 in fair agreement with the value calculated by Gray and Pearson.[1]

In an important work Pearson and Gray [1] have recently dealt with the calculation of the charge distribution in some simple halides of divalent metals. For mercury(II) chloride they deduce a value of the "ionic character" of the Hg—Cl bond as 0.54. The polarity of the bonds of this molecule has been experimentally investigated with the nuclear quadrapole resonance technique (Zeeman effect), by Negita, Tanaka, Okuda and Shimada.[2] They obtained the value 0.525 for the "ionic character" of $HgCl_2$.

This good agreement between theoretical predictions and experimental observations give us an excellent opportunity to test an alternative way of studying the bond polarity, namely that of infrared intensity measurements.

It must be noted that many inherent difficulties are associated with this method. However, it was felt important to investigate the possibilities of even a very crude calculation technique.

It has been deduced [3] that the infrared absorption intensity of the ith vibrational mode is given by

$$A_i = \frac{N\pi}{3 \times 10^3 \cdot c^2} \left(\frac{\partial \mu}{\partial Q_i} \right)^2 \tag{1}$$

where Q_i is the normal coordinate of that mode and μ is the dipole moment of the molecule.

From measurements of A_3, the intensity of the asymmetric stretching vibration, of a linear molecule XMX, one can derive the value of $|\partial \mu / \partial r|$.

Details of such calculations are given in the work of Robinson.[4] (Cf. also Ref. 5).

The first obstacle now arises. What part of $|\partial\mu/\partial r|$ can be attributed to the variation of the bond length of a bond with fixed charges and what part corresponds to the variation of these charges as the bond length varies.

In want of more detailed information we choose to neglect the latter effect and thus adopt a "fixed charge model". This is probably not as drastic as may be thought as we already know from the work cited [1,2] that the degree of covalency is not very great so that the possibility of polarity variation is consequently not as high as in a more covalently bonded molecule.

Remembering that we study the asymmetric stretching vibration, one obtains from the adopted model

$$|\partial\mu/\partial r| = 2\,\sigma \qquad (2)$$

if σ is the charge on each chlorine atom.

The other obstacle is that of the unquestionable influence of the solvent on the absolute intensity of any absorption band.

Many relationships have been put forward (cf. Ref. 6) to correlate the intensities measured in condensed phases to those in gas phase, based primarily on variation with the refractive index. Present opinion, however, favours intermolecular forces as playing a more important role compared to the effect due to the bulk medium.[6] This generalisation seems also to hold for solvent-induced frequency shifts.[7] This has led us to base the calculations on measurements in such solvents where solvent-HgCl$_2$ interaction was minimized.

As a measure of low solvent-solute interaction we have chosen the half-width of the absorption band. From the work of Shimozawa and Wilson [8] it follows that the broadness of an absorption band of a stretching vibration is a measure of the ease of rotation of the molecule in question. Consequently we regard the possibility of easy rotation as a measure of the absence of any more profound solute-solvent interactions.

EXPERIMENTAL

The spectra were run between 500 and 250 cm^{-1} on a Perkin Elmer 521 Spectrophotometer flooded with dried air and run at a low scanning speed and expanded wave number scale. The cells were of a type to be described in detail in another paper,[9] the main feature being that no part of the solution was in contact with corrosive metal. Platinum or teflon spacers were used (75 and 100 μ) and the actual thickness of the spacers were measured interferometrically by placing them between CaF$_2$-plates of the same size as the polythene windows used. The windows were cut from 2 mm high density polythene sheets previously pressed between glass plates at elevated temperature to produce optical flatness. No efforts were made to termostate the cells.

