

Fig. 1.—Infrared spectra of EDTA and its sodium salts in the crystalline state: A, H_4Y ; B, D_4Y ; C, $Na_2H_2Y \cdot 2H_2O$; D, $Na_2D_2Y \cdot 2D_2O$; E, Na_4Y .

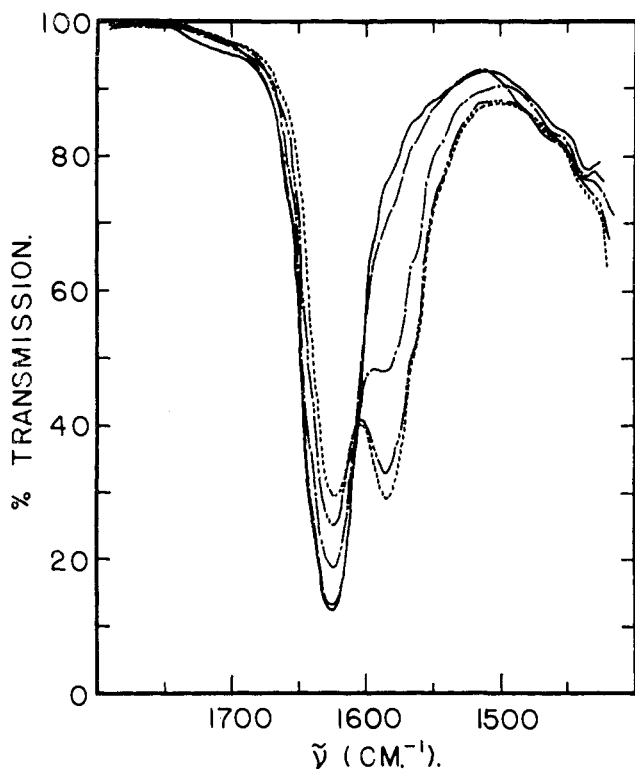


Fig. 2A.—Infrared spectra of EDTA in D_2O solutions: —, pH 3.9; - - -, 5.3; ·····, 6.3; - · - ·, 7.1; - - - - -, 7.8.

tive to deuteration, as is indicated in Fig. 1. These observations suggest that the 1635 cm.^{-1} band may result from a combination of OH bending and some other vibration.

The monosodium salt NaH_3Y is unknown and it was therefore not possible to study the H_3Y^- ion in the

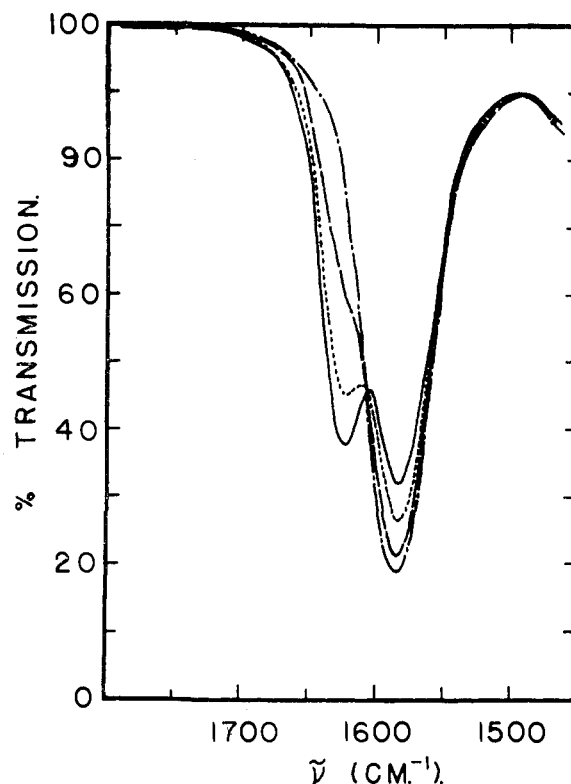
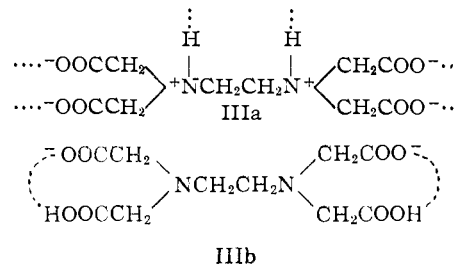


