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Properties of Electrolytic Solutions. XIII. Freezing Points of Solutions in Benzene[1]

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I. Introduction

In an earlier number of this series, Kraus and Vingee[3] have described an apparatus for determining the freezing points of solutions in ordinary solvents down to concentrations as low as 10^{-3} N and have presented data for the freezing point of solutions of tetraisoamylammonium nitrate in dioxane. Their results indicate that the electrolyte is highly associated even at relatively low concentrations. The present investigation was undertaken for the purpose of supplying data as to the state of electrolytes in solution in benzene, for which solvent there are available both conductance[2,4] and dielectric constant[5] data. The method employed was essentially the same as that of Kraus and Vingee, except that certain improvements were made to increase the precision of the measurements. Some of the earlier measurements, however, were carried out with the apparatus in its original form.

II. Apparatus, Procedure and Materials

Apparatus.—Only such elements of the apparatus will be described as have been modified over that of Kraus and Vingee. The freezing point tubes were placed in a bath whose temperature was automatically controlled to ±0.002°. The temperature was set at that point at which the heat introduced by the stirrers was just compensated by the radiation losses to the surrounding bath.

The vacuum-jacketed containers, in which the freezing point tubes were placed, were provided with hard rubber tops which were hollowed out and filled with sil-o-cel. Experience had shown that, using solid tops, enough heat was conducted through these tops to keep the upper part of the cells at a temperature below the equilibrium temperature.

A great variety of stirrers was tested out with a view to obtaining the most efficient stirring. In the end, it was found that the best results were obtained with the multiple two vane stirrers of Kraus and Vingee at approximately 700 r. p. m. The stirrers were mounted at intervals on a drill rod of 1.5 mm. diameter and were silver plated to avoid reaction with the solute, particularly in the case of silver perchlorate.

Multiple Thermocouples.—In some of the earlier measurements, a multiple thermocouple of twelve junctions was employed. Its construction was identical with that described by Kraus and Vingee. In later experiments, a new multiple thermocouple of thirty-six copper–constantan junctions was constructed in which special provisions were made to provide for ready heat transfer between the couples and the solution. The junctions were mounted in two layers, one behind the other, in longitudinal grooves in a small hard rubber cylinder and were tied in place with silk thread. The hard rubber cylinder slipped over a silver tube of 0.5 mm. thickness and 8 cm. length. The leads from the junctions were tied to the silver tube. The silver tube fitted closely over a solid silver cylinder the lower end of which was soldered to the bottom of the platinum casing in which the thermocouple system was contained. The diameter of the casing was 8 mm. and the upper portion was constructed of German silver.

The constants for the two multiple thermocouples were determined by means of a calibrated platinum resistance thermometer; they were: for the twelve junction couple,

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[1] This paper embodies a portion of the material presented as a thesis by Forrest M. Batson in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University.

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[3] Kraus and Vingee, THIS JOURNAL, **56**, 511 (1934).

[4] Fuoss and Kraus, *ibid.*, **55**, 3614 (1933).

[5] Kraus and Hooper, *Proc. Nat. Acad. Sci.*, **19**, 939 (1933).

0.002353° per microvolt and, for the thirty-six junction couple, 0.0007291° per microvolt.

Procedure.—The procedure was the same as that of Kraus and Vingee. About 225 g. of benzene was used in each of the cells, approximately 40% being present as solid. The concentration of the solutions was determined by withdrawing several samples of the final solution, of about 20 g. each, and analyzing for the solute. Excepting in the case of silver perchlorate, the benzene was evaporated and the amount of salt determined by weight. The samples of silver perchlorate solution were shaken with water and the silver precipitated as silver chloride and weighed. In case the most concentrated solution was too dilute to permit of accurate analysis, a weighed quantity of triphenylmethane was added prior to withdrawing the samples. The ratio of total solute to solvent was then determined as described above.

Excepting silver perchlorate, known weights of solute were added in the solid form. Silver perchlorate was added in solution in benzene, corrections being made for the amount of benzene introduced with the solute and for the benzene melted due to addition of the warm solution. For the heat of fusion of benzene, the value 30.2 cal./g. was used.

