

It is necessary to offer some explanation for the fact that the rotation due to the constant concentration of the dextro-triethylenediamine cobaltic ion should not be the same in all the solutions examined. Since the cation comes from a highly ionized hydroxide it seems hardly plausible to attribute the differences to incomplete ionization of the salts. Any variable of this type should cause the curve to show a shape similar to that of the curve for the dissociation constants of the acids, that is, a decrease from propionate to butyrate and an increase from butyrate to valerate corresponding to the higher dissociation constant of butyric acid.

The most probable explanation for the effect of the optically inactive anions upon the active cation seems to be the formation of secondary sphere coördination complexes. Brintzinger and Osswald<sup>7</sup> report compounds of this type with triethylenediamine cobaltic ion and oxalate, phosphate and arsenate ion. Such a phenomenon would explain the effect of increasing chain length

(7) Brintzinger and Osswald, *Z. anorg. allgem. Chem.*, **224**, 283-288; **225**, 33-37, 365-368 (1935).

and simple ring closure. The additional effect due to the appearance of the asymmetric carbon from the valerate up the series is undoubtedly due to asymmetric induction of the type observed by Pfeiffer and Quehl<sup>8</sup> with zinc and cadmium complex salts of camphorsulfonic acid and  $\alpha$ -bromcamphor- $\pi$ -sulfonic acid.

### Summary

1. Optically active triethylenediamine cobaltic hydroxide was prepared for the first time and its optical rotation and stability to racemization determined.

2. The optical rotations of the aliphatic acid salts: acetate, propionate, butyrate, valerate, caproate, heptoate and pelargonate, of triethylenediamine cobaltic hydroxide were determined.

3. The effect of chain length upon molecular rotation in this series was shown to be consistent with the postulate that a ring form is present in butyrate and larger ions.

(8) Pfeiffer and Quehl, *Ber.*, **64B**, 2667-2671 (1931); **65B**, 560-565 (1932).

BETHLEHEM, PA.

RECEIVED JULY 24, 1940

[CONTRIBUTION FROM INSTITUT DE CHIMIE, MONTPELLIER, FRANCE]

## Molecular Refraction of Ions of *l*-Aspartic Acid

By V. A. PERTZOFF

Molecular refraction has been extensively used for determining the atomic arrangement in organic compounds. In such investigations the atomic refractivities of Roth and Eisenlohr have been widely used. These refractivities, derived from the study of non-ionic compounds, are of little use in calculating the molecular refractions of organic ions, in particular of amino-acids, since ionization has a considerable effect on refraction. It will be shown presently that the molecular refraction of amino-acid salts may be calculated by using both the atomic refractivities of Roth and Eisenlohr and the refractivities of certain organic and inorganic ions.

Determinations of the refractive indices were carried out in a Pulfrich refractometer. Mercury and sodium lamps were used as a source of light. Refractivities of two ions of *l*-aspartic acid, representing two types of ionization, were studied: the monosodium salt in water and the di-sodium salt in 0.5 molar sodium hydroxide.

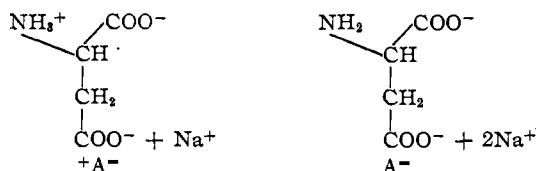
Molecular refractions of the salts were calculated with the help of the Lorentz-Lorenz equation for mixtures. Data and results of calculations, ex-

TABLE I

Ion	Concn., molar	Wave length, Å.	REFRACTION OF IONS OF <i>l</i> -ASPARTIC ACID			
			Refractive index =0.00003	Molecular refraction Lorentz eq.	Calcd., see text	
$+A^- + Na^+$	3.0044	5893	1.40528	28.67		
		5461	1.40791	28.92		
		4358	1.41540	29.41		
	1.9914	5893	1.38304	28.88	28.83	
		5461	1.38488	29.02		
		4358	1.39185	29.52		
	0.9977	5893	1.35855	28.87	28.83	
		1.9943	5893	1.39115	30.24	
			5461	1.39300	30.36	
4358	1.40031		30.93			
0.9955	5893	1.36589	30.35	30.35		
	5461	1.36756	30.45			
	4358	1.37416	31.01			
0.4983	5893	1.35219	30.39	30.35		

cept the densities which will be published shortly in conjunction with a study of optical rotations, are found in Table I.

