radicals. It has already been shown[2] that reaction (6) has a low steric factor, *i.e.*, about two collisions in 10^4 lead to reaction in spite of the low activation energy. If this same factor is assumed for (8), pre-exponential term for (7) is very low, of the order of 10^9 sec.$^{-1}$ instead of the usual value of about 10^{13} sec.$^{-1}$ for many unimolecular reactions. However, HCO has few vibrational degrees of freedom and quite possibly the dissociation rate will depend markedly on total pressure. If this is true, the constant for (7) will be complex, and statements concerning activation energy and steric factors must be made with care.

The same type of reasoning when applied to reaction (2) shows the pre-exponential factor to be about 10^{12} sec.$^{-1}$. Thus this radical with its larger number of degrees of freedom may decompose by a more nearly unimolecular process. It is safe to say that CH_3CO radicals decompose more rapidly than HCO radicals at a given oxygen pressure in spite of their higher activation energy for decomposition.

One further uncertainty exists concerning the mechanism as postulated, and this concerns the fates of the OH and HO_2 radicals. If either of these abstracts hydrogen or regenerates oxygen directly or indirectly, some uncertainties in the interpretation would exist. On the other hand, at the temperatures covered by these experiments a chain reaction has not been initiated, and for this reason it seems probable either that these radicals disappear mainly by combination with each other, or that eventually they react with the mercury vapor in the system. In this respect acetone–oxygen mixtures behave very differently from diethyl ketone–oxygen mixtures which will be discussed in a later paper.[13] Any hydrogen abstraction by either OH or HO_2 would presumably lead to the same acetonyl radical as results from methane formation and consequently could lead to a chain reaction. Some evidence that this type of thing occurs at 250° and higher has been noted.

(13) Work being performed by Dr. A. Finkelstein in this Laboratory.

ROCHESTER, NEW YORK RECEIVED JULY 5, 1951

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

A Study of Interactions between Dipole Molecules in Benzene Solution by a Cryoscopic Method[1]

BY BERNARD C. BARTON,[2] DAVID A. ROTHROCK, JR., AND CHARLES A. KRAUS

The interaction between dipolar molecules in benzene solution has been investigated by the cryoscopic method. The freezing point depression of seventeen dipolar substances has been measured as a function of concentration. In addition, the freezing point depression has been determined for equimolar mixtures of several pairs of dipolar molecules. If $r = \Delta T/\Delta T_0$ is the ratio of the depression for a given solution to that of an ideal solution then, in general, the results conform to the linear relation, $r = 1 - b'm$, where m is the formal concentration and b' is a constant which serves as a measure of the degree of interaction. With equimolar mixtures of two different dipolar molecules, measurable interaction occurs between molecules of different species.

I. Introduction

In an ideal system, the freezing point depression, ΔT_0, of a dilute solution is directly proportional to its concentration, or

$$\Delta T_0 = am \tag{1}$$

where m is the formal concentration and a is the freezing point constant. In the case of a solute consisting of polar molecules, the freezing point depression, ΔT, is usually less than ΔT_0, the depression for an ideal solution at the same concentrations. As a first approximation we might express the result by means of a quadratic equation of the form

$$\Delta T = am - bm^2 \tag{2}$$

where b is a constant which will be the larger the greater the interaction between the solute molecules. In practice, it is more convenient to examine values of the ratio $r = \Delta T/\Delta T_0$ rather than of ΔT, itself. Expressed in this manner, equation (2) becomes

$$r = \Delta T/\Delta T_0 = 1 - b'm \tag{3}$$

where the constant b' is the slope of the curve relating r with m and serves as a measure of the interaction between the dipole molecules.

There are numerous data in the literature which show that the freezing point depression for solutions of dipolar molecules is less than that of corresponding solutions of an ideal substance.[3] However, the available data, for the most part, relate to relatively concentrated solutions and their precision is not sufficiently high to permit of determining how closely they conform to equation (3). Furthermore, it seemed of interest to examine how the deviations from ideal systems may be dependent upon the dipole moments of the dissolved molecules. Accordingly, we have measured the freezing point depression of some seventeen polar substances in benzene, chiefly in the concentration range of 0.01–0.1 m. In addition, we have measured the freezing point depression of solutions of several sets of two different dipolar substances for the purpose of determining the interaction between molecules of different species.

