Studies on the Extractive Behaviour of 12-Heteropoly Acids.
Part II: Extraction of 12-Molybdophosphoric, 12-Tungstosilicic and 12-Molybdosilicic Acids

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The extractive behaviour of 12-molybdophosphoric ($H_3PMo_{12}O_{40}$), 12-molybdosilicic ($H_4SiMo_{12}O_{40}$) and 12-tungstosilicic ($H_4SiW_{12}O_{40}$) acids into various organic solvents have been studied. The order of extraction of $H_3PMo_{12}O_{40}$ into oxygenated organic solvents is very similar to that of $H_3PW_{12}O_{40}$. The oxygenated organic solvents extract $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ better than $H_4SiM_{12}O_{40}$ and $H_4SiW_{12}O_{40}$. Equilibria involved in the extraction process are discussed and the extraction constants have been calculated. Extraction data give support to the view that 12-heteropoly acids are extracted into oxygenated organic solvents in the form of solvated ion pairs. From 0·5. M LiCl solution, salts of the type $LiH_2M_{12}O_{40}$ and $LiH_3M_{12}O_{40}$ are extracted into the organic phase (where M = Mo or W).

The extraction of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) into oxygenated organic solvents is reported in an earlier communication and the mechanism of the extraction process has been discussed.[1] The mechanism of the extraction of other 12-heteropoly acids has, however, not been studied and so it is of interest to know their extractive behaviour. In the present paper, the results of extraction studies with 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$), 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$) and 12-molybdosilicic acid ($H_4SiMo_{12}O_{40}$) are examined.

EXPERIMENTAL

Apparatus and experimental procedures are described in the previous paper.[1]

Chemicals used were of A.R. grade. Solvents were distilled in an all glass apparatus and the distillate collected at their boiling points were used in extraction studies. Radio-isotopes were supplied by the Bhabha Atomic Research Centre, Trombay. 12-Molybdo-phosphoric acid,[2] 12-tungstosilicic acid[3] and 12-molybdosilicic acid[3] were prepared by the methods reported in the literature. These acids were labelled with P^{32} or W^{185} and Mo^{99} by adding 2 mc of P^{32} or W^{185} or Mo^{99} solution to the initial reaction mixture. All solutions were prepared in dust-free double distilled water. The strength of stock solutions was checked by analysing for P or Si and Mo or W.[4]

1. V. I. Lakshmanan and B. C. Haldar, *Jour. Indian Chem. Soc.*, 1969, **46**, 512.

2. H. Wu., *J. Biol. Chem.*, 1920, **43**, 189.

3. H. S. Booth, Inorganic Synthesis, Vol. I, p. 127, 128. McGraw-Hill Book Company, Inc., New York and London, 1939.

4. A. Vogel, "A Text Book of Quantitative Inorganic Analysis", London, Longmans Green and Co., 1959.

RESULTS AND DISCUSSION

Chemical analysis (Table I) and spectral data confirm that 12-molybdophosphoric, 12-tungstosilicic and 12-molybdosilicic acids are extracted into the oxygenated organic solvents. The molar conductance of $H_3PMo_{12}O_{40}$ (41·6 mhos for $2·16 \times 10^{-4}$ M solution), $H_4SiMo_{12}O_{40}$ (95 mhos for $1·38 \times 10^{-4}$ M solution), and $H_4SiW_{12}O_{40}$ (94·4 mhos for $2·44 \times 10^{-4}$ M

TABLE I

Analysis of Organic and Aqueous Phases after extraction of 12-Heteropoly acids with organic solvents

12-Heteropoly Acids	Solvent	Phase	Molar Conc. of P or Si	Molar Conc. of W or Mo	Ratio of P or Si to Mo or W
$H_3PMo_{12}O_{40}$	Methyl ethyl ketone	Aqueous	1.42×10^{-2}	1.70×10^{-1}	11.9
		Organic	4.90×10^{-2}	5.6×10^{-1}	11.8
	Ethyl acetate	Aqueous	1.21×10^{-2}	1.42×10^{-1}	12.0
		Organic	1.32×10^{-3}	1.59×10^{-2}	12.1
$H_4SiW_{12}O_{40}$	Methyl ethyl ketone	Aqueous	1.39×10^{-2}	1.69×10^{-1}	11.8
		Organic	6.0×10^{-3}	7.2×10^{-2}	12.0
$H_4SiMo_{12}O_{40}$	,,	Aqueous	7.41×10^{-3}	8.91×10^{-2}	12.0
		Organic	6.80×10^{-3}	8.10×10^{-2}	11.8