Fig. 2B.—Infrared spectra of EDTA in D_2O solutions: —, pH 8.6; - - -, 9.1; ·····, 9.8; - · - ·, 12.2.

solid state. As is shown in Fig. 1, the disodium salt $Na_2H_2Y \cdot 2H_2O$ exhibits two bands at 1672 and 1624 cm.^{-1} in the crystalline state. Chapman⁵ attributed the former (observed at 1668 cm.^{-1}) to the un-ionized and the latter (observed at 1637 cm.^{-1}) to the ionized carboxyl group, respectively, and suggested the hydrogen bonded structure indicated by IIIb. It should



be noted, however, that the frequencies of 1668 and 1637 cm.^{-1} are too low and too high for type A and type C carboxyl groups, respectively. In this investigation, it is found that the band at 1672 cm.^{-1} is not a carboxyl stretching band since it disappears upon deuteration and dehydration, as is shown in Fig. 1. Thus the structure compatible with the present infrared study is IIIa, containing the maximum number of zwitterion groups.

Figure 2 (A and B) shows the infrared spectra of EDTA obtained at various pH values in aqueous solution. At pH $4.0 \sim 5.3$, only one band is observed at 1624 cm.^{-1} (type B). Since the dinegative anion is predominant in this pH range, the structure of H_2Y^{2-} ion in aqueous solution must be IIIa. As the pH of the solution increases further, a new band appears at 1585 cm.^{-1} , and the band at 1622 cm.^{-1} becomes weaker. Finally, at pH 9.8 , only one band is observed at 1585 cm.^{-1} . These observations are in agreement with IV and V as the structures of the tri- and tetra-negative anions, respectively.

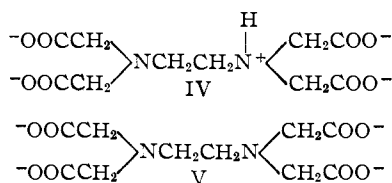


Figure 3 shows a plot of the peak intensities of the 1623 and 1585 cm^{-1} bands against the $p\text{H}$ of the solution.⁷ From this plot, it is possible to calculate approximate pK values by taking the $p\text{H}$ value at the midpoint of the two extreme intensities for each dissociation step.⁸ From the curve obtained for the 1585 cm^{-1}

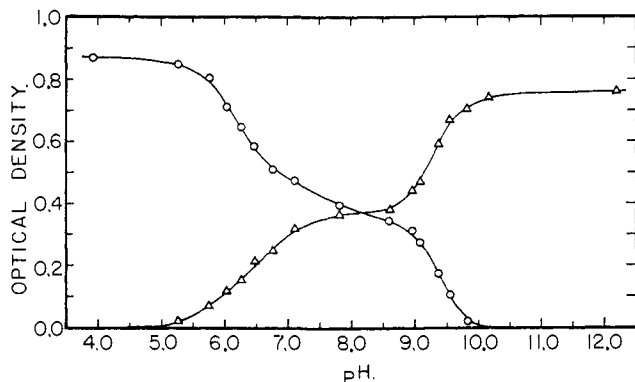
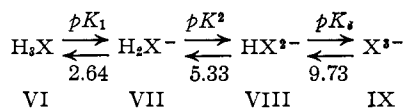


Fig. 3.—Absorbance of carboxylate bands of EDTA as a function of $p\text{H}$: —○—, 1623 cm^{-1} band; —△—, 1585 cm^{-1} band.

