Anal. Calcd. for $C_{12}H_{16}O_3N_2$: C, 60.98; H, 6.82; N, 11.86. Found: C, 61.08; H, 6.97; N, 11.98, 12.11.

Hydrochloride, precipitated from ethanol solution by dry acetone, m. p. 205.5–207°.

Anal. Calcd. for $C_{12}H_{17}O_3N_2Cl$: N, 10.28. Found: N, 10.15, 10.41.

β-Alanyl-β-phenyl-β-alanine.—Microscopic narrow prisms from 60% alcohol, m. p. 235–236° with effervescence, yield 75%.

Anal. Calcd. for $C_{12}H_{16}O_5N_2$: C, 60.98; H, 6.82; N, 11.86. Found: C, 60.87; H, 6.95; N, 11.83, 11.87.

Hydrochloride, obtained as crystalline material by repeated precipitation from a concentrated methyl alcohol solution by dry acetone, m. p. 180–182°.

Anal. Calcd. for $C_{12}H_{17}O_3N_2Cl$: N, 10.28. Found: N, 10.36.

Attempts at Ring Closure with the Dipeptides and with Diaminoacetone.—When a sample of each of the peptides described above was dissolved in 98.6% formic acid and the solution boiled for thirty to ninety minutes, the peptide was recovered in 60 to 80% yield on evaporation of the solvent. Similarly, when a mixture of the sulfate of diaminoacetone[14] and dry sodium formate was heated under varying conditions with 95% formic acid, no pyrimidine was isolated.[15] In this case, however, there was evidence of considerable change, the nature of which has not been determined.

Summary

1. The synthesis of the peptides β-alanylglycine, β-alanyl-β-phenyl-α-alanine, and β-alanyl-β-phenyl-β-alanine has been accomplished through the carbobenzoxy derivatives, but not by the amination of the corresponding β-halogen acyl amino acids.

2. These peptides do not combine with formic acid to give pyrimidines.

[14] Obtained from diaminoacetone hydrochloride, prepared according to Koessler and Hanke, THIS JOURNAL, **40**, 1718 (1918); and Adams, Chiles and Rassweiler, "Organic Syntheses," Coll. Vol. I, p. 9.

[15] From the thesis of Kathleen Spencer, presented to the Women's College of the University of Delaware in partial fulfilment of the requirements for the A.B. degree with distinction in chemistry, 1937.

NEWARK, DELAWARE RECEIVED JULY 17, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

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

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

I. Introduction

In previous papers of this series[3,4] an apparatus has been described for the determination of freezing points of dilute benzene solutions and data have been presented for a few quaternary ammonium salts in the concentration range 0.001 to 0.025 *N*. Geddes[5] and Kraus have shown that ammonium salts may be divided into three general classes according to their polarization–concentration curves. The purpose of the present investigation was to determine the freezing-point curves of a typical salt from each of these groups. Several improvements were made on the freezing-point apparatus as described by Batson and Kraus.[4] The accuracy of the results was determined by numerous measurements of the freezing-point curve for triphenylmethane, a normal solute. When the reproducibility of results with the improved apparatus had been established, the freezing-point curves were determined for solutions of tri-*n*-butylammonium picrate, tri-*n*-butylammonium iodide, and tetra-*n*-butylammonium perchlorate.

II. Materials, Apparatus and Procedure

Materials: Benzene.—Thiophene-free benzene was purified by the method described by Batson and Kraus.[4] Fractional crystallization was found to be superior to distillation as a method of purification. The pure product was stored over sodium–lead alloy (NaPb) in an all-glass still.

Triphenylmethane.—After four recrystallizations from ethyl alcohol, the product had a constant melting point of 92.5°.

Salts.—The tri-*n*-butylammonium picrate was prepared by Professor Fuoss by the method described by Kraus and Fuoss;[6] m. p. 106°. Tri-*n*-butylammonium iodide was prepared by J. A. Geddes by the addition of hydriodic acid to an ether solution of tributylamine. The crude compound was recrystallized from ethyl acetate; m. p. 102°. The tetra-*n*-butylammonium perchlorate was prepared in Rogers Laboratory by the method described by Luder, P. B. Kraus, C. A. Kraus and Fuoss;[7] m. p. 207°.

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[1] This paper is an abstract of a portion of a thesis presented by David A. Rothrock, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1936.

[2] Metcalf Fellow in Chemistry at Brown University.

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

[4] Batson and Kraus, *ibid.*, **56**, 2017 (1934).

[5] Geddes and Kraus, *Trans. Faraday Soc.*, **32**, 583 (1936).

