^{31}P NMR Study of organophosphonate protonation equilibrium at high pH

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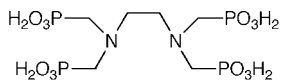
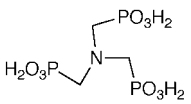
A ^{31}P NMR technique was used to determine the protonation constants of the organophosphonates 1-hydroxyethane-1,1-diphosphonic acid (HEDPA, H_4L), nitrilotri(methylenephosphonic acid) (NTPH, H_6L) and 1,2-diaminoethane-*N*,*N*,*N*′,*N*′-tetra(methylenephosphonic acid) (EDTPH, H_8L) at 24 °C and I = 3.4–3.5 mol dm^{-3} $(CH_3)_4NCl$ over the range pH 11–14.5. For the dissociation of the aliphatic hydroxy group of HEDPA log $K(H_{-1}L + H \rightleftharpoons L) \geqslant 14.6$ while for NTPH and EDTPH log $K(L + H \rightleftharpoons HL)$ was found to be 14.2(0.1) and 13.8(0.1), respectively. The influence of $(CH_3)_4NCl$ content on ^{31}P NMR chemical shifts was demonstrated.

Organophosphonate chelating compounds, particularly 1-hydroxyethane-1,1-diphosphonic acid (HEDPA, H_4hedpa, H_4L), nitrilotri(methylenephosphonic acid) (NTPH, H_6ntph, H_6L) and 1,2-diaminoethane-*N*,*N*,*N*′,*N*′-tetra(methylenephosphonic acid) (EDTPH, H_8edtph, H_8L) are widely used in a broad variety of applications.[1–5] Annual industrial output of organophosphonates is in the thousands of tons.[3,6] A fruitful implementation of organophosphonates requires reliable data on the stability constants of the corresponding complexes. These permit modelling and prediction of the technological, environmental and pharmaco-kinetic equilibrium. As phosphonates are hardly biodegradable, chemical speciations based on numerical chemical equilibrium data are of extreme importance for such applications as environmental science, waste management, agriculture, scale inhibition, magnetic resonance imaging, behaviour of radiopharmaceuticals in blood plasma, along with many others.[7–10]

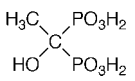
The H_nL and ML stability constants published for HEDPA, NTPH and EDTPH are rather controversial.[11] The main source of errors in pK_i values arises from ignorance of competitive background cation complexation[12] and the use of inadequate techniques in the high pH range. Another source of discrepancies is attributed to the (hypothetical) dissociation of the aliphatic hydroxy group of HEDPA. The first communication, more than 100 years ago, on the salts of this compound claimed to isolate the penta-basic solid salt of HEDPA.[13] However, numerous attempts to repeat this result have all failed[14] and a thorough calorimetric study revealed no evidence of HOC group dissociation up to pH 13.[15]



EDTPH



NTPH



HEDPA

The X-ray structures for HEDPA complexes CuH_2-hedpa(bipy)·$3H_2O$,[16] K_4Na_2Cuhedpa·$6H_2O$,[17] CaH_2-hedpa·H_2O,[18] Er(H_3hedpa)H_2hedpa·$5H_2O$,[16] $(NH_4)_3MoO_2$-H_3(hedpa)$_2$·$6.75H_2O$[19] and $Na_4NH_4MoO_2$-(Hhedpa)hedpa·$5H_2O$[20] indicate that the hydroxy group is in most cases either not coordinated at all or that it coordinates without dissociation. ESR data on aqueous solutions of V(IV)-HEDPA complexes also do not reveal any deprotonation of the alcoholic group below pH 12, although the complexes formed are very stable.[21] The formation of $MH_{-1}L$ species could therefore probably be neglected in stability constant evaluations for normal and protonated complexes of alkaline earth cations, 3d cations (M^{2+}) and f cations (M^{3+}). At the same time, the penta-basic HEDPA anion was found by X-ray analysis of the Mo(VI) complexes $[C(NH_2)_2]_5[WO_3(H_{-1}$hedpa)]·$4.5H_2O$[22] and $K_8Mo_6O_{17}(H_{-1}$hedpa)$_2$·$10H_2O$,[23] and by means of ESR in aqueous solutions of $[VOH_{-1}$hedpa$]^{3-}$ at pH 12–14.[21] This raises the problem of determining a reasonable log K_{-1} value for $H_{-1}L + H \rightleftharpoons L$.