solution) in nitrobenzene solution indicates that $H_3PMo_{12}O_{40}$, like $H_3PW_{12}O_{40}$, dissociates into two ions, while $H_4SiW_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ dissociate into three ions.[5] The extraction of $H_3PMo_{12}O_{40}$ resembles to that of $H_3PW_{12}O_{40}$. The resemblance is so close that the order of extractions (Table II) into the oxygenated organic solvents and the various equilibria proposed[1] to account for the extraction of $H_3PW_{12}O_{40}$ also hold good for $H_3PMo_{12}O_{40}$. Further, the values (Table III, IV, V) of the extraction constant for $H_3PMo_{12}O_{40}$ are comparable to those reported for $H_3PW_{12}O_{40}$[1]. These findings support the view that the extractive behaviour of these two acids is similar and $H_3PMo_{12}O_{40}$, like $H_3PW_{12}O_{40}$, is extracted in the form of solvated ion pairs by oxygenated organic solvents. This is also expected on the basis of their similarity in crystal structure, basicity and chemical behaviour in aqueous solution.

5. R. A. Robinson and R. H. Stokes, "Electrolytic Solutions", London, Butterworth Scientific Publications, 1959.

6. W. G. Gordy, *J. Chem. Phys.*, 1939, 7, 93.

7. "International Critical Tables of Numerical Data Physics and Technology". McGraw-Hill Book Company, Inc. New York, Vol. III, 1929.

TABLE II

Extraction coefficients of 12-Heteropoly acids between organic solvents and aqueous solution.

Initial concentration of 12-Molybdophosphoric acid $= 6 \cdot 3 \times 10^{-3}$ M.

12-Molybdosilicic acid $= 7 \cdot 8 \times 10^{-3}$ M.

12-Tungstosilicic acid $= 3 \cdot 1 \times 10^{-3}$ M.

Solvent	$E_{H_3PMo_{12}O_{40}}$	$E_{H_4SiW_{12}O_{40}}$	$E_{H_4SiMo_{12}O_{40}}$
O-dichloro benzene	$<5.0 \times 10^{-5}$	$<7.0 \times 10^{-5}$	$<3.7 \times 10^{-5}$
Benzene	$<1.0 \times 10^{-5}$	$<7.0 \times 10^{-5}$	$<2.8 \times 10^{-5}$
Chloroform	$<1.0 \times 10^{-5}$	$<7.0 \times 10^{-5}$	$<5.1 \times 10^{-5}$
Carbon tetrachloride	$<1.1 \times 10^{-5}$	$<7.1 \times 10^{-5}$	$<4.4 \times 10^{-5}$
Amyl acetate (AmAc)	1.9×10^{-2}	1.7×10^{-4}	2.26×10^{-4}
Nitrobenzene (NB)	0.21	3.08×10^{-3}	4.2×10^{-3}
Ethyl acetate (EtAc)	0.23	3.9×10^{-4}	8.5×10^{-4}
Methyl iso-butyl ketone (MIBK)	1.08	7.0×10^{-3}	1.1×10^{-2}
Methyl ethyl ketone (MEK)	1.58	0.18	0.42
Iso-Amyl alcohol (Iso-AmOH)	3.7	1.06×10^{-2}	1.1×10^{-2}
Octanol (OctOH)	9.6	1.04×10^{-3}	2.5×10^{-3}
Butanol (BuOH)	9.2	1.32	4.28

