Physical and Inorganic Chemistry

Complexes of Hydrogen Chloride and Hydrogen Bromide with Aromatic Hydrocarbons in n-Heptane Solution[1,2]

Herbert C. Brown and John J. Melchiore[3]

Contribution from the Richard B. Wetherill Laboratory of Purdue University, Lafayette, Indiana.   Received July 28, 1965

The Henry's law constants for hydrogen chloride and hydrogen bromide in n-heptane and in 0.5 M n-heptane solutions of benzene, toluene, m-xylene, and mesitylene have been determined at -78.5, -63.5, and $-45.2°$. A steady increase in the solubility of each gas is noted at each temperature, corresponding to the relative basicity of the aromatic hydrocarbons involved. This increased solubility is attributed to the formation of a 1:1 π-complex between the hydrogen halide and the aromatic molecule. Dissociation constants and thermodynamic data are calculated for the reaction, ArH·HX(soln.) $\rightleftharpoons$ ArH(soln.) $+$ HX(soln.). The thermodynamic stability of the π-complexes formed depends upon the electron-donating ability of the aromatic as well as the polarity of the hydrogen halide molecule. Thus, with a given hydrogen halide, the stability of the complexes increases in the order: benzene $<$ toluene $<$ m-xylene $<$ mesitylene, and a quantitative difference in stability of about 0.1 kcal./mole is observed between each successive member of this series. With a given aromatic, hydrogen chloride forms a more stable complex than hydrogen bromide, and the difference in stability between the two halide complexes of a given aromatic is observed to be approximately 0.2 kcal./mole. It is suggested that these complexes involve a type of hydrogen bonding between the proton of the hydrogen halide and the π-electron cloud of the aromatic ring.

Introduction

A number of workers have demonstrated the formation of complexes between hydrogen chloride or hydrogen bromide and various aromatic compounds, beginning with the discovery of solid complexes of hydrogen bromide with ethylbenzene, m-xylene, and mesitylene by Maass and co-workers.[4,5] By studying freezing point–composition diagrams, Maass and others showed the existence of solid 1:1 complexes of hydrogen bromide with the aromatics mentioned above. They also found evidence for solid 2:1 complexes formed between toluene or ethylbenzene and hydrogen bromide, with the respective compositions, (toluene)₂·HBr and (ethylbenzene)₂·HBr.[6] O'Brien and co-workers[7] measured the partial pressure of hydrogen chloride over a number of solvents. They found that Henry's law was obeyed in the aromatic solvents and proposed that a hydrogen bond was formed between hydrogen chloride and the solvent molecules. From infrared absorption studies on solutions of hydrogen chloride in nitrobenzene and o-nitrotoluene, Gordy and Martin[8] found that the fundamental vibrational band of hydrogen chloride shifted appreciably to lower frequencies. These shifts were interpreted as being caused by hydrogen bond formation between hydrogen chloride and the solvents. They proposed that the shifts of the hydrogen chloride band could be

(1) The Catalytic Halides. XXVIII.

(2) Based on a thesis submitted by J. J. Melchiore in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Graduate research assistant, 1954–1957, on Project No. AT(11-1)-170 supported by the Atomic Energy Commission; Purdue Research Foundation Fellow, 1954–1956.

(4) (a) O. Maass and J. Russell, J. Am. Chem. Soc., 40, 1561 (1918); (b) O. Maass, E. H. Boomer, and D. M. Morrison, ibid., 45, 1433 (1923).

(5) For detailed references to earlier work, see L. J. Andrews, Chem. Rev., 54, 713 (1954).

(6) For convenience, the complexes of the types (aromatic)·HX and (aromatic)₂·HX will be referred to as the 1:1 and 2:1 complexes, respectively.

(7) S. J. O'Brien, J. Am. Chem. Soc., 63, 2709 (1941); S. J. O'Brien, C. L. Kenny, and R. A. Zuercher, ibid., 61, 2504 (1939); S. J. O'Brien and J. B. Byrne, ibid., 62, 2063 (1940).

(8) W. Gordy and P. C. Martin, J. Chem. Phys., 7, 99 (1939); W. Gordy, ibid., 9, 215 (1941).