The data for all substances and their equimolar mixtures here reported follow relation (3). As Lassettre[3] has shown, the linear dependence of the ratio M/M_0 (or r) on m may be accounted for satisfactorily by assuming successive association

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(1) This paper is based on a portion of a thesis presented by Bernard C. Barton in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1939.

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

(3) E. N. Lassettre, *Chem. Revs.*, **20**, 259 (1937); THIS JOURNAL, **59**, 1383 (1937).

equilibria among aggregates of all orders. For the case of the dilute solutions of the present investigation, association probably does not proceed beyond the dimer stage. Our results suggest that we are dealing with a dimer–monomer equilibrium. Furthermore, aside from the magnitude of the slope, the same law seems to apply, whether or not association is due to the interaction between dipoles or to hydrogen bonding.

II. Materials, Apparatus and Procedure

(1) **Materials.** **Benzene.**—Thiophene-free benzene was purified by the method described by Batson and Kraus.[4] The middle fraction was fractionally crystallized until a substantially constant melting point of between 5.49° and 5.51° was obtained. It was stored over sodium-lead alloy (NaPb) until used.

Solutes.—Substances employed as solutes were mainly Eastman Kodak Co. products which were purified by conventional means; when possible, the final recrystallizations were made from benzene. Melting points were found to accord with values reported in the literature.

(2) **Apparatus and Procedure.**—The apparatus employed in this study has been described in earlier papers.[4,5] Temperature differences were measured with a 36-junction copper–constantan thermal constructed by Dr. F. M. Batson. The couple was recalibrated in a manner designed to minimize any error due to the non-linearity of the e.m.f.–temperature relation in the temperature range employed. For the small temperature differences encountered in this research, it was sufficiently accurate to express the e.m.f. as a quadratic function of temperature.

(3) **Procedure.**—The procedure employed in preparing solutions for measurements was essentially the same as that described in earlier papers. To determine the concentration of the solution, two samples of approximately 20 cc. each were withdrawn from the freezing point cell into quartz pipets; the solvent was evaporated in an air stream and after pumping off residual solvent, the weight of the solute was determined. In cases where the concentrations were too low to permit of accurate determination by weighing or when the solute was volatile, a weighed quantity of triphenylmethane was added, samples were withdrawn as described above and analyzed for total solute or for triphenylmethane. A correction was applied for the heat effect accompanying the solution of the triphenylmethane.

III. Results

(1) **Hexaethylbenzene.**—In previous investigations, the cryoscopic constant of benzene was determined by means of triphenylmethane as ideal solute.[4,5] Although solutions of this substance showed ideal behavior and led to reproducible values, the material possesses the disadvantage that it retains benzene very tenaciously. Accordingly, it was thought worthwhile to search for another substance which would behave ideally without introducing the difficulties incident to triphenylmethane.

The freezing point constant of benzene has been redetermined with hexaethylbenzene as the ideal solute. In use, this substance proved more convenient than triphenylmethane since it does not retain benzene. The data for a series of determinations are given in Table I; the concentrations recorded in the following tables are expressed as formula weights per 1000 g. of solvent.

TABLE I

FREEZING POINT DEPRESSION OF SOLUTIONS OF HEXAETHYLBENZENE IN BENZENE

m	ΔT	Const.	Dev., %
0.02857	0.1455	5.093	+0.10
.04092	.2083	5.085	− .06
.04160	.2116	5.086	− .04
.04338	.2209	5.092	+ .08
.05647	.2869	5.079	− .18
.06625	.3377	5.093	+ .10
Mean		5.088	Av. dev. 0.1%

The precision of the measurements is seen to be of the order of 0.1%. The mean value of the cryoscopic constant was found to be 5.088 and this value has been used in all computations. This value may be compared with the values 5.065, obtained by Kraus and Vingee[5a] and 5.075, obtained by Batson and Kraus.[4] It may be pointed out that hexaethylbenzene does possess the disadvantage of being slightly volatile. Loss of material during an analysis would tend to yield a somewhat high value of the constant whereas retention of solvent would tend to yield a low value. It may well be that the true value lies somewhere between 5.075 and 5.090. Davison[6] reports the value 5.088.