In most of the experiments, successive quantities of solute were added until a sufficiently large quantity of solute was present so that the resulting solution could be analyzed. This method has the disadvantage that any fluctuations in temperature or any melting of solvent during the course of the measurements, which extend over a period of several hours, reduces the precision of the measurements. The best results are obtained by determining the freezing point at a single concentration and then adding triphenylmethane for the purpose of determining the concentration of the solution. In this case, the time required for the temperature measurements is not over five or ten minutes, depending on the solubility of the solute.

Materials. Benzene.—After the usual preliminary purification, the benzene was boiled over sodium–lead alloy (NaPb) and fractionally distilled, the middle portion being retained. After repeating this process several times, the benzene was fractionally crystallized until a constant melting point was obtained.

Triphenylmethane was recrystallized from alcohol, m. p. 92.2°. Silver perchlorate was prepared according to the method of Hill.[6] Tri- and tetraisoamylammonium salts were prepared after the method of Kraus and Fuoss.[7]

III. Results

A. Triphenylmethane.—To determine the reliability of the method and to recheck the freezing point constant of benzene, the freezing points of a series of solutions of triphenylmethane in benzene were determined. The data are given in Table I. Concentrations in this and in the following tables are expressed in formula weights per 1000 g. of solvent.

B. Electrolytes.—The freezing points of solutions of the following electrolytes were determined: silver perchlorate, tetraisoamylammonium thiocyanate, triisoamylammonium picrate, tetraisoamylammonium picrate. The results are tabulated below. In determinations C to G, inclusive, for tri-isoamylammonium picrate, only a single addition of electrolyte was made. In all the determinations of tetraisoamylammonium picrate, triphenylmethane was added to the solution in each case. This was necessary because

TABLE I

FREEZING POINTS OF SOLUTIONS OF TRIPHENYLMETHANE

Formula weight, 244.12 (36 junctions)

No.	Concn.	ΔT	Mol. wt.	% dev.
A 1	0.000313	0.00158	244.5	+0.16
2	.000634	.00322	243.5	− .24
3	.000986	.00497	245.4	+ .53
4	.02481	.1263	243.1	− .41
B 1	.000704	.00354	246.3	+ .90
2	.001714	.00864	245.5	+ .57
3	.004096	.02082	243.5	− .24
4	.04375	.2214	244.6	+ .20
C 1	.02798	.1421	243.7	− .16
D 1	.002450	.01242	244.1	± .00
2	.02516	.1274	244.4	+ .12

TABLE II

FREEZING POINTS OF SOLUTIONS OF SILVER PERCHLORATE

Formula weight 207.34 (12 junctions)

No.	Concn.	ΔT	Mol. wt.
A 1	0.00300	0.0120	308.5
2	.00484	.01602	317.6
3	.00650	.02106	324.6
4	.00909	.02861	334.0
5	.01744	.05090	360.3
B 1	.00163	.00619	277.2
2	.00315	.01094	302.2
3	.00474	.01574	316.4
4	.00618	.02005	324.1
5	.00836	.02619	335.6
6	.01114	.03405	343.9
7	.01549	.04595	354.3

TABLE III

FREEZING POINTS OF SOLUTIONS OF TETRAISOAMYLAMMONIUM THIOCYANATE

Formula weight 356.42 (12 junctions)

No.	Concn.	ΔT	Mol. wt.
A 1	0.00199	0.00233	1547
2	.00402	.00372	1950
3	.00586	.00461	2295
4	.01119	.00697	2900
5	.01467	.00826	3210
6	.01825	.00925	3564
7	.02131	.00962	4002
B 1	.00136	.00181	1358
2	.00333	.00327	1841
3	.00729	.00537	2454
4	.01198	.00725	2985
5	.01592	.00859	3549

[6] Hill, THIS JOURNAL, **43**, 254 (1921).

[7] Kraus and Fuoss, *ibid.*, **55**, 21 (1933); see also footnote 2.