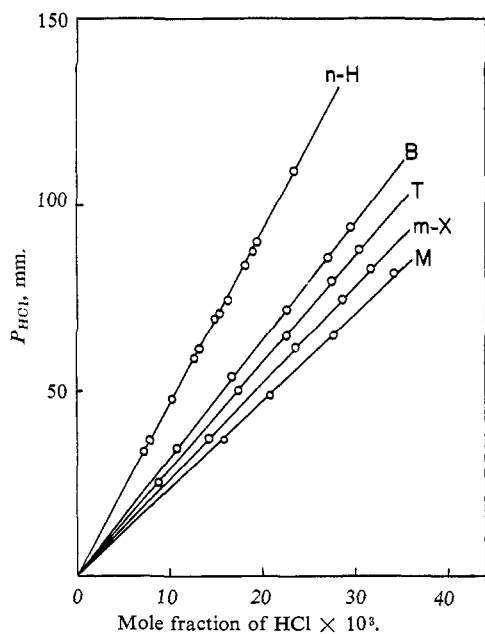Figure 1. Solubility of hydrogen chloride at $-78.5°$ in n-heptane (n-H), and in 0.5 M n-heptane solutions of benzene (B), toluene (T), m-xylene (m-X), and mesitylene (M).

used to compare basicities of weak bases. Plyler and Williams[9] studied the infrared absorption spectra of hydrogen chloride in benzene. The absorption band of hydrogen chloride shifted to lower frequencies, as compared to the gaseous state, again indicating a hydrogen bond interaction between benzene and hydrogen chloride.

Our earlier study[10] of the solubility of hydrogen chloride in n-heptane solutions and in toluene solutions of aromatic compounds established the existence in solution of 1:1 π-complexes of hydrogen chloride with a number of aromatic compounds, with the following order observed for the relative basicity of typical aromatic hydrocarbons: benzene < toluene < m-xylene < mesitylene. It was suggested that π-complexes were formed involving the formation of a hydrogen bond between the hydrogen chloride molecule and the π-electrons of the aromatic ring.

Cook[11] studied the shift in the infrared fundamental stretching frequency of hydrogen chloride in its complexes with alkylbenzenes. He correlated the observed shift in frequency with the basic strengths of the aromatics involved. The order of the relative basicity observed for benzene, toluene, m-xylene, and mesitylene was the same as that reported in our previous paper.[10] Cook likewise concluded that complex formation involved a hydrogen bond between the proton of hydrogen chloride and the π-electrons of the aromatic ring. Josien and others[12] also studied the relative basicity of aromatic compounds and other electron donor molecules toward complex formation with hydrogen halides by infrared measurements. The relative basicity observed for benzene, toluene, m-

xylene, and mesitylene again agreed with that reported in our previous paper.[10]

From the literature cited, it is evident that an interaction occurs between hydrogen halides and aromatic hydrocarbons to form molecular complexes, and the relative tendency of aromatic hydrocarbons to form such complexes is that shown above. Unfortunately, however, the precise formulation of the complexes of hydrogen halides with toluene is uncertain. As mentioned above, the complexes have been formulated as both 1:1 and 2:1 derivatives: (toluene)·HCl[10] and (toluene)$_2$·HBr.[4] Furthermore, Cook and others[13] demonstrated the existence of solid 1:1 complexes of hydrogen chloride with benzene, toluene, p-, o-, and m-xylenes, and mesitylene from freezing point–composition diagrams. For toluene, however, an additional solid complex, (toluene)$_2$·HCl, was also reported to exist.[13] On the other hand, Terres and Assemi[14] observed only the formation of solid 1:1 complexes of hydrogen chloride with alkylbenzenes from studies on melting point curves of the binary mixtures.

It appeared of interest therefore to examine the interaction of hydrogen halides with aromatic hydrocarbons in dilute n-heptane solution in order to establish whether the 2:1 complexes exist in solution. It was also of interest to determine the thermodynamic stabilities of the complexes involved, as well as the quantitative differences in basicity among various aromatic hydrocarbons. Furthermore, a comparison of the stabilities of hydrogen chloride complexes with those of the corresponding hydrogen bromide complexes was undertaken to gain information as to the precise nature of the interaction between the hydrogen halide molecule and the aromatic component.

Results

The Systems. Hydrogen Chloride–Aromatic Hydrocarbons in n-Heptane. Hydrogen chloride dissolved in n-heptane and in n-heptane solutions of the aromatic hydrocarbons examined to give clear colorless solutions. The solubility of hydrogen chloride in n-heptane and in 0.5 M n-heptane solutions of benzene, toluene, m-xylene, and mesitylene was determined at -78.5, -63.5, and $-45.2°$. The Henry's law constants ($P_{HCl} = kN_{HCl}$) were obtained from plots of the pressure of hydrogen chloride, P_{HCl}, *vs.* the mole fraction of hydrogen chloride in solution, N_{HCl}, which yielded straight lines passing through the origin in all cases.

Accurate determination of the solubility was important, since the values of the Henry's law constants thus obtained were to be used later in the calculation of the dissociation constants of the molecular complexes. Consequently, an effort was made to determine the Henry's law constants with a precision of 1%.

The results of the solubility measurements are summarized in Table I. Typical results, exemplified by data obtained at $-78.5°$, are shown graphically in Figure 1.

The heat of solution of hydrogen chloride in each solvent system, listed in Table I, was obtained by plotting the logarithm of the observed Henry's law constant against reciprocal temperature.

