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Mercuric Halide Association in Aromatic Solvents

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The possibility of mercuric halide self-association in benzene, toluene, xylene and mesitylene was studied by vapor pressure osmometry. The association was found to be dimeric for chloride and bromide, and dimeric and possibly trimeric for the iodide. Association constants at two temperatures and thermodynamic parameters were calculated.

Introduction

Mercuric halides are often quoted[1–4] as textbook examples of linear molecules with *sp* hybridization. Their stereochemistry, however, should include consideration of distorted-octahedral configurations[5–6], as well as the possibility of *ds* hybridization.[7–8]

There is much evidence, despite some experimental uncertainty, that in the gas phase the mercuric halides are monomeric[9] and have a linear structure.[10–13] However, there are indications that in other phases they tend to associate; even in inert gas matrices which create circumstances close to those of the gas phase, but at low temperature, several investigators claim[14–15] that there are dimeric and polymeric species of mercuric halides. In melts, vibrational spectra,[16–17] conductivity and viscosity measurements[18] also indicate intermolecular interactions. The crystal structure of the solids (except the red iodide) is a molecular one,[19–21] with, obviously, considerable intermolecular interaction. As to mercuric halide solutions in aqueous and organic solvents, however, the available literature[22–41] concerning solute self association and solute–solvent interactions is somewhat contradictory.

Some of the results[22–25] indicate self association, while others[26–30] disprove it. Indications are found in the literature[24,26,31–37] of interactions between the solute molecules and the various solvents. From certain organic solvents, adducts of mercury halides with solvent molecules have been isolated,[33,38–39] and some of them have a halogen-bridged polymeric structure which nevertheless preserves the basic linearity of the mercuric halide molecules.[38,40–41]

In the present work we undertook to study possible solute self-association in some aromatic solvents. This information is necessary for the proper interpretation of mercuric halide–organic solvent interactions, and, ultimately of course, for the characterization of these solution systems.

The aromatic solutions are of particular interest since the mercuric halides are soluble enough in methylbenzenes[34] and since the experimental results in such systems were rather controversial.[25–26,34–35,42–43]

We decided to measure a colligative property, which in dilute solutions allows determination of self-association equilibria without being directly dependent on possible solute–solvent interactions. Nevertheless, to examine the possible influence of such interaction effects on the possible oligomerization, we chose to investigate four aromatic solvents, differing only by the number of attached methyl groups, namely benzene, toluene, *p*-xylene and mesitylene.

Experimental

The measurement method chosen was vapor-pressure osmometry.[44–47] The rapidity of this method permitted repeated measurements at all concentrations with quite good precision (~ ± 2%). This was done by releasing a new drop several times, and the mean of all the separate readings was taken. From the results in diluted solutions one may reach conclusions concerning solute self-association.

The method of "vapor membrane" osmometry has been described elsewhere.[44,46] We shall only mention here that the selectivity of this "membrane" depends on the vapor pressures of the solvent and of the solute, which must differ considerably. In our systems this was achieved by measuring at higher temperatures (56° C, 65° C) for *p*-xylene and mesitylene than for benzene and toluene (42° C, 56° C) which have higher vapor pressure (the vapor pressure, ~ 0.3 mmHg, of the mercuric halides varies with temperature very slowly in this range).

We used a commercial version (Hitachi Perkin–Elmer, model 115) of the "Hill–Baldes" temperature gradient osmometer, measuring resistance (ΔR, in scale units), which is proportional to the temperature gradient. This gradient depends on the vapor pressure lowering of the solution which is proportional to the number of the solute particles. Using suitable calibration solutions (we used benzil in the same solvents) one gets from the measured ΔR for each stoichiometric concentration A, the corresponding osmometric concentration m.

For each run 200–300 mg of crystalline (Merck, analytical) mercuric halide were weighed on a Mettler 20 HT balance (0.01 mg precision), then about 50 ml solvent (Fluka Purissim) were added and the sample was reweighed. The solution was shaken 3–4 hours to ensure total dissolution (the solutions were prepared in concentrations slightly below the solute solubility[34]: about 16–20 milimolal for chloride and bromide and about 4–5 milimolal for iodide).

The solution was then diluted (one part in ten, two parts in ten, and so on) to obtain a series of ten equally-spaced concentrations, and the entire series was measured on the osmometer on the same day. At each of the above steps care was taken to prevent evaporation from the vessels and absorption of humidity into them.

