[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES OF HARVARD UNIVERSITY]

The Surface Tension of Aqueous Solutions of Dipolar Ions

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I. Problem

It is a commonplace that the surface tension of aqueous solutions of practically all organic compounds is less than that of water, though a curious exception is afforded by certain sugars.[1,2] It was long ago pointed out by Traube[3] that the lowering of surface tension associated with a given molar concentration of the solute increases in a regular way with the number of carbon atoms in the members of a homologous series. On the other hand, the surface tension of solutions of inorganic salts, and indeed of most strong inorganic electrolytes, is greater than that of the solvent. This means of course, in accordance with Gibbs' theorem, that these ions, in contrast to the organic compounds, are negatively adsorbed at the liquid surface.[4]

Now there is a class of organic molecules, most familiarly represented by the amino acids, which exist in solution preponderantly as dipolar ions, or zwitter ions.[5] These dipolar ions are exceptional above all for their extremely large electric moments, which are the basis of much of their behavior. Although they bear no net charge they have affinities with strong electrolytes. In regard to their structure and phenomena associated with solubility, they are susceptible to treatment in accordance with the concepts of the Debye–Hückel theory for strong electrolytes, with some modifications.[6,7] Thus their partial free energy in dilute solution may be shown to be proportional to the first power, and not the square root, of the ionic strength of the medium, as for ordinary ions.[6,7] Clearly these dipolar ions are of interest in the matter of surface tension. This is especially true of the aliphatic amino acids, which, as organic compounds, belong to a well-defined homologous series, while at the same time they are ions of an exceptional class, owing to their zero net charge and extremely large electric moments. By suitable choice from members of this group it is possible on the one hand to try the effect of varying the electric moment without altering the molecule in any other way, as for example when we pass from an α- to a β-form, or on the other hand, keeping the moment constant, to alter the length of the hydrocarbon chain.

There appear to be but two studies in the literature dealing with this question. Jones and Lewis,[8] by means of Sugden's bubble pressure method, showed that the surface tension of aqueous solutions of glycine was somewhat greater than that of pure water and that the surface tension passed through a slight maximum between a *p*H of 4 and 7. Unfortunately their results are only presented in the form of a small scale graph. Errera and Milliau[9] also report that the surface tension of glycine solutions is slightly greater (about 1%) than that of water, but they say that solutions of leucine, alanine, aspartic acid and asparagine are indistinguishable from water. They give no figures. The present paper contains the results of measurements of the surface tension of aqueous solutions of seven amino acids of varying size and moment, and of one other substance, glycine betaine, which is known to be a zwitter ion.

II. Materials and Methods

The amino acids were all obtained from the Laboratory of Physical Chemistry of the Harvard Medical School and all had been purified by recrystallization before measurements were made. Recrystallization of α-aminocaproic acid and β-alanine was especially necessary in order to obtain reproducible results. The betaine was the same preparation, several times recrystallized, which was previously studied by Edsall and Wyman.[10] The importance of careful purification of materials in these studies is very great, since

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(1) Traube, *J. prakt. Chem.*, **31**, 177 (1885).

(2) Clark and Mann, *J. Biol. Chem.*, **52**, 157 (1922).

(3) Traube, *Ann.*, **265**, 27 (1891).

(4) Onsager and Samara, *J. Chem. Phys.*, **2**, 528 (1934), have recently developed a theory first put forward by Wagner, *Physik. Z.*, **25**, 474 (1924), to account for this behavior. In its bare outline the theory is based on the Gibbs adsorption theorem and on the unequal distribution of ions between the interior and the surface of the liquid, calculated, in accordance with Debye's treatment of strong electrolytes, taking account of ionic atmospheres and image charges at the air–liquid interface, from the difference of potential energy between an ion at the surface and one in the interior. Whether or not it is correct in detail, this theory accounts for the increase of surface tension and points to a general method of attack on the problem of the surface tension of strong electrolytes.

(5) For a discussion of dipolar ions, see Cohn, *Ann. Rev. Biochem.*, **4**, 93 (1935).

(6) Scatchard and Kirkwood, *Physik. Z.*, **33**, 297 (1932).

(7) Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

(8) Jones and Lewis, *Biochem. J.*, **26**, 638 (1932).

(9) Errera and Milliau, *J. chim. phys.*, **30**, 726 (1933).

(10) Edsall and Wyman, THIS JOURNAL, **57**, 1964 (1935).

minute traces of surface active impurities may have appreciable effects.