[6] Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933).

[7] Luder, Kraus, Kraus and Fuoss, *ibid.*, **58**, 255 (1936).

Apparatus.—The apparatus was essentially the same as that described by Batson and Kraus.[4] However, several mechanical improvements were made in the setup. A geared stirring mechanism was constructed so that the heat of stirring would be the same in both cells. This eliminated the belt and pulley system which had been a source of difficulty. The gears were mounted on shafts two feet (61 cm.) above the surface of the thermostat. This made it possible to introduce or withdraw the thermocouple or platinum resistance thermometer without interrupting the stirring. The Dewar tubes were mounted on a brass carriage which could be lowered or raised in the constant temperature bath. The bath temperature could then be adjusted to the desired point before the cells were placed in the Dewar tubes and lowered into the bath.

Procedure.—About 225 g. of pure benzene was siphoned into each cell. A salt–ice bath was used to freeze approximately 75 g. of solid benzene in each cell. The cells were clamped in the Dewar tubes, lowered into the thermostat and stirring was begun. A very slow stream of dry air was passed into the cells to exclude moisture. It was found that, in order to compensate for the heat introduced by the stirring, the constant temperature bath required to be set at 4.20°.

The temperature difference between the two cells was observed by means of a 36-junction copper–constantan thermocouple. When a steady state had been maintained for half an hour, the system was assumed to be in equilibrium. The temperature change during this equilibrium period was less than 3×10^{-6} degree.

The solute, which had been compressed into pellets weighing between 35 and 45 mg., was added to one cell from a weighing tube. About twenty minutes were required to reëstablish equilibrium conditions. A second and larger sample was then added to obtain a concentration sufficiently high to allow accurate analysis. It was found that the greatest accuracy in results was obtained by determining only two points, one relatively dilute, the other about 0.02 *N*. When a final equilibrium was established, two samples of the solution were withdrawn for analysis. Special fused quartz pipets are best used for this purpose.

III. Results

The data for tri-*n*-butylammonium picrate are presented in Table I. The concentrations, *N*, expressed in moles per 1000 g. of solvent, and the corresponding observed temperature lowerings are listed in columns 1 and 2, respectively. In column 3 is given the ratio of observed temperature lowering to that of an ideal solute at the same concentration. The values for the *h*-function, which is given by the equation $h = j/(1 - 2j^2)$, are listed in column 4. *j* is the Lewis and Randall *j*-function ($j = 1 - \Delta T/\Delta T_0$). The last column shows the computed values of k_4, the dipole–quadrupole equilibrium constant.

In Tables II and III are presented the results of measurements with tri-*n*-butylammonium iodide and tetrabutylammonium perchlorate.

The freezing-point constant for benzene was taken as 5.070° per mole per 1000 g. of solvent. This is an average of the values determined by Batson and Kraus[4] and Kraus and Vingee.[3]

Table I

Freezing-Point Data for Tributylammonium Picrate Solutions in Benzene

$N \times 10^3$	$\Delta T \times 10^3$	$\Delta T/\Delta T_0$	h	k_4
1.293	6.428	0.9806	0.0210	...
1.889	9.484	.9903	.0101	...
3.048	15.024	.9722	.0299	0.091
4.116	20.130	.9646	.0381	.096
5.291	25.656	.9564	.0523	.091
8.067	38.816	.9480	.0632	.114
8.955	42.970	.9464	.0672	.119
11.200	52.374	.9223	.1089	.092
11.838	55.935	.9303	.0941	.113
13.747	63.107	.9054	.1437	.086
15.312	69.868	.9000	.1563	.088
16.813	76.444	.8968	.1639	.092
17.168	77.662	.8922	.1752	.088
18.384	83.173	.8924	.1750	.094

Table II

Freezing-Point Data for Tributylammonium Iodide Solutions in Benzene (Formula Weight, 313.15)

$N \times 10^3$	$\Delta T \times 10^3$	$\Delta T/\Delta T_0$	h	k_4	Mol. wt.
0.818	3.74	0.0123	0.1521	4.8	347.3
1.511	6.75	.8811	.2047	6.6	355.6
2.250	9.94	.8718	.2315	8.7	359.4
3.815	15.84	.8189	.4451	7.7	382.4
4.225	17.56	.8200	.4410	8.6	382.0
6.933	26.82	.7630	.8566	6.2	410.5
8.276	31.25	.7449	1.063	6.9	420.5
10.495	38.10	.7160	1.522	6.1	437.3
13.57	46.81	.6803	2.458	4.9	460.4
17.93	59.22	.6516	3.790	4.2	480.6
19.72	62.84	.6287	5.604	3.1	498.2

