

served the same type of water isotherm for degassed Spheron 6 that we find, but their isotherm indicates about twice as much water adsorption as we find in the range 0.5 to 0.7 p_0 . This is not disturbing, in view of the fact that their sample and ours were treated differently before the isotherm was determined. If we are correct in assuming that Spheron 6 particles have small cracks, the nature of the heat treatment will affect the porosity. After strong heating, in preparation of Graphon, all evidence of pores has disappeared.

For most of the Cabot carbon blacks that are thought to be essentially non-porous, the size of particles as computed from nitrogen areas is in good agreement with electron microscope values. Carbolac I is an exception. The electron-microscope arithmetic-mean diameter of the particles is 106 Å. The nitrogen area of about 1000 sq.m./g. gives a computed mean diameter of 26 Å. The discrepancy would correspond to a roughness factor of 4 for the nitrogen area.

The water isotherm for Carbolac I, Fig. 8, and the previously published water isotherm determined by Emmett and Anderson¹⁴ both show the type of rise we have attributed to the effects of capillaries. Comparison of the Carbolac I isotherm with that for Spheron 6 shows however an important difference. The rise for both starts at about 0.55 p_0 but for Carbolac I there is no flattening at or about 0.7 p_0 as is the case for the Spheron isotherm. This suggests that the capillaries to which we ascribe the rise are wider in the Carbolac particles than in the Spheron particles, and that there is a greater range of capillary widths. If these capillaries are filled by nitrogen at point B they may account for the large roughness factor.

An alternative explanation might be made for the capillary-like nature of the water adsorption by Carbolac I. This is that the capillaries might not be within the rather small granules but that they might be in the spaces between the granules. The ultimate particles of Carbolac I are very small and it might be that they fit closely enough together that the voids between particles are sufficiently narrow to act as capillaries in which vapor may condense. There is some indication for such condensation of vapor. When the sample bulb is removed for weighing after equilibration at high relative pressure with any of the vapors we have studied, it has been noted that the particles are agglomerated and stick together as a solid ball. This must be due to a film of liquid between the particles which acts as a binder. As soon as the relative pressure is lowered this clumping disappears.

Desorption Hysteresis.—When water vapor is desorbed from a carbon surface there is always a pronounced hysteresis, regardless of whether the sample is porous or not. Some speculation regarding the possible source of hysteresis in absence of pores has been previously published.⁹

In addition to "reversible hysteresis" in which the isotherm loop closes at a relative pressure near 0.4 p_0 water desorption isotherms also sometimes fail to rejoin the adsorption branch, even at zero pressure. This is, we believe, due to chemisorption or reaction with water during the period in which the vapor is in contact with carbon. Such an effect seems to be more pronounced when one starts with a surface which has some oxygen complex than with an initially clean surface.

CLAREMONT, CALIF.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. LIII. Molecular Weight of Salts in Benzene by the Cryoscopic Method¹

BY DAVID T. COPENHAFFER² AND CHARLES A. KRAUS

The molecular weights of triisomylammonium picrate, *n*-amyltri-*n*-butylammonium iodide, *n*-octadecyltri-*n*-butylammonium formate, tetraisoamylammonium thiocyanate and tetra-*n*-butylammonium thiocyanate have been determined in benzene up to the limit of their solubilities by a cryoscopic method. The molecular weights of equimolar mixtures of the last two salts have likewise been determined.

All these salts exhibit marked association in benzene solution, the degree of association being dependent on structural and constitutional factors. For the two thiocyanates and the iodide, the association number, *n* (ratio of observed molecular weight to formal weight) passes through a maximum at concentrations ranging between 0.12 and 0.28 molal; the association numbers, at the maximum, range between 21.9 and 31.9. The association number of tri-isoamylammonium picrate varies between 1.01 at 0.001 *m* and 1.58 at 0.1 *m*. Of the salts measured, octadecyltri-*n*-butylammonium formate exhibits the highest degree of association; at 0.001 *m*, *n* = 10.7; at 0.0033 *m*, *n* = 21.5.

The association number for the mixture of the two thiocyanates at a given total concentration is the mean of the value for the two components alone at the same concentration. The results of this investigation are discussed and correlated with the results of conductance measurements.