TABLE IV

FREEZING POINTS OF SOLUTIONS OF TRIISOAMYLAMMONIUM PICRATE

Formula weight 456.31 (12 junctions)

No.	Concn.	ΔT	Mol. wt.
A 1	0.000903	0.00442	472.8
2	.001780	.00882	468.0
3	.003830	.01882	471.2
4	.00624	.03012	479.4
5	.00896	.04264	485.9
6	.01175	.05513	492.9
7	.01505	.06941	501.5
B 1	.000704	.00362	449.6
2	.00163	.00835	456.4
3	.00347	.01718	467.4
4	.00610	.02965	476.1
5	.00851	.04082	482.6
6	.01126	.05323	489.3
C 1	.09013	.3155	660.9
D 1	.04805	.1967	565.2
E 1	.02547	.1134	519.7
F 1	.03348	.1452	533.5
G 1	.07798	.2868	629.1

TABLE V

FREEZING POINTS OF SOLUTIONS OF TETRAISOAMYLAMMONIUM PICRATE

Formula weight 526.39 (36 junctions)

No.	Concn.	ΔT	Mol. wt.
B	0.000345	0.00134	685.9
C	.000822	.00324	677.6
A	.001052	.00410	685.3
D	.002581	.00956	720.6
E	.003800	.01376	737.1

the solubility of the salt was too low to permit of direct determination of concentration.

IV. Discussion

We have no means for determining how nearly equilibrium is established between a solution and a solid phase with which it is in contact; we must determine the reliability of the method from the consistency of the experimental results. Probably, a precise equilibrium is never reached, but, if the two cells containing solvent and solution, respectively, are nearly identical, the deviation from equilibrium in the two will be nearly the same. The last column of Table I shows the deviation of the calculated molecular weight from the theoretical for triphenylmethane for the concentration range 3×10^{-4} *N* to 4.4×10^{-2} *N*. The mean deviation amounts to 0.32%, with three determinations, only, having a deviation between 0.53 and 0.90%. Down to a concentration of 2×10^{-3} *N* the method would seem to be reliable to approximately 0.2%. Below 10^{-3} *N* the actual deviations found are smaller than might be expected and are probably accidental. At the lowest concentration, 3×10^{-4} *N*, one might well expect deviations of the order of 1%.

The cryoscopic constant derived from the freezing point data of triphenylmethane has a value of 5.075°, which is in good agreement with the value 5.065° found by Kraus and Vingee.[3]

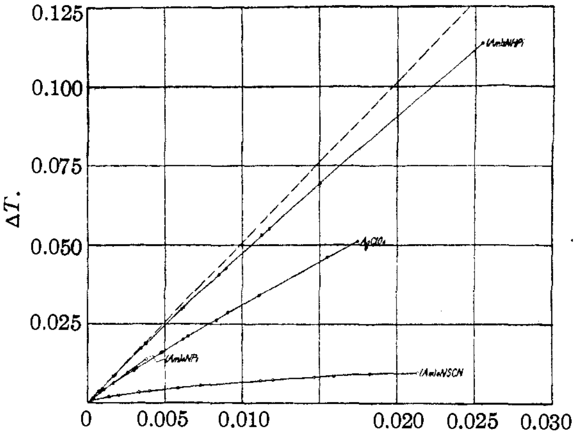

Fig. 1.—Freezing point curves of electrolytes in benzene.

The freezing point data for the several electrolytes are shown graphically in Fig. 1. The straight line represents the normal freezing point curve as determined for triphenylmethane. All the curves for the electrolytes lie below the normal curve but tend to approach the normal at low concentration: The deviations from normal depend very largely on the constitution and, particularly, the electrical symmetry of the ions. Electrolytes having ions which are electrically unsymmetrical exhibit a smaller deviation than those having symmetrical ions. Thus tri-isoamylammonium picrate, with two asymmetrical ions, deviates only slightly, even at a concentration as high as 0.01 *N*. Tetraisoamylammonium picrate which has only one asymmetrical ion, deviates much more largely but, in turn, deviates much less than tetraisoamylammonium thiocyanate which has two, at least relatively, symmetrical ions. Silver perchlorate exhibits approximately the same degree of deviation as does tetraisoamylammonium picrate. However, it may well be that quantum forces play a part in the formation of ion pairs.

