Studies on the Proton Transfer in Organic Salts by the Dipole Moment Measurements

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Kraus et al.[1] and Maryott[2] measured independently dipole moments of picrates of alkylamines in benzene and in dioxane solutions, and reported that the dipole moments measured lie between 12 and 13 *D*. As they recognized, these large dipole moments can be explained by assuming that the acid AH and the base B form an ion pair such as $A^-\ldots H\text{-}B^+$.

Such a proton transfer from acid to base in non-polar solvents may arise in systems composed of strong acid and strong base. On the other hand, a weak acid such as phenol and a weak proton acceptor such as acetone are known to combine by the usual hydrogen bond $A\text{-}H\ldots B$. In the latter case, the dipole moment usually increases only slightly because of the inductive effect or other intermolecular forces[3]. Hence we can expect the possibility of determining whether an acid-base pair is an ion pair or a hydrogen bonded complex by measuring its dipole moment. Such an investigation will be important for studying the strengths of acids and bases in non-polar solutions.

Customarily, the dissociation constants of acids and bases in aqueous solutions are respectively used as the measure of the acid and the base strength. But they are very complex in their nature, including not only the proton affinities of molecules (namely, the dissociation energies in vacuum) but also the heats of hydration and the entropy terms. On the other hand, in non-polar solvents, the energy and entropy of solvation for the ion pair formation are so small that they may be neglected in the first approximation.

Ultraviolet[4] and infrared[5] absorption measurements have also been used succesfully by some authors for the study of acid-base equilibria in non-polar solvents. However, these spectroscopic methods can be applied only to compounds having absorption bands which are easily measurable and vastly affected by the formation of the ion pair. The method of dipole moment measurement has no such limitations and may give in some cases a stronger evidence of the ion-par formation.

Experimental

Measurements of the dielectric constants were made with both the resonance method and the heterodyne beat method. The apparatuses used are described elsewhere[6,7]. Densities were measured with a picnometer.

Preparation and Purification of Materials.—Pyridinium picrate was prepared by mixing the methanol solutions of purified pyridine* and picric acid, followed by recrystallization from methanol, and dried in a vacuum desiccator. Anilinium picrate was prepared from the benzene solutions of aniline and picric acid by a similar method to that described above. Phenol was purified by fractional crystallization, then fused, dried with calcium chloride and distilled under a reduced pressure. Hexamethylenetetramine was recrystallized from ethanol and dried in a vacuum desiccator. Capric acid was purified by distillation. *p*-Nitrophenol was recrystallized from a ethanol-methanol mixture and dried. Triethylamine (the reagent of the Eastman Organic Chemicals Department) was dried with sodium hydroxide and distilled. Acetic acid and trichloroacetic acid are both the guaranteed reagent of the Wako Pure Chemical Industried Ltd. The former was dried with phosphorous pentoxide and distilled, while the latter was used without further purification. Monochloroacetic acid and dichloroacetic acid were purified by distillation under a reduced pressure. Dioxane, benzene and

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[1] C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956); G. S. Hooper and C. A. Kraus, *J. Am. Chem. Soc.*, **56**, 2265 (1934); J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936).

[2] A. A. Maryott, *J. Res. Nat. Bur. St.*, **41**, 1, 7 (1948).

[3] H. Baba and S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 3 (1951).

[4] A. Nisonoff, L. P. Kuhn and R. W. Gurney, *J. Chem. Phys.*, **20**, 985 (1952); M. M. Davies and H. B. Hetzer, *J. Res. Nat. Bur. St.*, **48**, 387 (1952); M. M. Davis and E. A. McDonald, ibid., **42**, 595 (1949).

[5] G. M. Barrow and E. A. Yerger, *J. Am. Chem. Soc.*, **76**, 5211, 5248 (1954); **77**, 4474, 6206 (1955); **78**, 5802 (1956).

[6] S. Nagakura and A. Kuboyama, *Repts. Inst. Sci. Technol. Univ. Tokyo*, **4**, 242 (1950).

[7] K. Kozima and T. Yoshino, *J. Am. Chem. Soc.*, **75**, 166 (1953).

* This was kindly offered by Dr. T. Tamura of this Laboratory.

carbon tetrachloride were dried with sodium, phosphorous pentoxide and calcium chloride, respectively, and distilled.