I. Introduction

Cryoscopic measurements by Kraus and Vingee³ with solutions of salts in dioxane and by Batson⁴

(1) This paper is based on a portion of a thesis submitted by David T. Copenhaffer in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1942. Paper LII, THIS JOURNAL, **73**, 3293 (1951).

(2) University Fellow in Brown University, 1940-1941. Metcalf Fellow, 1941-1942.

(3) C. A. Kraus and R. A. Vingee, THIS JOURNAL, **56**, 511 (1934).

(4) F. M. Batson and C. A. Kraus, *ibid.*, **56**, 2017 (1934).

and Rothrock⁵ with solutions of salts in benzene have shown that, in these solvents of low dielectric constant, association of ion pairs takes place to a measurable extent at concentrations as low as 0.001 *m*. At higher concentrations, the degree of association increases markedly, particularly with salts of large cations. However, these earlier measurements were not carried to concentrations above a few hundredths molal. It seemed of interest,

(5) D. A. Rothrock, Jr., and C. A. Kraus, *ibid.*, **59**, 1699 (1937).

therefore, to carry the measurements to the highest possible concentrations. At the same time, it was of interest to determine how the association of ion pairs is affected by various constitutional factors. Accordingly, cryoscopic measurements were carried out with benzene solutions of the following salts: tetraisoamylammonium thiocyanate, tetra-*n*-butylammonium thiocyanate, triisoamylammonium picrate, *n*-amyltri-*n*-butylammonium iodide and *n*-octadecyltri-*n*-butylammonium formate. Measurements were also carried out with equimolar mixtures of tetraisoamyl- and tetra-*n*-butylammonium thiocyanate.

II. Experimental

1. **Apparatus and Method.**—These were essentially the same as those of earlier investigations and their description need not be repeated here. The method consisted, essentially, in measuring the temperature difference between a solution and pure solvent by means of a 36-junction, copper-constantan thermal unit. Solution and solvent were contained in two glass cells of approximately 350 cc. capacity. Approximately 250 g. of benzene was introduced into each cell and about 75 g. was frozen to solid. The cells, provided with suitable covers and stirrers, were placed in silvered dewar tubes and the whole assembly was immersed in water whose temperature was maintained slightly below the freezing point of benzene. At the end of each determination, samples of solution were withdrawn into weighed pipets and, after evaporation of the solvent, the weight of salt was determined. For very dilute solutions, about 0.5 g. of hexaethylbenzene was added before withdrawal of the samples. The heat effect accompanying the introduction of the hexaethylbenzene was sufficient to melt 0.06 g. of benzene and had a negligible effect on the concentration of the solution as withdrawn.

The thermel was calibrated against a platinum resistance thermometer, a White double potentiometer being used in measuring the e.m.f. of the thermel.

The cryoscopic constant of benzene was redetermined using hexaethylbenzene as standard. The mean value of the constant for six determinations at six different concentrations, ranging from 0.013 to 0.058 molal, was found to be $5.089 \pm 0.005^\circ$. This value is in reasonably good agreement with earlier determinations^{4,5} in which triphenylmethane was used as standard and is in perfect agreement with the value of 5.088° found by Barton,⁶ who also used hexaethylbenzene as standard.

2. **Materials.**—Benzene was purified as described by Batson⁴; m.p. 5.49–5.51°. Hexaethylbenzene was recrystallized from benzene, m.p. 128.5–129.0° (cor.).

Tetraisoamylammonium thiocyanate was prepared according to the method of Kraus and Fuoss⁷ and was recrystallized from anhydrous ethyl acetate, m.p. 103.5–104° (cor.). Tetra-*n*-butylammonium thiocyanate was prepared and purified like the amyl derivative, m.p. 126.4–126.9° (cor.). Triisoamylammonium picrate was prepared by treating the acid with the amine in hot ethanol. It was recrystallized from 96% alcohol, m.p. 127.5–128° (cor.). *n*-Amyltri-*n*-butylammonium iodide was prepared by heating amyl iodide with an excess of amine to 60° for several weeks. It was recrystallized from anhydrous ethyl acetate, m.p. 109.3–109.9° (cor.). *n*-Octadecyltri-*n*-butylammonium formate was prepared by metathesis of the nitrate with potassium formate in absolute methanol. It was recrystallized from acetone containing a small amount of hexane, m.p. 87.5–89.5° (cor.). The potassium formate was dehydrated *in vacuo* at 100° until it contained only 5% water. The nitrate was prepared by metathesis of the iodide with silver nitrate and was purified by recrystallization from anhydrous ethyl acetate, m.p. 90° (cor.). The formate is not recrystallized readily, for which reason it is necessary to purify the intermediates with care.