(2) **Solutions of Single Dipolar Substances.**—The freezing point depression of solutions of various dipolar substances are recorded in Table II. The concentrations of the solutions in moles per 1000 g. of benzene appear in column 1, the freezing point lowering, ΔT, in column 2 and the ratio of the observed to the theoretical depression, r, in column 3.

TABLE II

FREEZING POINT DATA FOR SOME DIPOLAR MOLECULES IN BENZENE

m	ΔT	r
o-Dinitrobenzene		
0.05498	0.2635	0.934
.09165	.4230	.908
p-Dinitrobenzene		
0.05396	0.2708	0.987
.07667	.3835	.984
.08196	.4086	.981
.08265	.4123	.981
.09586	.4744	.973
2,6-Dinitrophenol		
0.03711	0.1852	0.982
.05382	.2663	.973
p-Nitrosodiethylaniline		
0.02828	0.1358	0.945
.0290	.140	.950
sym-Trinitrotoluene		
0.1445	0.7034	0.958
.2436	1.158	.935
.3562	1.647	.910
.4931	2.208	.881
o-Phenylenediamine		
0.02337	0.1131	0.952
.02624	.1257	.942
.03727	.1734	.915
m-Nitroaniline		
0.07830	0.3857	0.969
Picric acid		
0.06110	0.3017	0.971
o-Nitroaniline		
0.1063	0.5022	0.929
.2024	.9088	.883
m-Nitrophenol		
0.03699	0.1815	0.965
.04493	.2183	.956
.05944	.2853	.944
.06446	.3060	.934
Nitromethane		
0.1897	0.9211	0.954
.1902	.9242	.956
.4319	1.995	.909

(3) **Equimolar Mixtures of Dipolar Molecules.**—The freezing point of solutions of three pairs of dipolar substances and their equimolar mixtures are recorded in Table III. The value of m for mixtures is the total moles of solute per 1000 g. of benzene and this value is employed in evaluating r for the mixtures.

IV. Discussion

(1) **Solutions of a Single Molecular Species.**—In Fig. 1 are shown plots of the ratio $r = \Delta T/\Delta T_0$, as a function of the formal concentration m. The plots of 1A relate to the more dilute solutions, those of 1B relate to the more concentrated solutions. Within the experimental error, all plots are linear. The radii of the circles representing experimental points correspond to an error of 0.25% in the ratio, r. In only a few instances does the maximum deviation of the points from the straight lines exceed this value; this mean deviation is much less.

Values of the slopes, dr/dm, of the plots of Fig. 1 are collected in Table IV; included, in the last

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[4] F. M. Batson and C. A. Kraus, THIS JOURNAL, 56, 2017 (1934).

[5] (a) C. A. Kraus and R. A. Vingee, *ibid.*, 56, 511 (1934); (b) D. A. Rothrock, Jr., and C. A. Kraus, *ibid.*, 59, 1699 (1937).

[6] J. A. Davison, *ibid.*, 67, 228 (1945).