TABLE III

Determination of extraction constant for 12-Molybdophosphoric acid

Solvent	Conc. of 12-Molybdo-phosphoric Acid	$\log E$	$\log K = \log \dfrac{E}{(H^+)}$	Average $(\log K)$
MEK	6.3×10^{-3}	1.5052	2.45	
	”	0.3032	2.40	
	”	0.3345	2.44	2.46 ± 0.14
	1.59×10^{-2}	0.2853	2.60	
	3.36×10^{-1}	0.5340	2.40	
EtAc	2.5×10^{-4}	-0.6198	2.10	
	1.0×10^{-3}	-0.1423	3.10	3.04 ± 0.09
	2.5×10^{-3}	0.0645	3.00	
	5.0×10^{-3}	0.2810	2.95	
MIBK	2.5×10^{-4}	-0.5528	3.15	
	2.5×10^{-3}	-0.1206	3.30	3.02 ± 0.32
	5.0×10^{-3}	0.5705	2.70	
*Iso-AmOH	2.5×10^{-4}	-0.5279	4.20	
	1.0×10^{-3}	0.0294	3.35	
	2.5×10^{-3}	0.4928	3.71	3.74 ± 0.46
	5.0×10^{-3}	0.6590	3.71	

* Extraction carried out from $0 \cdot 5$ M LiCl solution.

TABLE IV

Determination of extraction constant for 12-Molybdophosphoric acid

Solvent	Conc. of 12-Molybdophosphoric Acid	$\log E$	$\log K = \log \dfrac{E}{(H^+)^2}$	Average $(\log K)$
EtAc	6.1×10^{-3}	-1.2443	2.79	2.84 ± 0.05
	1.34×10^{-3}	-0.9626	2.89	
	6.36×10^{-1}	0.7798	2.83	
Iso-AmOH	3.17×10^{-3}	0.5441	4.84	
	1.59×10^{-2}	0.5911	4.64	4.82 ± 0.18
	6.59×10^{-2}	0.6964	4.97	
MIBK	6.3×10^{-3}	0.0334	3.57	
	1.34×10^{-2}	0.0531	3.86	3.63 ± 0.23
	6.36×10^{-2}	0.4579	3.46	

TABLE V

Determination of extraction constant for 12-Molybdophosphoric acid

Solvent	Conc. of 12-Molybdophosphoric Acid	$\log E$	$\log K = \log E$	Average $(\log K)$
MEK*	2.50×10^{-4}	1.34	1.34	
	1.00×10^{-3}	1.34	1.34	1.35 ± 0.02
	2.50×10^{-3}	1.37	1.37	
	5.00×10^{-3}	1.33	1.33	
			$\log K = 2 \log E$	
NB*	2.5×10^{-4}	-0.8532	-1.71	
	1.00×10^{-3}	-0.8239	-1.65	-1.67 ± 0.04
	2.50×10^{-3}	-0.8237	-1.65	
			$\log K = \log \dfrac{E}{(H^+)}$	
NB	3.18×10^{-2}	-0.7455	0.12	0.11 ± 0.01
	6.36×10^{-2}	-0.0459	0.10	

* Extraction carried out from 0·5 M LiCl solution.