From each spectrum the quantity $\log\,(T_0/T)\times\varDelta\nu_{\frac{1}{2}}$ was calculated using as good an estimation of the base line of the spectrum that could be traced. This quantity was then plotted against concentration, and good straight lines resulted (Fig. 1). From the slopes the quantity $\varepsilon\times\varDelta\nu_{\frac{1}{2}}$ was calculated. Deviations from linearity only occurred when using methanol solutions, where the limit of $C_{\mathrm{HgCl_2}}^{-1}\times\log(T_0/T)\times\varDelta\nu_{\frac{1}{2}}$ when $C_{\mathrm{HgCl_2}}\to0$ was used for the calculation of $\varepsilon\times\varDelta\nu_{\frac{1}{2}}$. The reason for this deviation is probably small amounts of water causing a possible disproportionation of HgCl$_2$ into ionic species. It was found that the methanol solutions soon became nontransparent on standing in the open air, probably because of the strong absorption of water in this spectral region.
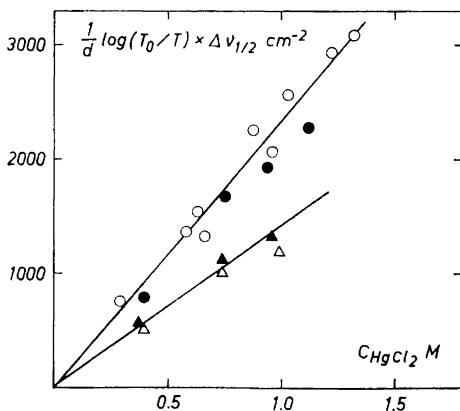
Fig. 1. Variation of $(1/d)$ log $(T_0/T) \times \Delta\nu_\frac{1}{2}$ for ethanol solutions ($\bigcirc$, $d=76$ μ; $\bullet$ $d=103$ μ) and for methylethylketone solutions ($\triangle$, $d=76$ μ; $\blacktriangle$ $d=103$ μ). Only a representative number of measurements leading to the value of $\varepsilon \times \Delta\nu_\frac{1}{2}$ are reported here.
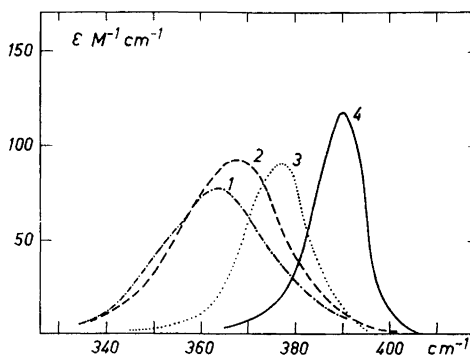
Fig. 2. Survey of the $HgCl_2$ asymmetric absorption band in ethanol (1), methanol (2), methylethylketone (3), and benzene (4).

The possibility that the organic solvents could cause the polythene windows of the cells to swell and thereby change the effective cell thickness was considered. However, had this been of any significance then the absorptivity should have been different when using different spacer thicknesses. But for the possible exception of the ketonic solvent no systematic variation of the observed absorbancies was found for the two spacers used (*cf.* Fig. 1).

The spectrum of the benzene solution was measured at only one concentration and with a (teflon) spacer of 1 mm.

Table 1. Spectral data of the $HgCl_2$ asymmetric stretching vibration.

Solvent	ν_{max} cm^{-1}	$\Delta\nu_\frac{1}{2}$ cm^{-1}	$\varepsilon \times \Delta\nu_\frac{1}{2}$ M^{-1} cm^{-2}	ε M^{-1} cm^{-1}
Ethanol	365	30	2350	77
Methanol	368	25	2300	93
"Butylcellosolve"*	364	24	2040	84
Acetonitrile	370	21	1450	68
Methylethylketone	377	16	1450	91
Benzene	390	13	1480	118

* 2-Butoxyethanol.

RESULTS

The experimental results of the absorption of the asymmetric stretching vibration of $HgCl_2$ measured in six different solvents are given in Table 1 and Fig. 2.

It follows from the suggested criterion on solute-solvent interaction, that the least degree of such interaction should be found in ethanol and the highest one in benzene. The latter finding at least is in accord with chemical intuition. We have then accepted the results obtained for ethanol solutions as the basis for the calculation of $|\partial\mu/\partial r|$. As stated above, the method of calculation follows that of Robinson.[4] Introducing the atomic masses in the G_{33} matrix it is easily found that $G_{33}^{-\frac{1}{2}} = 6.59_5 \times 10^{-12}$. The value of A in ethanol solutions, 0.835×10^4 M^{-1} cm^{-2}, then yields $|\partial\mu/\partial r| = 5.12 \times 10^{-10}$ e.s.u.

Consequently, from eqn. (2) one obtains $\sigma = 2.56 \times 10^{-10}$ e.s.u. and the fractional charge on the chlorine atoms as $\sigma/4.8 \times 10^{-10} = 0.53_5$. This value is in very good agreement with the ones previously reported.[1,2]

Certainly some correction should be made on the A value to compensate for bulk dielectric effects. However, as said before, the magnitude of this correction is uncertain. If one uses a relatively high value of the refractive index, say $n = 1.5$, the formula of Onsager [10] renders almost no change, whereas, e.g., that of Chako [11] gives a corrected value about 34 % less than observed, corresponding to a 16 % smaller value of σ, i.e. 0.46. Taking the mean of these corrections and considering the experimental uncertainties it results that $0.48 < \sigma < 0.56$, i.e. $\sigma = 0.52 \pm 0.04$ This result may be seen in contrast to the estimate $\sigma \simeq 0.25$ made by Braune and Linke [12] from a method that is essentially one of determinining the bond moment from observations on the bending vibration. This value is definitely not in agreement with theoretical [1] and experimental [2] findings. The results presented here, then strengthen the view that bond moments — and charges in a fixed charge model — are more safely arrived at from observations on asymmetric stretching vibrations than from those on the bending ones.

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