Table III

Freezing-Point Data for Tetra-*n*-butylammonium Perchlorate Solutions in Benzene (Formula Weight, 341.78)

$N \times 10^3$	$\Delta T \times 10^3$	$\Delta T/\Delta T_0$	Mol. wt.
1.09	1.84	0.333	1029
4.34	5.35	.243	1404
9.62	9.82	.202	1696
14.23	12.00	.166	2052

IV. Discussion

The reproducibility of the measurements with a normal solute was used to establish the accuracy of the results. In the case of thirteen separate determinations on triphenylmethane at sixteen different concentrations between 0.0008 and 0.02 normal, there were no deviations greater than 0.6% and in only three cases did the error exceed 0.2%. The values at the low concentrations, with one exception, showed as good agreement as those at higher concentrations. It may be safely assumed that the measurements are reliable to 0.2%. The mean deviation could be lessened by lowering the constant 0.1%, but since this lies within the experimental error, it seemed best to assume values as previously determined until more precise data are available.

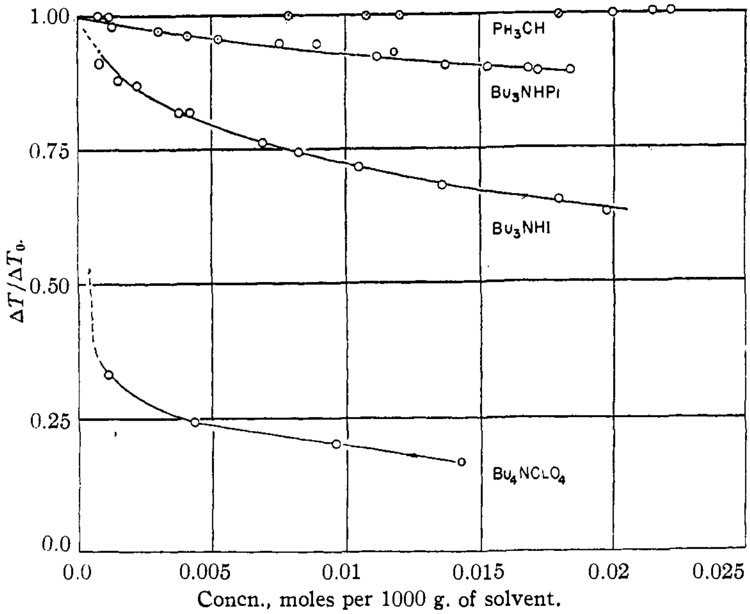

Fig. 1.—Freezing-point curves.

The data in the tables are plotted in Fig. 1. The $\Delta T/\Delta T_0$ ratios are plotted against molal concentrations. The horizontal line at the ratio value of unity is for normal substances. The values obtained for triphenylmethane, only a few of which are plotted, lie on this line within experimental error. The curves for the electrolytes deviate from the normal at higher concentrations, but as the concentration diminishes, the values tend toward unity. It has been shown by conductance measurements in benzene,[8,6] where the potential energy between ions is much greater than kT, that the relative number of simple ions is negligible for the concentration with which we are dealing. Consequently, the depression of the freezing point depends upon the number of unassociated dipoles and the number of higher complexes formed by combination of dipoles. The simplest case is that of an equilibrium between dipoles and quadrupoles, in which instance the curve has a simple form and the dissociation constant may be calculated. When the dipoles unite to form higher complexes than quadrupoles, there is no simple relationship by means of which an association constant may be determined.

Tributylammonium picrate exhibits the least association of the three electrolytes. This dipole has two unsymmetrical ions and should behave similarly to triisoamylammonium picrate for which data were obtained by Batson and Kraus.[4] Salts of this type follow a mass action relation for a dipole-quadrupole equilibrium. Fuoss and Kraus[9] have shown that for salts having such an equilibrium, the h-concentration plot should be a straight line. The slope of this line offers a direct means of obtaining k_4, the dipole-quadrupole equilibrium constant. Curve I of Fig. 2 is a plot of the h-function for tributylammonium picrate against molal concentration. The slope of the best straight line through the experimental points is 9.6. The equilibrium constant for the dissociation of quadrupoles to dipoles is $k_4 = 0.895/9.6 = 0.093$, where 0.895 is the density of benzene. The values of k_4, computed for each point, are given in Table I. The results are satisfactory since a small error in the measured