(9) E. K. Plyler and D. Williams, *Phys. Rev.*, **49**, 215 (1936).
(10) H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).
(11) D. Cook, *J. Chem. Phys.*, **25**, 788 (1956).
(12) M. L. Josien and G. Sourisseau, *Hydrogen Bonding, Papers Symposium, Ljubljana*, 129 (1957); *Chem. Abstr.*, **55**, 1185b (1961); M. L. Josien and J. Lascombe, *Coll. intern. centre natl. recherche sci.* (Paris), **77**, 137 (1959), *Chem. Abstr.*, **54**, 2936e (1960).

(13) D. Cook, Y. Lupien, and W. G. Schneider, *Can. J. Chem.*, **34**, 964 (1956).
(14) E. Terres and M. T. Assemi, *Brennstoff-Chem.*, **37**, 257 (1956).

Table I. Solubility Data for Hydrogen Chloride–Aromatic Systems

Compd. in 0.5 M n-heptane soln.	Henry's law constant (mm.) at			Heat of soln., kcal./ mole
	$-78.5°$	$-63.5°$	$-45.2°$	
n-Heptane	4630	7520	12270	-2.59
Benzene	3190	5660	9980	-3.03
Toluene	2880	5240	9440	-3.15
m-Xylene	2600	4890	8870	-3.25
Mesitylene	2350	4460	8400	-3.38

From an examination of Table I and Figure 1, it is evident that the solubility of hydrogen chloride is greater in the aromatic solutions than in pure n-heptane. Moreover, the solubility varies in a manner corresponding to the relative basicity already established by Brown and Brady[10]; that is, the solubility is greatest in the mesitylene solution and least in the benzene solution. Furthermore, there is a marked increase in the heat of solution in the aromatic solutions over that in pure n-heptane, and an additional regular increase in the heat of solution is noted as the series progresses from benzene to mesitylene. These observations indicate that an interaction is taking place between hydrogen chloride and the aromatic hydrocarbons in solution.

On the assumption that the increased solubility of hydrogen chloride in 0.5 M aromatic solution is due to the formation of 1:1 molecular complexes of the type ArH·HX[10] between hydrogen chloride and the aromatic molecules, the dissociation constants of the complexes, K_{diss}, were calculated.

$$\text{ArH·HX(soln.)} \rightleftharpoons \text{ArH(soln.)} + \text{HX(soln.)}$$

In this calculation we assumed that the solubility of hydrogen chloride in aromatic solutions would be essentially the same as in n-heptane itself if no interaction occurred between hydrogen chloride and the aromatic. This assumption may not be entirely correct, since the solvent properties of the various solutions probably differ slightly owing to factors other than the basicity of the medium. However, we dealt with dilute solutions of aromatics in n-heptane. The solvent properties of the solutions should be essentially the same as that of n-heptane, and therefore, only very small differences in solubility of hydrogen chloride would be expected in these solutions if no interaction occurred. For the calculation of the dissociation constants, we also assumed that the volume of the solution containing hydrogen chloride was essentially the same as the pure solvent system at a given temperature. This again might not be strictly correct, but since only a small amount of hydrogen chloride was present in solution, the volume change upon dissolution of hydrogen chloride should be very small.[15]

(15) The calculated dissociation constants decrease slightly with increasing concentrations of hydrogen chloride. A similar variation was observed previously.[10] This small variation may arise from neglect of the volume change accompanying solution of the hydrogen chloride, as well as from failure of the dilute solutions to exhibit strictly ideal behavior.
    The measured solubilities and the dissociation constants at $-78.5°$ were in excellent agreement with the values reported previously.[10] For example, the value of Henry's law constant here reported, 4630, may be compared with the earlier value, 4520. The present results reveal a somewhat higher precision, presumably the result of some of the refinements introduced in the procedure, as described in the Experimental Section.

Table II. Thermodynamic Data for the Dissociation of the Aromatic–Hydrogen Chloride Complexes in Solution

Compd. in 0.5 M n-heptane soln.	Temp., °C.	K_{diss}, mole/l.	$\Delta H°$, kcal./ mole	$\Delta F°$, cal./ mole	$\Delta S°$, e.u.
Benzene	-78.5	0.941		23.5	10
	-63.5	1.37	1.99	-132	10
	-45.2	2.00		-315	10
Toluene	-78.5	0.687		145	9.6
	-63.5	1.00	2.02	0	9.6
	-45.2	1.47		-176	9.6
m-Xylene	-78.5	0.519		254	9.5
	-63.5	0.786	2.10	100	9.5
	-45.2	1.13		-55.5	9.5
Mesitylene	-78.5	0.407		348	9.6
	-63.5	0.611	2.21	205	9.6
	-45.2	0.935		30.1	9.6

The results of the calculations are summarized in Table II.

