between the nitrobenzene dipole, with its negatively charged protuberance, and the tetrahedral cation does not seem unreasonable. But apparently a $Bu_4N^+\cdot(^-O_2N^+C_6H_5)\cdot Br^-(^+HO^-CH_3)$ structure is stable, while the cation–nitrobenzene grouping alone is not, because nothing unusual appears in the $\Lambda_0\eta$–x_1 curve at the methanol-rich end. It will be noted that the rise in K on the addition of methanol to nitrobenzene is gradual, as contrasted to the abrupt rise at the other end. The variation of equivalent ion size with solvent composition in an approximately isodielectric mixture can only mean that we should consider short range interaction between solvent and solute, in which the detailed structure of both must be taken into account. Again, we realize that further work with systematically varied solvent and solute geometries will be necessary to clarify some of the puzzles suggested by this work. In any case, it is significant to note that tetrabutylammonium bromide is a much stronger electrolyte in mixtures of nitrobenzene and methanol than it is in either solvent alone. The conclusion that interaction between anions and methanol on the one hand and between cations and nitrobenzene on the other, seems inescapable.

Acknowledgments.—We wish to express our gratitude to the Egyptian Government for the grant of a stipend which made this work possible. Thanks are also due to D. Edelson for measurements of the dielectric constants and to W. N. Maclay for the determinations of the viscosities herewith reported.

Summary

1. Densities, light absorption (λ 4000–4600), viscosities and dielectric constants of methanol–nitrobenzene mixtures have been determined at 25°.

2. The conductance of tetrabutylammonium bromide in these mixtures has been measured at concentrations below 0.001 N. Dissociation constants and limiting conductances were obtained by extrapolation to zero concentration.

3. Tetrabutylammonium bromide is a much stronger electrolyte in methanol–nitrobenzene mixtures than in either solvent alone. The mobility is markedly decreased by addition of methanol to nitrobenzene and the dissociation constant is abruptly increased by addition of nitrobenzene to methanol.

4. Neither hydrodynamic nor electrostatic properties of the electrolyte in the mixtures can be described by means of a continuum theory; rather, specific interaction, presumably determined by structural details of both solvent and solute, must be involved.

NEW HAVEN, CONNECTICUT RECEIVED AUGUST 3, 1949

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

A Contrast between Polyelectrolytes[1] and Simple Electrolytes[2]

BY DAVID EDELSON AND RAYMOND M. FUOSS*

Introduction

Concentrated solutions of simple electrolytes such as sodium chloride are characterized, from the theoretical point of view, by the large fluctuations in charge density which occur in the neighborhood of a given test ion. As a consequence, it is impossible to describe the behavior of such solutions in terms of a time average potential of an ionic atmosphere; the latter simply does not exist. It is the purpose of this paper to present some experimental data on solutions of another type of electrolyte, in which the local charge distribution resembles that in a concentrated solution of a one–one electrolyte, *regardless of the stoichiometric concentration of the salts in question.*

Chain polymers, such as polystyrene, in which some hundreds or thousands of atoms are held by primary valence bonds into single molecules, are quite familiar. Flory[3] has called attention to the fact that locally no dilute solution of a polymer exists, in the sense that a small exploring element of volume will either contain pure solvent or else concentrated polymer solution, depending on whether the element is "far" from a polymer molecule or "near" one. If an electrolyte with a skeleton structure similar to polystyrene is considered, we see that an analogous situation must obtain. If, for example, alkyl halide is added to polyvinylpyridine, we have a macromolecule in which every other carbon atom of a long chain carries a positive pyridonium ion; it is at once realized that these charges in the polycation can diffuse no farther apart than would correspond to maximum extension of the carbon backbone of the molecule, no matter how dilute the solution may be in terms of grams per unit volume. As a consequence of the high positive charge density localized in the polycation, we would expect a relatively large number of anions to accompany the polymeric ion, much as gegen ions accompany a protein molecule or soap micelle—with the important difference, however, that the gegen ions in the present case can diffuse into and through the coil of the poly-

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* Harvard College B.S. 1925.

[1] Project NR 054-002 of the Office of Naval Research.

[2] Presented at the 116th meeting of the American Chemical Society at Atlantic City, September 20, 1949, Symposium on Concentrated Electrolytes and Fused Salts.