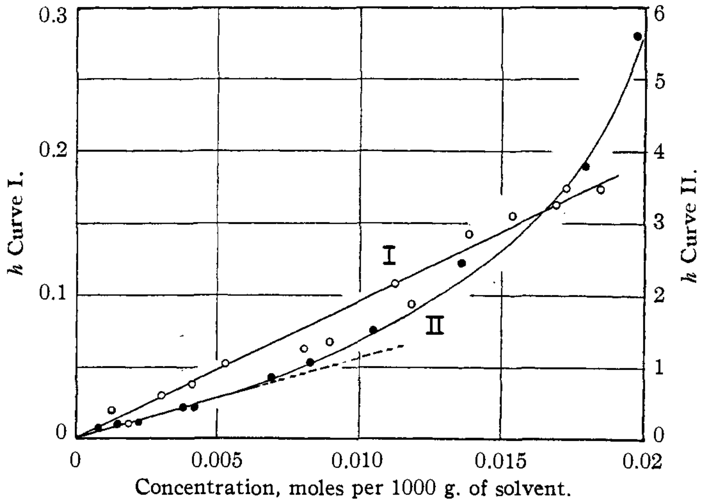

Fig. 2.—h-Curves: I, ○, tributylammonium picrate; II, ●, tributylammonium iodide.

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(8) Fuoss and Kraus, THIS JOURNAL, 55, 2387 (1933).

(9) Fuoss and Kraus, *ibid.*, 57, 1 (1935).

quantities is magnified many fold in the deviation function.

The diameter of the minor axis of the ellipsoidal model of this dipole may be calculated by the method of Fuoss and Kraus.[9] The slope of the h-curve is used to obtain an accurate value for the limiting tangent of the osmotic equation. For this calculation, the axial ratio is assumed to be one half ($\lambda = 1/2$). Using the value of polar moment obtained by Geddes and Kraus[5] ($\mu = 13.1 \times 10^{-18}$), we obtain 5.59 Å. as the value of the minor diameter, which is in good agreement with the value ($\lambda a = 5.02$ Å.) obtained from the polarization measurements.

Tributylammonium iodide is an ionic dipole molecule possessing a symmetrical negative ion and, therefore, according to the view of Batson and Kraus, it should associate to a greater extent than the corresponding picrate. In Fig. 1 the experimental curve for the iodide is seen to lie considerably below that of tributylammonium picrate.

Geddes and Kraus[5] found that the polarization of this compound is practically independent of concentration below 0.001 N, the upper concentration limit of their measurements. Since the freezing-point results show definitely that association occurs, we must assume that the quadrupoles and higher complexes are formed in such a way that the polarization remains constant. This condition is possible if the dipoles associate to form an equal number of quadrupoles joined in a parallel and anti-parallel position; that is, the number of quadrupoles having an enhanced moment just equals the number having zero moment so that the polarization remains constant. If this condition obtains, we should be able to determine, by use of the h-function, an equilibrium constant which is a mean constant for the two types of dipole–quadrupole equilibria. Curve II of Fig. 2 shows the plot of the h-function for tributylammonium iodide. It is observed that above 0.004 N the curve begins to deviate rapidly from a straight line. This may be ascribed to the formation of higher complexes among the various molecular species present as the concentration increases. For example, the formation of octopoles which have zero moment seems not unlikely. In the light of the above results, it seems probable that if polarization measurements were carried to higher concentrations, the values would decrease due to the presence of the large groups with zero moment.

The slope of the h-curve for the lower concentrations is 112. This gives a mean quadrupole dissociation constant of $k_4 = 0.0080$. The values given in Table II for k_4 are in fair agreement with this for concentrations below 0.004 N. In the case of a dipole which associates in two ways, the general theory is not adequate to account for the molecular interaction. However, an approximation of the minor diameter of the dipoles in the anti-parallel configuration may be made, if we assume that the dissociation constants for the two types of quadrupoles are equal. In this event, the constant for the anti-parallel quadrupole dissociation is 0.016 or twice that of the mean dissociation constant. Using this value of k_4, we obtain a value of 3.69 Å. for the minor diameter. This is a reasonable value, but may not be considered as rigorous since the assumed model is only a rough approximation. It seems probable that this type of dipole is better represented by an ovoid than an ellipsoid.

