These are two other interesting and significant features about this structure. The first is the coordination of the sodium which is six coordinated in the form of a somewhat distorted octahedron. The details are indicated in Figure 3 with the pertinent angles shown. The Na–O distances are remarkably uniform, varying only from 2.28 to 2.59 A.

The second significant feature is the very elaborate network of hydrogen bonding, which, when combined with the sodium coordination, makes an extremely tightly bonded crystal. For example, O(9) is hydrogen bonded to O(7), O(4), O(13) in addition to being bonded to carbon and coordinated to sodium. The hydrogen-bond distances are all between 2.69 and 2.89 A, indicating a generally strong hydrogen bonding.

The very low-temperature factors observed in Table I are a result of this tightly knit structure. Whether or not these truly represent the thermal vibrations, one would expect low-temperature factors for oxygen and phosphorus atoms held as tightly as these, the oxygens being held in some cases by five neighboring atoms.[8]

Acknowledgment. We thank the National Institutes of Health for Grant GM-08392-04, which has made this work possible. We also thank Mr. Merlyn Gunsch, who did some of the preliminary work on the crystal; the Montana State University Computing Center and Western Data Processing Center of UCLA for grants of computing time. Also, we wish to thank the University of Washington and Professor Lyle Jensen for the use of the densitometer used in measuring the intensities.

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[8] The low-temperature factors were considered in some detail in the refinement. They do not appear owing to either level to level scaling or the absorption of the crystal. The only unknown factors seem to be the form factors or the absorption due to the capillary, which seemed unlikely. Thus, we must assume that they are real or that some other unknown systematic error is involved.

Complexes of Aluminum Bromide with Aromatic Hydrocarbons in Solution[1,2]

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Contribution from the Richard B. Wetherill Laboratory, Purdue University, Lafayette, Indiana. *Received August 6, 1965*

Abstract: The interaction of aluminum bromide with aromatic hydrocarbons in solution has been studied by determining the apparent molecular weight of the aluminum bromide over a wide range of composition and temperature. The molecular weights were determined from the lowering of the vapor pressures and the depressions of the freezing point. At one extreme, aluminum bromide exhibits the dimeric molecular weight in benzene, with no evidence of dissociation over the concentration range examined. At the other extreme, the solute exhibits the monomeric molecular weight in mesitylene, the first clear case for dissociation of such a Lewis acid dimeric halide by a π donor. From variation in the apparent molecular weight with concentration, evidence was obtained as to the combination of the aromatic with aluminum bromide. The results of the present study indicate that at 70° aluminum bromide exists in the following forms in the respective aromatic solutions: Al_2Br_6 in benzene, a mixture of Al_2Br_6 and $ArH \cdot Al_2Br_6$ in toluene, $ArH \cdot Al_2Br_6$ in *m*-xylene, and a mixture of $ArH \cdot Al_2Br_6$ and $ArH \cdot Al_2Br_3$ in mesitylene. On the other hand, at 5°, the following species are indicated: $ArH \cdot Al_2Br_6$ in benzene, a mixture of $ArH \cdot Al_2Br_6$ and $ArH \cdot AlBr_3$ in toluene, and $ArH \cdot AlBr_3$ in either *m*-xylene or mesitylene. These results suggest that the equilibria, $Al_2Br_6(soln) + ArH(l) \rightleftharpoons ArH \cdot Al_2Br_6(soln)$ and $ArH \cdot Al_2Br_6(soln) + ArH(l) \rightleftharpoons 2ArH \cdot AlBr_3(soln)$, tend to shift to the right with the increasing basicities of the aromatics involved and with decreasing temperature of the solution. The order of increasing interaction of the aromatics with aluminum bromide at the temperatures examined is benzene < toluene < *m*-xylene < mesitylene.

In previous papers of this series,[6] we presented evidence for the existence of both 1:1 and 1:2 solid complexes, with the respective compositions $ArH \cdot AlBr_3$ and $ArH \cdot Al_2Br_6$, formed between aromatic hydrocarbons (ArH) and aluminum bromide. The fact that complexes of this composition exist in the solid phase does not ensure their existence in solution. Originally, we had become interested in these complexes while attempting to understand the part they played in the kinetics of the aluminum bromide catalyzed reaction of alkyl bromides with benzene and toluene in excess aromatic as the reaction medium.[7] Accordingly, we decided to explore the nature of the interaction of aluminum bromide with representative aromatic hydrocarbons in the aromatic as solvent.