[3] P. J. Flory, *J. Chem. Phys.*, **13** 453 (1945).

mer, which is a flexible unit with no fixed geometry. This association of charges of opposite sign will occur even in solvents of high dielectric constant, because the coulomb potential energy will be large compared to kT for at least $Z/2$ gegen ions, if Z is the degree of polymerization. In the space in the solvent between polyion clusters, only gegen ions will be found. In other words, the microscopic inhomogeneity in a dilute solution of polyelectrolyte appears at dimensions large compared to the size of ordinary ions; over regions of some hundreds of ångström units, we have structures which approximate droplets of concentrated solution, while between them are regions sparsely populated with ions of charge opposite to that on the polyion.

Suppose we consider a solution of polyelectrolyte of such a concentration that the spheres representing the space occupied by polycation coils begin to overlap. Then a given gegen ion will always be near a positive charge and we might expect some parallels between the behavior of this solution of polyelectrolyte and that of a solution of a simple electrolyte at an equivalent concentration where we have the *same number of ions per unit volume*. Below are presented data which verify this expectation in a qualitative way at least.

Experimental

Poly-4-vinyl-N-*n*-butylpyridonium bromide was prepared by heating 25.5 g. (0.24 monomole) of polyvinylpyridine with 75 cc. (0.71 mole) *n*-butyl bromide in 400 cc. of nitromethane at 60° for four days. The polyvinylpyridine was sample 422, prepared by Dr. U. P. Strauss[4]; it had an intrinsic viscosity of 1.64 in ethanol and a number-average (osmometer) molecular weight of 195,000, corresponding to $Z = 1860$. Excess butyl bromide and solvent were removed by vacuum evaporation; the residue was dissolved in ethanol and the polyelectrolyte was precipitated as a light tan powder by addition of dioxane. After vacuum drying, potentiometric titration gave 31.23% Br^-, *vs.* 32.86% calculated for $(CH_2CHC_5NC_4H_9Br)_\infty$.

Sodium polyacrylate solution was prepared by adding a stoichiometric equivalent of sodium hydroxide to a sample of aqueous polyacrylic acid (16% solids). The polyacrylic acid solution, as received, assayed 1.898 ± 0.017 monomoles of acid per kilogram, based on titration of a (quantitatively) diluted sample with standard caustic, using phenolphthalein as indicator. The stock solution used in our conductance work was 0.287 *N*; more dilute solutions were prepared by weight.

Conductance measurements were made at 25.00° in cells which consisted of two 1 × 8 cm. vertical tubes connected at the bottom by a tube of small bore (cell 1, 9 × 0.1 cm. connector; cell 2, 7.5 × 0.3 cm. connector). Platinum electrodes 8 × 12 mm. were dipped into the vertical tubes; since most of the resistance was concentrated into the connecting tube, the location of the electrodes and the depth of filling made very little difference (0.1 and 0.5% maximum for cells 1 and 2, respectively) in the cell resistance. The cells were standardized by comparison against a cell with constant $K = 2.5144$; for cell 1, $K = 451.6$, and for cell 2, $K = 79.91$. The electrodes were lightly platinized. Measurements were made at 2000 cycles on a bridge similar to that described by Shedlovsky.[5]

Viscosities were measured in a Bingham[6] viscometer at several rates of shear. The viscometer constant $(pt)_0$ for water at 25°, with pressure p in g./sq. cm. and t in seconds was 3210.

Results

The conductance data are given in Table I for the polybromide and the polyacrylate; for comparison, several solutions of sodium bromide in the same range of concentration were also measured. Solvent correction amounted to 1.5% for the most dilute solution and only 0.03% in the most concentrated. Equivalent conductances Λ for the polyelectrolytes were calculated on a stoichiometric monomole basis; *i. e.*, for the polybromide, the corrected specific conductance (times 1000) was divided by the number of equivalents c of bromide per liter. Densities are also given in Table I. As seen from Table II, the viscosities are non-Newtonian, especially for the polyacrylate. The average velocity gradients β were calculated by Kroepelin's[7] formula

$$\beta = 8V/3\pi r^3 t$$

where V is the volume flowing through a capillary of radius r in t seconds. The apparent relative viscosities of Table II were obtained by dividing the observed pt products by 3210, the corresponding value for water.