The data presented in ref. 11 indicate that for NTPH and EDTPH log $K(H + L \rightleftharpoons HL)$ is above 12 and potentiometry based on a glass electrode is not appropriate for correct estimation of these values.[24] At the same time the recent use of NMR[25–31] for these and related ligands also seems to be inadequate. None of the groups using NMR managed to reach the "plateau" where the chemical shift of the completely deprotonated ligand is clearly not dependent on pH (or at least to pass a half-neutralisation point) nor did they use constant ionic strength at high pH. In addition to this none of the data reported take into account possible complexation of background alkali cations by the ligand. For NTPH and EDTPH the failure of the protonation constant evaluation at pH 11–14 causes serious errors in log K_{ML} values.

The present paper is devoted to the NMR estimation of organophosphonate protonation constants in highly basic solutions in a 3.33 M $(CH_3)_4NCl$–$(CH_3)_4NOH$ medium known not to interact with phosphonates.

Experimental

Reagents

Reagent grade purity powder samples of organophosphonates have been supplied by Angarsk Chemical Plant, Russia (HEDPA), and Cheboksary Chemical Plant, Russia (NTPH). A powder sample of reagent grade purity EDTPH was kindly provided by Professor T. Kiss. All substances passed NMR analysis and then have been used without further purification. Ligand purity found: HEDPA >99% (^{31}P NMR); NTPH 96% (^{31}P NMR; a single impurity of 4% MIDPH phosphorus content is detected); EDTPH 95% (^{31}P NMR). As far as all the impurities are detected as separate NMR lines, they could not affect the accuracy of NMR measurements when pH >12 and organophosphonate concentration is less than 0.001 M.

Tetramethylammonium chloride, $(CH_3)_4NCl$ (Fluka, purum), was purified by dissolving 80 g of salt in 150 ml of hot methanol (Baker, p.a.). The hot solution was filtered and then 1350 ml of acetone (Merck, p.a.) was added by stirring. After cooling, the solution was filtered again, and the salt was washed with 50 ml of acetone and dried in a vacuum desiccator.

Tetramethylammonium hydroxide, $(CH_3)_4NOH \cdot 5H_2O$ (Fluka, purum), was used without further purification. The corresponding solutions were standardised by titration against 0.1 M HCl (Merck Titrisol®) and kept under argon. Solutions of hydrochloric acid were standardised against tris(hydroxymethyl)aminomethane. Both 3.33 M solutions of $(CH_3)_4NCl$ and $(CH_3)_4NOH$ have been analysed for Na, Ca and Mg content before use. The highest values of metal impurities measured (Na: 0.21 mmol dm^{-3}; Ca: 0.25 mmol dm^{-3}; Mg: 0.16 mmol dm^{-3}) are found to be satisfactory.

Sample preparation

The 3.45 M aqueous solutions of $(CH_3)_4NOH$ and $(CH_3)_4NCl$ as well as 0.2 M solutions of organophosphonic acids ($hedpa^{4-}$; $Hntph^{5-}$; $Hedtph^{7-}$) partly neutralised with $(CH_3)_4NOH$ have been prepared. In a series of samples the $(CH_3)_4NOH$ content was gradually varied from 0.01 to 3.33 M. At the same time the total ionic strength I and organophosphonate concentration were maintained constant within the series, correspondingly 3.4–3.5 mol dm^{-3} and 6.4 mmol dm^{-3}. For samples with 0.01–0.05 M $(CH_3)_4NOH$ the ligand concentration was taken at the level of 0.6 mmol ($I = 3.4$). A contribution from the organophosphonate proton could therefore be neglected, and the equilibrium content of free $[OH^-]$ was taken equal to the amount of $(CH_3)_4NOH$ added. The corresponding pH value was then derived using an appropriate pK_w. This approach eliminates the need for potentiometric measurements. The samples were allowed to equilibrate 12 h in closed tubes with a small air phase volume and then the chemical shifts were measured. Each run included 10 solutions of L, which span the range $14.5 \geqslant pH \geqslant 11$.