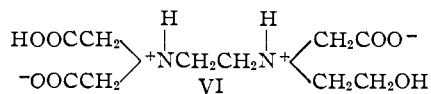
band, pK_3 and pK_4 are estimated to be 6.5 and 9.3, respectively. The former is in good agreement with that obtained by potentiometric studies (6.1) whereas the latter is about 0.8 unit smaller than that of potentiometric values (10.1). This discrepancy is understandable in view of the much higher concentrations used in this investigation, the absence of supporting electrolyte and the considerable differences in activity coefficients that would be expected.

N-Hydroxyethylethylenediaminetriacetic Acid (HEDTA).—The ionization constants reported for HEDTA from potentiometric studies⁹ are summarized as



where H_3X represents HEDTA.

Figure 4 (A and B) shows the infrared spectra of HEDTA at various $p\text{H}$ values in aqueous solution. In strongly acidic solution ($p\text{H}$ 2.1) where H_3X predominates, a band of medium intensity is observed at 1720 cm^{-1} , and a more intense band is found at 1625 cm^{-1} . From the frequencies and intensities of these two bands, it is concluded that the structure of H_3X is VI. In the crystalline state, H_3X has bands at 1705



(shoulder), 1667 (medium) and 1629 cm^{-1} (very strong). A zwitterion structure similar to VI is in accord with these observations, although, because of intermolecular interactions, the spectrum of the crystalline compound is more complicated than that of the aqueous solute.

(7) Since bands at 1623 and 1585 cm^{-1} partially overlap, the intensity of each band was estimated by assuming its shape to be symmetrical.

(8) K. Nakamoto and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 5837 (1959).

(9) S. Chaberek and A. E. Martell, *ibid.*, **77**, 1477 (1955).

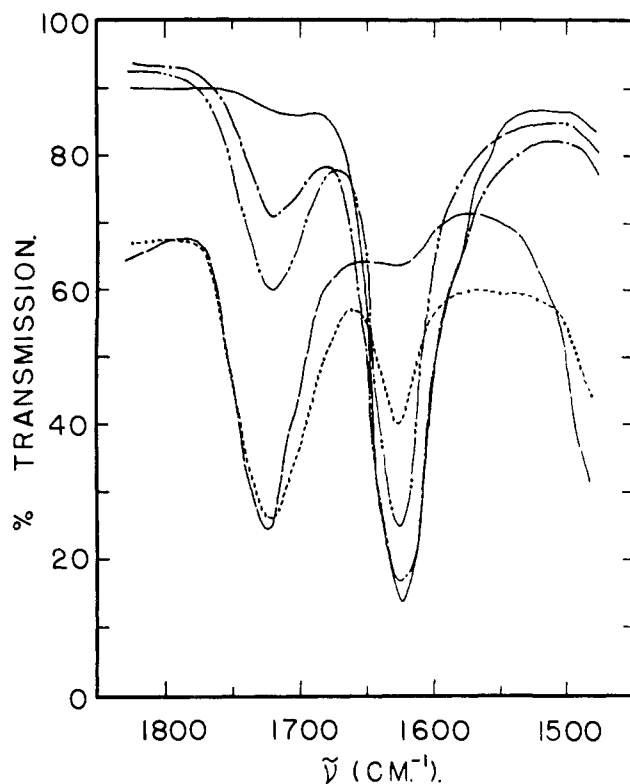


Fig. 4A.—Infrared spectra of HEDTA in D_2O solutions: —, $p\text{H}$ 0.02; ---, 1.1; —, 2.1; - - - -, 2.8; —, 4.0.