TABLE III

m	ΔT	r
1. *m*-Dinitrobenzene		
0.1114	0.5460	0.964
.1773	.8482	.941
.2779	1.285	.910
.3385	1.528	.888
2. *m*-Phenylenediamine		
0.06042	0.2902	0.945
.07713	.3658	.933
.09605	.4471	.916
Mixture of 1 and 2		
0.04501	0.2244	0.981
.05585	.2762	.973
3. *p,p'*-Dichlorodiphenyl		
0.04975	0.2481	0.981
.06160	.3059	.966
.08065	.3963	.967
4. Benzidine		
0.03708	0.1777	0.943
.04531	.2170	.942
Mixture of 3 and 4		
0.05934	0.2909	0.964
.06834	.3346	.963
.07166	.3482	.956
5. *p*-Dinitrodiphenyl		
0.03975	0.1986	0.983
.07172	.3559	.976
.07853	.3890	.975
6. *β*-Naphthylamine		
0.03669	0.1848	0.991
.05389	.2694	.984
.08080	.4006	.975
Mixture of 5 and 6		
0.04772	0.2393	0.987
.06632	.3290	.976
.06909	.3429	.976
.09163	.4539	.975
.09858	.4854	.969

column, are the polar moments of various compounds.

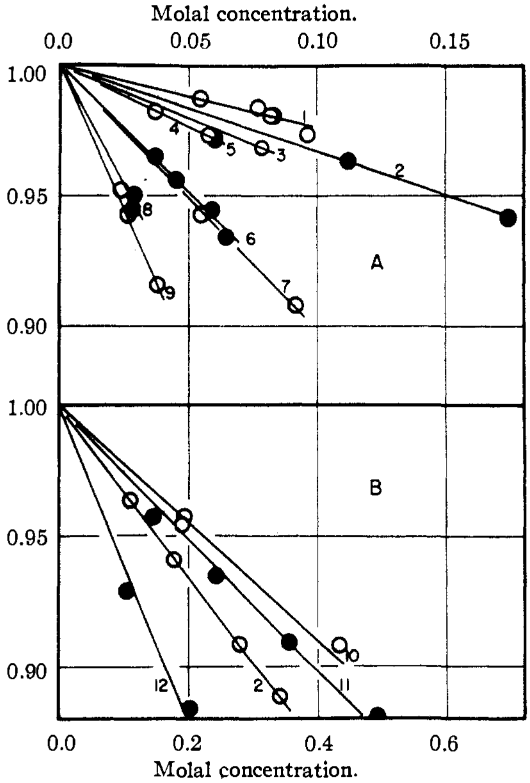

Fig. 1.—Plots of $r = \Delta T/\Delta T_0$ for dipole molecules in benzene: A: 1, *p*-dinitrobenzene; 2, *m*-dinitrobenzene; 3, *m*-nitroaniline; 4, 2,6-dinitrophenol; 5, picric acid; 6, *m*-nitrophenol; 7, *o*-dinitrobenzene; 8, *p*-nitrosodiethylaniline; 9, *o*-phenylenediamine. B: 10, nitromethane; 11, *sym*-trinitrotoluene; 2, *m*-dinitrobenzene; 12, *o*-nitroaniline.

TABLE IV

SLOPES OF FREEZING POINT CURVES AND DIPOLE MOMENTS OF VARIOUS MOLECULES

Substance	$-dr/dm$	$\mu \times 10^{18}$ [a]
o-Phenylenediamine	2.18	1.4
p-Nitrosodiethylaniline	1.83	7.0
Benzidine	1.50	1.3
o-Dinitrobenzene	1.02	6.0
m-Nitrophenol	0.97	3.9
m-Phenylenediamine	.89	1.8
o-Nitroaniline	.61	4.3
Picric acid	.46	...
2,6-Dinitrophenol	.46	...
m-Nitroaniline	.40	4.8
p,p'-Dichlorodiphenyl	.40	—0
m-Dinitrobenzene	.33	3.8
p-Nitrodiphenyl	.32	4.2
β-Naphthylamine	.32	1.8
sym-Trinitrotoluene	.25	...
p-Dinitrobenzene	.23	0.4
Nitromethane	.22	3.2

[a] Tables of Electrical Dipole Moments, Tech. Report No. 2, Lab. of Insulation Research, M.I.T., April, 1947.