TABLE I

CONDUCTANCE OF SALTS IN WATER AT 25°

c	ρ	Λ	c	ρ	Λ
Poly-4-vinyl-N-*n*-butylpyridonium Bromide					
0.2737	1.0167	24.44	0.01776	....	40.17
.1126	....	29.25			
.08721	....	30.71	.01630	....	40.54
.06571	....	32.25	.01231	0.9981	42.22
.04948	1.0007	34.09	.01076	....	42.75
.04241	....	34.97	.006946	....	44.77
.02742	....	37.58	.003954	....	46.92
Sodium Polyacrylate					
0.2873	1.0138	34.69	0.03919	....	36.37
.1257	....	36.40	.02620	....	36.73
.05780	....	36.25	.01551	0.9979	37.07
.04722	0.9997	36.93			
Sodium Bromide					
2.124	1.1615	78.06	0.4066	1.0291	99.2
1.029	1.0778	89.59	.2326	1.0155	104.2

TABLE II

VISCOSITIES OF POLYELECTROLYTES IN WATER AT 25°

Polybromide						Polyacrylate[a]	
$c = 0.2737$		$c = 0.04948$		$c = 0.01231$		$c = 0.04422$	
β	η_r	β	η_r	β	η_r	β	η_r
1573	7.963	3717	2.857	3070	1.868	675	19.52
1177	7.963	2566	2.836	2401	1.871	474	21.48
752	7.968	1651	2.834	1792	1.872	271	24.55
352	7.986	530	2.844	771	1.888		

[a] At $c = 0.2873$, $\beta = 51.7$, $\eta_r = 231$.

Discussion

The parent polymer from which the polybromide was prepared has a number average molec-

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(4) U. P. Strauss and R. M. Fuoss, *J. Polymer Sci.*, **4**, 457 (1949).

(5) T. Shedlovsky, THIS JOURNAL, **52**, 1793 (1930).

(6) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, N. Y., 1922, p. 76.

(7) H. Kroepelin, *Kolloid Z.*, **47**, 294 (1929).

ular weight of 195,000, corresponding to an average of about 2000 vinylpyridine units or 4000 carbon atoms per chain. Neglecting steric effects, the mean square diameter R of the random coil[8] representing the molecule will be

$$R = \left(\frac{1+p}{1-p}\,Na^2\right)^{1/2} = 138\ \text{Å}.$$

where p is $^1/_3$, the cosine of the normal angle between carbon atoms, N is 4000 and a is 1.54×10^{-8} cm., the C–C distance. A liter would contain 0.38×10^{21} cubes R on a side a with 2000 monomer units per polymer molecule, a solution 1.24 normal (on a monomole basis) would then be the order of concentration at which ideal 2000-mers would begin to overlap. Actually, the concentration at which our polyvinylpyridine coils would begin to interfere with each other would be lower than this, because the bulk of the pyridine units will cause the coil to open to a larger structure than that corresponding to the idealized model.

A considerably better estimate of the size of the parent polymer can be obtained from its intrinsic viscosity $[\eta]$, which, according to Debye[9] is a measure of the specific volume of the polymer in solution. We found $[\eta] = 1.64$, and 0.025 is the intrinsic viscosity in the same units for a suspension of Einstein spheres[10]; consequently 1.64/0.025 gives 65.6 cc./g. as the specific volume. Multiplying by the molecular weight of the monomer, this corresponds to 6.90 l./mole, or a 0.145 normal solution. The cubical cell available per polymer molecule is 282 Å. on a side, or about twice that for the ideal model.

When butyl bromide is added to polyvinylpyridine, the coil will expand still more; first, because the butyl groups obviously require space, and second, because electrostatic repulsion between the positively charged pyridonium nitrogens will favor more open configurations. Part of the latter term will be neutralized by the presence of bromide ions within the coil of the polymer. In order of magnitude, therefore, we might expect in solutions in the range of 0.01 normal and higher that polycation coils of different ions would be so close together that there would be no "empty" solvent between them. In other words, a bromide ion would always be near a positive charge, and approximately at the same order of distances as in a solution of sodium bromide of the same stoichiometric concentration. Indeed, the only difference (microscopically) between a 0.1 normal solution of sodium bromide and a 0.1 normal solution of polypyridonium bromide would be that the relative motion of the cations in the latter is restricted mechanically, while in the former, they are free-swimming entities like the anions. The anions in both solutions ought to behave much the same, except that motion of the anions in the polymeric solution would be somewhat hampered by the polymer chains which coil through the solvent through which the ions must migrate. The diffuse cation would presumably have a low mobility because it is spread out and would require many simultaneous coincidences to move in an electrical field; we therefore are tempted to assume that the transference number of the cation is nearly zero and that the observed conductance is primarily that due to the bromide ions. The fact that the equivalent conductances are so high, despite the high (macroscopic) viscosities of the solutions, lends reassuring support to this assumption.