NMR measurements

The $^{31}P\{^1H\}$ NMR spectra of organophosphonates (C_L = 0.0064 mol dm^{-3}) were recorded with a Bruker DRX500 instrument at 202.5 MHz with a 10 mm diameter sample tube in a thermostated room at 24(1) °C. A short acquisition times (4–5 min) provided no observable sample heating. The external standard, placed in a 2 mm coaxial inner tube, was a 2 : 3 v/v mixture of 85% phosphoric acid and D_2O (added for lock) and chemical shift values are reported relative to this reference. Downfield shifts are denoted as positive. Susceptibility corrections to the chemical shifts were neglected, being estimated as small for constant ionic strength and a comparatively narrow range of $\log[OH^-]$ variations within a sample series.

Measurements at pH 11–12 have been run with 0.0006 mol dm^{-3} ligand concentrations and the same acquisition time as for the other samples in order to exclude possible influence of the initial ligand solution on the total pH value. For ^{31}P NMR sample purity analysis, 0.2 M ligand concentrations have been used and the signal-to-noise ratio was not less than 200.

Data treatment and protonation constant evaluation

A constant ionic strength of $I = 3.4$ mol dm^{-3} (HEDPA, NTPH) and $I = 3.5$ mol dm^{-3} (EDTPH), maintained by $(CH_3)_4NCl$–$(CH_3)_4NOH$, was used throughout the measurements. These values include corrections for the phosphonate contribution. As long as phosphonate concentration $[L] \ll [(CH_3)_4NOH]$, the $\log[OH^-]$ has been taken equal to the initial $(CH_3)_4NOH$ content in a sample. Free hydrogen ion concentration was therefore obtained by a recalculation using $pK_w = 14.157$[32] for 25 °C and $I = 3.0$ M KCl. The known pK_w values for R_4NCl medium[33] span the range of $I = 0.1$–1.0 mol dm^{-3} and are not considered here.

The first two protonation steps of a completely deprotonated ligand L (NTPH, EDTPH) can be described by the reactions:

$$H^+ + L^{n-} \rightleftharpoons HL^{1-n} \qquad K_1$$

$$H^+ + HL^{1-n} \rightleftharpoons HL^{2-n} \qquad K_2$$

where $n = 6$ (NTPH) or 8 (EDTPH); for HEDPA:

$$H^+ + H_{-1}L^{5-} \rightleftharpoons L^{4-} \qquad K_{-1}$$

where $H_{-1}L^{5-}$ indicates an anion with complete dissociation of the aliphatic hydroxy group.

Owing to a 3–4 log units difference between K_1 and K_2 (and correspondingly for K_{-1} and K_1) an experimentally observed single time-averaged $^{31}P\{^1H\}$NMR chemical shift of "free" and proton-bonded ligand δ_{obs} can be given by a simple equation:

$$\delta_{obs} = (\delta_L + K_1[H^+]\delta_{HL})/(1 + K_1[H^+])$$

where δ_L represents the chemical shift of a free ligand L and δ_{HL} that of the monoprotonated species HL. The protonation constants K_1 (K_{-1}) have been calculated by the non-linear curve-fitting program SigmaPlot[34] with 10 experimental points for each curve.

