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Anomalous H/D Isotopic Substitution Effects in Aqueous Solutions of Ethylenediaminetetra-acetic Acid

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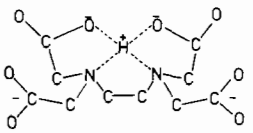
We have previously reported the Raman spectra of aqueous (H_2O) solutions containing the ions $HEDTA^{3-}$ (pH 8) and H_2EDTA^{2-} (pH 5) (H_4EDTA = ethylenediaminetetra-acetic acid), with Na^+ as counter ion [1]. The data were interpreted as favouring a folded configuration resulting from the formation of intramolecular hydrogen bonds between the carboxylate groups and protonated nitrogen atoms. The arrangement is analogous to that proposed for the ion $HCDTA^{3-}$ (CDTA = 1,2-cyclohexanediaminetetra-acetic acid) on the basis of PMR evidence [2].



The initial protonation of $EDTA^{4-}$ in H_2O solution is accompanied by a marked increase in the frequency of all the Raman active νC–H vibrations, apparently indicative of the involvement of both nitrogens in the initial protonation process [1, 3, 4]. The Na-23 NMR spectra [5] of these solutions also demonstrate that the process of monoprotonation completely displaces the Na^+ ion from its weak interaction with $EDTA^{4-}$. In D_2O the conversion of $EDTA^{4-}$ to $DEDTA^{3-}$ may be followed on the basis of the changes which occur in the $\nu_{asym}\,CO_2^-$ region of the IR spectrum: thus $EDTA^{4-}$ is characterised by a single band at 1580 cm^{-1} but $DEDTA^{3-}$ gives rise to two bands of similar intensity at 1580 and 1620 cm^{-1}; at pD 5 where D_2EDTA^{2-} is present solely the band at 1620 cm^{-1} remains [6, 7]. For the H_2O solutions the process of monoprotonation is also accompanied by a shift of the single Raman active νC–C vibration of the carboxylate arms; diprotonation to H_2EDTA^{2-} causes this band to split into two components [1]. However Krishan and Plane [8], who examined one $EDTA/Na^+/D_2O$ solution in the course of a Raman study of a range of EDTA containing solutions, reported that at pD 4 only one νC–C band was detectable as opposed to the two bands observed for the equivalent H_2O solution. In order to confirm and extend this apparently anomalous observation we have examined the Raman spectra of a series of $EDTA/Na^+/D_2O$ solutions from pD 4 to 12. These spectra show the same shifts of νC–H with pD as were observed for the H_2O solutions but a different pattern for the νC–C bands. Thus whereas the spectrum of aqueous $HEDTA^{3-}$ has only one νC–C band, that of $DEDTA^{3-}$ in D_2O has two; at pD 5 where D_2EDTA^{2-} is the main species only one νC–C band is present, confirming Krishnan and Plane's result (Table I).

PMR studies have determined [9] that the rate of deuteration of either the ethylenic, or the methylenic, protons in $EDTA/Na^+/D_2O$ solutions is negligible so that any H/D shifts in the vibrational spectra must be attributed to the formation of $N–D^+$ *vs.* $N–H^+$ bonds, or to the influence of interaction with the solvent. In order to ensure that we are indeed comparing like 'monoprotonated' and 'diprotonated' species we have made use of the internally consistent pD scale developed by Paabo and Bates [10] and also obtained the IR spectra of the D_2O solutions. By a comparison with the data obtained by Nakamoto *et al.* [7] it is possible to identify the solution at pD 8.45 as certainly containing the $DEDTA^{3-}$ ion. Unfortunately the strong H_2O band at 1650 cm^{-1} prevents complete observation of the changes

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TABLE I. νC–H and νC–C Frequencies in the Raman Spectra of $Na^+/EDTA/D_2O$ Solutions (cm^{-1}).

pD	νC–H					νC–C[a]	
12.60				2956(vs)	2853(vs)		918(s)
9.32			2984(sh)	2956(vs)	2856(s)		916(s, br)
8.45		3028(w)	2987(vs)	2956(w)	2870(w)	923(m)	908(s)
7.43		3020(m)	2976(vs)		2870(w)	926(s)	901(w)
6.30		3020(m)	2976(vs)			925(s, br)	
5.0		3018(m)	2976(vs)			930(s, br)	
4.32	3068(w)	3022(w)	2985(vs)			930(s, br)	

[a]At pH 8.47, in H_2O solution, νC–C is at 922 cm^{-1} and at pH 5.05 at 935 and 911 cm^{-1} [1].

in the IR carboxylate region which take place in H_2O as $EDTA^{4-}$ is converted to $HEDTA^{3-}$. For the former a shoulder at 1580 cm^{-1} is prominent; with mono-protonation this diminishes in intensity and the water peak increases in intensity, however at pH 8 the shoulder is still detectable. This observation, coupled with the changes in the νC–H region of the Raman spectra which are common to H_2O and D_2O solutions suggests that basically the same process takes place in both H_2O and D_2O. A preliminary examination of CDTA in H_2O and D_2O demonstrates that similar changes in the νC–H region occur with 'protonation', though for this system changes in the νC–C region are more complex and also complicated by the spectrum of the cyclohexane ring; detailed study requires higher resolution than we currently have at our disposal.

Previous studies of glucine and ethylenediamine in H_2O/D_2O solutions have resulted in assignments of N–H stretching modes above 3000 cm^{-1} and deformation modes at about 1600 cm^{-1} [3, 4]. While these assignments for both N–H and N–D frequencies are complicated by their proximity to the vibrational modes of H_2O and D_2O respectively, there is no evidence to suggest that N–D vibrations should occur at 900 cm^{-1}. It is thus clear that the changes in vibrational pattern which we record are not associated with normal isotopic H/D substitution displacements. Similarly anomalous changes were observed in the Raman spectra of glycine and ethylenediamine in H_2O/D_2O solutions and it appears that the effects may be specific to the formation of hydrogen and deuterium bonds. It seems likely that the differences at least in H_2O/D_2O/EDTA solutions, reflect a variation in the strain in the rings which are formed as a result of intramolecular hydrogen bonding. Such a result would ensure if, for example, hydrogen and deuterium bonds differed significantly in length in the respective ions. In view of the extensive use which is made of D_2O as a solvent for the NMR study of complex molecules it is desirable that the origin of these effects should be identified.

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References

1 R. H. Nuttall and D. M. Stalker, *J. Chem. Soc. Dalton*, 1884 (1977).
2 Y. Fujiwara and C. N. Reilley, *Anal. Chem., 40,* 890 (1968).
3 M. Takeda, R. E. S. Ivazo, D. Garfinkel, I. H. Scheinberg and J. T. Edsall, *J. Am. Chem. Soc., 80,* 3813 (1958).
4 S. A. S. Ghazanhafer, J. T. Edsall and D. V. Myers, *ibid., 86,* 559 (1964).
5 T. L. James and J. H. Noggle, *ibid., 91,* 3424 (1969).
6 D. T. Sawyer and J. E. Tackett, *ibid., 85,* 314 (1963).
7 K. Nakamoto, Y. Morimoto and A. E. Martell, *ibid., 85,* 309 (1963).
8 K. Krishnan and R. A. Plane, *ibid., 90,* 3195 (1968).
9 J. B. Terrill and C. N. Reilley, *Anal. Chem., 38,* 1876 (1966).
10 M. Paabo and R. G. Bates, *Anal. Chem., 41,* 283 (1969).