Experimental Results and Method of Calculation

The results of the measurements are given in Tables I–IX, where n_a and n_b are concentrations of acids and bases in unit of mole/g. of the solution, ε is the dielectric constant and v the specific volume. x_c in Table I denotes the concentration of the salt in unit of mole fraction. For the calculation of the dipole moments, the stoichiometric formation of the acid-base complex was assumed, irrespective of whether it is an ion pair or a hydrogen bond complex, because it is known that the equilibrium constant for the hydrogen-bond formation between acid and base molecules is very great[4,8]. As for the solution where the base is present excessively, therefore, the concentration of the free base was taken as equal to n_b-n_a**. For the hexamethylenetetramine-phenol system only, the dissociation is not small enough to be neglected. In this case, the concentration of the complex was calculated by use of the dissociation constant of the system determined by the previous infrared spectroscopic measurement[8].

If we assume that, in dilute solutions, the distances between dipoles are so large that their interactions are negligibly small, the polarization of the solution per one gram of the solution may be expressed as follows:

$$p=(\varepsilon-1)v/(\varepsilon+2)=\sum_j n_j P_j \tag{1}$$

TABLE I

PYRIDINIUM PICRATE

Solvent: dioxane. at 15°C

$x_c\times10^4$	v	ε
0.000	0.96321	2.239
2.376	0.96256	2.277
4.340	0.96182	2.305
6.824	0.96098	2.355

$\varepsilon=2.237+167.9\,x_c$

$v=0.96326-3.31\,x_c$

$P_c=2380,\quad \mu=10.43D$

TABLE II

ANILINIUM PICRATE

Solvent: dioxane. at 23°C

$n_c\times10^5$	v	ε	P_c
0.000	0.97134	2.2265	
1.343	0.97025	2.3030	980
2.696	0.96890	2.4262	1218

P_c(average) = 1099 $\quad\mu=7.0D$

TABLE III

TRICHLOROACETIC ACID-TRIETHYLAMINE

Solvent: dioxane. at 20°C

$n_a\times10^5$	$n_b\times10^5$	v	ε	P_c
0.000	0.000	0.96771	2.2253	
0.5739	2.283	0.96818	2.3003	2130
1.856	4.774	0.96804	2.4329	1784

P_c(average) = 1957 $\quad\mu=9.6D$

TABLE IV

DICHLOROACETIC ACID-TRIETHYLAMINE

Solvent: dioxane. at 25°C

$n_a\times10^5$	$n_b\times10^5$	v	ε	P_c
0.000	0.000	0.97360	2.2258	
1.293	8.318	0.97619	2.3286	1290
2.261	14.548	0.97791	2.3953	1201
4.019	25.86	0.98124	2.5191	1375

P_c(average) = 1289 $\quad\mu=7.76D$

TABLE V

MONOCHLOROACETIC ACID-TRIETHYLAMINE

Solvent: dioxane (the same material as used in the above system). at 25°C

$n_a\times10^5$	$n_b\times10^5$	v	ε	P_c
1.714	9.800	0.97654	2.3461	1134
2.748	16.95	0.97900	2.4173	1110
4.959	34.23	0.98498	2.5610	1049

P_c(average) = 1098 $\quad\mu=7.15D$

TABLE VI

ACETIC ACID-TRIETHYLAMINE

Solvent: benzene. at 25°C

$n_a\times10^5$	$n_b\times10^5$	v	ε	P_c
0.000	0.000	1.14427	2.2724	
0.5453	1.784	1.14445	2.2826	388
1.336	3.761	1.14467	2.2943	349
2.780	8.790	1.14505	2.3206	360

P_c(average) = 366 $\quad\mu=3.96D$

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8) H. Tsubomura *J. Chem. Phys.*, **23**, 2130 (1955).

** Barrow et al. have proposed, by the measurements of the infrared spectra of carboxylic acid-amine systems in non-polar solvents, that in the solution there are two molecular species, I and II, which have the composition of $(\mathrm{Acid})_2\cdot$Amine and Acid · Amine, respectively. In this paper, the dipole moment of the carboxylic acid-amine complex was calculated under the assumption that all the acid molecules in the solution are converted into species II. For the dioxane solutions of triethylammonium salts of mono-, di- and tri-chloroacetic acids, this assumption seems to be valid because it is known that many carboxylic acids exist as monomers in dioxane solution[9], and under such a condition the formation of I is considered to be impossible. As for the case of acetic acid-triethylamine-benzene system, the validity of the assumption is not quite sure. In carrying out the measurement of this system, therefore, we made the concentration of triethylamine many times greater than that of acetic acid in order to increase the concentration of species II. Hence, even if the species I exists in the solution, its concentration will be small compared with the total acid concentration, and it is considered that the conclusion given later is essentially unaltered.

9) R. J. W. Le Fèvre and H. Vine, *J. Chem. Soc.*, **1938**, 1795.