The dissociation constants calculated from the experimental data exhibit reasonable constancy over the range of hydrogen chloride concentration studied (see Table V). This then indicates that the assumption made in formulating the complexes as 1:1 derivatives, ArH·HX, must be correct. Furthermore, the dissociation constants of the complexes thus calculated obeyed the van't Hoff equation from which the heats of dissociation of the complexes, $\Delta H°$, were calculated. From the dissociation constants at each temperature, the standard free energy changes for the dissociation reaction, $\Delta F°$, were calculated. Finally, from a knowledge of $\Delta H°$, $\Delta F°$, and the temperature, the standard entropy changes for the dissociation, $\Delta S°$, were calculated. The results of these calculations are also presented in Table II.

Hydrogen Bromide–Aromatic Hydrocarbons in n-Heptane. Similar studies were carried out on the systems of hydrogen bromide–aromatic hydrocarbons in n-heptane. Hydrogen bromide dissolved in n-heptane and in n-heptane solutions of benzene, toluene, m-xylene, and mesitylene to give clear colorless solutions. The Henry's law constants and the heats of solution of hydrogen bromide in n-heptane and in 0.5 M n-heptane solutions of the aromatics examined were obtained (Table III and Figure 2). From an examination of the data, it is again evident that an interaction is taking place between hydrogen bromide and the aromatics in solution.

Table III. Solubility Data for Hydrogen Bromide–Aromatic Systems

Compd. in 0.5 M n-heptane soln.	Henry's law constant (mm.) at			Heat of soln., kcal./ mole
	$-78.5°$	$-63.5°$	$-45.2°$	
n-Heptane	1090	1970	3740	-3.28
Benzene	850	1630	3230	-3.54
Toluene	779	1530	3110	-3.67
m-Xylene	714	1460	2990	-3.80
Mesitylene	657	1380	2830	-3.89

Again, on the assumption that the increased solubility of hydrogen bromide in 0.5 M n-heptane solutions of aromatics was due to the formation of 1:1 molecular
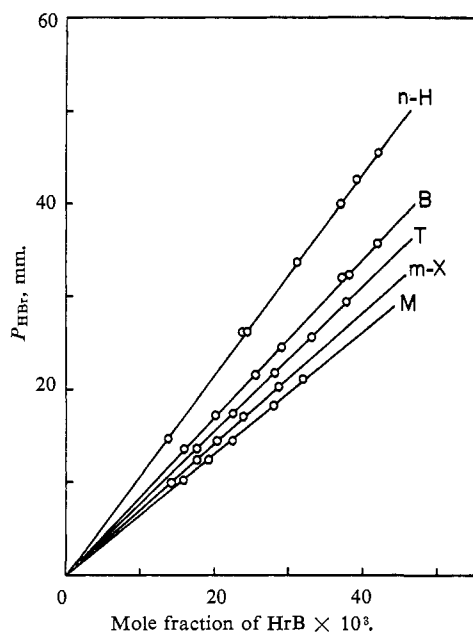
Figure 2. Solubility of hydrogen bromide at $-78.5°$ in n-heptane (n-H), and in 0.5 M n-heptane solutions of benzene (B), toluene (T), m-xylene (m-X), and mesitylene (M).
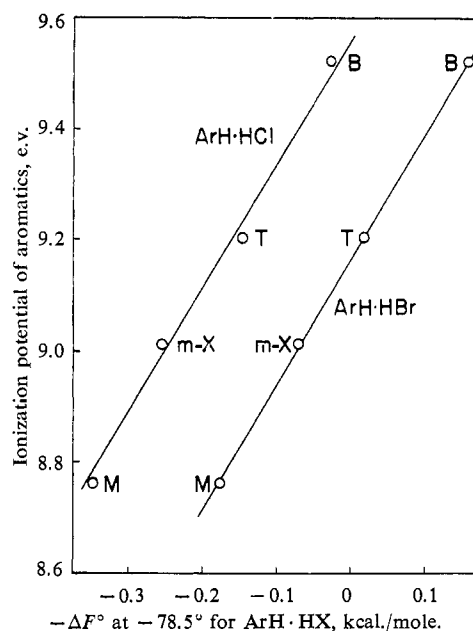

Figure 3. Correlation of the free energies of dissociation of the hydrogen halide–aromatic complexes with the ionization potentials of the corresponding aromatics: benzene (B), toluene (T), m-xylene (m-X), and mesitylene (M).

complexes of the type ArH·HX between hydrogen bromide and the aromatic molecules, the dissociation constants of the complexes were calculated. The dissociation constants thus obtained were also found to exhibit reasonable constancy over the range of hydrogen bromide concentration studied (see Table V). This implies the existence of the 1:1 molecular complexes in the solutions investigated. The values of $\Delta H°$, $\Delta F°$, and $\Delta S°$ for the dissociation were also calculated and are summarized in Table IV.