III. Results

The results of cryoscopic measurements are presented in Table I. The molal concentration in

formula weights per 1000 g. of solvent is given in column 1, the freezing point depression in column 2 and the association number (*n*), the ratio of the apparent molecular weight to the formula weight, in column 3. In computing the association number, 5.085° was employed for the cryoscopic constant.

TABLE I
CRYOSCOPIC DATA FOR SALTS IN BENZENE

<i>m</i>	ΔT°	<i>n</i>	<i>m</i>	ΔT°	<i>n</i>
1. Tetraisoamylammonium thiocyanate			2. Tetra- <i>n</i> -butylammonium thiocyanate		
0.02009	0.00939	10.9	0.00128	0.00263	2.48
.02912	.01119	13.2*	.00404	.00716	2.86
.03945	.01188	16.9	.02309	.01660	7.05
.04149	.01212	17.4*	.02365	.01667	7.21
.04515	.01213	18.9	.04895	.02018	12.3
.05860	.01323	22.5	.07624	.02305	16.8
.07734	.01573	25.0 ^c	.1119	.02732	20.8
.1230	.02426	25.8 ^a	.1688	.03142	27.3
.1678	.03383	25.2 ^a	.1941	.03301	29.9
.2361	.05851	20.5 ^d	.2236	.03694	30.8
.2515	.07038	18.2 ^e	.2808	.04474	31.9
.3274	.1154	14.4 ^a	.3579	.05833	31.2
.3329	.1192	14.2 ^e	.4412	.07439	30.2
.4256	.1880	11.5 ^a	.5115	.09017	28.8
			.5613	.1040	27.5
			.6327	.1245	25.9
			.7531	.1685	22.7
3. Equimolar mixtures of 1 and 2			4. <i>n</i> -Octadecyltri- <i>n</i> -butylammonium formate		
0.00103	0.00195	2.68	0.00091	0.00044	10.6
.00275	.00451	3.71	.00204	.00074	14.0
.00723	.00694	5.30	.00300	.00080	19.1
.02151	.01297	8.43	.00326	.00077	21.5
5. Tri-isoamylammonium picrate			6. <i>n</i> -Amyltri- <i>n</i> -butylammonium iodide		
0.00462	0.02334	1.01	0.00093	0.00157	3.02
.00896	.04264	1.06	.00232	.00339	3.48
.02678	.1158	1.18	.00600	.00748	4.08
.06054	.2272	1.35	.01495	.01212	5.02
.06248	.2329	1.36	.03534	.02230	8.06
.07382	.2637	1.42	.05485	.02628	10.6
.09886	.3258	1.54	.06930	.02842	12.4
.1068	.3442	1.58	.09409	.02982	16.0
.1398	.4141	1.72	.0990	.03038	16.6
.1454	.4262	1.74	.1084	.03138	17.6
.1911	.5123	1.90	.1244	.03268	19.4
.2029	.5341	1.93	.1567	.03769	21.1
.2527	.6162	2.09	.2246	.05221	21.9
.3037	.6967	2.22	.3150	.07466	21.5
.3194	.7242	2.24	.3804	.09700	19.9
.3525	.7717	2.32	.4998	.1492	17.0
.3606	.7849	2.34			
.3788	.8141	2.37			
.4332	.8980	2.45			
.4447	.9154	2.47			
.5034	1.0062	2.54			
.5214	1.0362	2.56			
.5360	1.0562	2.58			
.5374	1.0594	2.58			
.5335	1.0820	2.60			
.6230	1.2022	2.64			

(6) B. C. Barton, Thesis, Brown University, 1939.

(7) C. A. Kraus and R. M. Fuoss, *THIS JOURNAL*, **55**, 21 (1933).

^a Obtained in collaboration with Dr. B. C. Barton.

IV. Discussion

In a non-polar solvent, such as benzene, with a low dielectric constant, the forces due to the ions of a dissolved salt are much greater than they are in polar solvents of high dielectric constant. Moreover, the interaction of ions with solvent molecules, which may be marked in the case of polar solvents, are virtually negligible in the case of non-polar solvents. In non-polar solvents, we should, therefore, expect to find the interactions between ions to be greatly enhanced.