In fact, the literature contains a number of conflicting reports as to the precise nature of the interaction of aluminum bromide with aromatic hydrocarbons in solution. For example, from molecular weight determinations by the freezing point depression method, Van Dyke[8] obtained a value of 534.0 for the molecular

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[1] The Catalytic Halides. XXX.

[2] Based on a thesis submitted by S. U. Choi in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Research Assistant (1953–1956) on Project No. AT(11-1)-170 supported by the Atomic Energy Commission.

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[5] Postdoctorate Research Associate (1952–1954) on Project No. AT (11-1)-170, supported by the Atomic Energy Commission.

[6] (a) S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 903 (1966); (b) H. C. Brown and W. J. Wallace, *ibid.*, **75**, 6265 (1953).

[7] H. C. Brown and H. Jungk, *ibid.*, **77**, 5584 (1955); **78**, 2182 (1956).

[8] R. E. Van Dyke, *ibid.*, **72**, 3619 (1950).

weight of aluminum bromide in benzene solution, in agreement with the theoretical value, 533, for the aluminum bromide dimer. From a similar study, Ulich[9] obtained values somewhat smaller than 533, which he attributed to partial dissociation of the dimeric aluminum bromide into the monomeric form in the benzene solution. Other evidence supporting the existence of aluminum bromide as a dimer in benzene solution appears in the parachor measurements of Poppick and Lehrman,[10] and the molar refraction determination by Korshak, Lebedev, and Fedoseev.[11]

On the other hand, as a result of their dipole moment measurements, Ulich and Nespital[12] concluded that 1:1 addition compounds, $D \cdot AlBr_3$, of aluminum bromide with organic donor molecules, D, were present in solution. Similar results were obtained by Sheka[13] on other aluminum bromide addition compounds. In a more comprehensive dipole moment study, Nespital[14] found the molar polarization of aluminum bromide in benzene solution to decrease appreciably with increasing concentration and attributed this phenomenon to an equilibrium between dimeric and monomeric aluminum bromides in solution, the latter being complexed with benzene. Similar results were realized by Photnikov, Sheka, and Yankelevich.[15]

Attempts were also made to study the interaction of aluminum bromide with aromatic hydrocarbons in solution by spectrophotometric methods. Eley and King[16] reported that benzene solution of aluminum bromide showed a characteristic absorption band at 2785 A, and attributed this to an aluminum bromide complex in solution

$$Al_2Br_6 + nC_6H_6 \rightleftharpoons (C_6H_6)_n \cdot Al_2Br_6$$

where the value of n was presumed to be 1 by analogy with other aromatic molecular complexes, such as $C_6H_6 \cdot I_2$.[17] Luther and Pockels[18] also carried out similar studies on systems of aluminum bromide with benzene and toluene and concluded that in excess aromatic the interaction of aluminum bromide with the aromatic was not based upon the existence of binary complexes in solution, but only upon the statistical clustering between the components.

In hope of clarifying these conflicting reports, we undertook to investigate the molecular species present in solutions of aluminum bromide in a series of aromatics: benzene, toluene, *p*- and *m*-xylenes, and mesitylene. Preliminary results revealed that aluminum bromide exhibits the dimeric molecular weight in benzene and the monomeric value in mesitylene with intermediate stages indicated for the intervening aromatics. This was an unexpected development. Previously, only typical Lewis bases with available lone pairs, such as methyl bromide[19] or dimethyl ether,[20] had been demonstrated to be capable of dissociating aluminum bromide dimer.

We then faced the question of how to establish whether a molecule of aromatic was associated with each molecule of aluminum bromide dimer or monomer in solution. We decided to utilize a technique which had been applied previously to the addition compounds of aluminum bromide with methyl bromide[19a] and of gallium chloride with alkyl chlorides.[21]

In this procedure the molecular weight of the solute is determined as a function of the mole ratio of the Lewis base (solvent) to the acceptor molecule. If 1 mole of the solvent is coordinated with the acceptor, then the molecular weight, calculated on the basis of the original number of moles of donor introduced, will exhibit a decrease in value with increasing concentrations. In such a case, correction of the data for the mole of solvent coordinated with the acceptor will lead to a constant value of the molecular weight, essentially independent of concentration.