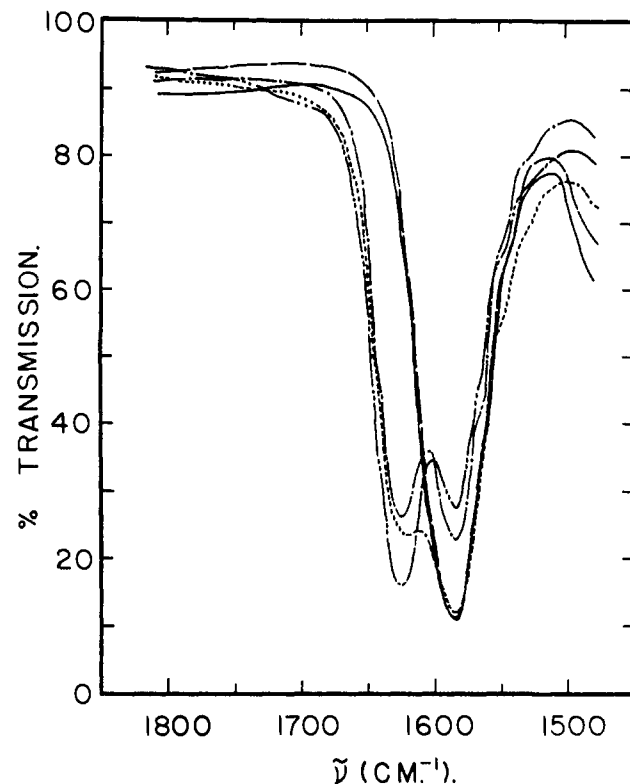


Fig. 4B.—Infrared spectra of HEDTA in D_2O solutions: - - - -, $p\text{H}$ 5.6; ---, 7.5; - - - -, 9.1; —, 11.5; —, 12.8.

As the $p\text{H}$ increases from 2.8 to 4.0, the band at 1720 cm^{-1} (type A) becomes weaker and the band at 1624 cm^{-1} (type B) becomes stronger. Thus the structure of the mononegative ion which predominates in this

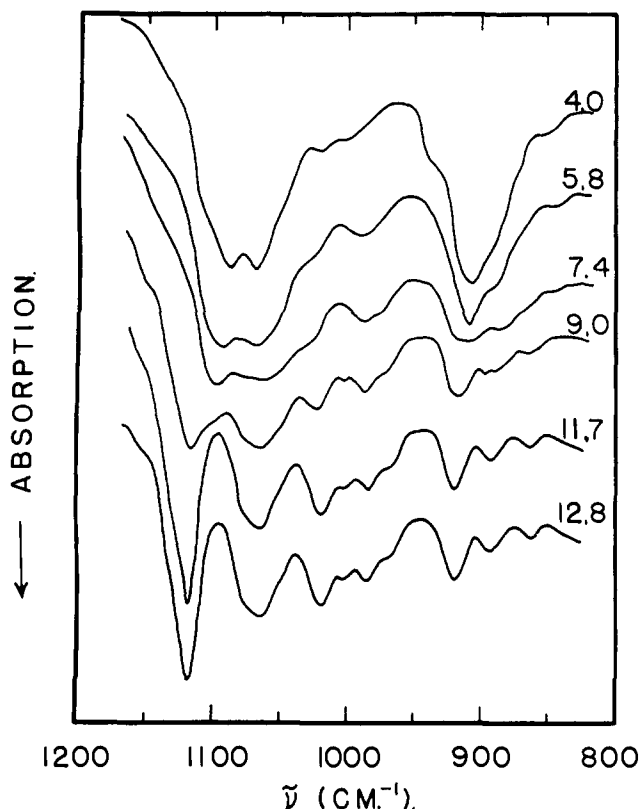
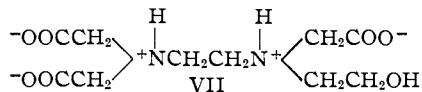
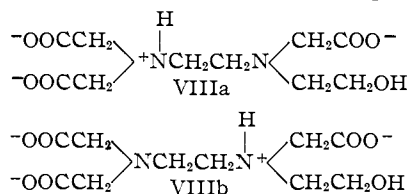


Fig. 5.—Infrared spectra of HEDTA in the low frequency region (pH is indicated).

range must be VII. At pH 5.6, a new type C band ap-



pears at 1583 cm^{-1} . At pH 7.5, where HX^{2-} is completely formed, the bands at 1624 and 1583 cm^{-1} have about the same intensity. Its structure may be either VIIIa or VIIIb; VIIIa has two type B and one



type C group, whereas VIIIb has one type B and two type C carboxyl groups. As is seen in Fig. 4, the band at 1620 cm^{-1} (type B) is stronger than the band at 1583 cm^{-1} (type C). Since the intensity of both type carboxyl bands per group is approximately the same, the observed spectra favor an equilibrium between VIIIa and VIIIb, with a higher proportion of VIIIa. This result seems reasonable since the nitrogen attached to a hydroxyethyl group is less basic than that attached to a $\text{CH}_2\text{-COO}^-$ group. At pH 11.5, the band at 1620 cm^{-1} disappears completely, corresponding to the complete formation of X^{3-} (IX).