The agreement of the experimental data and calculated values was tested by plotting the observed and calculated chemical shifts as a function of $-\log[H^+]$. Standard deviations were estimated to be 0.06 (NTPH) and 0.05 (EDTPH). The chemical shift δ_L for EDTPH was determined by both direct observation of the "plateau" at pH *ca.* 14.3–14.5 and *via* non-linear curve-fitting, while for NTPH it was calculated using a half-neutralisation point. For HEDPA the experimental curve gives no clear evidence that a half-neutralisation point is passed up to the highest experimentally available pH level. The experimental results are presented in Tables 1–3 along with literature values[9,14,26–28,30,35–47] and in Figs. 1 and 2.

Results and discussion

HEDPA

Unlike other organophosphonates, ^{31}P NMR of HEDPA has a low sensitivity to the variations of pH. The influence of $(CH_3)_4NCl$ content on the chemical shifts of phosphonic groups was therefore checked for this particular case, Table 1, and δ_{obs} was found to be dependent not only on pH but also on $[(CH_3)_4N^+]$ concentration. The 0.18 ppm shift caused by

Table 1 Dependence of the ^{31}P NMR chemical shift of a 0.005 M HEDPA in 0.26 mol dm^{-3} $(CH_3)_4NOH$ solution on $(CH_3)_4NCl$ concentration

$[(CH_3)_4N^+]$/ mol dm^{-3}	δ^a
0.26	18.640
2.84	18.458

^{a} $\neq 0.004$.

an increase of $[(CH_3)_4N^+]$ from 0.26 M to 2.84 M at a constant pH 13.4 is found to be larger than the 0.08 ppm shift that one can see when pH changes from 13 to 14.6 at constant $I = 3.4$ mol dm^{-3}. This effect indicates that ^{31}P NMR titrations with variable $[(CH_3)_4N^+]$ content could be misleading.

The data presented in Fig. 1 demonstrate that deprotonation of the HOC group starts when $\log[OH^-] > -0.7$ (pH >13.5) and even at the highest pH 14.6 that we managed to achieve the half-neutralisation point is still unlikely to have been reached. The value reported in Table 2 is therefore an approximate lower limit of the true one. The disagreement with the values previously reported[14,44] is understandable due to the inappropriate technique used in these papers.

NTPH and EDTPH

The observed chemical shifts (Table 3) of both $Hntph^{5-}$ and $Hedtph^{7-}$ (pH 11–13) are in a reasonable agreement with those reported elsewhere.[25,26,30,31,37,45] The titration curves give clear evidence of EDTPH being completely deprotonated already at pH 14.4 ($\log[OH^-] \approx 0.3$), while for NTPH only a half-neutralisation point could be passed up to pH 14.6. A first glance at Table 2 and Fig. 2 gives a somewhat unexpected result. NTPH forms slightly stronger complexes with proton, whereas EDTPH demonstrates lower affinity towards H^+ although the formal negative charge of its anion $[edtph^{8-}]$ is 2 units higher. An explanation of this is difficult as long as particular structures are not available.

Comparison with the corresponding X-ray structures of carboxy analogues and of some other organphosphonates suggests possible reasons. In crystals of nitrilotriethanoic (NTA, H_4nta) and ethylendiaminetetraethanoic (EDTA, H_4edta) acids an acidic proton located on a nitrogen atom always reveals chelated structures forming 3 additional H bonds with other donor groups of the same molecule so that the total coordination capacity of such a proton is equal to 4.[48] In the case of EDTA two 5-membered rings are formed and each of two protons participates also in one 8-membered ring with an acetic group from the opposite site of the molecule.