Several series were prepared from solvents which were further purified by drying over sodium and distilling, but since the results deviated by no more than $\Delta R \sim \pm 0.5$ (scale units), *i.e.* $\sim \pm 1\%$, from results obtained without this treatment, it was discontinued.

Calculations and Results

The stoichiometric (A) and osmometric (m) concentrations are given by the following power series of the monomeric concentration (a):

$$A = a + 2b_2a^2 + 3b_3a^3 + \cdots n\, b_na^n$$
$$m = a + b_2a^2 + b_3a^3 + \cdots b_na^n$$

and the coefficients b_i are the overall association constants of the following equilibria:

$$2a \overset{b_2}{\rightleftharpoons} a_2 \qquad b_2 = \frac{a_2}{a^2}$$
$$3a \overset{b_3}{\rightleftharpoons} a_3 \qquad b_3 = \frac{a_3}{a^3}$$
$$\vdots \qquad\qquad \vdots$$
$$na \overset{b_n}{\rightleftharpoons} a_n \qquad b_n = \frac{a_n}{a^n}$$

The monomeric concentration is a fraction of the osmometric, thus $a = zm$ $(0 < z \leqq 1)$, and one may get the actual monomeric concentration for each osmometric one by computing the corresponding z from

$$\ln z = \int_0^m \frac{\alpha^{-1}-1}{m}\,dm$$

(α is the aggregation number defined by $\alpha = \frac{A}{m}$)

Out of sets of osmometric and monomeric concentrations, the association constants b_i have been computed by minimalization of an error function Φ[48–51]:

$$\delta\Phi = \delta \sum_j (m_j^{obs} - m_j^{calc})^2 = 0$$

(j runs over all concentrations)

m_j^{calc} is obtained from

$$m_j^{calc} = a_j + \sum_{i=2}^{n} b_ia_j^i$$

and

$$m_j^{obs} = \frac{\Delta R_j}{k} \quad \text{(k is the calibration constant)}$$

thus

$$\Phi = \sum_{j=1}^{p} \left[\frac{\Delta R_j}{k} - (a_j + \sum_{i=2}^{n} b_ia_j^i)\right]^2$$

On equating all the partial derivatives to zero and rearranging, the so-called normal equations are obtained:

$$pb_1 + a_j^2b_2 + \cdots\cdot a_j^nb_n = \frac{\Delta R_j}{k}$$
$$a_j^2b_1 + a_j^4b_2 + \cdots a_j^{n+2}b_n = a_j^2\frac{\Delta R_j}{k}$$
$$a_j^nb_1 + a_j^{n+2}b_2 + \cdots a_j^{n+n}b_n = a_j^n\frac{\Delta R_j}{k}$$

In matrix notation $A\vec{B} = \vec{Y}$, A being the matrix of coefficients, $\vec{B}$ the vector of the unknown parameters $b_1 \cdots b_n$, and $\vec{Y}$ the right-hand-side vector.

Thus, $\vec{B} = A^{-1}\vec{Y}$, and a FORTRAN program called NONLSQ was used on a CDC 6600 computer to solve this equation iteratively.

Obviously, a solution of this kind necessitates the predetermination of n, which is the degree of the polynomial m_j^{calc}, and thus the degree of the association. However, to determine n is the aim of this study (beside computing the numerical values of $b_1 \cdots b_n$). We solved this problem by running NONLSQ with a degree (Q) of the polynominal increasing from Q = 2 to Q = 9 and taking for n the Q giving the lowest Φ_{min} (Figure 1).

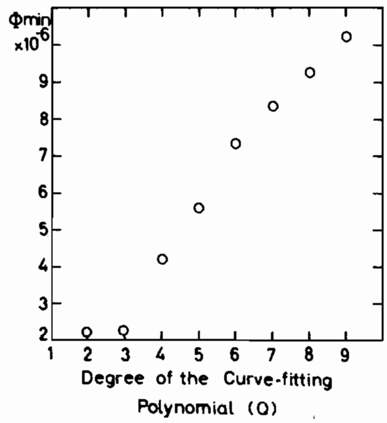


Figure 1. The error-function minimalization curve.

A polynomial $\mu_1=\frac{m-a}{a}=b_1+b_2a+b_3a^2+\cdots$ was used instead of $m=a+b_2a^2+b_3a^3+\cdots$, and b_1 which theoretically should be zero, had non-zero values due to experimental errors. By inserting this b_1, we diminished the possibility of the incorporation of such errors into the other parameters $b_2\cdots b_n$. For the computation of the monomeric concentration a, and for the successive runs of NONLSQ needed to select the optimal Q, a special FORTRAN program was written.

