mal potential of the cell[7] and for the limiting values of the ionization constant and the pH. However, each group of constants when used in the Debye–Hückel equation to fit observed activity coefficients will yield slightly different values for a_i and higher terms, depending upon the range of the concentration chosen.

Summary

Numerical values of A and B in the Debye–Hückel equation for activity coefficients in terms of unit volume of solution and unit weight of solvent, and of $2.30259RT/F$ for use in e. m. f. equations, are given at temperatures from 0 to 100°. The natural constants were chosen from the tabulations of Birge and of Wensel. Contributions of dielectric constant of the medium and of resonance of the ions to the higher terms of Debye–Hückel equations are discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HARVARD MEDICAL SCHOOL.]

Raman Spectra of Amino Acids and Related Compounds. VI. Sarcosine, Ethanolamine, Choline, Betaine and Betaine Derivatives[1]

BY JOHN T. EDSALL

In previous papers of this series[1,2] the effect of ionization of the carboxyl and amino groups, and of methylation of the amino group, has been systematically studied by observations of the Raman spectra of amines, carboxylic acids, and amino acids. Certain characteristic relations between variation of spectrum and variation of structure were observed. The present study, which deals with several compounds more complex in structure than those earlier reported, shows that many of the same correlations may be clearly traced even in the complicated spectra here reported. Closely related substances, such as choline and betaine, are also found to show striking and characteristic differences in Raman spectra. All the spectra here reported were obtained in aqueous solution.

The **experimental technique** has already been fully described.[1,2,3] The **materials** employed were as follows: (1) **Sarcosine** (Hoffman–La Roche) was used without further purification, in aqueous solution, 20% by weight. Sarcosine hydrochloride solution was prepared from sarcosine by adding an equivalent quantity of hydrochloric acid, plus excess hydrochloric acid, to a concentration of approximately 0.5 molar. This excess acid served to repress the ionization of the carboxyl group, so that the observed spectrum should arise only from the sarcosine cation, not from isoelectric sarcosine. Hydrochloric acid dissolved in water at this concentration gives rise to no Raman lines. The final solution of the hydrochloride contained about 20% of sarcosine by weight; it was shaken with norit and filtered several times through a no. 42 Whatman filter paper, directly into the Raman tube, to remove traces of suspended particles and give an optically clear solution. This procedure for clarification of solution has been generally employed in these studies.

(2) **Betaine hydrochloride** (m. p. 246–247°) (Eastman Kodak Co.) was used without further purification in 35% solution by weight, containing excess hydrochloric acid (1 molar). **Betaine** (m. p. 293–294°) was prepared from

TABLE I

RAMAN SPECTRA OF SARCOSINE AND SARCOSINE HYDROCHLORIDE IN AQUEOUS SOLUTION

$(CH_3)^+NH_2\cdot CH_2COOH$		$(CH_3)^+NH_2\cdot CH_2COO^-$	
Sannié and Poremski	Edsall	Sannié and Poremski	Edsall
369 (4)	368 (2)	369 (4)	370 (3)
486 (1b)	490 (2)	487 (2b)	490 (2)
516 (0)	...	...	...
585 (0b)	568 (2)	601 (2b)	596 (1b)
...	675 (1/2)	680 (vb?)	679 (1/2b)
843 (1)	841 (1)	867 (1b)	867 (1/2)
909 (5)	903 (3)	927 (6)	930 (4)
965 (3)	964 (2)	964 (3)	960 (1)
...	...	996 (1)	...
1059 (5)	1055 (2)	1054 (1)	1053 (4)
1116 (?)	...	1105 (5b)	...
1153–74 (1b)	1163 (1)	1151–68 (2d)	1167 (1)
1291 (1)	1254 (1)	...	...
...	1284 (1)	1292 (2)	...
...	...	1309 (5)	1320 (3b)
...	...	1408 (8b)	1408 (6b)
1425 (2)	1429 (2)	...	...
1469 (5)	1464 (3)	1467 (8)	1468 (4)
1602 (0vb)	1622 (1vb)	1610–15 (3)	1633 (2vb)
1737 (3b)	1732 (1b)	...	...
...	2840 (2)	2837 (1)	2833 (1/2)
2932 (?)	...	2922 (1)	...
2977 (3)	2979 (6)	2974 (10)	2969 (8)
3034 (?)	3049 (3)	3038 (4)	3044 (2)

(1) The preceding paper of this series is by J. T. Edsall and H. Scheinberg, *J. Chem. Physics*, **8**, 520 (1940). Some of the data in the present communication were briefly discussed in *Proc. Am. Soc. Biol. Chem.* (1938); see *J. Biol. Chem.*, **123**, xxxiii (1938); also Table IV in reference 2c below.