Now the above argument may be repeated, with the roles of anion and cation reversed for solutions of sodium polyacrylate; we are led to the hypothesis that, in this range of concentration, the conductance is due mostly to the cations, which behave approximately like sodium ions in a one–one electrolyte of the same concentration.

Figure 1 is a test of these hypotheses. The top curve (1) is the conductance curve of sodium bromide[11] and the lower two (3, 4) those of the two polyelectrolytes investigated. Curve 2 is the sum of curves 3 and 4, and according to the arguments presented above, should represent the conductance of sodium bromide in an aqueous medium containing an organic solute which partially blocks the motion of the ions. It will be seen that curve 2 is nearly parallel to curve 1, over the observed range, differing from it by a factor of two, which seems reasonable for the relative (microscopic) viscosity of the polymer medium with respect to water.

In Fig. 2, the change of the product of equivalent conductance and viscosity is shown as a function of concentration for sodium bromide and for the polybromide. For the former, we find a typical pattern: a small decrease at low concentrations due to the relatively rapid decrease of equivalent conductance with increasing concentration, followed by an increase, as the viscosity increase gains control. The total change of $\Lambda\eta$ in this range of concentration, however, only amounts to about 10%. The situation in the case of the polybromide is strikingly different; here, the $\Lambda\eta$ product increases rapidly with increasing concentration over the accessible range. This effect is due to the very rapid increase of macroscopic viscosity η with increasing concentration; as we have already mentioned, the viscosity measured in a capillary viscometer does not seem to be the proper figure to use as a measure of the hydrodynamic resistance which a small ion encounters in moving through a solvent medium which is essentially a tangle of polymer chains (of molecular dimensions in cross section) suspended in water. For the small ion, the local motion of segments of the chains is hydrodynamically significant, while the whole aggregate is determinative for the behavior

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(8) W. Kuhn, *Kolloid Z.*, **68**, 2 (1934).

(9) P. Debye, letter quoted by L. H. Cragg, *J. Colloid Sci.*, **1**, 465 (1946).

(10) A. Einstein, *Ann. Physik*, **19**, 289 (1906); correction, *ibid.*, **34**, 591 (1911).

(11) "International Critical Tables," Vol. VI, p. 235.

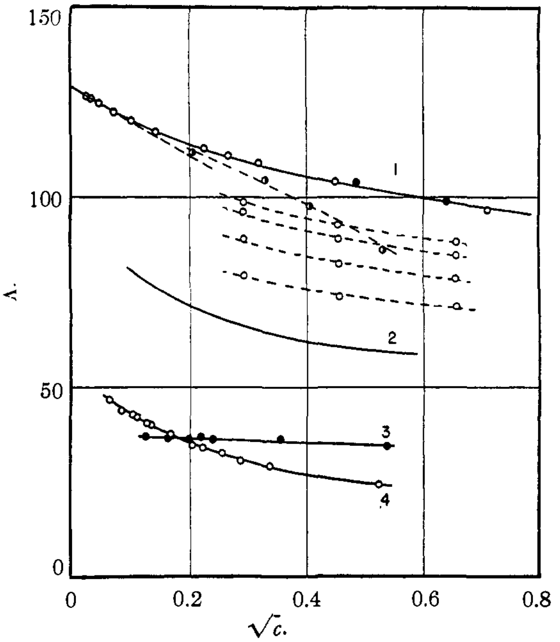

Fig. 1.—Conductance curves: 1, sodium bromide, solid circles from Table I, open circles, "I. C. T.," Vol. VI, p. 235; 2, sum of 3 and 4; 3, sodium polyacrylate; 4, polybromide; dotted curves, sodium bromide in polyvinyl alcohol solutions.