Table IV. Thermodynamic Data for the Dissociation of the Aromatic–Hydrogen Bromide Complexes in Solution

Compd. in in 0.5 M n-heptane soln.	Temp., °C.	K_{diss}, mole/l.	$\Delta H°$, kcal./ mole	$\Delta F°$, cal./ mole	$\Delta S°$, e.u.
Benzene	−78.5	1.51		−159	9.0
	−63.5	2.05	1.59	−298	9.0
	−45.2	2.75		−458	9.0
Toluene	−78.5	1.05		−17.8	9.6
	−63.5	1.45	1.85	−156	9.5
	−45.2	2.10		−335	9.6
m-Xylene	−78.5	0.831		71.7	9.8
	−63.5	1.24	1.98	−89.7	9.9
	−45.2	1.75		−255	9.8
Mesitylene	−78.5	0.636		175	9.7
	−63.5	0.960	2.06	14.4	9.7
	−45.2	1.38		−145	9.7

Discussion

Relative Basicity of the Aromatic Hydrocarbons. The solubility of each hydrogen halide in n-heptane increased by the addition of aromatics to the solution, and this increase in solubility varies in a manner corresponding to the basic properties of the aromatic molecules. Thus, qualitatively from the Henry's law constant data, the following order of basicity is observed: benzene $<$ toluene $<$ m-xylene $<$ mesit-

ylene. This qualitative order of basicity is consistent with the results obtained previously,[10] and is also exactly what would be expected from considerations of the cumulative inductive effect of the methyl groups in the aromatic molecules.

The increase in solubility of the hydrogen halides in these aromatic solutions is attributed to 1:1 complex formation, and the dissociation constants and the heats of dissociation of each hydrogen halide complex are calculated on this basis. From the results (Tables II and IV), it is seen that the difference between the heats of dissociation of each hydrogen halide complex with the successive aromatics, from benzene to mesitylene, is of the order of 0.1 kcal./mole.

It has been suggested that the stability of a molecular complex should be related to the ionization potential of the electron donor molecule.[16] It was therefore desirable to see if such a relationship exists in the present data. The ionization potentials[17] of the aromatics studied were plotted against the values of $\Delta F°$ obtained at $-78.5°$ for the hydrogen chloride and hydrogen bromide complexes (Figure 3). From the plots it is evident that a good linear relation exists between the ionization potential of the aromatics and $\Delta F°$ for the dissociation of the hydrogen halide complexes, in accordance with the predictions of the theory.[16] This then indicates that the values of $\Delta F°$, and hence, K_{diss}, can be considered as a quantitative measure of the relative basicity of aromatic hydrocarbons.

Nature of the Hydrogen Halide–Aromatic Complexes. The molecular complexes formed between hydrogen halides and aromatic hydrocarbons must involve an

(16) R. S. Mulliken, *J. Am. Chem. Soc.*, 74, 811 (1952); *J. Phys. Chem.*, 56, 801 (1952).

(17) H. Baba, I. Omura, and K. Higashi, *Bull. Chem. Soc. Japan*, 29, 521 (1956). The following values (in e.v.) are reported as the ionization potentials: benzene, 9.52; toluene, 9.20; m-xylene, 9.01; and mesitylene, 8.76.

Table V. Comparison of Equilibrium Constants[a] for the Toluene–Hydrogen Halide Systems at $-78.5°$

HX	HX, mole/l.	Complex, mole/l.	1:1 complex		2:1 complex	
			Toluene, mole/l.	K_{diss}, mole/l.	Toluene, mole/l.	K_{diss}, mole²/l.²
HCl	0.150	0.0938	0.407	0.651	0.313	0.157
	0.135	0.0841	0.417	0.669	0.332	0.177
	0.110	0.0678	0.433	0.704	0.364	0.216
	0.0846	0.0523	0.448	0.726	0.396	0.254
			Average	0.688		0.201
			Mean deviation	4%		17%
HBr	0.245	0.100	0.401	0.98	0.301	0.221
	0.215	0.0882	0.413	1.01	0.325	0.257
	0.188	0.0767	0.425	1.04	0.349	0.299
	0.159	0.0645	0.437	1.07	0.373	0.342
	0.126	0.0503	0.451	1.13	0.401	0.404
			Average	1.05		0.304
			Mean deviation	4%		17%

[a] Calculated under the assumptions of two different complexes, the 1:1 and 2:1 complexes.

interaction of the hydrogen halide with the π-electrons of the aromatic molecule. Such complexes have been termed π-complexes, to differentiate them from the σ-complexes in which complete transfer of the proton to the aromatic ring occurs.[10] A close examination of the dissociation constants and the heats of dissociation of both hydrogen chloride and hydrogen bromide complexes shows that, thermodynamically, these π-complexes are relatively unstable compared to normal chemical compounds, with the heats of dissociation of the complexes in solution being quite low, of the order of 2 kcal./mole. It is also noteworthy that the thermodynamic stability of the π-complexes formed in each series is increased regularly by the introduction of methyl groups into the benzene ring, the increase in stability being about 0.1 kcal./mole per methyl group.