1. **Association at Low Salt Concentrations.**—Conductance measurements⁷⁻¹⁰ have shown that in benzene, at concentrations below $1 \times 10^{-5} N$, salts exist largely as ion pairs or ion dipoles. The fraction of salt existing as free ions amounts to one part per million or less. At these concentrations the ions are in equilibrium with ion pairs in accordance with the law of mass action. In the neighborhood of $1 \times 10^{-5} N$, the conductance passes through a minimum due to interaction between ions and ion dipoles; thereafter the conductance increases with increasing concentration to reach significant values at high concentrations. This indicates a considerable increase in the concentration of ions with increasing salt concentration although we do not know, precisely, either their nature or their number.

Molecular polarization values¹¹⁻¹³ derived from dielectric constant measurements likewise have provided clear proof that below about $1 \times 10^{-4} N$ all salts (in benzene) exist substantially completely as ion dipoles. With increasing concentration, the polarization decreases, indicating association of dipoles to quadrupoles. For salts with large ions and intermediate dipole moments, the equilibrium between dipoles and quadrupoles follows the law of mass action. For salts with large cations and small anions the polarization falls off more rapidly, indicating the formation of aggregates more complex than quadrupoles. On the whole, the relation between molecular polarization and concentration for different salts is markedly dependent on constitutional and dimensional factors and is in accord with the view that properties are governed by electrical forces.

At higher concentrations of salts in benzene, molecular weight determinations would appear to provide more information as to the state of salts in solution than would other methods. Let us first consider the molecular weights at relatively low concentrations. In Table II are given values of the association number, n , for all the salts that have been measured in this Laboratory; values of n at 0.001 and 0.01 m are given in columns 2 and 3, respectively. In column 4 are given the dipole moments of the salts in benzene.

Depending on the extent of their association, we may divide the salts into five types as indicated

(8) R. M. Fuoss and C. A. Kraus, *THIS JOURNAL*, **55**, 3614 (1933).

(9) W. F. Luder, P. B. Kraus, C. A. Kraus and R. M. Fuoss, *ibid.*, **58**, 255 (1936).

(10) L. E. Strong and C. A. Kraus, *ibid.*, **72**, 166 (1950).

(11) G. S. Hooper and C. A. Kraus, *ibid.*, **56**, 2265 (1934).

(12) J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 586 (1936).

(13) C. A. Kraus and G. S. Hooper, *Proc. Nat. Acad. Sci.*, **19**, 939 (1933).

TABLE II

ASSOCIATION NUMBERS OF SALTS IN BENZENE

Salt	n at		$\mu \times 10^{18}$	Salt type
	$m = 0.001$	$m = 0.01$		
Am ₃ NHPi	1.01 ^{a,c}	1.07	13.3 ^a	A
Bu ₃ NHPi	1.01 ^b	1.07	13.1 ^a	A
Bu ₃ NHI	1.12 ^b	1.4	8.09 ^a	B
AgClO ₄	1.15 ^c	1.7	10.7 ^c	B
Am ₄ NPi	1.3 ^c	..	18.3 ^d	C
Am ₄ NCNS	3.2 ^{a,c}	7.8	15.4 ^a	D
Bu ₄ NCNS	2.4 ^a	4.2	..	D
Bu ₄ NClO ₄	3.0 ^b	5.0	14.1 ^e	D
Am·Bu ₃ NI	3.1 ^a	4.4	..	D
Octd·Bu ₃ NCOOH	10.7 ^a	E

^a This investigation. ^b Ref. (5). ^c Ref. (4). ^d Ref. (12). ^e Ref. (13).

in column 5. The cryoscopic behavior of solutions of these salts may be correlated with their dipole moments and other constitutional factors.