The results of the computations showed the existence of dimerization in the solutions of the iodide in mesitylene, and of the chloride and bromide in each of the four aromatic solvents. The iodide also apparently trimerizes in benzene, toluene and para-xylene.

The computed stepwise association constants ($K_i=\frac{b_i}{b_{i-1}}$) are presented in Table I, with their standard error. There are fairly large standard errors in the case of the iodide. This is to be expected considering the relatively low solubility of the iodide in those solvents, so that almost the entire measured concentration range in this case was close to the instrument's sensitivity limit. Consequently, one must be very careful in the interpretation of the results in the mercury iodide system.

Thermodynamic values (Table II) were computed from the association constants at two temperatures, according to the relations $\Delta G=-RT\ln K$; $\Delta H=-R\frac{\ln K(T_2)-\ln K(T_1)}{1/T_2-1/T_1}$; $\Delta S=\frac{\Delta H-\Delta G}{T}$. It must be mentioned that enthalpy changes calculated from equilibrium constant measurements, rather than from direct calorimetry, are generally considered to be unreliable[52] since it can be shown that ΔH is very sensitive to un-

TABLE I. Mercuric Halide Association Constants.

	Benzene		Toluene		*p*-xylene		Mesitylene	
	42.1°C	55.6°C	42.1°C	55.6°C	55.6°C	64.9°C	55.6°C	64.9°C
Mercuric Chloride								
K_2	65±2	3900±45	108±4	57±2	446±14	324±9	840±20	709±10
Mercuric Bromide								
K_2	14.5±0.5	975±20	185±9	53±2	900±40	298±8	380±10	512±4
Mercuric Iodide								
K_2	17±4	1±1.5	8.5±0.5	1±2	1±0.8	49±2	718±8	536±170
K_3	1213±400	3400±5000	247±18	–	1900±1500	20±6	–	–

TABLE II. Thermodynamic Values of Mercuric Halide Association.[a]

	Benzene		Toluene		*p*-xylene		Mesitylene	
	42.1°C	55.6°C	42.1°C	55.6°C	55.6°C	64.9°C	55.6°C	64.9°C
Mercuric Chloride								
ΔG_2	–2.62	–5.37	–2.94	–2.60	–3.99	–3.88	–4.40	–4.41
ΔH_2	61.6		–9.8		–7.6		–4.1	
ΔS_2	204		–22		–11		1	
Mercuric Bromide								
ΔG_2	–1.68	–4.50	–3.24	–2.59	–4.45	–3.83	–3.87	–4.19
ΔH_2	64.1		–18.9		–26.3		7.5	
ΔS_2	209		–50		–67		35	
Mercuric Iodide								
ΔG_2	–1.76	0	–1.33	0	0	–2.61	–4.30	–4.22
ΔH_2	–42.8		–32.1		–93.3		–7.0	
ΔS_2	–130		–98		284		–8	
ΔG_3	–4.45	–5.31	–3.45	0	–4.94	–2.01		
ΔH_3	15.5		–83.4		–109.4			
ΔS_3	63		–254		–318			

[a] Free energy and enthalpy change values are given in kcal/mol and entropy changes in cal/mol degree.

certainty in the determination of K. In our case while the K and ΔG values have relative errors of about 2–4% (except iodide), the errors in ΔH are about 20%.

The reproducibility of the results was determined as follows: entirely new solutions were prepared, readings were made with new calibration, and the association constants were recalculated for each solution series. The results turned out to be reproducible within a range of 5–16%.

Discussion

In a paper regarding the dipole moment of mercuric chloride in benzene,[25] solute self-association was suggested, based on measurement of average molecular weight and on comparison of the experimental Kerr constant to the calculated one. Later, the reliability of these calculations was questioned,[26] and moreover, there are experimental results contradicting the existence of mercuric halide self-associates in benzene and in other organic solvents.[27–30]

The results of the present work indicate clearly that mercuric halide self-association in methyl benzenes does exist. Measurements in series of concentrations and a polynomial selection-method of computation (as detailed above) enabled us to determine the species that exist in associative equilibrium in the solutions. Dimers of the mercuric halides were shown to exist and in the case of the iodide there may be even trimeric species. The comparison of the numerical values of the association constants obtained in the four solvents (which are quite similar, being of a homologous series) indicates that the amount of self-association in those solvents is different despite their close similarity. This difference indicates that perhaps there is a stabilization of the dimer by the solvent, and this effect varies with the number of the methyl groups attached to the benzene ring.