After a preliminary trial with Sugden's method it was decided to use the drop weight method as being simpler and giving more reproducible results.[11] The surface tension of the solutions was calculated from the weights of the drops of solution and of water falling from a given tip by means of the equation

$$\gamma = \frac{w}{w_0}\frac{\psi_0}{\psi}\gamma_0$$

in which γ denotes surface tension, w the weight of a single drop, ψ the corresponding correction factor as given by Harkins and Brown, and the subscript $_0$ refers to water. The surface tension of water was taken as 71.97 at 25°. For any particular case the value of ψ is determined by the ratio of the radius of the tip to the cube root of the volume of the drop, and in order to determine ψ it is therefore necessary to know the density of the liquid. The densities used in the calculation of the values of the surface tension given below were taken directly from the data given by Wyman and McMeekin[12] in the case of glycine and α-aminobutyric acid and were calculated from the partial molal volumes in the other cases—for betaine from the volume given by Edsall and Wyman;[10] otherwise from the figures of Cohn, McMeekin, Edsall and Blanchard.[13] In calculating the density of the solutions of ϵ-aminocaproic acid studied over a wide range of *p*H no attempt was made to distinguish between the isoelectric material and its salts since it was apparent that the effect of this on the values of the surface tension would be less than the experimental error. Indeed the tips were so chosen that ψ was relatively insensitive, and consequently varied but little between pure water and the most concentrated solution—the greatest variation was from 0.6022 to 0.6033, in the case of α-aminobutyric acid.

Three different tips were used, one of monel metal, one of Pyrex, and one of fused quartz. The radii of these were 0.4701 ± 0.0003, 0.476 ± 0.002 and 0.4770 ± 0.0003 cm., respectively. The monel metal and quartz tips were turned or ground so as to be of accurately circular cross section; the Pyrex tip was made from a selected piece of Pyrex rod and was less exact; yet on the whole it gave the best results and was used in the majority of the determinations. The fact that it was less round than the others did not appear to affect the consistency of the results and any possible error in the calculation of the surface tension arising from uncertainty as to the proper value to use for the radius in reckoning the values of ψ was negligible. The monel metal tip was difficult to clean and there was often trouble in getting the liquids to wet the face of the tip. It was found that this tip did better if the face was electrolytically coated with a light deposit of platinum black. It proved difficult to grind the face of the quartz tip sufficiently rough to provide for good wetting without chipping the edges. This problem of ensuring that the drops, particularly the first one, completely wet the tip proved to be the most troublesome feature of the manipulations, more so than that of adjusting the rate of drop formation.

The measurements were all made at 25° and the apparatus containing the liquid was always placed in the thermostat at least fifteen minutes before the first drop was formed in order to make sure of temperature equilibrium.

All hydrogen-ion concentrations were determined with a glass electrode, in connection with a circuit similar to that described by DuBridge and Brown,[14] making use of a type F. P. 54 General Electric tube. The electrode was calibrated with standard buffers before or after measurements.

III. Results

The results obtained on six isoelectric amino acids and on isoelectric betaine, are given below in Table I and are shown graphically in Fig. 1. Except in one case, each point is based on several determinations which agree to about 0.1% or better. It may be seen from Fig. 1 that in every case the relation between surface tension and concentration is linear within the limits of error. At their worst the experimental points depart from the straight lines by slightly more than 0.1%.

Glycine, α-alanine, β-alanine, and β-aminobutyric acids all behave like inorganic salts in that the surface tension of their solutions is greater than that of water. The effect however is less pronounced than in the case of most of the latter substances. Thus even for glycine the increment

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[11] For a discussion of this method see Harkins and Brown, THIS JOURNAL, **38**, 246 (1916), and **41**, 520 (1919).

[12] Wyman and McMeekin, *ibid.*, **55**, 908 (1933).

[13] Cohn, McMeekin, Edsall and Blanchard, *ibid.*, **56**, 784 (1934).

[14] DuBridge and Brown, *Rev. Sci. Instruments*, **4**, 532 (1933).

TABLE I

SURFACE TENSION OF SOLUTIONS OF ISOELECTRIC MATERIALS AT 25°

Concentrations are expressed in moles per liter. Values of $\Delta\gamma/\Delta c$, the increment of surface tension per mole of solute, reckoned from the straight lines in Fig. 1, are given in parentheses after the name of each compound. The surface tension of water is 71.97