The oxygenated organic solvents extract (Table II), $H_4SiMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ less efficiently than $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$. This may be attributed to the fact that the anions of 12-molybdo- and 12-tungsto-silic acids in aqueous solution carry more charge than those of 12-molybdo- and 12-tungsto-phosphoric acids. Since 12-heteropoly acids are extracted in the form of solvated ion pairs, it is reasonable to assume that their extractions are mainly determined by the dielectric constant and bisicity of the solvent. Apparently, the extraction of $H_3PMo_{12}O_{40}$, the combined effect of dielectric constant and basicity make nitrobenzene ($\epsilon = 34.8$ at 25° and basicity[6] $= 28$) as good an extractant as ethyl acetate ($\epsilon = 6.4$ at 25° and basicity[6] $= 84$). If the charge on the anions of $H_4SiMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ is higher than that on the anion of $H_3PMo_{.2}O_{40}$, then the dielectric constant of the solvent will have more pronounced effect on the extractions of $H_4SiMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ than on the extraction of $H_3PMo_{12}O_{40}$. This is reflected in the better extractions of $H_4SiW_{12}O_{40}$ and $H_2SiMo_{12}O_{40}$ into nitrobenzene than into ethyl acetate. Again, $H_3PMo_{12}O_{40}$ is extracted better into octanol ($\epsilon = 10.1$ at 20°, basicity higher than methyl ethyl ketone) than into methyl ethyl ketone ($\epsilon = 18.1$ at 25°, basicity $= 77$), whereas $H_4SiMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ are extracted much less efficiently into the former than into the latter. These findings appear to support the above explanation based on the relative importance of basicity and dielectric constant of solvents in determining the extraction of differently charged anions from aqueous solution. Butanol, which has dielectric constant[8]
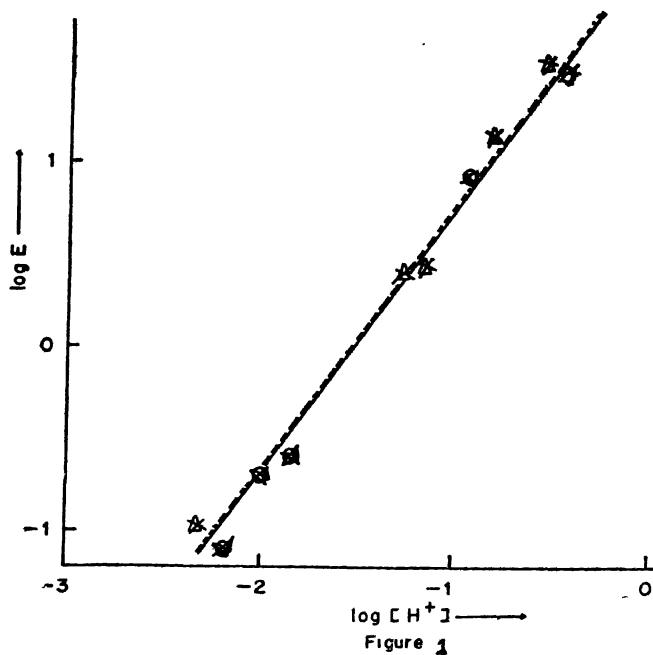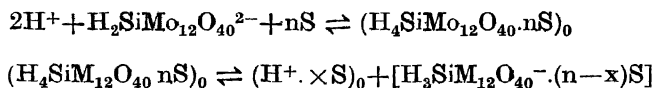

Fig. 1 : Effect of Hydrogen ion concentration on the Extraction Coefficient of 12-Tungstosilicic Acid and 12-Molybdosilicic Acid between Methyl Ethyl Ketone and Aqueous Acid Solution. Initial Concentration of 12-Tungstosilicic Acid $= \triangle 3.1 \times 10^{-3} M$ $O 1.55 \times 10^{-3} M$, Slope $= 1.7$. Initial Concentration of 12-Molybdosilicic Acid $= \times 1.55 \times 10^{-3} M \triangle \pm 3.70 \times 10^{-4} M$, Slope $= 1.7$.

8. R. C. Weast, "Hand Book of Chemistry and Physics", 48th Ed. 1967-68. Published by the Chemical Rubber and Company.

($\epsilon = 17\cdot1$ at 25°) close to that of methyl ethyl ketone and basicity presumably higher than that of methyl ethyl ketone is found to be a much better extractant than methyl ethyl ketone for the four 12-heteropoly-acids $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$.

In the extractions of $H_4SiW_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ by methyl ethyl ketone, the plot (Fig. I) of log E versus log $(H^+)_{aq}$ is a straight line of slope equal to $1\cdot7$. The variation of E with respect to $(H^+)_{aq}$ can be explained by assuming that the following equilibria are involved in the extraction process.

$$2H^+ + H_2SiMo_{12}O_{40}{}^{2-} + nS \rightleftharpoons (H_4SiMo_{12}O_{40}.nS)_0$$

$$(H_4SiM_{12}O_{40} \; nS)_0 \rightleftharpoons (H^+.\times S)_0 + [H_3SiM_{12}O_{40}{}^-.(n-x)S]$$

where M = W or Mo.