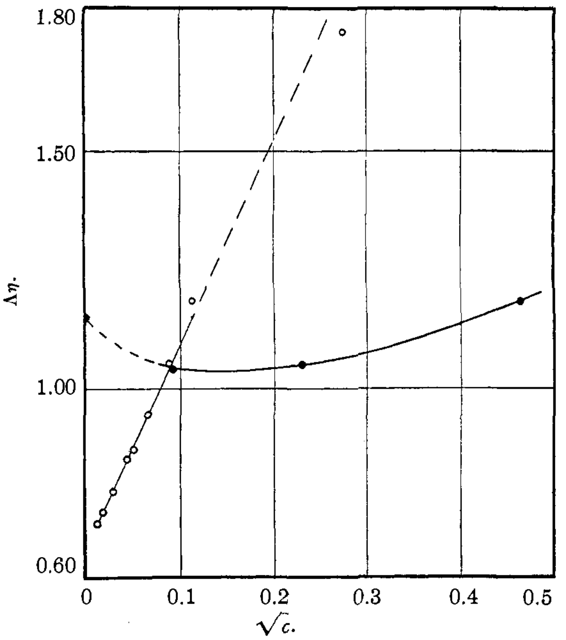

Fig. 2.—Change of $\Lambda\eta$ with concentration: open circles, polybromide; solid circles, sodium bromide, ("I. C. T.," Vol. VI, p. 235 and Vol. V, p. 15). Viscosity in centipoises in ordinate scale.

of the solution in the viscometer. Figure 2 thus lends support to the suggestion that most of the conductance in this range of concentration is due to the bromide ions.

The hypothesis that the presence of chain molecules in solution does not decrease the mobility of small ions in anything like the degree to which they increase the macroscopic viscosity may be tested experimentally by measuring the conductance of a simple electrolyte in the presence of a neutral chain electrolyte. The data shown as dotted curves in Fig. 1 are conductance curves for sodium bromide in various solutions of polyvinyl alcohol (Elvanol 71–24). The half black points give the conductance curve which is obtained when a 0.2881 *N* solution of sodium bromide in a polyvinyl alcohol solution with relative viscosity 12.9 is diluted; the initial conductance is lower than that of sodium bromide in water at the same concentration, but far above what would be computed on the basis of a constant $\Lambda\eta$ product. On dilution, both conductance and viscosity approach that of sodium bromide in water, as might be expected. The set of four parallel dotted curves are for sodium bromide in aqueous polyvinyl alcohol as solvent, where the concentration of polyvinyl alcohol was kept constant for each curve. The relative viscosities run from 1.2 for the top curve, through 2.0 and 8.0 to 40 for the bottom curve of this set. Again we see that the conductance of the sodium and of the bromide ions is of the same order of magnitude as in pure water for solvent, despite a forty-fold change of bulk viscosity. The gradual decrease of Λ with increasing polyvinyl alcohol content is due to the local interference of *segments* of the polyvinyl alcohol chains with the motion of the ions, while the high bulk viscosity is due to the necessity of moving whole polymer molecules in a viscometer. The dotted curves indeed bear a striking resemblance to curve 2, which, as we mentioned above, represents essentially the conductance of sodium bromide in a medium containing interfering chain molecules. (Numerical data are omitted here; we plan to present a systematic study of this and similar systems containing simple electrolytes and neutral chain molecules in a later paper.)

No attempt has been made to extrapolate the curves for the polyelectrolytes to zero concentration. At any finite concentration, the field around the polyion in any configuration will be so high that some gegen ions will be in the vicinity, and in effect nullify part of the charge of the polyion, as far as interaction with an external field is concerned. In the hypothetical limit of zero concentrations, by definition gegen ions will be at an infinite distance; for this case, we would expect intramolecular repulsion to cause the polyion to extend itself to a rod-like structure and for this, an estimate of limiting conductance can be made. If we represent the polybromide ion by an ellipsoidal rod 5000 Å. long and 10 Å. in diameter, Perrin's formula[12]

$$\frac{D}{D_0} = \frac{\rho^{2/3}}{\sqrt{1-\rho^2}} \ln \frac{1+\sqrt{1-\rho^2}}{\rho} \qquad (1)$$

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(12) F. Perrin, *J. Phys. Radium*, **7**, 1 (1936).