(2) (a) J. T. Edsall, *J. Chem. Physics*, **4**, 1 (1936); (b) **5**, 225 (1937); (c) **5**, 508 (1937).

(3) J. T. Edsall and E. L. Sagall, THIS JOURNAL, **65**, 1312 (1943).

TABLE II

RAMAN SPECTRA OF BETAINE, BETAINE HYDROCHLORIDE, AND CHOLINE CHLORIDE IN AQUEOUS SOLUTION

S. and P. = Sannié and Poremski. S., S. and W. = Slovokhotova, Syrkin and Wolkenstein. E. = Edsall (present investigation).

Betaine $(CH_3)_3N^+ \cdot CH_2 \cdot COO^-$			Betaine Hydrochloride $(CH_3)_3N^+ \cdot CH_2COOH$		Choline Chloride $(CH_3)_3N^+ \cdot CH_2 \cdot CH_2OH$
S. & P.	S., S. & W.[a]	E.	S. & P.	E.	E.
330 (3b)	327 (2)	341 (1/2b)	330 (1)	338 (1)	331 (0)
368 (4b)	367 (2)	376 (0b)	369 (1)	381 (1)	383 (1/2)
429 (2)	425 (1)	425 (0)	425 (1)	443 (1b)	432 (0)
449 (2)	446 (0)	...	444 (0)	...	462 (1/2)
543 (4b)	537 (2)	546 (1)	543 (2b)	545 (1)	553 (1/2)
609 (1b)	...	627 (0b)	589 (0)	...	...
...	702 (0)	736 (0)	685 (1b)	700 (1)	713 (5)
784 (10)	779 (10)	778 (3)	782 (10)	780 (4)	769 (1/2)
902 (5)	896 (5)	901 (1)	894 (4)	894 (1)	877 (2)
940 (5)	934 (4)	...	931 (4)	930 (1)	...
961 (6)	957 (4)	962 (2vb)	959 (5)	962 (2)	955 (4)
984 (5)	999 (0)	...	991 (1b)	997 (1/2)	...
1013–33 (2b)	1007 (1)	...	...	...	1009 (1/2)
...	1031 (1)	...	...	...	1058 (1)
...	1096 (2)	...	...	...	1089 (1/2)
1137 (2)	1124 (1)	1143 (1/2b)	1135 (1)	1136 (1/2)	1142 (2)
1218 (3)	1216 (1)	1219 (1/2b)	1219 (2)	1218 (1)	1209 (0)
1246 (0)	1265 (1)	...	...	...	1239 (1/2)
1284 (0)		...	...	1290 (0)	1278 (1/2)
1341 (5b)	1336 (7b)	1335 (2)	1330 (1)	1337 (1/2)	1342 (1)
1403 (5)	1394 (2b)	1403 (2)	...	...	...
1423 (4)	1416 (2)	...	1423 (1)	1419 (1)	...
1459 (10)	1451 (8b)	1453 (2)	1454 (9)	1453 (4)	1450 (5)
1478 (4)	1472 (1)	...	1480 (1)	...	1478 (0)
1638 (1b)	1653 (0)	1638 (0vb)	1640 (0vb)	...	...
...	...	...	1739 (2b)	1751 (1b)	...
2840 (3b)	...	2824 (0)	2830 (2b)	2831 (2)	2835 (3)
...	...	...	2889 (0?)	...	...
2947 (5)	...	2937 (2)	2945 (3b)	2937 (2b)	2937 (4)
2976 (8)	2974 (10b)	2982 (3b)	2982 (8)	2983 (5b)	2986 (6)
3040 (7)	3035 (10b)	3043 (3b)	3043 (6)	3049 (4b)	3044 (6)