Glycine[a] ($\Delta\gamma/\Delta c$ = +0.92)

c	0.502	1.035	1.185	1.360	1.517
γ	72.43	72.86	73.14	73.15	73.47

α-Alanine[b] ($\Delta\gamma/\Delta c$ = +0.58)

c	0.50	1.00	1.39
γ	72.27	72.54	72.79

α-Aminobutyric acid[b] ($\Delta\gamma/\Delta c$ = −0.41)

c	0.38	0.845	1.185	1.245
γ	71.80	71.63	71.49	71.43

α-Aminocaproic acid[b,c] ($\Delta\gamma/\Delta c$ = −23)

c	0.025	0.051
γ	71.23	70.90

Betaine[b] ($\Delta\gamma/\Delta c$ = −0.14)

c	0.44	0.88
γ	71.95	71.79

β-Alanine[b] ($\Delta\gamma/\Delta c$ = +0.77)

c	0.237	0.475	0.949	1.390
γ	72.19	72.36	72.62	72.99

β-Aminobutyric acid[b] ($\Delta\gamma/\Delta c$ = +0.05)

c	0.5	1.0	1.5
γ	72.03	72.04	72.04

ϵ-Aminocaproic acid[b] ($\Delta\gamma/\Delta c$ = −0.25)

c	0.545	0.763	1.09
γ	71.88	71.80	71.66

[a] Measurements with monel metal tip. [b] Measurements with Pyrex tip. [c] Measurements with quartz tip.

of surface tension per mole of solute[15] is but 0.97 as compared with a value of 1.64 for sodium chloride or a value of 3.04 for magnesium chloride, a uni-divalent salt; for β-aminobutyric acid it is but 0.05.

If we compare the four α-amino acids, or the two β-acids, studied, it is clear that increasing the length of the carbon chain when the electric moment is kept constant has the effect of depressing the molar increment of surface tension, as in the case of other homologous series; and the data on the α-acids indicate that the depressing effect of each additional carbon atom increases geometrically, at least approximately so, with the number of atoms introduced, as has been observed in other series more extensively studied.[16] In this connection the behavior of betaine is of interest. Betaine ($(CH_3)_3{}^+NCH_2COO^-$) differs from glycine owing to the substitution of three methyl groups for the three hydrogens attached to the positively charged nitrogen atom. It therefore contains three more CH_2 groups than glycine, and since its electric moment is known to be very nearly if not quite the same as that of α-amino acids,[10] it might be supposed that it would behave like α-aminovaleric acid. Although we have not determined the surface tension–concentration curve for this amino acid, it is safe to predict that it lies between curves of α-aminobutyric and α-aminocaproic acids. Actually the curve for betaine lies well above that for α-aminobutyric acid. The implication of this is that a CH_2 group which is itself a part of the structure of a changed group contributes quite differently to the properties of the molecule than one which belongs to a hydrocarbon residue.

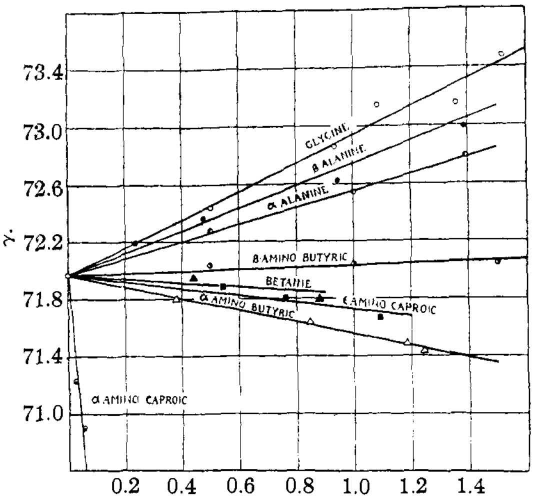

Fig. 1.—Graph of data in Table I.

The effect of increasing the dipole moment without otherwise altering a molecule is to increase the molar increment of surface tension,

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(15) In what follows this quantity is referred to as the molar increment of surface tension, for brevity.

(16) Szgszkowski's data [*Z. physik. Chem.*, **64**, 385 (1908)] on normal fatty acids show that in dilute solutions, where the surface tension may be regarded as linear in the concentration, the molar surface tension increments decrease geometrically with the number of CH_2 groups in the molecule, the ratio for the series being about 3.4. This is equivalent to the statement that the differences, taken as positive, between the molar surface tension increments of successive members of the series increase in the same ratio, 3.4. In the case of the α-amino acids the molar surface tension increments themselves change from positive to negative values so that we must consider the differences. Data for one member of the series, α-aminovaleric acid, are lacking, which leaves only three differences to be considered. These may be fitted moderately well by assuming a ratio of 3.8. If we use a value of 0.30 instead of the observed value of 0.34 for the first difference, we may calculate expected values of the molar surface tension increments as +0.92, +0.62, −0.52, −21.4. These are in fairly good agreement with the values given in Table I.

that is, to rotate the curve counter-clockwise and make the substance behave more like an inorganic salt. This may be seen by comparing the curves for α- and β-alanine, α- and β-aminobutyric acid, or, better still, α- and ε-aminocaproic acid.