An important difference is also to be noted between the stabilities of hydrogen chloride complexes and of the corresponding hydrogen bromide complexes. For any given aromatic donor molecule, hydrogen chloride forms a thermodynamically more stable complex than hydrogen bromide, the difference in stability being of the order of 0.2 kcal./mole. Dissociation constants, $\Delta H°$, and $\Delta F°$, all support the conclusion that the hydrogen chloride complexes are more stable than the corresponding hydrogen bromide complexes. These data therefore contradict O'Brien's claim[18] that hydrogen bromide interacts twice as strongly with aromatics as hydrogen chloride.

At first glance, it seems peculiar that hydrogen chloride should form the stronger complexes, since hydrogen chloride is normally considered to be a weaker acid than hydrogen bromide. Indeed, there is considerable evidence that hydrogen bromide is a stronger acid than hydrogen chloride in circumstances where ionization occurs.[19] However, it should be recognized that the formation of these π-complexes does not involve transfer of the proton of the hydrogen halide molecule. The phenomenon appears to be related more closely to the hydrogen bond forming ability of the molecule than to its acid properties. Consequently, it would appear that the dipole moments of the two molecules might provide a more realistic

measure of their relative ability to form π-complexes with aromatics than their acid dissociation constants.

Zahn[20] reports the dipole moments of gaseous hydrogen chloride and hydrogen bromide to be 1.03 and 0.78 D., respectively, while Fairbrother[21] reports a value of 1.32 D. for hydrogen chloride in benzene and a value of 1.01 D. for hydrogen bromide in benzene. Therefore, hydrogen chloride has the larger dipole moment both in the gaseous state and in benzene solution. If π-complex formation involves essentially an electrostatic interaction between the negative π-electron cloud of the aromatic ring and the positive end of a hydrogen halide dipole to form a hydrogen bond, then the more polar hydrogen chloride would be expected to form the stronger hydrogen bond and the correspondingly more stable complex with a given electron donor. Experimentally, hydrogen chloride was observed to form the more stable complexes. Therefore, it appears that π-complex stability depends not only upon the basic property of the aromatic donor molecule but also upon the polarity of the hydrogen halide acceptor molecule.

The $(Toluene)_2 \cdot HX$ Complexes. In addition to the 1:1 hydrogen chloride–toluene solid complex, Cook and others[18] reported the existence of a 2:1 solid complex with the composition of $(toluene)_2 \cdot HCl$. Maass and others[4] reported a similar solid complex with hydrogen bromide, $(toluene)_2 \cdot HBr$. To see if such complexes exist in solution, equilibrium constants at $-78.5°$ for the assumed reaction

$$(toluene)_2 \cdot HX(soln.) \rightleftharpoons 2 \text{ toluene(soln.)} + HX(soln.)$$
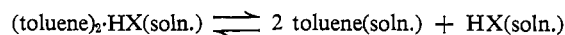
were calculated and compared with the values obtained previously by assuming the 1:1 complexes. The results are presented in Table V. From this comparison it is seen that equilibrium constants calculated on the assumption of 2:1 complexes do not exhibit satisfactory constancy. Therefore, it is concluded that such 2:1 complexes do not exist in any significant concentration in solution. The solid 2:1 complexes reported in the literature are presumably lattice compounds which owe their stability to crystal lattice forces.

(18) S. J. O'Brien and E. G. Bobalek, *J. Am. Chem. Soc.*, **62**, 3227 (1940).
(19) See, for example, R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

(20) C. T. Zahn, *Phys. Rev.*, **27**, 455 (1926).
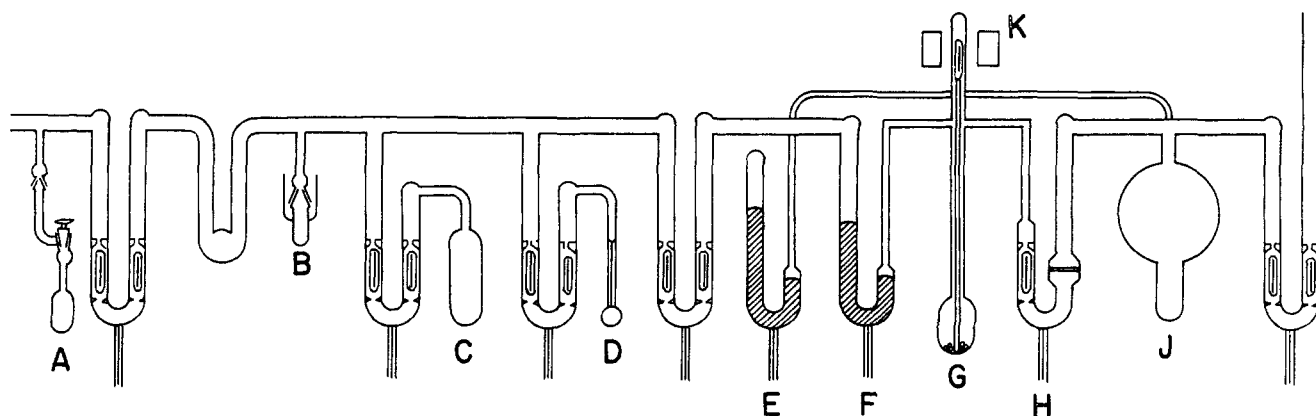(21) F. Fairbrother, *Trans. Faraday Soc.*, **30**, 862 (1934).