The compounds of Table IV are listed in the order of decreasing slope. They fall, roughly, into three groups depending on the value of dr/dm. For the first group $dr/dm > 1$, for the second, it varies between 1 and 0.4 and for the last, it is less than 0.4. While there is little correlation between slopes and dipole moments of individual substances, the average values of dipole moments for the three groups is 4.0, 3.6 and 2.7×10^{-18}, respectively. The two compounds of greatest moment, 7.0 and 6.0×10^{-18}, appear in the first group and *p*-dinitrobenzene ($\mu = 0.4 \times 10^{-18}$) in the last group, with a slope of only 0.23. On the other hand, nitromethane ($\mu = 3.2 \times 10^{-18}$) has a slope of only 0.22.

While the dipole moments of solute molecules lead to interactions that cause deviation from the freezing point depression of an ideal substance, other factors may lead to a similar result. In the case of amines and phenolic compounds, hydrogen bonding may occur, leading to association, as is the case with the carboxylic acids.

An examination of the slopes of the isomeric diamino- and dinitrobenzenes throws some light on this question. In Table V are collected values of dr/dm and of polar moments for these compounds.

TABLE V

SLOPES AND ELECTRIC MOMENTS FOR ISOMERIC DIAMINO- AND DINITROBENZENES

	Diaminobenzenes		Dinitrobenzenes	
	$-dr/dm$	$\mu \times 10^{18}$	$-dr/dm$	$\mu \times 10^{18}$
o-	2.18	1.4	1.02	6.0
m-	0.89	1.8	0.33	3.8
p-	(1.3)[a]	1.5	0.23	0.4

[a] From less precise data by B. C. Barton, Thesis, Brown University, 1939.

The high values of dr/dm for the diamines are noteworthy as are the low values for the corresponding dinitro compounds. In the case of the nitro compounds, the slopes parallel the electric moments; this is not true in the case of the amino compounds. As with the nitro compounds, there is a substantial decrease in slope on going from the ortho- to the meta-diamine; but the slope of the para compound is higher than that of the meta compound. However, it is possible that the polar moments of these diamines, as determined in benzene, may in themselves reflect association; the low value for the ortho compound, for example, may be a result of internal compensation.

Berger[7] has examined a considerable number of polar molecules in benzene solution by the ebullioscopic method. In most cases his *r vs. C* curves do not extrapolate to the origin and a comparison with our measurements cannot be made. In general, he found marked deviations from ideal systems.

Most of the molecules for which solutions have been measured have two polar groups which, in some cases, oppose and, in others, reinforce each other. It seems that we may safely conclude that, for the most part, interaction takes place between individual dipoles in the molecules rather than between the molecules as a whole. Thus, we find a notable example in *p,p'*-dichlorodiphenyl, whose polar moment is zero but $\mathrm{d}r/\mathrm{d}m = 0.40$. In this case, interaction must occur between individual dipoles of two molecules. At least in part, the larger value of $\mathrm{d}r/\mathrm{d}m$ for *p*-phenylenediamine may be accounted for in this way. One conclusion that may be safely drawn is: *the molecular weight of compounds containing dipoles cannot be satisfactorily determined by cryoscopic or other similar methods, except at very low concentrations.*

(2) Equimolar Mixtures of Dipole Molecules.—If we have an equimolar solution of two dipole molecules of total concentration m, and if we assume that solutions of each molecular species conform to equation (2), then, if no interaction takes place between the molecules of different species, we have

$$\Delta T_{1,2} = \Delta T_1 + \Delta T_2 \qquad (4)$$

and

$$r = 1 - m(b_1' + b_2')/4 \qquad (5)$$

where numerals 1 and 2 refer to species 1 and 2, $\Delta T_{1,2}$ is the freezing point depression of the mixture and r, again, is the ratio of the observed to the theoretical freezing point depression. If interaction occurs, we should expect $\mathrm{d}r/\mathrm{d}m$, as observed, to be greater than $(b_1' + b_2')/4$.