TABLE VII

p-NITROPHENOL-TRIETHYLAMINE

Solvent: dioxane. at 20°C

$n_a\times10^5$	$n_b\times10^5$	v	ε	P_c
0.000	0.000	0.96825	2.2299	
0.9517	1.3826	0.96836	2.2689	721
1.1935	1.7125	0.96843	2.2786	720

P_c(average) = 721 $\mu=5.57D$

TABLE VIII

PHENOL-HEXAMETHYLENETETRAMINE

Solvent: carbon tetrachloride. at 27°C

$n_a\times10^5$	$n_b\times10^5$	$1/v$	ε	P_c
0.000	0.000	1.58062	2.2179	
2.721	0.000	1.57852	2.2310	77.3*
2.711	2.535	1.57791	2.2402	158
2.727	1.661	1.57475	2.2364	151

P_c(average) = 155 $\mu=2.05D$

* Molecular polarization of phenol. From it the dipole moment of phenol is calculated to be 1.55*D*.

TABLE IX

CAPRIC ACID-HEXAMETHYLENETETRAMINE

Solvent: carbon tetrachloride (the same material as used in the above system). at 27°C

$n_a\times10^5$	$n_b\times10^5$	$1/v$	ε	P_c
1.820	2.271	1.57475	2.2256	136

$\mu=1.50D$

TABLE X

	P_E+P_A	μ
pricric acid[a]	43.0	1.55
phenol	28.0	1.55
p-nitrophenol[b]	37.2	5.0
acetic acid[c]	12.8	1.7
monochloroacetic acid[9]	17.9	2.6[d]
dichloroacetic acid[9]	23.0	2.6[d]
trichloroacetic acid[9]	28.1	2.6[d]
capric acid[e]	49.6	1.7
hexamethylenetetramine[11]	41.0	0.0
triethylamine[10]	33.7	0.8
pyridine[f]	24.0	2.2
aniline[g]	32.0	1.9

a The P_E+P_A of this compound is estimated from those of *p*-nitrobenzene, and *p*-nitrophenol. The dipole moment is taken equal to that of phenol.

b Donle and Gehrckens, *Z. phys. Chem.*, **B18**, 316 (1932).

c C. T. Zahn, *Phys. Rev.*, **37**, 1516 (1931); Wilson and Wenzke, *J. Chem. Phys.*, **2**, 546 (1934).

d Taken as equal to the moment of the ethyl ester.

e The P_E+P_A of this compound is calculated by use of the polarizations of atoms. The moment is assumed as equal to that of acetic acid.

f Leis and Curran, *J. Am. Chem. Soc.*, **67**, 79 (1945).

g Kumler and Halverstadt, ibid., **63**, 2182 (1941).

TABLE XI

Acid	Base	(Debye units)		
		μ_{obs}	μ_s	$\Delta\mu$
picric acid	pyridine	10.43	3.4	7
picric acid	aniline	7.0	1.8	6
trichloroacetic acid	triethylamine	9.6	3.0	8
dichloroacetic acid	triethylamine	7.76	3	7
monochloroacetic acid	triethylamine	7.15	3	6.5
acetic acid	triethylamine	3.96	2.2	3
p-nitrophenol	triethylamine	5.57	5.4	0.3
capric acid	H. M. T.*	2.05	1.55	0.5
phenol	H. M. T.	1.50	1.70	−0.2

* Hexamethylenetetramine

where n_j denotes the n value of each component, and P_j is its molecular polarization. In general, there are four components in the solution: the solvent, the free acid, the free base and the complex. From Eq. 1, the molecular polarization of the complex, P_c, can be calculated, when the polarizations of the other components are known. The polarization of the solvent is derived from the measurement of the pure solvent. The P_j values of the free acid and base need not be very accurate, because their concentrations in the solution are very small. The P_j value of triethylamine was set equal to 46.6 cc. for the benzene solution[10], and to 47.2 cc. in the dioxane solution. The latter value was obtained from the measurement of ε and v of the dioxane solutions of triethylamine. For the system composed of hexamethylenetetramine and phenol, the polarization of the former was taken as

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[10] K. Higasi, *Sci. Pap. Inst. Phys. Chem. Res.*, **31**, 311 (1937).

41.0 cc.[11] and that of the latter was experimentally obtained with the present sample of phenol (Table VIII).