[a] Slovokhotova, Syrkin and Wolkenstein have reported, in the spectrum of isoelectric betaine in water, a number of weak lines in addition to those listed in the table above. Their values are as follows: 347 (1), 480 (00), 498 (1), 807 (1) 833 (1), 848 (1), 862 (1), 874 (0), 1169 (2), 1438 (0), 1556 (0), 1572 (0), 1590 (0), 1609 (0). Sannié and Poremski have studied betaine in methanol solution, with results practically identical with those obtained in water.

the hydrochloride by treatment with silver oxide, and recrystallized from alcohol and ether. It was studied in 25% aqueous solution. (3) **Choline chloride** (Hoffman-La Roche) was once recrystallized from alcohol and ether; studied in 40% aqueous solution, containing hydrochloric acid (0.5 *N*); solution extremely clear. (4) **Dimethyl phenyl betaine hydrochloride**[4] was prepared from dimethylaniline and chloroacetic acid, and recrystallized three times from 80% alcohol, with the addition of ether (m. p. 196–197°, dec.); studied in 22% solution, containing 0.5 *N* hydrochloric acid. The free betaine was obtained from the hydrochloride by treatment with silver oxide, and studied in 36% solution. (5) **Pyridine betaine hydrochloride**[4] was prepared from pyridine and chloroacetic acid, and recrystallized three times from alcohol; studied in 55% solution containing 0.5 *N* excess hydrochloric acid. (6) **Ethanolamine hydrochloride** (Hoffman-La Roche) was used without further purification in 40% solution with 0.5 *N* hydrochloric acid. (7) **Ethylenediamine dihydrochloride** (Eastman Kodak Co.) was twice recrystallized from alcohol–water, and studied in 35% solution with 0.2 *N* hydrochloric acid.

The **experimental results** are presented in Tables I, II, III and IV. Sarcosine and betaine, and their hydrochlorides, have also been studied by Sannié and Poremski[5]; and betaine has been studied by Slovokhotova, Syrkin and Wolkenstein.[6] Their results are given in Tables I and II, with our own measurements.

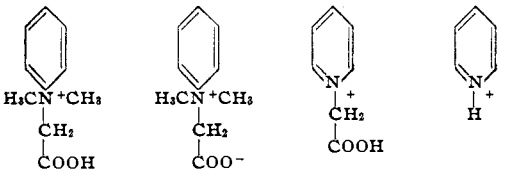
(4) J. T. Edsall and J. Wyman, Jr., THIS JOURNAL, **57**, 1964 (1935).

(5) C. Sannié and V. Poremski, *Bull. Soc. Chim.*, **8**, 702 (1941).

(6) N. A. Slovokhotova, J. K. Syrkin and M. V. Wolkenstein, *Compt. rend acad. sci. U. R. S. S.*, **35**, No. 5, 146 (1942).

TABLE III

RAMAN SPECTRA OF DIMETHYLPHENYL BETAINE HYDROCHLORIDE, DIMETHYLPHENYLBETAINE, PYRIDINE BETAINE HYDROCHLORIDE AND THE PYRIDINIUM ION



239 (2b)	...	260 (1b)	...
379 (1)	380 (2b)	395 (1/2)	396 (3)
...	463 (1/2b)	463 (1/2)	516 (1)
547 (1/2b)	544 (1)	...	569 (1)
615 (3)	615 (3)	602 (0)	...
...	...	646 (2)	638 (2)
727 (4)	728 (6)	776 (1/2)	...
...	...	849 (1)	870 (1)
891 (1b)	904 (2)	900 (1)	...
970 (1)	968 (2)	971 (1/2)	952 (0)
1003 (6)	1003 (7)	...	...
1033 (6)	1033 (7)	1028 (6)	1013 (10)
...	...	...	1066 (1)
1116 (3)	1119 (4)	...	1135 (1)
1161 (1/2b)	1170 (1)	...	1187 (1)
1201 (2b)	1202 (3)	1205 (5)	1218 (2)
1327 (0b)	1330 (3b)	1349 (1/2)	1347 (1)
...	1404 (3b)	...	...
1468 (3b)	1465 (3b)	1502 (0)	1500 (2)
1597 (5)	1598 (5)	1589 (1)	1582 (2)
...	...	1641 (2)	...
1750 (0vb)	...	1732 (1/2)	...
2613 (1/2)	...	...	...
2825 (1/2)	...	...	...
2986 (6b)	2980 (7b)	2972 (4)	...
3049 (1b)	3044 (3)	...	3035 (5)
3090 (6)	3088 (8)	3106 (5)	3095 (5)