In Table VI are presented values of $\mathrm{d}r/\mathrm{d}m$ for three pairs of dipole molecules. The values for the pure compounds are given in column 2, the observed values for the mixtures are given in column 3 and in the last column are given values of $\mathrm{d}r/\mathrm{d}m$ calculated on the assumption that no interaction occurs between the molecules of different species in the mixtures. The results are plotted in Fig. 2, where the broken lines correspond to values for the mixtures computed on the assumption of no cross interactions.

TABLE VI

COMPARISON OF OBSERVED AND COMPUTED VALUES OF $\mathrm{d}r/\mathrm{d}m$ FOR MIXTURES

	$-\mathrm{d}r/\mathrm{d}m$		
Compound	Pure sub.	Mixt. (obsd.)	Mixt. (calcd.)
p,p'-Dichlorodiphenyl	0.40	0.59	0.48
Benzidine	1.50		
m-Dinitrobenzene	0.33	.46	.31
m-Phenylenediamine	.89		
p-Dinitrodiphenyl	.32	.32	.16
β-Naphthylamine	.32		

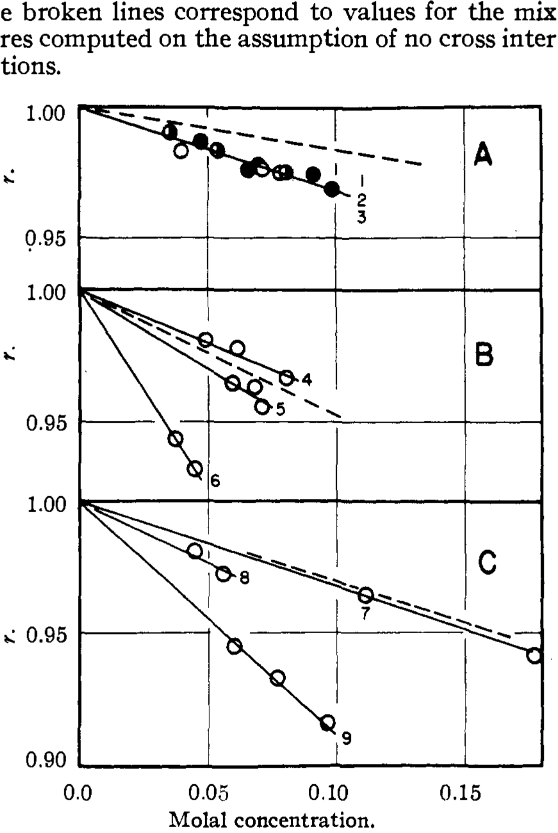

Fig. 2.—Plots of $r = \Delta T/\Delta T_0$ for dipolar molecules and their equimolar mixtures: A: 1, ○, *p*-dinitrodiphenyl; 2, ◑, *β*-naphthylamine; 3, ●, equimolar mixture. B: 4, *p,p'*-dichlorodiphenyl; 5, equimolar mixture; 6, benzidine. C: 7, *m*-dinitrobenzene; 8, equimolar mixture; 9, *m*-phenylenediamine.

As may be seen from the figure as well as from the table, interaction occurs between molecules of different species to a measurable extent. The most interesting mixture is that of *p*-dinitrodiphenyl and *β*-naphthylamine (Fig. 2-A). At the same total concentrations, the freezing points of solutions of the two pure compounds as well as those of their equimolar mixtures are the same within the limit of experimental error. This means that the molecules of any one species interact with molecules of the other species to the same extent as they do with molecules of their own kind.

Although a few exploratory investigations of mixtures in benzene[8] and other solvents[9] have been made earlier, they lack the precision necessary to permit of careful analysis. Further investigations along these lines might well serve to enhance our knowledge of molecular interaction.

PROVIDENCE, R. I. RECEIVED JANUARY 22, 1951

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[7] G. Berger, *Z. physik. Chem.*, **B22**, 253 (1933).

[8] F. A. Landee and I. B. Johns, THIS JOURNAL, **63**, 2895 (1941).

[9] J. Meisenheimer and O. Dorner, *Ann.*, **482**, 139 (1930).