It need not be emphasized that this technique must be used with caution. Justification for its applicability in the present study is provided by the remarkable constancy in the molecular weight values as the concentration is varied over wide ranges and in the consistency of the results.

Results

The molecular weight of aluminum bromide in aromatic solutions was determined by either the vapor pressure depression method (VP method) or the freezing point depression method (FP method). In the former procedure, the vapor pressure depression was measured by the direct reading of a differential manometer (VP–M method) or the indirect method based on the ultraviolet spectrophotometric determination of the aromatics (VP–UV method).[6a]

The System: Benzene–Aluminum Bromide. The molecular weight of aluminum bromide in benzene solution was determined at 70° by the VP–M method. Some typical data are shown in Table I. The values of the apparent molecular weight (MW_a),[22] calculated on the assumption of no complex formation between aluminum bromide and the aromatic solvent, are listed in the fifth column of Table I. A value of 536 ± 2, averaged from 14 measurements, was obtained for the MW_a in excellent agreement with the theoretical value, 533, for dimeric aluminum bromide. It is therefore concluded that aluminum bromide exists primarily as an uncomplexed dimer in benzene solution at 70°.

The molecular weight of aluminum bromide in benzene solution was determined also by the FP method to see if the variation of temperature affected the results. Data of some typical measurements are included in Table I. The MW_a values obtained at this temperature, 510 ± 7, were somewhat smaller than the theoretical value, 533. Therefore, the molecular weight MW_2[19]

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[9] H. Ulich, *Z. Physik. Chem.* (Bodenstein Festband), 423 (1931).

[10] I. Poppick and A. Lehrman, *J. Am. Chem. Soc.*, **61**, 3237 (1939).

[11] V. V. Korshak, N. N. Lebedev, and S. D. Fedoseev, *J. Gen. Chem. USSR*, **17**, 575 (1947); *Chem. Abstr.*, **42**, 1217 (1948).

[12] H. Ulich and W. Nespital, *Z. Elektrochem.*, **37**, 559 (1931).

[13] I. A. Sheka, *Russ. J. Phys. Chem.* **16**, 99 (1942); *Chem. Abstr.*, **37**, 6538 (1943).

[14] W. Nespital, *Z. Physik. Chem.*, **B16**, 153 (1932).

[15] V. A. Plotnikov, I. A. Sheka, and Z. A. Yankelevich, *Mem. Inst. Chem. Technol., Akad. Sci. Ukr. SSR*, **4**, 363 (1938); *Chem. Abstr.*, **32**, 7791 (1938).

[16] D. D. Eley and P. J. King, *J. Chem. Soc.*, 4972 (1952).

[17] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

[18] H. Luther and G. Pockels, *Z. Elektrochem.*, **59**, 159 (1955).

[19] (a) H. C. Brown and W. J. Wallace, *J. Am. Chem. Soc.*, **75**, 6270 (1953); (b) D. G. Walker, *J. Phys. Chem.*, **64**, 939 (1960).

[20] D. G. Walker, *ibid.*, **65**, 1367 (1961).

[21] H. C. Brown, L. P. Eddy, and R. Wong, *J. Am. Chem. Soc.*, **75**, 6275 (1953); R. Wong and H. C. Brown, *J. Inorg. Nucl. Chem.*, **1**, 402 (1955).

[22] The values of molecular weight calculated on the assumptions of the formation of no complex, 1:1 complex, and 1:2 complex will be referred to as MW_a, MW_1, and MW_2, respectively.