A.—Salts with large unsymmetrical cations and large anions having polar moments of about 13×10^{-18} . Triisoamylammonium picrate is an example of this class; association at 0.001 m is just appreciable and at 0.01 m it is 7%. The equilibrium between dipoles and quadrupoles follows the law of mass action.⁵

B.—Salts with large unsymmetrical cations and small anions and having polar moments in the neighborhood of 8×10^{-18} . The tri-*n*-butylammonium halides are examples of this type. For the iodide, the association is 12% at 0.001 m and 40% at 0.01 m . The dipole-quadrupole equilibrium does not conform to the law of simple mass action except, perhaps, at very low concentrations.⁵ Silver perchlorate appears to fall into this class.¹⁴

C.—Salts of large symmetrical cations and large anions and having moments in the neighborhood of 18×10^{-18} . Tetraisoamylammonium picrate is the only example of this type in Table II; it is associated to the extent of 30% at 0.001 m and 40% at 0.0038 m , its solubility limit.⁴

D.—Salts of large symmetrical cations and small anions having moments in the neighborhood of 15×10^{-18} . Tetraisoamylammonium thiocyanate is a typical example, its association number at 0.001 m is 3.2 and at 0.01 m it is 7.8. These salts are definitely associated beyond the quadrupole stage of 0.001 m and association increases rapidly with increasing concentration.

E.—Highly associated salts. Of this type we have only a single example, *n*-octadecyltri-*n*-butylammonium formate. At 0.001 m its association number is 11; at 0.0032 m it is 21.5.

The association of ion dipoles is clearly governed by two factors; the dipole moment of the ion pair and the size and symmetry of the ions. Thus, tetraisoamylammonium picrate, with a moment of 18×10^{-18} , shows an association of 30% at 0.001 N while triisoamylammonium picrate, with a moment of 13×10^{-18} , shows an association of 1% at 0.001 m and 7% at 0.01 m . On the other hand, tri-*n*-butylammonium iodide with a polar moment of only 8×10^{-18} shows an association of

(14) The silver ion complexes with benzene and it is not unlikely that this complex is present in the aggregates found by means of cryoscopic measurements. R. E. Rundle and J. H. Goring, *THIS JOURNAL*, **72**, 5337 (1950).

12% at 0.001 *m* and 40% at 0.01 *m*. The smaller size of the iodide ion leads to a larger association although the moment of the salt is much smaller than that of the corresponding picrate. Constitutional factors are probably most important in regulating the extent of association; the extraordinarily high association of *n*-octadecyltributylammonium formate may, perhaps, in part, be ascribed to the presence of the long alkyl chain.

Preliminary data were obtained with mixtures of two quaternary ammonium thiocyanates. As may be seen in Fig. 1, the curve for the mixtures lies between those of the two pure components. The association number of the mixture is much greater than that computed on the assumption that no interaction occurs between unlike dipoles. Actually, the experimental curve for the mixture is represented very precisely by the expression $n_{1,2} = (n_1 + n_2)/2$ where $n_{1,2}$, n_1 and n_2 are the association numbers of the mixture and of the two thiocyanates at the total concentration *m*. From the above results, it seems reasonable to conclude that both salt species are present in the aggregates, probably in equimolar proportion. If $n_1 > n_2$, for the pure salts, and if n_{1a} and n_{2a} are the association numbers of the two salts in the mixed aggregates, then, $n_{1a} < n_1$ and $n_{2a} > n_2$. This case is somewhat similar to that observed by Barton⁶ with mixtures of *p*-nitrodiphenyl- and β -naphthylamine.

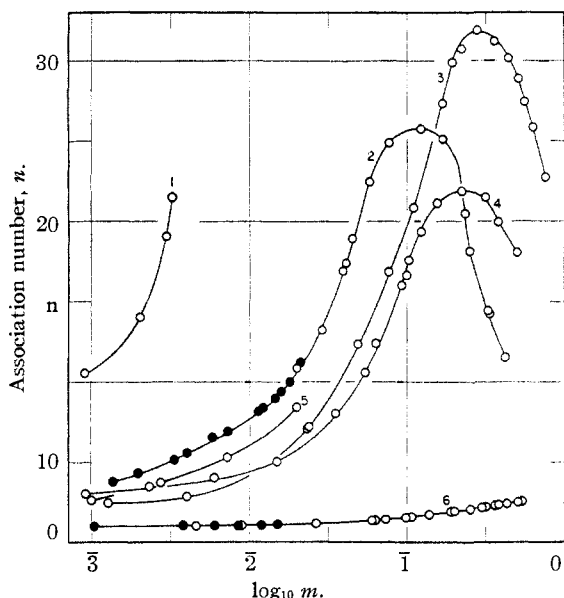


Fig. 1.—Association numbers of salts in benzene at the freezing point: 1, octadecyltributylammonium formate; 2, tetraisoamylammonium thiocyanate; 3, tetra-*n*-butylammonium thiocyanate; 4, *n*-amyltri-*n*-butylammonium iodide; 5, equimolar mixture of 2 and 3; 6, triisoamylammonium picrate: O, this investigation; ●, Batson and Kraus (ref. 3).