Figure 4. Apparatus for the determination of the Henry's law constants.

Experimental Section

Apparatus for Determination of the Henry's Law Constants. The apparatus used in the present study was essentially the same as that reported previously,[10] with minor modifications. The portion of the vacuum line used for determination of the Henry's law constant is shown diagramatically in Figure 4.

Materials. Hydrogen chloride was prepared by dropping concentrated reagent hydrochloric acid into concentrated reagent sulfuric acid. The gas was condensed in the vacuum line with liquid nitrogen. Purification inside the line was effected by taking a middle fraction as the gas distilled from a Dry Ice bath. The gas was stored in a large storage bulb in the line.

Hydrogen bromide was prepared, purified, and stored in the vacuum line by the method described in other papers of this series.[22,23]

Phillips research grade *n*-heptane (99%) was distilled through a Todd column (50 theoretical plates), passed through a 3-ft. silica gel column, and stored over calcium hydride. Ultraviolet absorption spectra of the resulting *n*-heptane showed the absence of any olefin or aromatic and carbonyl compounds. The refractive index measured was $n^{20}D$ 1.3873. A large sample was introduced into the vacuum line over Drierite and fractionated again in the line. The middle fraction was found to be tensiometrically homogeneous, having a vapor pressure of 11.4 ± 0.2 mm. at 0° and 35.5 ± 0.2 mm. at 20°. This sample was stored in the line.

Aromatic hydrocarbons (benzene, toluene, *m*-xylene, and mesitylene) used in the present study were all high purity (99.9 mole %) samples supplied by the National Bureau of Standards[24] and were therefore used without additional purification.

Procedure for Determination of the Henry's Law Constants. The procedure for determination of the Henry's law constants was modified somewhat from that described in a previous paper of this series.[10]

Tube B was removed from the line, and the aromatic compound being studied was carefully weighed into the tube. After weighing, the tube was returned and the aromatic degassed and transferred into the bottom portion of tube D by the usual vacuum technique.[25]

Then *n*-heptane, which was stored in tube C, was condensed into D. When bulb D was about three-fourths full, the transfer was stopped, the mercury float valve adjoining D closed, and the contents of the bulb allowed to warm up to room temperature. Gentle tapping of bulb D ensured mixing of the aromatic with *n*-heptane. A Dry Ice bath in a clear dewar flask was replaced around D and *n*-heptane carefully condensed into D to a predetermined etched mark on the capillary portion of D. The volume of D to the etched mark had been determined before the tube was sealed to the line. The capillary portion of D was also previously calibrated similarly. By placing successively the −63.5 and −45.2° baths contained in clear dewar containers around D, and observing the corresponding rise of the liquid above the etched mark with a Gaertner cathetometer, the volume of the solution was determined at each temperature. Thus, a solution of an aromatic in *n*-heptane with known concentration (0.5000 ± 0.0008 *M*) and volume at each temperature was prepared in the line.

The solution was transferred to the weighing tube A, which was then removed from the line, weighed, and returned to the line. From the difference in weight, the weight of the solution and, hence, the weight of *n*-heptane could be determined. The solution was then transferred to the solubility tube G, a constant temperature bath (−78.5, −63.5, and −45.2°) raised around tube G to a predetermined mark, and about 0.5 hr. allowed for temperature equilibrium to take place. The stirrer was operated by a solenoid K, connected to an electric repeat-cycle timer. Efficiency of stirring was increased by the presence of several glass beads in the bottom of tube G.

The pressure of the hydrogen halide in the storage system J, whose volume had previously been determined, was read and the room temperature measured. Then a large excess of hydrogen halide was transferred from bulb J to the solubility tube G, by condensing hydrogen halide in J with liquid nitrogen, followed by lowering the mercury in valve H sufficiently so that the gas warming up in J would bubble gently through the mercury into tube G. Stirring was continued in G for about 0.5 to 1 hr. The pressures of the hydrogen halide in G and J were read on manometers E and F. From the pressure of the hydrogen halide in J and the

(22) S. U. Choi and H. C. Brown, *J. Am. Chem. Soc.*, **85**, 2596 (1963).
(23) H. C. Brown and W. J. Wallace, *ibid.*, **75**, 6268 (1953).
(24) This supply is gratefully acknowledged.