The extraction coefficient, E, may be written in the form

$$E = K_1[H^+]^2_{aq}\left[1 + \frac{K_2}{[H^+]_0} \right] \qquad \qquad .. \;(1)$$

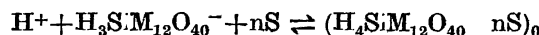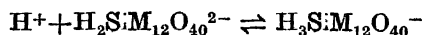where
$$K_1 = \frac{[H_4SiM_{12}O_{40}.nS]_0}{[H^+]^2_{aq}[H_2SiM_{12}O_{40}{}^{2-}]_{aq}}$$

and

$$K_2 = \frac{[H^+.nS]_0[H_3SiM_{12}O_{40}{}^-]_0}{[H_4SiM_{12}O_{40}]}$$

When the extracted species is completely dissociated in the organic phase, E should be proportional to $\dfrac{[H^+]^2_{aq}}{[H^+]_0}$ and so, the value of the slope obtained by plotting log E against log $[H^+]_{aq}$ should be less than 2. If the dissociation of the extracted species in the organic phase is negligible, the slope would attain the value of 2. Since $H_4SiMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ dissociate into three ions in nitrobenzene, it is quite plausible that they dissociate at least partially in methyl ethyl ketone, the dielectric constant of which is as high as $18\cdot51$ at 25°. However, the existence of the following equilibria in the aqueous phase,

$$H^+ + H_2SiM_{12}O_{40}{}^{2-} \rightleftharpoons H_3SiM_{12}O_{40}{}^-$$

$$H^+ + H_3SiM_{12}O_{40}{}^- + nS \rightleftharpoons (H_4SiM_{12}O_{40} \; nS)_0$$

can also provide explanation for the observed effect of hydrogen ion concentration on the extraction coefficients of $H_4SiMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$. With methyl ethyl ketone as an extractant from $0\cdot5$ M LiCl medium, the extraction coefficients (Table VI) appear to remain constant with increase in the initial aqueous phase concentrations of $H_4SiW_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$. Since chemical analysis data (Table VII) suggest the extraction of salts such as $LiH_3SiW_{12}O_{40}$ and $LiH_3SiMo_{12}O_{40}$ from LiCl medium, the following equilibria may be postulated to represent the extraction process,
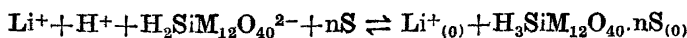
$$Li^+ + H^+ + H_2SiM_{12}O_{40}{}^{2-} + nS \rightleftharpoons Li^+{}_{(0)} + H_3SiM_{12}O_{40}.nS_{(0)}$$

TABLE VI

Extraction of 12-Heteropoly acids by methyl ethyl ketone from 0·5 M LiCl solution

Heteropoly Acid	Conc. of 12-Heteropoly Acid $\times 10^3$	E_{MEK}
$H_4SiMo_{12}O_{40}$	0.18	0.63
	1.80	0.61
	3.60	0.59
$H_4SiW_{12}O_{40}$	0.925	0.91
	1.850	0.94

TABLE VII

Analysis of organic phase after extraction of 12-Heteropoly acids from 0·5 M LiCl solution

Solvent	12-Heteropoly Acid	Molar Conc. of Li^+	Motor Conc. of P(V) or Si(IV)	Molar Conc. of W(VI) or Mo(VI)	Ratio of Li : P(V) or Si (IV) : W(VI) or Mo(VI)
MEK	$H_3PMo_{12}O_{40}$	1.36×10^{-2}	1.41×10^{-2}	1.7×10^{-1}	0.9 : 1 : 12.1
	$H_4SiW_{12}O_{40}$	1.21×10^{-3}	1.34×10^{-3}	1.66×10^{-2}	0.90 : 1 : 12.1
	$H_4SiMo_{12}O_{40}$	8.2×10^{-4}	9.0×10^{-4}	1.68×10^{-2}	9.90 : 1 : 12.1
EtAc	$H_3PMo_{12}O_{40}$	3.5×10^{-3}	3.25×10^{-3}	4.02×10^{-2}	1 : 1.05 : 12

Assuming that the salt $LiH_3SiM_{12}O_{40}$ dissociates completely into Li^+ and $H_3SiM_{12}O_{40}^-$ in the organic phase, it can be shown that

$$E^2 = K_3 \qquad \qquad .. \quad (2)$$

where $\qquad K_3 = \dfrac{(Li^+)_0 \, (H_3SiM_{12}O_{40}^-.nS)_0}{(H^+)_{aq} \, (H_2SiM_{12}O_{40}^{2-})_{aq}} = \text{constant},$

Equation (2) predicts that E should remain constant at different initial concentrations of $H_4SiW_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ as observed experimentally (Table VI). It appears that the extraction behaviour of $H_4SiW_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ in LiCl medium lends support to the view that the extracted species undergoes ionization in methyl ethyl ketone.