2. Association at Higher Concentrations.—

In Fig. 1, the results of the present investigation are presented in graphical form, the association number, *n*, being plotted as a function of the logarithm of the molal salt concentration.

Let us first consider the three quaternary ammonium salts of Class D. The association num-

bers increase rapidly as concentration is increased until a maximum is reached between 0.12 and 0.28 molal; thereafter the association number decreases rapidly. The association numbers at the maximum are of the same order of magnitude but differ for different salts. Values for the maximum are collected in Table III.

TABLE III

Salt	Concn. at max. <i>m</i>	<i>n</i> at max.
(<i>i</i> -Am) ₄ NCNS	0.12	25.8
(<i>n</i> -Bu) ₄ NCNS	.28	31.9
(<i>i</i> -Am)(<i>n</i> -Bu) ₃ NI	.22	21.9

Inspection of Fig. 1 and Table III will show that constitutional factors play an important role in the association process. Association progresses more rapidly with tetraisoamylammonium thiocyanate than it does with the corresponding tetra-*n*-butyl salt; the maximum is reached at a markedly lower concentration but the association at the maximum is notably lower than for the butyl salt. At the highest concentration at which the first salt was measured (0.42 molal), its association number is 11.5 while that of the second salt at the same concentration is 30.5.

It remains to consider whether or not the high association values might be due to some source of error. In the case of tetraisoamylammonium thiocyanate, for example, the concentration at the maximum is only 0.12 molal and, whether the association numbers are precise or somewhat in error, thermodynamically the solution is very dilute. We need also to consider the possibility that the concentration of ions is sufficiently great to lead to significant deviations from the laws of dilute solutions. The equivalent conductance of the tetraamyl salt at the maximum point is less than 0.1; considering the viscosity of the solution to be approximately twice that of benzene,¹⁰ we might expect that the number of ions would amount to not more than one in 500 molecules of solute, which would yield an ion concentration in the neighborhood of 0.0002 *m*. It is scarcely conceivable that the ions at this concentration could have a predominant effect on the osmotic properties of the solution.

It may be noted, in connection with the conductance of these solutions, that symmetrical quaternary ammonium salts with small anions (Type D) have complex conductance curves, with several inflection points appearing between the minimum, at extremely low concentrations and the maximum, at relatively high concentrations. A correlation is found to exist between the concentrations of the maxima in the freezing point curves and the points of inflection exhibited at the high concentration end of the conductance curves. Thus, for the tetra-*n*-butyl- and tetraisoamylammonium thiocyanates and *n*-amyltri-*n*-butylammonium iodide, the concentrations of the maxima as given in Table III lie at 0.28, 0.12 and 0.22 *m*, respectively; the concentrations of the inflection points of the conductance curves are 0.27, 0.14 and 0.25 *m*, respectively.¹⁰ It may be noted

further, that, while the conductance curve for tri-isoamylammonium picrate is of simple form, the conductance increasing regularly with increasing concentration,^{7,10} the association of this salt, as shown by freezing point measurements, is much less pronounced than is that of the other salts shown in Fig. 1.

While the building up of the ion dipoles to complex structures with increasing concentration follows fairly logically on the basis of existing concepts, the rapid dissociation of the complexes at concentrations above that of the maximum does not follow simply on a similar basis. There is reason for believing that this building down of the complexes is due to a modification of the forces acting between the dipoles and, indeed, between the ions themselves.