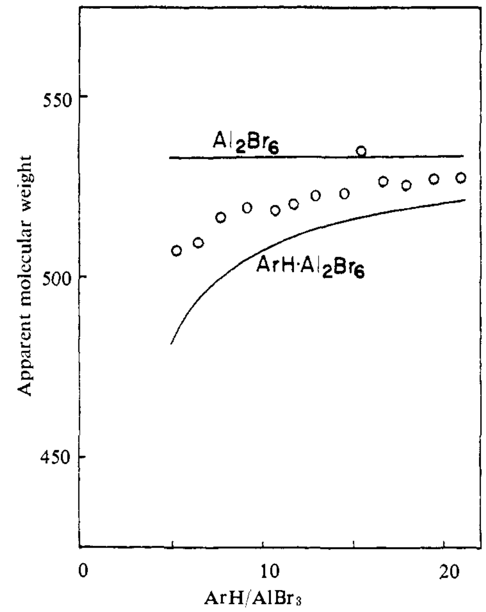

Figure 1. Variation of apparent molecular weights of aluminum bromide in aromatic solution with the mole ratio of aromatic/$AlBr_3$. The two lines represent the theoretical values of the apparent molecular weight in cases that aluminum bromide exists in solution as an uncomplexed dimer and a 1:2 complex, respectively. Experimental points with toluene at 70° are shown by circles.

Table I. Molecular Weight of Aluminum Bromide in Benzene Solution

Temp, °C	Mole ratio, benzene/$AlBr_3$	Vapor pressure depression, mm	Freezing pt depression, °C	MW_a	MW_2
70[a]	22.0	12.1		539	
	18.5	14.5		532	
	16.1	16.5		539	
	13.9	19.0		535	
	11.3	23.3		533	
	8.57	30.3		535	
	6.17	41.0		537	
			Average	536 ± 2[c]	
Ca. 5[b]	20.9		1.64	500	520
	31.9		1.03	530	540
	40.5		0.84	510	520
	44.1		0.76	520	530
	54.8		0.62	510	520
	75.4		0.4	530	530
			Average	510 ± 7[d]	520 ± 5[d]

[a] VP–M method; vapor pressure of benzene observed at 70° = 550.7 mm. [b] At the freezing temperature of benzene; FP method; ΔH_f = 2351 cal/mole.[28] [c] Averaged from 14 measurements, some being excluded from this table. [d] Averaged from 11 measurements, some being excluded from this table.

was again calculated assuming that 1 mole of benzene was effectively removed to form a 1:2 complex in solution. The values of MW_2 thus obtained (the last column of Table I) exhibited slightly better constancy and were closer to the theoretical value 533. However, the experimental value of 520 ± 5, averaged from 11 measurements, was still significantly lower than 533. This may be due to experimental uncertainty or it may be the result of a slight dissociation of the 1:2 complex into the 1:1 complex in solution. However, it appears safe to conclude that the 1:2 complex must be the predominant molecular species present in solution at the lower temperature, approximately 5°.

The System: Toluene–Aluminum Bromide. The molecular weight measurements were carried out on this system at 70° by the VP–M method. Data for some typical measurements are summarized in Table II. The values of MW_a obtained were somewhat smaller than the theoretical value for dimeric aluminum bromide, 533, whereas the values of MW_2 were greater than 533. It must be noted, however, that the value of MW_a decreases with increasing concentration of aluminum bromide in toluene solution. If it is assumed that either an uncomplexed dimer of aluminum bromide or a 1:2 complex is a true picture of the molecular species present in the solution, the value of MW_a must vary with the aluminum bromide concentration in the manners indicated by the two respective lines in Figure 1. The values obtained experimentally, however, fall between these two limiting cases. It appears therefore that aluminum bromide exists in toluene solution at 70° as an equilibrium mixture of both an uncomplexed dimer and a 1:2 complex.

$$Al_2Br_6(soln) + ArH(l) \rightleftharpoons ArH \cdot Al_2Br_6(soln) \quad (1)$$

Table II. Molecular Weight of Aluminum Bromide in Toluene Solution at 70°

Mole ratio, toluene/$AlBr_3$	Vapor pressure depression, mm[a]	MW_a	MW_2
22.8	4.39	530	542
18.0	5.57	525	540
15.6	6.32	535	552
13.1	7.68	522	542
10.7	9.33	518	542
7.81	12.6	516	551
5.43	18.0	507	556
	Average	522 ± 6[b]	545 ± 5[b]

[a] VP–M method; vapor pressure of toluene observed at 70° = 203.7 mm. [b] Averaged from 14 measurements, some being excluded from this table.