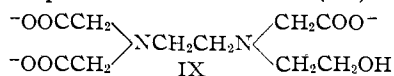
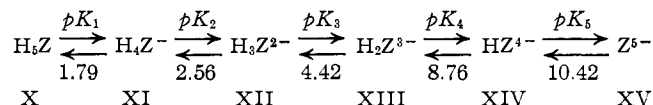


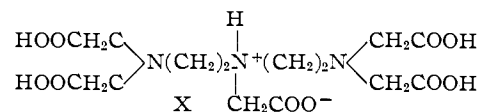
Figure 5 shows the infrared spectra of HEDTA in $1200\text{-}800 \text{ cm}^{-1}$ region. At pH 9.0, new bands appear at approximately 1140 , 1040 , 940 , 880 and 863 cm^{-1} . As stated previously for a different ligand, these vibrations should be ascribed to the absorption of the $>\text{N-CH}_2\text{-CH}_2\text{-OH}$ group as a whole, and the appear-

ance of new bands at high pH should be ascribed to the loss of positive charge on the nitrogen atoms in the ionization process VII \rightarrow VIII \rightarrow IX rather than to the ionization of the hydroxyethyl hydrogen.

Diethylenetriaminepentaacetic Acid (DTPA).—Potentiometric measurements¹⁰ give the following ionization constants for DTPA



where H_5Z represents DTPA. The spectrum of aqueous H_5Z was not obtained because of its low solubility. In the crystalline state, however, it has three bands of about the same intensity at 1731 , 1700 and 1634 cm^{-1} . Thus the most probable structure in the crystalline compound may be X. An alternative structure X'

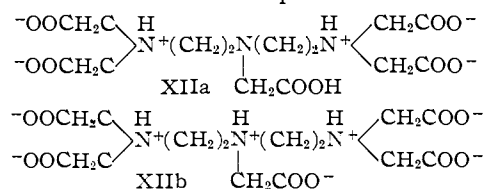


(not shown) would have a dipolar group involving one of the terminal nitrogen atoms. Structure X is favored over X' from a symmetry viewpoint. The bands at 1731 and 1700 cm^{-1} correspond to four type A carboxyl groups and the band at 1634 cm^{-1} corresponds to one type B carboxyl group. The splitting of type A band into two peaks may be ascribed to the difference of crystal environment in these four carboxyl groups of X.

Other structures having positive charges on the terminal nitrogen atoms can be ruled out on the basis of the relative intensities of these three bands. Structure X' has one $>\text{N}^+\text{-CH}_2\text{COOH}$ (type A'), three $>\text{N-CH}_2\text{-COOH}$ (type A) and one $>\text{N}^+\text{-CH}_2\text{COO}^-$ (type B) groups. The type A' carboxyl group usually absorbs at a higher frequency ($1750\text{--}1730 \text{ cm}^{-1}$) than the type A carboxyl group ($1730\text{--}1700 \text{ cm}^{-1}$), although the intensities of the absorption bands of both types of groups are approximately the same. Therefore an attempt to assign the band at 1731 cm^{-1} to type A', and the band at 1700 cm^{-1} to type A, of X', does not correlate with the observed intensity pattern. Other alternative structures may be ruled out in a similar manner.

For the aqueous solute at pH 3.6 where the H_3Z^{2-} ion predominates, a weak band at 1710 and a strong band at 1626 cm^{-1} are observed, as is shown in Fig. 6.