These cases are, perhaps, understood more readily from the point of view of Strong and Kraus¹⁰ who look upon concentrated benzene solutions as solutions of benzene in the fused salt. The fused salt is completely dissociated into its ions and there is no interaction between individual ions; rather, the ions, so to speak, float in a field due to all the ions in a given small volume. If benzene molecules are introduced, these will serve to separate the ions, reducing and, perhaps, distorting the field

in which the ions float. If sufficient benzene is introduced, the field will be weakened to such an extent that interaction will take place between individual ions with the resulting formation of ion pairs. The formation of ion pairs will tend to lower the conductance. On addition of larger quantities of benzene, the ion pairs will begin to interact with one another to form quadrupoles and more complex structures. This building up process will continue until a point is reached where the building down process sets in as a result of ordinary kinetic interactions. In other words, with increasing additions of benzene, association first increases, reaches a maximum and then decreases.

In solutions of salts in a non-polar solvent, such as benzene, we are dealing with interactions that have their seat in the charges on the ions. The solvent takes little or no part in these interactions, it serves merely as a medium in which the ions may exist without precipitation as a solid phase. The properties of these systems must ultimately be traceable to the ions of the electrolytes in solution. The correctness of this view is borne out by the sensitivity of the properties of these solutions to the constitutional and structural features of the ions that are involved.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

The Association Constants of Several Carboxylic Acids in Benzene as Determined Cryoscopically

BY BERNARD C. BARTON¹ AND CHARLES A. KRAUS

The apparent molecular weight of five carboxylic acids has been determined in benzene in the concentration range 0.01–0.1 molal. Constants have been derived for the monomer–dimer equilibrium. With the exception of hydrocinnamic acid, the order of these constants is the same as that of their ionization constants in water. The constant for benzoic acid at the freezing point of benzene is in agreement with that obtained by Wall, *et al.*, at higher temperatures by a vapor tension method.

I. Introduction

At the time that this investigation was initiated, there were no reliable data relating to the association of carboxylic acids in benzene. In the meantime, Gross and co-workers² have determined the association of acids at 25° by means of dielectric constant measurements. Wall and co-workers³ have made similar determinations at several temperatures by means of a differential vapor tension method. More recently, Wolf and Metzger⁴ have determined association constants of several acids at two temperatures.

While carboxylic acids are highly associated in benzene at concentrations where measurements can be most conveniently made (0.01 to 0.1 *m*), it appeared that fairly reliable constants could be obtained by the cryoscopic method in view of the precision with which freezing point depressions could be determined.

(1) University Fellow in Brown University, 1936–1939, inc.

(2) (a) A. A. Maryott, M. E. Hobbs and P. M. Gross, *J. Chem. Phys.*, **9**, 408 (1941); (b) H. A. Pohl, M. E. Hobbs and P. M. Gross, *Ann. N. Y. Acad. Sci.*, **40**, 389 (1940).

(3) (a) F. T. Wall and P. E. Rouse, Jr., *THIS JOURNAL*, **63**, 3002 (1941); (b) F. T. Wall and F. W. Baines, *ibid.*, **67**, 898 (1945).

(4) K. L. Wolf and G. Metzger, *Ann.*, **563**, 157 (1949).

II. Experimental

1. **Apparatus and Materials.**—The apparatus and techniques employed were the same as those developed in this Laboratory for determining the molecular weight of electrolytes in benzene. The experimental details have been described in earlier papers.⁵

The following acids were employed after recrystallization from benzene: benzoic, m.p. 128.5–129.0°; *o*-bromobenzoic, m.p. 148.9°; hydrocinnamic, m.p. 48.0–48.5°; cinnamic (*trans*), m.p. 131.0–131.5°; phenylpropionic, m.p. 135–136°. Benzene was purified as described in earlier papers.⁵

2. **Results.**—In Table I are recorded values of $r = \Delta T/\Delta T_0$, the ratio of the observed depression to that of an ideal substance at the same concentration. The concentration, *m*, is expressed as moles of solute per 1000 g. of benzene. The freezing point constant has been taken to be 5.085°/mole/1000 g. solvent.⁶

III. Discussion

The dissociation constants of the dimers are best evaluated by graphical methods. If *K* is the dissociation constant of the dimer, *m* is the stoichiometric concentration of the acid in moles per 1000

(5) (a) C. A. Kraus and R. A. Vingee, *THIS JOURNAL*, **56**, 511 (1934); (b) F. M. Batson and C. A. Kraus, *ibid.*, **56**, 2017 (1934); (c) D. A. Rothrock, Jr., and C. A. Kraus, *ibid.*, **59**, 1699 (1937).

(6) B. C. Barton and C. A. Kraus, *ibid.*, **73**, unpublished (1951).