If we accept the ionization proposed by Bjerrum, we are studying the refractions of the following ions



For convenience of calculation we may split the Na aspartate into four components:  $\text{Na}^+$ ,  $\text{NH}_3^+$ ,  $>\text{CH}-\text{COO}^-$  and  $-\text{CH}_2-\text{COO}^-$ . Fajans<sup>1</sup> in a summary of his own and other investigations, gives the following refractions:  $\text{Na}^+ = 0.20$ ,  $\text{NH}_4^+ = 4.31$ ,  $\text{CH}_3\text{COO}^- = 14.36$  (5893 Å.). The two last values differ from the desired values by one or two hydrogen atoms. Taking the atomic refractivity of hydrogen as 1.10<sup>2</sup> we obtain by subtraction:  $\text{NH}_3^+ = 3.31$ ,  $>\text{CH}-\text{COO}^- = 12.16$  and  $-\text{CH}_2\text{COO}^- = 13.26$ . The sum of these refractions, including  $\text{Na}^+$ , is 28.83. This is in good agreement with the experimental value in more dilute solution of 28.87. The agreement should be better for the value obtained in less concentrated solutions since the refractions derived by Fajans were obtained from a study of dilute solutions.

A similar calculation may be carried out for the di-sodium salt. The components  $>\text{CH}-\text{COO}^-$  and  $-\text{CH}_2-\text{COO}^-$  remain the same, but in place of the ionized group  $-\text{NH}_3^+$  we have  $-\text{NH}_2$ .

(1) Fajans, *Z. physik. Chem.*, **B24**, 103 (1934).

(2) Landolt-Börnstein, "Physik.-Chem. Tabell.," Vol. 2, 1923, p. 985.

According to Fajans<sup>2</sup> the molecular refraction of  $\text{NH}_3$  is 5.63. Subtracting 1.10 we obtain for the group  $-\text{NH}_2$  4.53. The sum, including two  $\text{Na}^+$  is 30.35, which again is in good agreement with the experimental value in more dilute solution (30.39).

It may be asked whether the method employed here is capable of distinguishing between the Bjerrum type of ionization and the so called "classical" one. According to the classical ionization we are studying the refractions of  $\text{HOOC}-\text{CH}(\text{NH}_2)-\text{CH}_2-\text{COO}^- + \text{Na}^+$ . Above is the necessary information to calculate the molecular refraction. It is 28.99. The highest value obtained experimentally was 28.88. Bjerrum's ionization accounts a little better for the experimental results, but the difference is small. It is small due to the fact that in this case, the suppression of a negative charge lowers the refraction to about the same extent that the suppression of a positive charge raises it, the difference is only 0.16.

The molecular refraction of the amino-acid ion itself may be calculated for any wave length, by subtracting 0.20 or 0.40 from the figures given in Table I, the dispersion of  $\text{Na}^+$  being negligible.<sup>3</sup>

The results indicate that the ion  $\text{A}^-$  has a slightly greater dispersion than the ion  $^+\text{A}^-$ .

### Summary

With the help of data for the refractivities of ions the molecular refractions of certain ions of l-aspartic acid have been calculated and the significance of the calculated values to the structure of these ions has been pointed out.

HUBBARDSTON, MASS.

RECEIVED AUGUST 2, 1940

(3) Kruis and Geffcken, *Z. physik. Chem.*, **B34**, 51 (1936).