Of the many possible structures for the H_3Z^{2-} ion, XIIa and XIIb are the most probable on the basis of



the infrared spectrum, since no bands for type C carboxyl group ($1585\text{--}1575 \text{ cm}^{-1}$) are observed. The appearance of a weak band at 1710 cm^{-1} definitely indicates the presence of XIIa.

The percentage of XIIa can be calculated in the following way. For most of the compounds studied, the optical density of type A carboxyl band per group is 0.055 ± 0.005 for 0.11 mole/liter solution with a cell of 0.021-mm . thickness. Under the same conditions, the optical density of the type A band of DTPA is 0.040 . Thus the percentage of XIIa at pH 3.6 is estimated to be $(0.041/0.055) \times 100 = 75\%$. This conclusion is

(10) S. Chaberek, A. E. Frost, M. A. Doran and N. J. Bicknell, *J. Inorg. Nucl. Chem.*, **11**, 184 (1959).

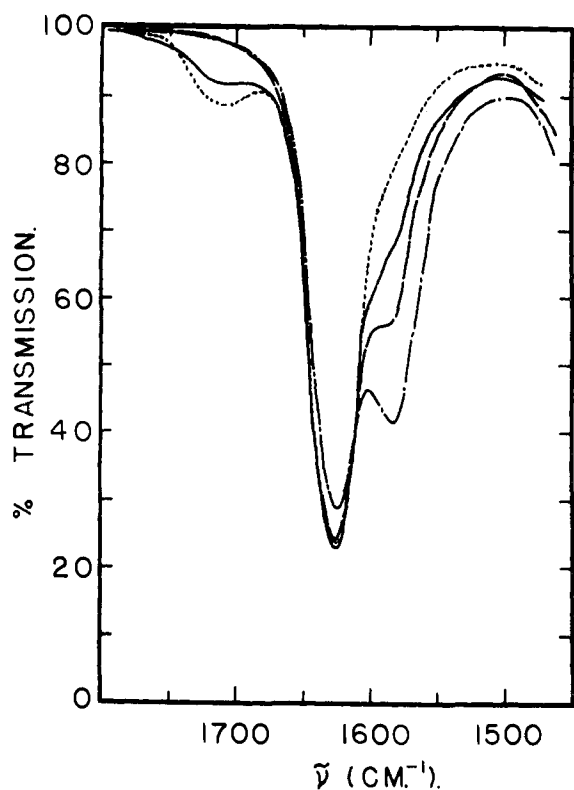


Fig. 6A.—Infrared spectra of DTPA in D₂O solution: ----, pH 3.6; —, 4.4; — · —, 6.8; - - - -, 8.4.

reasonable since the central nitrogen atom in XIIa is only very weakly basic (or the ammonium form XIIb is highly acidic) because of the coulombic and inductive effects of the terminal positive nitrogen atoms.

On the basis of this determination of the relative concentrations of XIIa and XIIb, the microscopic equilibrium constants for the second and third dissociation step can now be calculated. The results are given in Table I.

TABLE I

MICROSCOPIC EQUILIBRIUM CONSTANTS FOR THE SECOND AND THIRD DISSOCIATION STEPS OF DTPA

Constant	Equilibrium expression ^a	Value (pK _x)
K ₂	$\frac{([\text{XIIa}] + [\text{XIIb}][\text{H}^+])}{[\text{XI}]}$	2.56
K _a	$\frac{([\text{XIIa}][\text{H}^+])}{[\text{XI}]}$	2.69
K _b	$\frac{([\text{XIIb}][\text{H}^+])}{[\text{XI}]}$	3.16
K ₃	$\frac{([\text{XIII}][\text{H}^+])}{([\text{XIIa}] + [\text{XIIb}])}$	4.42
K _c	$\frac{([\text{XIII}][\text{H}^+])}{[\text{XIIa}]}$	4.30
K _d	$\frac{([\text{XIII}][\text{H}^+])}{[\text{XIIb}]}$	3.82

$$^a K_Z = \frac{[\text{XIIa}]}{[\text{XIIb}]} = \frac{K_a}{K_b} = \frac{K_d}{K_c} = 3.0.$$