Similar studies were carried out at lower temperatures. The results are summarized in Table III. It is evident from the table that the value of MW_a of aluminum bromide in toluene solution decreases with decreasing temperature, the same being observed in the benzene solution. This decrease in the MW_a value is presumed

Table III. Molecular Weight of Aluminum Bromide in Toluene Solution at Various Temperatures

Temp, °C	Mole ratio, toluene/$AlBr_3$	MW_a	No. of measurements	Method
70[a]	5–23	522 ± 6	14	VP-M
50	9–13	479 ± 7	2	VP-M
18.9	7–22	460 ± 10	7	VP-M
18.9	7–22	450 ± 10	7	VP-UV
0	10–18	350 ± 20	6	VP-UV

[a] Data of Table II.

to be due to the dissociation of the 1:2 complex into the 1:1 complex in solution.

$$ArH \cdot Al_2Br_6(soln) + ArH(l) \rightleftharpoons 2ArH \cdot AlBr_3(soln) \qquad (2)$$

Hence, it appears that in the toluene solution of aluminum bromide, the equilibria 1 and 2, shown above, will shift more to the right at lower temperature, and therefore the 1:2 complex will dissociate more into the 1:1 complex with decreasing temperature, corresponding to the smaller values of molecular weight observed at lower temperatures.

The System: *m*-Xylene–Aluminum Bromide. The studies were extended to this system. The results obtained at 70 and 0° are summarized in Table IV. The value of MW_2 observed at 70°, 529 ± 4, is in excellent agreement with the theoretical value 533, and the value of MW_1[22,23] at 0°, 256 ± 20, agrees with the theoretical value, 267. Hence, it appears that the 1:2 complex is the predominant molecular species present in the solution at 70°, and the 1:1 complex at 0°. The large temperature variation of the molecular weight observed here is again attributed to the dissociation of the 1:2 complex into the 1:1 complex at lower temperature, according to equilibrium 2.

Table IV. Molecular Weight of Aluminum Bromide in *m*-Xylene Solution

Temp, °C	Mole ratio, *m*-xylene/ $AlBr_3$	Vapor pressure depression, mm	MW_a	MW_2 or MW_1
70[a]	21.9	1.76	508	520
	16.7	2.29	509	525
	13.4	2.81	515	534
	10.3	3.67	505	531
	7.00	5.45	487	525
	4.89	7.82	472	527
		Average	502 ± 14[c]	529 ± 4[c]
0[b]	16.4	0.115	214	231
	14.5	0.116	235	253
	12.7	0.148	208	229
	11.1	0.151	234	258
	9.38	0.179	229	257
	7.75	0.178	279	313
		Average	232 ± 16[d]	256 ± 20[d]

[a] VP–M method; vapor pressure of *m*-xylene observed at 70° = 75.2 mm. [b] VP–UV method; vapor pressure of *m*-xylene observed at 0° = 1.62 mm. [c] Averaged from 12 measurements, some being excluded from this table. [d] Averaged from 11 measurements, some being excluded from this table.

The System: *p*-Xylene–Aluminum Bromide. In a previous study,[6a] a major difference was observed between the behaviors of *m*- and *p*-xylenes as to their relative ability to form solid π complexes with aluminum bromide. Therefore, we undertook the investigation of the molecular species present in *p*-xylene solution of aluminum bromide. The results of the molecular weight determination by the FP method reveal that the value of MW_2 is 530 ± 3, in good agreement with the theoretical value, 533. This indicates that the 1:2 complex is present in solution at the freezing temperature of *p*-xylene, around 13°.

The System: Mesitylene–Aluminum Bromide. Studies were extended further to this system. The results obtained at 70 and 0° (Table V) reveal that aluminum bromide exists as a mixture of 1:1 and 1:2 complexes in mesitylene solution at 70°, and primarily as a 1:1 complex at 0°. The large temperature dependence thus observed is again attributed to equilibrium 2.