Kraus et al.[1] stated that, for solutions of some salts with large dipole moments, the measured molecular polarization of the salt decreases rapidly with increasing concentration even in the range of the concentration of 10^{-4} mole fraction. They attributed this as due to the association of the polar salts. Maryott[2] observed, however, that the molecular polarizations of similar salts are nearly constant up to more concentrated solutions, when dioxane is used as the solvent. Also, in the present measurement with the pyridinium picrate solutions, it was found that the P_c values obtained from each solution by use of Eq. 1 agree well with that derived by the method of Halverstadt and Kumler[12]. From these facts, it may be inferred that the effect of association is negligibly small in the dioxane solutions with the range of concentration of the present measurements. In the present investigation, salts with large dipole moments are measured in the dioxane solutions, while other salts (or hydrogen bonded complexes) with smaller dipole moments, where the effect of association will be small, are measured in benzene or carbon tetrachloride solutions. The P_c values obtained by use of Eq. 1 are, therefore, considered to be a good approximation to the true P_c values. They are listed in Table II–IX. The P_c value given in Table I is that obtained by Halverstadt and Kumler's method.

The orientation polarization of the salt was calculated by subtracting from P_c the electronic and atomic polarization of the complex, which were assumed as equal to the sum of those of the free acid and base. The values used were taken from literatures and reproduced in Table X, where the dipole moments of free acids and bases are also listed. The dipole moments of the acid-base complex calculated from the orientation polarizations thus obtained are given in Table I–IX.

Discussion

If the dipole moments of the acid and base in the complex remain the same as those of the free acid and base, the dipole moment of the complex will be given by the vector sum of these two moments. Let it be called the structure moment and denoted by μ_s. Now, if the observed dipole moment of an acid-base complex is very large compared with its structure moment, the complex is conceivably an ion pair. In order to calculate the structure moments, it is assumed that none of the acid and base molecules changes the structure on the complex formation, and that the OH……N group is on a straight line. The direction of the dipole-moment vectors of the polar molecules are estimated on the basis of the bond moment data and the consideration of the resonance moments. Based on these assumptions, the structure moments are obtained as shown in Table XI. It is readily seen that the first five systems given in Table XI have the form of the ion pair, and that the last three systems are essentially hydrogen bonded complexes.

From the theoretical point of view, the dipole moment produced by the proton transfer can be estimated by assuming the electronic structure of the ion pair as follows:

$$O^{-}\ldots\ldots H{-}N^{+}$$

where the $H{-}N^{+}$ bond is purely covalent. The O……N distance may be taken as 2.6 Å, because the lengths of the OH……N hydrogen bonds are in general about 2.8Å, and a slight contraction is expected in the case of the ion pair. Hence, if we assume, as a first approximation, that the positive and the negative charge are, respectively, centered at the nitrogen and the oxygen nucleus, the dipole moment arising from this proton transfer is calculated as $4.80\times10^{-10}\times2.6\times10^{-8}=12.5D$. Actually, even in the case of a complete proton transfer, the dipole moment due to the proton transfer is conceivable somewhat smaller than this value, because the electronic cloud of the two molecules would be distorted so as to decrease the strong field of the dipole produced by the transfer.

Thus we have seen that there is a large dipole moment in the ion pair directed along the OH……N straight line with the positive end on the nitrogen atom. In Table XI, $\Delta\mu$ represents the dipole moment with the above-mentioned direction, whose magnitude is so determined that the vector sum of this and μ_s is equal to the observed moment of the complex. For the tri-*n*-butylammonium picrate, the

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[11] R. J. W. Le Fèvre and G. J. Rayner, *J. Chem. Soc.* **1938**, 1921.

[12] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

dipole moment of which was determined by Maryott as 11.9 *D*, the $\Delta\mu$ value is calculated to be 9.6 *D*. If one assumes that this complex is a pure ion pair, then, by inspection of the $\Delta\mu$ values in Table XI, it may be confimed that pyridinium picrate, trichloroacetic acid-triethylamine complex, and dichloroacetic acid-triethylamine complex are almost complete ion pairs. As for the two systems, anilinium picrate, and monochloroacetic acid-triethylamine complex, it is recognized that the $\Delta\mu$ values are a little smaller than those for the above mentioned complexes. In regard to the arbitrariness of the calculated $\Delta\mu$ values, however, it will be rather safe to make no distinction between these five systems***.