At pH 4.4, a new type C band appears at 1585 cm.⁻¹. At pH 6.8 where the H₂Z³⁻ ion predominates, two bands are observed, a very strong band at 1625 cm.⁻¹ and a weak band at 1587 cm.⁻¹. Of the possible structures XIIIa and XIIIb, XIIIa has four type B and one

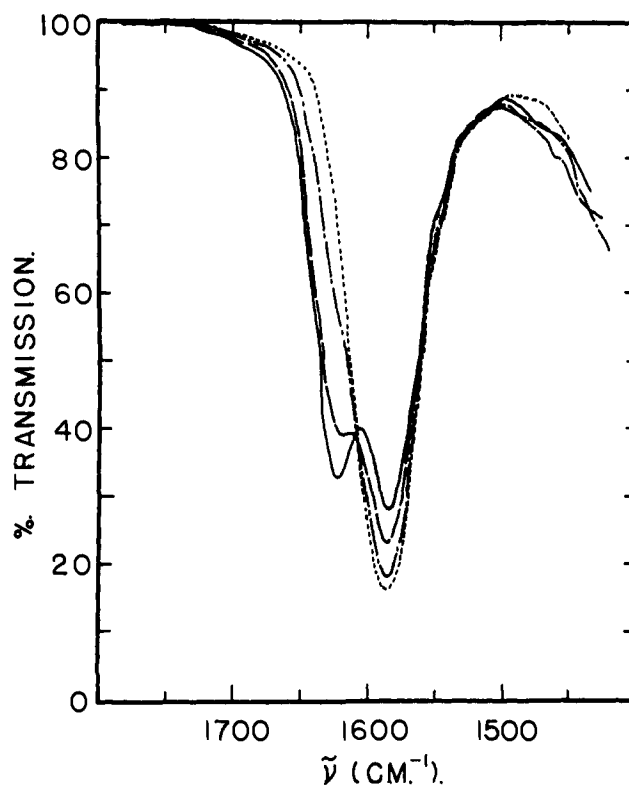
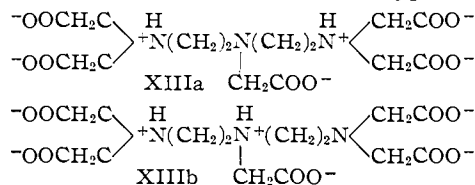
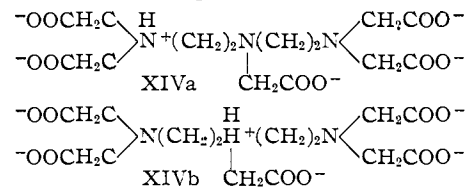


Fig. 6B.—Infrared spectra of DTPA in D₂O solution: —, pH 9.0; ----, 9.3; — · —, 9.9; - - - -, 11.6.

type C bands, whereas XIIIb has three type B and two type C carboxyl groups. Figure 6 indicates that the ratio of optical density of the type B (1620 cm.⁻¹) to type C (1585 cm.⁻¹) band is 4.1. Therefore XIIIa seems to be indicated. Structure XIIIa is also favored since it has the charge distribution with minimum energy.

At pH 9.3 where the HZ⁴⁻ ion is predominant, the band at 1624 cm.⁻¹ becomes weaker and the band at 1585 cm.⁻¹ becomes stronger. Figure 6 shows that the ratio of optical density of these two bands is 2 to 1 at this pH. Of the two possible structures, XIVa and



XIVb, for the HZ⁴⁻ ion, XIVa is more compatible with the observed spectrum than XIVb, since the former has two type B and three type C bands, whereas the latter has one type B and four type C carboxyl groups. Structure XIVa is also favored by the greater coulombic attraction between the positive ammonia and negative carboxylate groups in this structure. At pH 11.6, only one band is observed at 1584 cm.⁻¹ (type C), indicating complete formation of the Z⁵⁻ ion (XV).