Table V. Molecular Weight of Aluminum Bromide in Mesitylene Solution

Temp, °C	Mole ratio, mesitylene/ $AlBr_3$	Vapor pressure depression, mm	MW_2 or MW_1
70[a]	14.0	1.39	423
	12.8	1.55	412
	10.7	1.79	426
	8.73	2.25	416
	6.30	3.17	410
		Average	416 ± 4[c]
0[b]	12.4	0.036	270
	11.8	0.035	280
	10.8	0.037	290
	9.61	0.045	270
	8.11	0.047	310
		Average	280 ± 10[d]

[a] VP–M method; vapor pressure of mesitylene observed at 70° = 30.7 mm. [b] VP–UV method; vapor pressure of mesitylene observed at 0° = 0.443 mm. [c] Averaged from eight measurements, some being excluded from this table. [d] Averaged from nine measurements, some being excluded from this table.

Discussion

The results of the present study may be fitted by the assumptions that at 70° aluminum bromide exists as an uncomplexed dimer in benzene solution, a mixture of uncomplexed dimer and 1:2 complex in toluene, a 1:2 complex in *m*-xylene, and a mixture of 1:2 and 1:1 complexes in mesitylene.

As studied previously,[6a] a steady increase in the ability to form solid π complexes with aluminum bromide is observed from benzene to toluene, to *m*-xylene, and to mesitylene. The crystal lattice energies of the solid complexes do not appear to play a major role on the relative stability of the aluminum bromide–aromatic solid complexes, as discussed in a previous paper of this series.[6a] Hence, it seems reasonable to assume that the relative ability of each aromatic to form the solid aluminum bromide complexes is reflected in its ability to complex with the aluminum bromide in solution. The following equilibrium is, therefore, expected to shift more to the right with the aromatics in the order indicated above.

$$Al_2Br_6(soln) + ArH(l) \rightleftharpoons ArH \cdot Al_2Br_6(soln)$$

The previous study[6a] also indicates that the weaker aromatic bases form π complexes readily with aluminum bromide dimer, but that only the two most basic aromatic hydrocarbons examined, *m*-xylene and mesitylene, appear capable of dissociating the dimeric aluminum bromide molecule to form solid 1:1 complexes. It appears reasonable to assume that the same tendency will also be present in solution. Therefore, the fol-

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(23) An identical equation can be used for the calculation of both MW_1 and MW_2 (see Experimental Part).

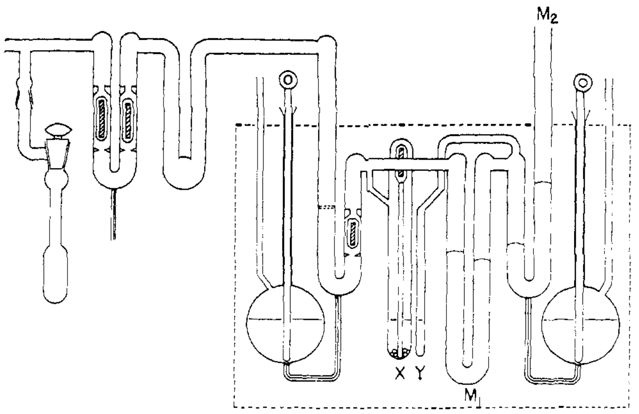


Figure 2. Apparatus for the molecular weight determination by the direct, manometric reading of vapor pressure depressions.

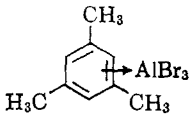
lowing equilibrium is also expected to shift more to the right with the more basic aromatics.

$$\text{ArH}\cdot\text{Al}_2\text{Br}_6(\text{soln}) + \text{ArH}(\text{l}) \rightleftharpoons 2\text{ArH}\cdot\text{AlBr}_3(\text{soln})$$

It is therefore rationalized that the following represents the order of increasing interaction with aluminum bromide in solution: benzene < toluene < *m*-xylene < mesitylene. This is consistent not only with their relative ability to form solid π complexes with aluminum bromide but also with their relative ability to form π complexes with hydrogen halides in solution.[24]

The results of the present study indicate that at 0° aluminum bromide exists as a 1:2 complex in benzene (I), a mixture of 1:2 and 1:1 complexes in toluene, and a 1:1 complex in either *m*-xylene or mesitylene (II).