(25) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

room temperature, the amount of the gas in J at any time was easily determined. The difference between the initial amount of the gas in J and the amount at any given time represents the amount of the gas present in G.

After recording pressures on E and F and the room temperature, the tube G was maintained at Dry Ice temperature, while the gas in J was condensed with a liquid nitrogen bath. The mercury in valve H was lowered sufficiently so that a small amount of hydrogen halide in G would bubble slowly into J. The coarse sintered glass disk in the right-hand side of valve H prevented mercury from being carried over into J. The valve H was then closed and the constant temperature bath once again raised around tube G. The gas in J was allowed to warm to room temperature, and, after equilibrium had been established in tube G, pressures and room temperature were again recorded. Additional quantities of hydrogen halide were removed from the solubility tube in the manner just described until a sufficient number of points (usually about four) had been taken so that a plot of pressure of hydrogen halide in G vs. mole fraction of the hydrogen halide in solution could be made. Data for a typical determina-

Table VI. Solubility of Hydrogen Chloride in 0.5 M n-Heptane Solution of Benzene at $-78.5°$

P_{HCl}, mm.	HCl in soln., mmoles	N_{HCl} × 10^{3a}	Henry's law const., mm.
94.00	1.151	29.59	3180
85.65	1.046	26.97	3180
71.40	0.869	22.51	3170
53.45	0.641	16.70	3200
34.60	0.410	10.75	3220
			Av. 3190

^{a} Benzene = 2.413 mmoles; n-heptane = 35.31 mmoles.

tion of the solubility of hydrogen chloride in 0.5 M n-heptane solution of benzene at $-78.5°$ are summarized in Table VI.

The following materials were used for the constant temperature baths: Dry Ice at sublimation pressure of 760 mm., $-78.5°$; chloroform solid–liquid slush, $-63.5°$; and chlorobenzene solid–liquid slush, $-45.2°$. The apparatus used to maintain Dry Ice at sublimation pressure of 760 mm. was adequately described previously.[10]

Equilibria in Solution. I. Ion Solvation and Mixed Solvent Interaction

Donald J. Glover

Contribution from the U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland. Received August 2, 1965

A maximum in the pk values of 2,2',4,4',6,6'-hexanitrodiphenylamine (HND) is observed in the system dioxane–water. The maximum is attributed to the solvation of hydrogen ion by water or dioxane in excess of a dioxane–water complex. The complex consists of two molecules of dioxane and one of water. The fact that there is a decrease in k_w of water of about 7×10^3 in going from water to 70% dioxane, while the k of HND decreases by only two- to threefold, is explained by solvation effects. The anion of HND is not considered to be further solvated than un-ionized HND, while the hydroxide ion is thought to be solvated with more than one molecule of solvent.

Although the law of mass action is used to express equilibria in solution, no general attempt to incorporate the solvent into the expression has been made. There have been correlations of acid ionization data in various solvents, the most notable being the work of Grunwald and co-workers.[1]

Much has been written about the effect of changes in dielectric constant on ionization constants. Usually a plot of pk vs. the reciprocal of the dielectric constant is presented, which is based on the Born equation.

Invariably, these plots are linear *only* over a very small range of dielectric constant change. As Harned and Owen[2a] observed, when the plots are extended over a great range such as represented by going from water to 82% dioxane–water, the linearity fails. Such a plot is improved by considering the addition of a water concentration term.[3] Even here the extension of the linear plot is not great.

It would seem that a consideration of the direct participation of the solvent in the ionization would lead to a better understanding of the solvent composition and the composition of ion solvates. For example, such a participation might be implied by the finding of Harned and Owen[2b] that a plot of pk vs. mole fraction of dioxane gives a nearly linear plot.

The marked changes in ionization in the system dioxane–water make this system particularly intriguing. Generally, a neutral proton acid decreases in strength from its value in water as the dioxane concentration is increased to 82%, a decrease of 10^5 or 10^6 being usual. It is not unusual for the same decrease to be observed

(1) (a) H. P. Marshall and E. Grunwald, *J. Am. Chem. Soc.*, 76, 2000 (1954); (b) E. Grunwald and B. J. Berkowitz, *ibid.*, 73, 4939 (1951); (c) B. Gutbezahl and E. Grunwald, *ibid.*, 75, 559 (1953).

(2) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958: (a) p. 682; (b) p. 662; (c) p. 756.

(3) M. Yasuda, *Bull. Chem. Soc. Japan*, 32, 429 (1959), introduces (HOH) into the ionization expression for a weak acid in order to get a better plot of pk vs. the reciprocal of the dielectric constant. Curvature still occurs at high concentrations of organic solvent.