gives the diffusion constant **D** in terms of the axial ratio $\rho = 10/5000$ and $\mathbf{D}_0$, the diffusion constant of the equivalent sphere of radius $a_0 = 5000 \rho^{2/3}/2 \approx 40$ Å. Assuming Stokes' model, we find

$$D_0 = kT/6\pi\eta a_0 = 0.61 \times 10^{-6} \text{ cm.}^2/\text{sec.} \quad (2)$$

using the familiar Einstein relationship between diffusion coefficient and friction coefficient. Substituting numerical values, $\mathbf{D}/\mathbf{D}_0 = 0.110$ and $\mathbf{D} = 6.7 \times 10^{-8}$. The mobility u in c. g. s. units is then

$$u = Q\mathbf{D}/300kT \quad (3)$$

where Q is 2000 times the electron charge and the factor of 300 converts to practical units from e. s. u. For the rod-like model, we have

$$u = 0.0052 \text{ (cm./sec.)/(volt/cm.)}$$

and on multiplying by the faraday

$$\lambda^+ = 500$$

We would accordingly expect a limiting equivalent conductance of the order of 600, *i. e.*, far above the top of the scale of Fig. 1, for the polybromide. As has already been mentioned, however, we do not expect to find even the beginning of the predicted sharp rise in conductance at any experimentally accessible concentration. On the basis of this calculation, a large Wien effect should appear for polyelectrolytes of this type, but for ordinary low voltage conductance, the $\Lambda-\sqrt{c}$ curves experimentally observed will probably seem to approach the limiting conductance of the gegen ion as their limit.

Acknowledgment.—We are grateful to the Minnesota Mining and Manufacturing Company for a sample of polyacrylic acid, and to E. I. du Pont de Nemours and Company for a sample of Elvanol 71-24.

Summary

1. Conductances and viscosities of poly-4-vinyl-N-*n*-butylpyridonium bromide and of sodium polyacrylate in water at 25° in the moderately concentrated range (up to 0.3 normal) have been measured.

2. In the upper part of this range of concentration, interionic distances, both in the polyelectrolyte and in solutions of one-one electrolytes, become of the same order.

3. The experimental results suggest that in the polyelectrolyte gegen ions behave much like the same ions in simple electrolytes, except that their transference number is nearly unity.

NEW HAVEN, CONNECTICUT RECEIVED OCTOBER 29, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Adiabatic Compressibility of Aqueous Solutions of Some Simple Amino Acids and Their Uncharged Isomers at 25°[1]

BY FRANK T. GUCKER, JR.,*[2] FRANK W. LAMB, GLENN A. MARSH AND ROBERT M. HAAG

For a number of years various thermodynamic properties of solutions of simple amino acids and their uncharged isomers have been studied in this Laboratory in order to determine the influence of the dipole moment of the amino acids. We have found that the apparent molal heat capacities and volumes[3,4] and the heats of dilution[5] of glycine and glycolamide, and the apparent molal heat capacities and volumes of *dl*-α-alanine, β-alanine and lactamide,[6] are linear functions of the molality in dilute solutions, and sometimes over a considerable range of concentration. The interpretation of most of these results was discussed[7] on the basis of the theory developed by R. M. Fuoss[8] for the mutual interaction of pairs of spherical solute molecules each containing a central point dipole, as modified by J. G. Kirkwood[9] to take into account the discontinuity of the dielectric constant between the surface of the solute molecule and the solvent. This theory predicts an increase of all of these apparent molal properties which is linear with the concentration in the infinitely dilute solution, and limiting slopes which are proportional to the fourth power of the dipole moment, divided by the molecular volume. Rough agreement with this theory is shown by most of the solutions. A consideration of the energy of charging the dipolar ion also affords an explanation of the limiting value of the apparent molal volumes and heat capacities. The present paper describes the extension of our experimental work to the determination of the compressibility of some of these solutions, which may be given a similar theoretical treatment since the apparent molal compressibility is simply the negative of the pressure coefficient

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* Harvard University Ph.D. 1925.

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(3) F. T. Gucker, Jr., W. L. Ford and C. E. Moser, *J. Phys. Chem.*, **43**, 153 (1939).

(4) F. T. Gucker, Jr., and W. L. Ford, *ibid.*, **45**, 309 (1941).

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(6) F. T. Gucker, Jr., and T. W. Allen, *ibid.*, **64**, 191 (1942)

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(8) R. M. Fuoss, THIS JOURNAL, **58**, 982 (1936).

(9) J. G. Kirkwood, *Chem. Revs.*, **19**, 275 (1936).