The deviations in the case of tetraisoamylammonium thiocyanate are very striking. The mean molecular weight at a concentration of 0.021 *N* is 4000, or approximately eleven times the formula weight. The actual freezing point lowering (at 0.021 N) amounts to only 0.0096°, which is barely within the limits of sensitivity of ordinary freezing point methods.

Bearing in mind the fact that the solutions with which we are here dealing are extremely dilute with respect to ions, it seems that the deviations from the ideal curve can be due only to interactions between the ion pairs as has been suggested by Fuoss and Kraus.[4] When the ions are symmetrical, the pairs readily build up to higher aggregates—quadrupoles and multipoles. At very low concentrations, the observed molecular weight should approach the formula weight as a limit; which is the case, except with salts having large symmetrical ions, like tetraisoamylammonium thiocyanate, where the limiting curve is not approached even at concentrations as low as 10^{-3} N. The other three electrolytes exist largely as ion pairs below 10^{-3} N.

The difference between the behavior of electrolytes having symmetrical and unsymmetrical ions is likewise exhibited in other of their properties as, for example, their conductance and their dielectric constant effects. As was shown by Fuoss and Kraus, conductance curves of electrolytes having symmetrical ions exhibit two inflection points at concentrations above the minimum. In other words, there is a region in which the conductance increases only slowly with increasing concentration. This corresponds to the region in which dipoles are disappearing from the solution and multipoles are being formed. The conductance curve of electrolytes with asymmetrical ions is everywhere convex toward the concentration axis at higher concentration.

As Kraus and Hooper have shown, the dielectric constant of solutions of electrolytes with asymmetrical ions increases approximately linearly with concentration. On the other hand, in the case of electrolytes with symmetrical ions, the dielectric constant increase falls off rapidly with increasing concentration, the curves being strongly concave toward the axis of concentration.

Our results would seem to show that, at concentrations between 10^{-3} and 10^{-4} N, electrolytes in solution exist largely in the form of ion pairs, which form more complex aggregates at higher concentrations, the complexity increasing the more rapidly the greater the electrical symmetry of the ions.

V. Summary

Improvements are described in an apparatus for determining the freezing point of solutions in benzene at low concentrations.

The freezing point constant of benzene has been redetermined and found to be 5.075°.

The freezing points of solutions of triisoamylammonium picrate, silver perchlorate, tetraisoamylammonium picrate and tetraisoamylammonium thiocyanate have been determined.

At very low concentrations, the freezing point curves approach the ideal linear slope, based on the formula weight of the electrolyte. At higher concentrations, the deviations increase and are greatest for electrolytes having electrically symmetrical ions, and smallest for electrolytes having asymmetrical ions.

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Activation Energies of Reactions Involving Oxygen. I. The Reaction $O + H_2 = H_2O$

BY RICHARD S. BEAR[1] AND HENRY EYRING

For several years one of us,[2] in collaboration with others, has been interested in developing quantum mechanical methods of calculating activation energies for chemical reactions. Hitherto no satisfactory procedure has been devised whereby systems containing oxygen can be studied in this manner. This paper discusses the reaction $O + H_2 = H_2O$, determining activation energies of excited and normal oxygen atoms with hydrogen molecules.

The results obtained herein seem of general importance in that they demonstrate a method for handling a system in which polar forces are important and indicate the treatment of a reaction during which a change in multiplicity takes place.

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(1) National Research Fellow in Chemistry.

(2) Eyring and Polanyi, *Z. physik. Chem.*, **B12**, 279 (1931); Eyring, THIS JOURNAL, **53**, 2537 (1931); Sherman and Eyring, *ibid.*, **54**, 2661 (1932); Kimball and Eyring, *ibid.*, **54**, 3876 (1932); Eyring, Sherman and Kimball, *J. Chem. Phys.*, **1**, 586 (1933).