I



II

From the comparison of results obtained at 70 and 0°, it appears that the two equilibria, mentioned above, tend to shift more to the right, not only with increasing interaction between aluminum bromide and the aromatics involved, but also with decreasing temperature of the solution. This temperature dependence implies that the forward reactions of both equilibria must be exothermic.

From the present study it appears that a 1:1 complex is present in the *m*-xylene solution of aluminum bromide at 0°, but a 1:2 complex in the *p*-xylene solution at approximately 13°. Therefore, it appears that *m*-xylene interacts more strongly with aluminum bromide in solution than does *p*-xylene. This is consistent with the relative abilities of the xylenes to form solid π complexes with aluminum bromide, noted previously.[6a]

Experimental Section[25]

Materials. Aluminum bromide was purified in the method described in previous papers of this series.[6] The high-purity samples of aromatic hydrocarbons used in the present study, except for the freezing point depression experiments, were supplied by the National Bureau of Standards.[26] Benzene (thiophene free) was fractionated through a Todd column rated at approximately 50 theoretical plates. The center cuts ($n^{20}\text{D}$ 1.5007) were retained, stored in the vacuum line, and used for the freezing point depression experiments. A value of 99.75 mole % was obtained for its purity by the cooling curve method.[27] *p*-Xylene (Phillips Petroleum Co., research grade) was dried with calcium hydride and stored in the vacuum line. A purity of 99.86 mole % was observed by the cooling curve method.[24] The observed value of the refractive index was $n^{20}\text{D}$ 1.4957.

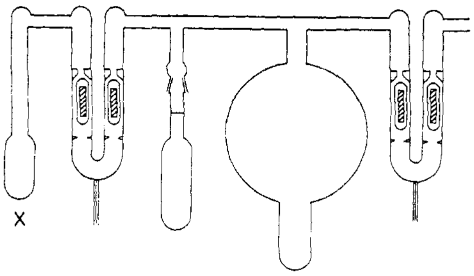


Figure 3. Apparatus for the accurate measurement of low vapor pressures of aromatic hydrocarbons.

Constant Temperature Baths. Warm baths were obtained by heating a water bath to the desired temperature which was controlled to within ±0.05° by means of a temperature regulator. Cold baths used were prepared from the solid–liquid slushes of the following substances: acetophenone, 19°; and ice–water, 0°.

Molecular Weight Determination by Manometric Readings of Vapor Pressure Depression (VP–M Method). The apparatus used in this procedure is shown diagramatically in Figure 2. A solution with an accurately known concentration of aluminum bromide in the aromatic hydrocarbon was prepared in the reaction vessel X by the procedure described previously.[6] A small quantity of the pure aromatic was introduced into vessel Y under vacuum. The entire apparatus was then kept in a bath at the desired temperature (shown by the dotted line in Figure 2). After sufficient time had elapsed (about 0.5 to 1 hr), both the vapor pressure of the aromatic and the vapor pressure depression were measured by direct reading of the manometers M_2 and M_1, respectively. The meniscus correction, due to the depression of mercury in a glass tube, was applied to the manometer readings when they were low enough to be affected by this correction. For higher values of the vapor pressure of the aromatic, the rise of mercury in the longer limb of the manometer M_2 was prevented by admission of dry air. In this way all of the mercury was maintained within the bath at the desired temperature. The pressure of the air admitted was measured by another manometer (not shown in Figure 2) and this value added to the readings of the manometer M_2 after an application of a correction for the difference in temperature between the two manometers.

In order to vary the composition of the solution, the bath was removed, the apparatus was cooled down to room temperature, and a small quantity of the aromatic was then transferred from the reaction vessel to the weighing tube. The above-mentioned procedure was then repeated for the measurement of the vapor pressure and the new vapor pressure depression.

From the observed values of the vapor pressure of the aromatic, P_o, and the vapor pressure depression, ΔP, the molecular weight of aluminum bromide was calculated utilizing the equations

$$\text{MW}_a = \frac{P_o - \Delta P}{\Delta P}\left(\frac{w}{n}\right)$$

$$\text{MW}_1\,(\text{or MW}_2) = \frac{P_o}{\Delta P}\left(\frac{w}{n}\right)$$

where w is the weight of aluminum bromide introduced and n the number of moles of the aromatic present in the liquid phase.