Data for the pyridinium ion (pyridine hydrochloride) from H. J. Bernstein and W. H. Martin, *Trans. Roy. Soc. Canada*, (III) Section III, **31**, 95 (1937); other data from the present study. For new data on pyridine and its derivatives, see also E. Herz, L. Kahovec and K. W. F. Kohlrausch, *Z. physik. Chem.*, **53B**, 124 (1943).

TABLE IV

RAMAN SPECTRA OF ETHANOLAMINE HYDROCHLORIDE AND ETHYLENEDIAMINE DIHYDROCHLORIDE

$HO \cdot CH_2CH_2 \cdot NH_3^+$	$^+H_3N \cdot CH_2CH_2 \cdot NH_3^+$
321 (1vb)	371 (0b)
494 (1vb)	481 (1)
842 (1)	826 (2)
872 (5)	929 (2)
1018 (2)	991 (1)
1069 (4)	1055 (3)
1135 (0)	...
1275 (2)	1252 (0b)
1325 (3)	1340 (3)
1468 (6)	1462 (3)
1638 (1vb)	1615 (2vb)
2906 (3)	...
2969 (6)	2989 (6b)

Discussion

The agreement between the different authors who have studied sarcosine and betaine is generally good. Except for a few broad or faint lines, the measurements of a given frequency commonly do not differ by more than 5 cm.$^{-1}$. In the case of betaine, the other workers have reported a double or triple frequency near 960 ± 30 cm.$^{-1}$; also they report two pairs of lines, one in the region between 1390 and 1420 cm.$^{-1}$, another in the region between 1450 and 1480 cm.$^{-1}$. Our own observations show only one line in each of these three regions; probably the other authors employed spectrographs of higher dispersions than ours, and succeeded in resolving doublets which were unresolved in our work. Slovokhotova, Syrkin and Wolkenstein[6] also report a number of weak frequencies (Table II, footnote) not observed by Sannié and Poremski[5] or by us.

Sannié and Poremski report a strong line at 1105 in sarcosine, of which we have observed no indication. Since our results are generally in excellent agreement with theirs, it is possible that this frequency as given in their paper is a misprint.

We may note certain correlations between spectrum and structure, which are in accord with the rules already deduced[1,2]: (1) compounds containing an undissociated carboxyl group give a characteristic Raman frequency between 1720 and 1750 cm.$^{-1}$, in aqueous solution.[7] This vanishes when the carboxyl group is ionized. On the other hand, frequencies near 1400, and sometimes near 1330, appear on ionization of the carboxyl group.[2c] (2) Three characteristic frequencies—near 2840, 2980 and 3040—appear in all compounds containing one or more methyl groups attached to a positively charged nitrogen; commonly a fourth frequency, near 2925, appears also. The intensity of the line at 3040, relative to that of the line at 2980, increases with the number of methyl groups so attached.[1,2b]

The spectrum of N-dimethylphenylbetaine is clearly in large part the spectrum of the aromatic portion of the molecule; similarly the spectrum of pyridine betaine is largely very similar to that of the pyridinium ion. The latter relation is indicated in Table III.

(7) In pure liquid fatty acids, this frequency lies at a lower level, near 1660 cm.$^{-1}$ (see (2a)).

The spectrum of choline is closely similar to that of betaine, as would be expected from their similarity of structure. However, there are some very striking differences. Both compounds show lines in the regions 700–715 and 770–785 cm.$^{-1}$. In betaine the higher of these frequencies is by far the more intense; in choline, the lower. In choline, no lines at 1400 or near 1740 are found; whereas they are strongly present in betaine and its hydrochloride, owing to the presence of the carboxyl group.