In Table II and Fig. 2 are given data showing the change of surface tension with *p*H for a solution of ε-aminocaproic acid containing 0.2431 mole per liter. Figure 2 also contains, in the upper portion, a graph of the titration data obtained incidentally in the course of these measurements. The full curve, with which the experimental points are in fairly good agreement, is calculated from the two *pK* values of 4.43 and 10.75 given for this amino acid by Edsall and Blanchard.[17]

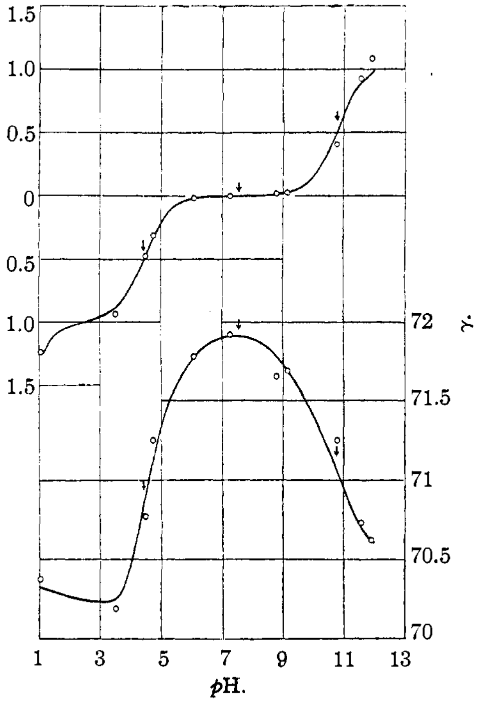

Fig. 2.—Lower curve: Surface tension of a 0.2431 molar solution of ε-aminocaproic acid as a function of *p*H. Upper curve: Titration of ε-aminocaproic acid (0.2431 molar). The ordinates give moles of acid or base per mole amino acid. The smooth curve is based on *pK* values of 4.43 and 10.75. The isoelectric point (7.59) and the *pK* values are indicated by arrows.

TABLE II

SURFACE TENSION OF ε-AMINOCAPROIC ACID SOLUTIONS AS A FUNCTION OF *p*H AT 25°

The total concentration of amino acid is 0.2431 mole per liter throughout. In column 1 the amount of acid or base present is expressed in terms of moles per mole of amino acid.

Amount of acid (−) or base (+)	*p*H	γ
−1.234	1.05	70.38
−0.944	3.52	70.19
− .474	4.50	70.77
− .308	4.74	71.24
− .021	6.07	71.78
0	7.26	71.92
+ .019	8.80	71.65
+ .020	9.16	71.69
+ .405	10.80	71.25
+ .925	11.58	70.73
+1.091	11.90	70.62

The data extend over somewhat more than the full titration range and show that the surface tension is a maximum at or close to the isoelectric point (*p*H = 7.59). There is a marked drop of surface tension with addition of acid or base amounting to about 2.4% when the isolectric material is converted completely into the hydrochloride, and a drop of about 1.7% when it is converted to the sodium salt. This is in general agreement with the results of Jones and Lewis[8] on glycine. As nearly as can be judged from their small scale graph there is roughly a 1% decrease in the surface tension of a 1.5 molar solution when the isoelectric amino acid is converted into the hydrochloride or sodium salt.[18]

This phenomenon is of interest since it shows the effect of the dipole moment as contrasted with the single charge of the anion or cation on the molar increment of surface tension. The increment is greater for the dipolar ion than for the simple ion, the more so for ε-aminocaproic acid where the moment is large than for glycine where it is relatively much smaller. In fact it appears from the figures given above, rough as they are in the case of glycine, that the increase in the surface tension increment of a 1 molar solution due to converting the cation or anion into the dipolar ion is about six times as great for ε-aminocaproic acid as for glycine. It is worth bearing in mind here the great size of the moments involved. Thus the moment of glycine has been estimated as in the neighborhood of 15×10^{-18} e. s. u. That of the caproic acid is much larger.[5]

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(17) Edsall and Blanchard, THIS JOURNAL, **55**, 2337 (1933).