Among the remaining four systems, acetic acid-triethylamine has an appreciable $\Delta\mu$ value. It seems that in this complex there is an "incomplete proton transfer" that may be explained by either of the following two theories. The one is that the ground state of such a complex may be represented by the resonance,

$$\mathrm{O{-}H\ldots\ldots N \rightleftarrows O^{-}\ldots\ldots H{-}N^{+}}$$

in which the contributions of the two resonance structures have the same order of magnitude. This occurs in the cases where the potential curve for the proton in the complex has a single minimum near the center of the O......N straight line. Another explanation is that there is a tautomeric equilibrium between the ion pair and the hydrogen bonded complex. In this case, the potential curve has two minima: one near the oxygen atom and the other near the nitrogen atom, and the proton oscillates between them. At the moment, it is difficult to decide which is the correct theory. Anyway, it may be inferred from the dipole moment that acetic acid-triethylamine complex is more like a hydrogen bonded complex than an ion pair.

Relation between the Dipole Moment and the Proton Affinity.—The energy required for the proton transfer reaction, $\mathrm{AH+B=A^{-}\ldots\ldots H{-}B^{+}}$, in vacuo, is generally expressed as follows,

$$E=PA(A^{-})-PA(B)+E_{i.p.} \qquad (2)$$

where $PA(A^{-})$ is the energy required to remove proton from the acid AH, that is, the proton affinity of the anion A^{-}, and $PA(B)$ is that of the base B. $E_{i.p.}$ is the energy necessary for bringing the anion and cation from infinite separation to the position which they occupy in the ion pair. In the non-polar solvents, where solvation energy is small, the above formula may be applied approximately with no alteration. Assuming that $E_{i.p.}$ is constant for all the acid-base pairs that have the common O...H...N groups, the energy to produce an ion pair becomes the smaller, the smaller $\{PA(A^{-})-PA(B)\}$ is. $PA(A^{-})$ and $PA(B)$ are, respectively, related to the acid and base strength, and, therefore, it may be interesting to compare the ability of the ion-pair formation and the dissociation constants of acid and base in aqueous solutions.

Fig. 1 was drawn under this supposition, where the two axes indicate $-\log K_a$ and $-\log K_b$ of the acid and the base of a given complex. The systems which are concluded to have the structure of the ion pair are denoted by a small circle and those which are concluded to have the structure of the hydrogen bonded complex are denoted by the symbol ×. Acetic acid-triethylamine complex is regarded to be in the intermediate state. It can be seen that there is certainly a relation

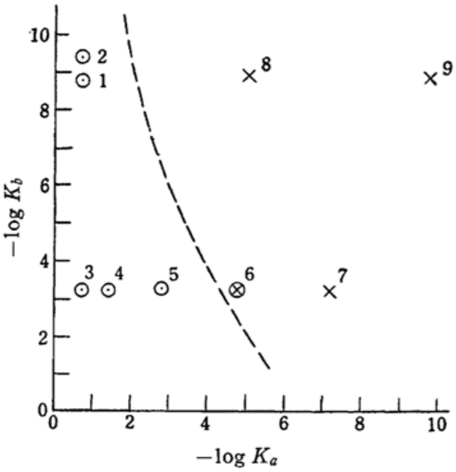

Fig. 1. Relation between the structure of acid-base complexes and the acid and base strength of their component molecules.

1. picric acid-pyridine
2. picric acid-aniline
3. trichloroacetic acid-triethylamine
4. dichloroacetic acid-triethylamine
5. monochloroacetic acid-triethylamine
6. acetic acid-triethylamine
7. *p*-nitrophenol-triethylamine
8. capric acid-hexamethylenetetramine
9. phenol-hexamethylenetetramine

*** For the case of mono- and dichloroacetic acid, the results of calculation of $\Delta\mu$ become more ambiguous owing to the possible existence of the rotational isomers.

between the ability to form ion pairs and the pK values. And the curve drawn in the figure may show roughly the limit of the pK's of acids and bases to produce ion pairs.

Shirai[13] has recently measured dipole moments of salts of dodecylamine with various carboxylic acids of the general formula $C_nH_{2n+1}COOH$ in benzene solution. The obtained values range between $1.5D$ and $2.2D$. These values are much smaller than the dipole moment of acetic acid-triethylamine complex obtained in the present measurement, showing that the dodecylamine-carboxylic acid complexes are essentially hydrogen bonded complexes. This result may be interpreted as showing that dodecylamine is less basic than triethylamine, a result that is reasonable from the electronic theory.

In the polar solvents, the proton transfer is very much facilitated because of the large solvation energy. In the present investigation, it was observed that the dioxane solution of *p*-nitrophenol and triethylamine, which does not form the ion pair and has a faint yellow color, becomes very intensely yellow when diluted with methanol. This shows that the acid-base pair will become the ion pair or solvated ions in the more polar solvent, methanol.

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13) M. Shirai, *Sci. Pap. Coll. Gen. Educ., Univ. Tokyo*, **6**, 147 (1956).