Tetrabutylammonium perchlorate is an electrolyte having relatively symmetrical ions. The polarization curve for this compound diminishes rapidly as the concentration is increased. This indicates that the dipoles must be building up in some manner to lower the total moment. The results of freezing-point measurements show a marked association even at 0.001 N. At 0.014 N (the limit of solubility), the apparent molecular weight is six times the formula weight. This means that, on the average, six dipoles are associated into one aggregate. This type of association, which has been observed also in the case of thiocyanates, obviously does not follow any sort of simple mass action relation. The conductance of tetrabutylammonium perchlorate in benzene has been measured in this Laboratory;[7] it exhibits a conductance curve where the rise in conductance, after passing the minimum at a concentration of 10^{-5} N, is very gradual up to 10^{-3} N, after which the conductance increases rapidly. These results support one another and bear out the view of Batson and Kraus concerning the dependence of association of ion pairs upon the configuration of their constituent ions.

V. Summary

Some improvements in the apparatus for determining the freezing points of dilute solutions are described.

The $\Delta T/\Delta T_0$-concentration curves were determined for tributylammonium picrate, tributylammonium iodide and tetrabutylammonium perchlorate in the concentration range of 0.001 to 0.02 N. All three electrolytes exhibit marked association. The results for tributylammonium picrate are in accord with a mass action equilibrium between dipoles and quadrupoles over the entire concentration range measured. At lower concentrations, the results for tributylammonium iodide are in accord with a dipole–quadrupole equilibrium, but, at higher concentration, more complex structures are formed. To account for the polarization curve of the iodide, two types of quadrupoles must be assumed to be formed. In the case of the perchlorate, highly complex structures are formed even at low concentrations.

PROVIDENCE, R. I. RECEIVED JUNE 29, 1937

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Electrical Properties of Solids. I. Experimental Methods

BY RAYMOND M. FUOSS

I. Introduction

Recent technical developments in the synthesis of high polymer plastics have opened a new field for investigation, that of the electrical properties of amorphous solids. At the present time, their behavior in a. c. and d. c. fields is not understood because very little reliable experimental work is available. One serious source of error is due to the obvious fact that the sample does not make molecular contact with the electrodes. In this paper it will be shown that the error due to series air film capacity between electrodes and sample may be eliminated by extrapolation to infinite thickness and results on two amorphous solids, fused quartz and Pyrex glass, will be given to illustrate the method.

II. Apparatus and Materials.—The Schering bridge[1] has unfortunately been neglected as a tool in physical chemical research. It furnishes a reliable means of obtaining accurate values for both dielectric constant and conductance, when at least half of the current is carried capacitatively.

The bridge is shown schematically in Fig. 1. S is a guarded air capacitor whose nominal value is 100 $\mu\mu$f. R_3 and R_4 are decade resistance boxes (0 to 10,000 in 0.1 Ω steps) whose quadrature terms are negligible in the frequency range used. C_3 is a fixed 1000 $\mu\mu$f condenser and C_4 is a decade capacity 0–1000 $\mu\mu$f plus a vernier capacity 0.3–2.0 mμf. When tan δ is so small that less than 0.3 mμf would be required in the 4-arm for balance, C_3 is thrown parallel to R_3 in order to increase the value of C_4 to a readable figure. F is a variable resistance in the guard line (to be described later) which may be substituted for R_3 by a selector switch to the amplifier as shown. The latter has three stages; the input is filtered. The bridge voltage is supplied by a set of alternators and transformers which cover the ranges 15–500 cycles at 10–25,000 volts and 500–2000 cycles at 10–10,000 volts.

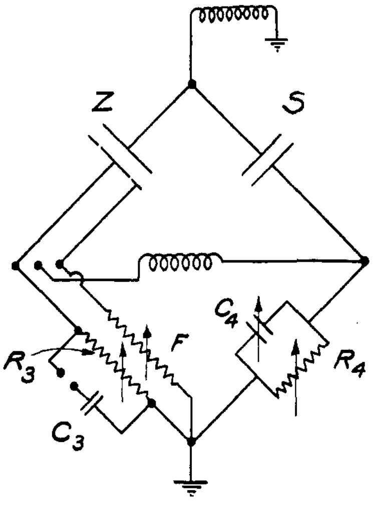

Fig. 1.—The Schering bridge.

The cells are shown in simplified cross section in Fig. 2. The test electrode T is 2.999_0 in. (7.617 cm.) in diameter and the guard ring G is 3.040 in. (7.722 cm.) inside and 4.000 in. (10.16 cm.) outside diameter. The two are mounted rigidly on a mycalex plate 0.5 in. (1.27 cm.) thick. The high potential electrode H and both T and G are hollow, to permit the circulation of oil pumped from a thermostat. In order to prevent temperature gradients in the oil line, due to dif-

[1] Hague, "Alternating Current Bridge Methods," Pitman, London, 1932, pp. 241 ff.