Thus we may suggest a model of mercuric halide associates in methylbenzenes which consists of mercuric halide dimers interacting with molecules of the methylbenzenic solvent. There are a few experimental results, besides ours, which support this suggestion:

(i) There are indications that mercuric halides tend to associate in all phases, except the gaseous one.[9,14–25,38,40–41] In the gaseous phase self-association fails to occur, perhaps because of a rapid decrease in stability of the associate with increasing temperature (*cf.* the association in inert gas matrices at low temperature[14–15]).

(ii) A variety of mercuric halide complexes were isolated from different solvents and their structure was investigated.[33,36,38–41] All of them have solvent molecules attached, and some have a polymeric structure.

(iii) The vibrational frequency of the mercuric halides in different solvents exhibits a shift from the gaseous frequency towards the values in the condensed phases, thus indicating intermolecular interactions.[16,36–37,53–55] Furthermore, this shift increases with increasing donor character of the solvent; for instance, it is small in carbon tetrachloride and large in pyridine.

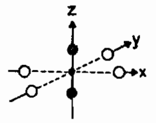
(iv) There are indications of solute–solvent interactions from results of various experimental methods, *e.g.* u.v. spectroscopy,[35] dipole moments,[26,56–57] and solubility.[34]

(v) C.T. bands found in methylbenzenic solutions of mercuric halides[35] were reported to exist in the gaseous phase[43] and so have to be assigned to intramolecular, rather than intermolecular, charge transfer. However, there is an increase in the intensity on going from the gaseous to the solution bands. It is perhaps possible that, the transfer in the gaseous phase being from the halide to the mercury, the added intensity in solution is due to *inter*molecular interactions between halide and mercury, thus indicating dimeric structures, which do not exist in the gaseous phase.

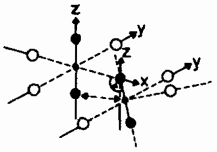
We have no direct proof from this study about the geometry of the monomeric and dimeric mercuric halide species found to exist in equilibrium in the methylbenzenes, and to interact with solvent molecules. Nevertheless, there is evidence in favour of a tentative structure (Figure 2 a–b):

(i) The mercuric halides have a distorted octahedral stereochemistry in the crystalline phase[5–6,19–20] and in the polymeric solvated structure in the halomercurate complexes.[5–6]

(ii) The bonding between two adjacent mercury atoms is by a bridging halogen. The existence of such bonding has been proved in the case of the polymeric backbone of the various halomercurate complexes by ^{35}Cl quadrupole resonance[40,58–60] and by other experimental methods.[6,15,38,41]



a) Solvated Monomer



b) Solvated Dimer

Figure 2. Suggested structures for solvated mercuric halide. ●, Mercury; ◍, Halogen; ○, Solvent molecule; α, Tetrahedral angle; ←-→, Electrostatic attraction distorting the ideal tetrahedral angle.

(iii) Some time ago, *ds* hybridization was proposed[7–8] to explain the distorted octahedral coordination of the mercury atom. It enables the mercury halides to preserve a digonal structure even in condensed phases in which they polymerize. The electronegative halogen atoms create a sufficiently high positive charge on the mercury to make *ds* mixing possible,[7–8] with the $\frac{1}{2}\sqrt{2}\,(d_{z^2} - s)$ orbital charge concentrated in the xy plane. This leads to strong binding of two ligands along the z axis, while in the xy plane, due to the higher electron density, four ligands may be attached more weakly.

Obviously, the structure suggested in Figure 2 is speculative and needs further investigation. This could be done by measuring experimental properties which should be different in the monomer and in the dimer, if their structures are as we have suggested. Such properties are the dipole moment (which should be zero for the centrosymmetric monomer but not for the dimer), and the intensity of the C.T. bands (which should increase on dimerization). The values of these properties should thus depend on the dimer concentration, and should therefore vary with the stoichiometric concentration, according to the dimerization constants. Although both dipole moments and spectra have been measured, no such concentration-dependent effects have been studied.

There are two points in our results for which we have no explanations. First, the trimerization of the iodide; however, the results in the iodide systems are of low precision as explained in the previous section. Second, we did not obtain clear trends in the thermodynamic values, neither with respect to the three halogens, nor with respect to the solvents. Perhaps this indicates that the number of the methyl groups of the solvent, and the change of the halogen, affect the monomer–dimer and solvation–desolvation equilibria in more than one way.

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