Molecular Weight Determination by Ultraviolet Spectrophotometric Measurements of Vapor Pressure Depressions (VP–UV Method). Two units of the apparatus shown in Figure 3 were assembled in such a manner that the two vessels containing the aluminum bromide solution and the pure aromatic (corresponding to X at Figure 3) were placed in a single bath. After sufficient time (up tc about 1 hr) had elapsed for the system to attain thermal

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[24] H. C. Brown and J. J. Melchiore, *J. Am. Chem. Soc.*, **87**, 5269 (1965); H. C. Brown and J. D. Brady, *ibid.*, 74, 3570 (1952).

[25] For further detail on the experimental procedure and numerical data consult S. U. Choi's Ph.D. Thesis, Purdue University Library.

[26] This assistance is gratefully acknowledged.

[27] K. L. Nelson, *Anal. Chem.*, **29**, 512 (1957).

equilibrium, the pressures of the aromatic present in the gaseous phase of the two vessels were measured by the procedure described previously.[6a] From the values of the two pressures thus obtained, the values of P_0 and ΔP were calculated, and therefore the molecular weight of aluminum bromide calculated, assuming Raoult's law to hold.

Molecular Weight Determination by Freezing Point Depression (FP Method). The apparatus used in this procedure is shown diagramatically in Figure 4. A known amount of aluminum bromide was introduced into the reaction vessel E, and the aromatic to be studied was then transferred from the storage tube F to the reaction vessel, both being carried out under vacuum. After the transfer, the stopcock C was closed. The volume of the aromatic transferred was measured by the difference between the two readings of the meniscus of the liquid hydrocarbon in vessel F. The entire apparatus was then removed from the vacuum line at the two ball joints A and D. A platinum resistance thermometer was placed in the narrow well B, and a bath containing a suitable coolant placed around the reaction vessel with an air jacket. The cooling curve was then recorded on the chart of Speedomax recorder. Thus, the freezing points of the solution, and, therefore, the values of the freezing point depression, ΔT_f, were measured. The mole fraction of the aromatic solvent, N_1, was then calculated by the equation

$$\ln N_1 = \frac{\Delta H_f}{R T_0^2} \Delta T_f$$

where ΔH_f is the heat of fusion of the solvent and T_0 the freezing point of the pure solvent, expressed on the absolute scale. These two quantities were obtained from the literature.[28]

In order to vary the composition of the solution, the stopcock C was opened and a small quantity of the aromatic was transferred from the storage tube to the reaction vessel. The above procedure was then repeated to measure the freezing point of the solution.

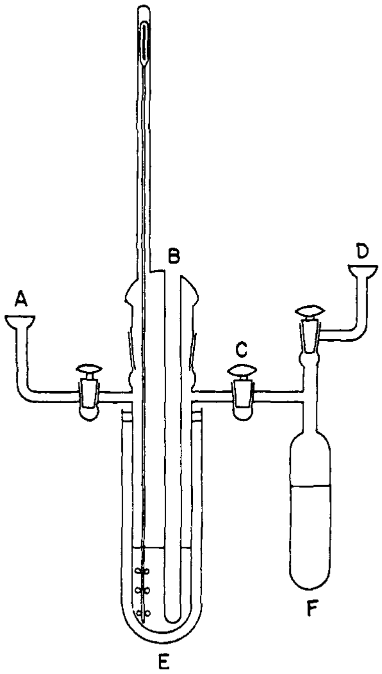

Figure 4. Apparatus for the molecular weight determination by the freezing point depression method.

The molecular weight of aluminum bromide was calculated by the equations

$$\mathrm{MW_a} = \frac{w}{n[(1/N_1) - 1]};\quad \mathrm{MW_1\ (or\ MW_2)} = \frac{w}{n(1 - N_1)}$$

where w is the weight of aluminum bromide introduced and n the number of moles of the aromatic present in the reaction vessel.

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[28] "Selected Values of Properties of Hydrocarbons," National Bureau of Standards Circular C461, U. S. Government Printing Office, Washington, D. C., 1947.