Summary

1. Raman spectra are reported for choline chloride, ethanolamine hydrochloride, sarcosine, betaine and certain betaine derivatives and their hydrochlorides; also for the hydrochloride of ethylene diamine.

2. Certain correlations between Raman spectrum and structure, previously found in certain simpler compounds, are shown also to be present in the substances studied here.

BOSTON, MASS. RECEIVED JUNE 4, 1943

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE UNIVERSITY OF IOWA]

Hexahydroxybenzene and Some of its Derivatives[1]

BY IRA E. NEIFERT AND EDWARD BARTOW

Hexahydroxybenzene, $C_6H_6O_6$, was first prepared by Lerch[2] from potassium carbonyl, $K_6C_6O_6$. Nietzki and Benckiser[3] obtained hexahydroxybenzene by the action of a zinc chloride–hydrochloric acid solution on triquinoyl. They found it difficult to separate hexahydroxybenzene, prepared from potassium carbonyl and hydrochloric acid, from its first oxidation product, tetrahydroxyquinone.

Gelormini and Artz[4] stated that some hexahydroxybenzene may have been produced in the oxidation of *i*-inositol, cyclohexanehexol, $C_6H_6(OH)_6$, with nitric acid. They obtained several compounds related to tetrahydroxyquinone, one of which was hexahydroxybenzene acetate. No free hexahydroxybenzene was reported.

It was our thought that the separation would be unnecessary, if the tetrahydroxyquinone formed could be reduced completely to hexahydroxybenzene, the hexahydroxybenzene might be prepared by reduction of tetrahydroxyquinone made from *i*-inositol, which, because of its composition and cyclic structure, and absence of a metal, is an ideal material for the preparation of tetrahydroxyquinone and hexahydroxybenzene.

The purpose of this research was to prepare hexahydroxybenzene from *i*-inositol, to prepare derivatives and study their properties. *i*-Inositol was prepared in sufficient quantity from starch factory steep water by the method of Bartow and Walker[5a,b] modified by Hoglan and Bartow.[6] Tetrahydroxyquinone was prepared by oxidizing *i*-inositol with concentrated nitric acid, neutralizing with sodium bicarbonate, and then adding the crystals to one part of 45% hydriodic acid (sp. gr. 1.50) and ten parts of hydrochloric acid (sp. gr. 1.19), heating the mixture and stirring for half an hour. Crystals of tetrahydroxyquinone are obtained on cooling.

Sometimes these crystals are brown, but if an equal volume of water is added and the mixture warmed and stirred for about fifteen minutes, coal-black crystals are obtained. These crystals should be filtered out on a Büchner funnel, washed with a little water to dissolve any crystals of sodium chloride and sodium iodide, then with cold alcohol and finally with ether. Since tetrahydroxyquinone is somewhat more soluble in alcohol and ether than in water, excessive amounts should not be used. The combined filtrate and wash liquids may be evaporated on a steam-bath and more of the tetrahydroxyquinone will crystallize out. The yield is approximately 80% of the theoretical. The apparent catalytic effect of the hydriodic acid is the important part of the above method. Fair yields have been obtained when dilute hydrochloric acid (6 *N*) has been substituted for the concentrated hydrochloric acid, provided hydriodic acid is used in conjunction with it. Diluted acid is not recommended.

(1) Original manuscript received August 10, 1939.

(2) J. U. Lerch, *Ann.*, **124**, 20–42 (1862).

(3) R. Nietzki and Th. Benckiser, *Ber.*, **18**, 499–515 (1885).

(4) O. Gelormini and N. E. Artz, THIS JOURNAL, **52**, 2483–2494 (1930).

(5) (a) E. Bartow and W. W. Walker, *Ind. Eng. Chem.*, **30**, 300–303 (1938); (b) U. S. Patent 2,112,553, March 29, 1938.

(6) F. S. Hoglan and E. Bartow, *Ind. Eng. Chem.*, **33**, 2397 (1939).