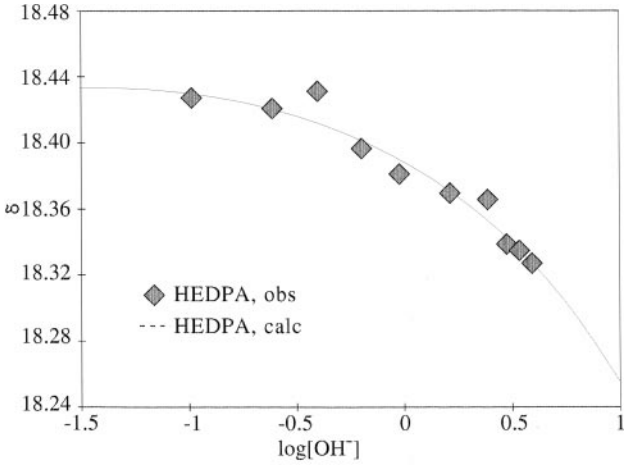


Fig. 1 Variation of ^{31}P NMR chemical shift of HEDPA with hydroxide concentration, log $[OH^-]$.

In the case of phosphorylated amines formation of even a single 5-membered ring is sterically hindered, while the simultaneous formation of two such rings involving $-PO_3^{2-}$ groups meets additional electrostatic resistance. In fact, no chelation was initially observed for crystalline H_6ntph. Later, 5-membered H-rings have been found for H_6ntph, H_8edtph and some other organophosphonates.[48] Generally the tendency of nitrogen proton chelation should increase as the ligand becomes less protonated. A cyclic configuration in HL is expected to be flexible and to involve sequentially several phosphonate fragments.[48] Actually, such dynamic chelation in aqueous solutions is responsible for the high log K_1 values of organophosphonates when compared with their carboxy analogues.

Table 2 Equilibrium constants of organophosphonates

Ligand	Method[a]		I/mol dm^{-3}	T/°C	Equilibrium	log K	Reference
HEDPA	^{31}P NMR	C	3.4; $(CH_3)_4NCl$	24	$L_{-1}H + H \rightleftharpoons L$	>14.6	This work
	Glass electrode,	C	0.1; KCl	25		11.13	44
	Glass electrode,	A	*ca.* 0.04; KOH	20		11.96	14
NTPH	^{31}P NMR,	C	3.4; $(CH_3)_4NCl$	24	$L + H \rightleftharpoons HL$	14.2 ± 0.1	This work
	^1H NMR,	C	0.1; NaOH–KNO_3	Room		13.3	27
	^{31}P NMR,	C	0.1; KNO_3	0		13.1	25
	^{31}P NMR,	C	0.1; KOH	25		12.7	26
	Glass electrode,	C	0.1; KOH, KNO_3	25		12.8	37
	Glass electrode,	C	0.1; KNO_3	25		12.5	47
	Glass electrode,	C	0.2; KOH, KCl	25		12.30	39
	Glass electrode,	C	1.0; KNO_3	25		12.34	42
	Glass electrode,	A	0.1; KCl	25		12.1	40
	NMR,	?	?	28		11.5	45
	Glass electrode,	C	0.1; $(CH_3)_4NCl$	20		10.9	41
	Glass electrode,	C	0.15; NaCl	37		10.67	9
EDTPH	^{31}P NMR,	C	3.5; $(CH_3)_4NCl$	24	$L + H \rightleftharpoons HL$	13.8 ± 0.1	This work
	^1H NMR,	C	*ca.* 1; KOH–KNO_3	Room		14.0	28
	Glass electrode	C	3.0; KNO_3	25		12.36	36
	Glass electrode,	C	*ca.* 0.1; KNO_3	25		13.14	36
	Glass electrode,	C	*ca.* 0.1; KNO_3	25		13.07	32
	Glass electrode,	A	0.1; KNO_3	25		12.10	38
	Glass electrode,	C	3.0; KNO_3	25		12.01	46
	Glass electrode	C	0.1; KCl	25		10.60	35
	Glass electrode,	C	0.15; NaCl	37		10.67	33

[a] Symbol "C" indicates that the corresponding stability constants are given in terms of concentration, while those marked with "A" are in terms of activity.