(18) Jones and Lewis [*Biochem. J.*, **26**, 632 (1932)] have shown that the surface tension of dispersions of lecithin in water, though less than that of water, is a maximum at *p*H = 2.8. This is close to the estimated isoelectric point of lecithin, which presumably exists as a dipolar ion. The surface tension of solutions of proteins and peptones is less than that of water, but there is disagreement among observers as to whether it is a maximum or a minimum at the isoelectric point. See Johnston, *ibid.*, **21**, 1314 (1927); Botazzi, in Alexander, "Colloid Chemistry," D. Van Nostrand Co., New York, 1919, Chap. VII; Berczeller, *Biochem. Z.*, **53**, 215 (1913); Errera and Milliau;[9] Loebel, *J. Phys. Chem.*, **32**, 763 (1928); Artom, *Arch. Sci. Biol.* (Ital.), **14**, 327 (1930).

It is striking that the molar increment of surface tension of the hydrochloride or sodium salt of ϵ-aminocaproic acid is very much less negative than that of isoelectric α-aminocaproic acid and therefore *a fortiori* presumably less negative than that of its salts. This is an illustration of the fact pointed out by Cohn[5] on the basis of a systematic study of solubilities that the effect of a CH_2 group situated between polar groups (whether or not they bear a free charge) is different from that of one located in a hydrocarbon residue in the molecule.

As a result of the application of a new and exceedingly accurate method of measuring surface tension Jones and Ray[19] report a very curious phenomenon shown by aqueous solutions of inorganic salts. The surface tension–concentration curves, which are linear at ordinary concentrations, do not continue straight back to the ordinate axis, but dip down so as to show negative surface tension increments when the solutions are very dilute. It would be of importance in any theoretical interpretation of surface tension to know whether or not dipolar ions behave in the same way, and it is hoped in the future to study the problem by this more accurate method.

Summary

Measurements of the surface tension of aqueous solutions of seven amino acids of differing size and moment and of glycine betaine have been made with the drop weight method. In the case of four of the amino acids the surface tension is greater than that of water; in the other cases it is less. In these dipolar ions there appears to be an antagonism between the effect of the electric moment which tends to increase the surface tension, and the size and number of organic groups in the molecule which tend to lower it. The effect of converting an amino acid into its hydrochloride or its sodium salt is to lower the surface tension of the solution.

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[19] Jones and Ray, THIS JOURNAL, **57**, 957 (1935).

The Electromotive Force of the Cell Zn-Hg (2 phase) | $ZnSO_4$ (m) $PbSO_4$ (s) | Pb-Hg (2 phase) and its Temperature Coefficient at 25° and Concentrations from 0.05 to 1.5 Molal[1]

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Determinations of the e. m. f. of the cell

$$\text{Zn-Hg (2 phase)} \mid ZnSO_4\ (m)\ PbSO_4\ (s) \mid \text{Pb-Hg (2 phase)} \qquad (1)$$

corresponding to the chemical reaction

$$\text{Zn (satd. amalg.)} + PbSO_4\ (s) = ZnSO_4\ (m) + \text{Pb (satd. amalg.)} \qquad (2)$$

have been reported by Bray[3] at 25° for molalities from 0.0005 to 3.5, and by Cowperthwaite and La Mer[4] at 0, 12.5, 25, 37.5 and 50° for molalities from 0.0005 to 0.01, also 0.02 and 0.05 molal at 0, 25 and 50°.

In the present paper are given some e. m. f. measurements on cell (1) for the molalities 0.0512, 0.150, 0.510 and 1.501 at the temperatures 15, 25 and 35°.

Experimental Part

Preparation of Materials.—Lead sulfate of definite crystalline form was prepared from *pro analysi* reagents in the way recommended by Bray[3] and stored under doubly distilled water until needed. Zinc sulfate stock solution was made up from Kahlbaum "zur analyse" reagents and doubly distilled water, and analyzed by the zinc ammonium phosphate method as well as by weighing in the form of zinc sulfate after evaporation and heating on addition of some drops of sulfuric acid.

Four per cent. lead amalgam and 4% zinc amalgam were made up with *pro analysi* metals and redistilled mercury as described by Cowperthwaite and La Mer,[4] filtered hot through capillary tubings and stored under a slight excess pressure of purified nitrogen.

Tank nitrogen was purified from oxygen by the wet combustion method described by Van Brunt,[5] using a nitrogen lift pump to circulate the ammonia–ammonium carbonate solution over the copper wire gauze filling of the absorption tower.

Experimental Method.—The cell was similar to that used by Cowperthwaite and La Mer,[4] with

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[1] This work was aided by a grant from "Anna Paus's Legat."

[2] Research Chemist, Norsk Hydro-Elektrisk Kvaelstofaktieselskab, Oslo.

[3] U. B. Bray, THIS JOURNAL, **49**, 2372 (1927).

[4] I. A. Cowperthwaite and V. K. La Mer, *ibid.*, **53**, 4333 (1931).

[5] C. Van Brunt, *ibid.*, **36**, 1448 (1914).