The extraction of $H_4SiW_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ by nitrobenzene from aqueous solution may be represented as,
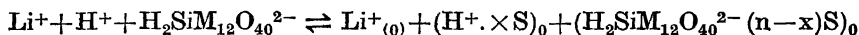
$$2H^+ + H_2SiM_{12}O_{40}^{2-} + nS \rightleftharpoons 2(H^+ \times S)_0 + [H_2SiM_{12}O_{40}^{2-}(n-x)S]_0$$
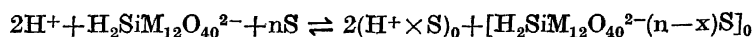
The extraction equilibrium constant can be written as,

$$K_4 = E^3 \qquad \qquad .. \quad (3)$$

where $\qquad K_4 = \dfrac{(H^+ \times S)_0^2 (H_2SiM_{12}O_{40}^{2-}(n-x)S]_0}{(H^+)_{aq}^2 (H_2SiM_{12}O_{40})_0^{2-}} = \text{constant}$

The validity of equation (3) is confirmed by experimental data summarized in Table VIII. If the extraction is carried out from $0.5\ M$ LiCl medium, then the extraction equilibrium may be expressed as,

$$Li^+ + H^+ + H_2SiM_{12}O_{40}{}^{2-} \rightleftharpoons Li^+{}_{(0)} + (H^+.\times S)_0 + (H_2SiM_{12}O_{40}{}^{2-} \cdot (n-x)S)_0$$

and the extraction coefficient is given by

$$E^3(H_2SiM_{12}O_{40}{}^{2-})_{aq} = K_5 \qquad\qquad .. \quad (4)$$

where $\qquad K_5 = \dfrac{2(Li^+)_0(H^+.\times S)_0(H_2SiM_{12}O_{40}{}^{2-}.(n-x)S)_0}{(H^+)_{aq}(H_2SiM_{12}O_{40})^{2-}} = $ constant.

According to expression (4), E^3 should be inversely proportional to $(H_2SiM_{12}O_{40}{}^{2-})_{aq}$. Extraction data shown in Table IX, indicates that the value of $E^3\ (H_2SiM_{12}O_{40}{}^{2-})_{aq}$ remains fairly constant over the limited concentration range studied.

TABLE VIII

Extraction coefficient of 12-Heteropoly acids as a function of its initial aqueous phase concentration

12-Heteropoly Acid	Conc. of 12-Heteropoly Acid (in molarity) $\times 10^3$	$E_{NB} \times 10^3$
$H_4SiW_{12}O_{40}$	20.0	0.21
	50.0	0.20
	200.0	0.19
$H_4SiMo_{12}O_{40}$	1.9	3.90
	2.8	4.20
	14.0	4.20
	24.0	3.86

TABLE IX

Extraction of 12-Heteropoly acids by nitrobenzene from $0.5\ M$ Lithium chloride solution. Temperature $= 29° \pm 1°$

12-Heteropoly Acid	Initial Conc. of 12-Heteropoly Acid $\times 10^3$	Conc. of 12-Heteropoly acid in equilibrated aqueous phase $\times 10^3$ $(H_2SiM_{12}O_{40}{}^{2-})_{aq}$	E_{NB}	$\log[E^3 \times (H_2SiM_{12}O_{40}{}^{-2})]$
$H_4SiW_{12}O_{40}$	1.80	0.178	1.22×10^{-2}	-9.49
	0.37	0.3675	7.35×10^{-3}	-9.77
	0.925	0.9196	5.66×10^{-3}	-9.48
	1.85	1.841	4.32×10^{-3}	-9.66
$H_4SiMo_{12}O_{40}$	0.18	1.752	$1.8\ \times 10^{-2}$	-8.99
	1.80	1.771	1.69×10^{-2}	-8.07
	3.60	3.586	3.61×10^{-3}	-9.8

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