Table 3 ^{31}P NMR chemical shifts of NTPH and EDTPH in $(CH_3)_4NCl$–$(CH_3)_4NOH$ aqueous solutions[a]

Ligand	Species	pH	δ
NTPH	L	16.6[b]	18.77[b]
	HL	11.0	6.13
EDTPH	L	15.6[b]	16.57[b]
	HL	11.0	11.43

[a] Values are calculated by SigmaPlot. [b] Conventional values, obtained with SigmaPlot by extrapolation of the experimental curve.

The probability of one H-cycle formation for *N*-methyl-*N*,*N*-di(methylenephosphonic acid) (MIDPH) is twice, and for NTPH three times as high as that for aminomethylenephosphonic acid (AMPH). This tentative scheme is in qualitative agreement with log K_1 values reported: 10.04 (AMPH, $I = 0.1$, 25 °C[49]), 12.1 (MIDPH, $I = 0.1$, 25 °C[26]), 14.1 (NTPH, $I = 3.4$, 24 °C, this work).

The fact that NTPH has a slightly higher affinity towards proton than EDTPH could be due to the inability of the latter to arrange simultaneously the same number of phosphonate groups for proton chelation. In the case of the monoprotonated EDTPH species ($Hedtph^{7-}$) the nearest proton chelation sphere is likely to be similar to that of MIDPH. This failure of EDTPH to arrange for proton chelation similar to that of NTPH is probably compensated by a statistic factor: the proton is interchangeably chelated by the "right" and "left" sides of the ligand. This intramolecular migration of a proton gives some extra stabilisation and leads in turn to the almost equal values of log K_1 for NTPH and EDTPH, Table 2.

In comparing the available literature values of the protonation constants of NTPH and EDTPH with the present results, those that used a glass electrode and sodium salt as background medium show the largest and quite understandable disparity. NMR-based log K_1 values[25–27] seem to be also underestimated due to inappropriate background cation (Na^+, K^+), variable ionic strength and inability to reach the half-neutralisation point. Data presented in refs. 27 and 28 appear to have come the closest, mostly due to the self-compensation of several errors. In ref. 28 the authors report log $K_1 = 14.0$ but they used a variable ionic strength of 1–10 mol dm^{-3} maintained by KOH within an uncertain and uncontrolled $D_2O : H_2O$ ratio in the presence of *tert*-butanol as the internal standard. The ligand concentration was 0.1 M, which is comparable with the amounts of free base added. An examination of this paper reveals that the titration was not complete and the "real" log K_1 under the experimental conditions should have been even higher. An extrapolation of data presented here to a common background medium $I = 0.1$ mol dm^{-3} represents a significantly complicated, although feasible procedure, which is outside of the frame of the present communication. The expected value seems unlikely to be much lower than that reported here for $I = 3.4$–3.5 mol dm^{-3}.

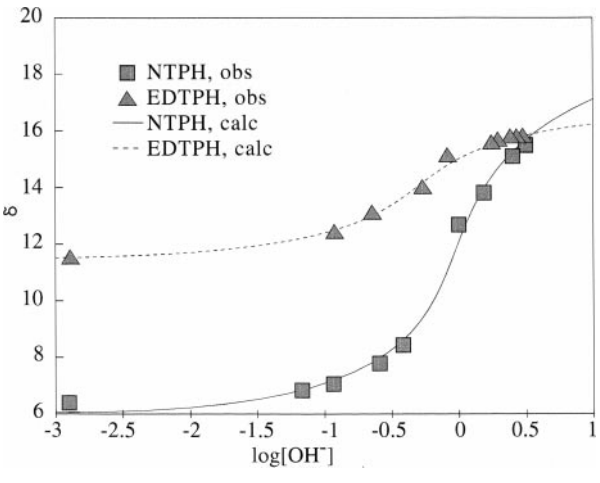


Fig. 2 Variation of ^{31}P NMR chemical shifts of NTPH and EDTPH with hydroxide concentration, log [OH^-].

Acknowledgements

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