April, 1993] © 1993 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 66, 1111—1115 (1993) 1111

A Hydrophobicity Scale of Heteropoly- and Isopolyanions Based on Voltammetric Studies of Their Transfer at the Nitrobenzene/Water Interface

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(Received October 22, 1992)

A hydrophobicity scale of heteropoly- and isopolyanions is proposed on the basis of voltammetric studies concerning their transfer at the nitrobenzene (NB)/water (W) interface. For polyanions of various size and ionic charge ($z=-2$ to -6), the standard ion-transfer potential ($\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^{\ominus}$), which is related to the Gibbs free energy of the transfer as $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^{\ominus}=-\Delta G_{\mathrm{tr}}^{\ominus,\mathrm{O}\rightarrow\mathrm{W}}/zF$ (F, the Faraday constant), depends linearly on the quantity $|z|/n^{2/3}$ (n, the number of oxygen atoms in the polyanion structure), which should be proportional to the surface charge density of the polyanion. The value of $|z|/n^{2/3}$ may provide a useful criterion for evaluating the hydrophobic (or hydrophilic) properties of polyanions, including the stability in solutions and extractability into organic solvents.

Heteropolyanions[1,2] are widely used as acid and redox catalysts for various synthetic reactions in both heterogeneous and homogeneous systems;[3] they have also played important roles in the analysis of such oxoanions as orthophosphate and silicate ions. While trying to understand these catalytic and analytical processes, detailed solution studies of heteropolyanions were carried out using electrochemical and spectroscopic techniques. One of the important facts obtained is that although certain heteropolyanions, like $[\mathrm{PMo_{12}O_{40}}]^{3-}$, are unstable in water, they are stabilized by the addition of water-miscible organic solvents, such as 1,4-dioxane and acetone.[4—11] It should also be noted that in recent synthetic studies[12] a wide variety of new heteropolyanions, e.g., $[\mathrm{S_2Mo_{18}O_{62}}]^{4-}$, $[\mathrm{S_2VMo_{17}O_{62}}]^{5-}$, $[\mathrm{VMo_{12}O_{40}}]^{3-}$, and $[\mathrm{P_2Mo_{18}O_{61}}]^{4-}$ (containing $\mathrm{P_2O_7}^{4-}$), have been successfully prepared from mixed aqueous solutions. Thus, although many heteropolyanions possess hydrophobic characteristics, there has been no available measure for evaluating the affinity of heteropolyanions to organic solvents.

Over the past several years, we employed a novel voltammetric technique[13—15] (so-called, "ion-transfer voltammetry") in order to study the transfer of heteropoly- and isopolyanions at the interface between two immiscible electrolyte solutions (ITIES), viz., the nitrobenzene (NB)/water (W) interface.[16—19] Moderately hydrophobic or semi-hydrophobic polyanions, such as $[\mathrm{SiW_{12}O_{40}}]^{4-}$, $[\mathrm{P_2Mo_{18}O_{62}}]^{6-}$, and $[\mathrm{Mo_6O_{19}}]^{2-}$, produced voltammetric waves due to their transfer across the ITIES. Through analyses of the voltammetric waves, the values of the standard ion-transfer potential ($\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^{\ominus}$), which is related to the standard Gibbs free energy of transfer by Eq. 3 (see below), were determined for the polyanions of various size and ionic charge. As for the determined $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^{\ominus}$-values, a simple linear dependence on the surface charge densities of polyanions has been observed.[20] On the basis of this finding, we will hereinafter propose a hydrophobicity scale of heteropoly- and isopolyanions.

Experimental

Chemicals. The tetrabutylammonium ($\mathrm{TBA^+}$) salt of $[\mathrm{VMo_5O_{19}}]^{3-}$ was prepared as described previously.[21]

The $\mathrm{TBA^+}$-salt of α-$[\mathrm{Mo_8O_{26}}]^{4-}$ was obtained as follows: 10 g of $\mathrm{(NH_4)_6Mo_7O_{24}\cdot 4H_2O}$ was dissolved in 100 ml of water. After filtration of the turbidity, the pH of the solution was adjusted to 5.5—6.5 with 1 M NaOH (M= mol dm^{-3}). The addition of tetrabutylammonium bromide produced white precipitates. They were collected by filtration, washed with ethanol and then dried at 50°C. The identification of the salt was based on an elemental analysis and IR spectroscopy.[22] Found: C, 35.42; H, 6.74; N, 2.59; Mo, 35.89%. Calcd for $\mathrm{C_{64}H_{144}N_4Mo_8O_{26}}$: C, 35.70; H, 6.74; N, 2.60; Mo, 35.64%. IR (cm^{-1}) 950 (w), 923 (vs), 912 (vs), 905 (vs), 854 (s), 806 (vs), 665 (vs), 560 (w), 502 (w) (vs=very strong; s=strong; w=weak). In TG-DTA no evolution of water was observed up to 220°C.

The other chemicals were described in a previous paper.[19]

Electrochemical Measurements. In studying of the transfer of $[\mathrm{VMo_5O_{19}}]^{3-}$ and α-$[\mathrm{Mo_8O_{26}}]^{4-}$ at the NB/W interface, the following electrochemical cell (cell A) was used:

	I	II	III	IV	V	
	0.02 M	0.1 M	0.1 M	0.05 M	0.05M	
Ag/	TPnACl,		TPnATPB,	$\mathrm{MgCl_2}$,	$\mathrm{MgCl_2}$,	AgCl/
AgCl	0.1 M	TPnATPB	x mM	0.5 M	0.5 M	Ag,
	$\mathrm{MgSO_4}$		polyanion	$\mathrm{MgSO_4}$,	$\mathrm{MgSO_4}$	
	(W)	(NB)	(NB)	buffer (W)	(W)	

Here, TPnACl denotes tetrapentylammonium chloride and TPnATPB tetrapentylammonium tetraphenylborate. The polyanion was added to phase-III as the $\mathrm{TBA^+}$-salt,[23] and its transfer across the interface (area, 12.6 mm^2) between phases III and IV was examined. The pH of phase IV was adjusted with a $\mathrm{CH_3COOH}$–$\mathrm{(CH_3COO)_2Mg}$ buffer ($[\mathrm{CH_3COO^-}]=0.1$ M) or HCl (at pH<3). The electrolytic cell was water-jacketed in order to maintain the temperature at 25±0.1°C. For further details, see Ref. 19.

Results

The voltammetric determinations of $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^{\ominus}$ for the polyanions at the NB/W interface were previously described in detail,[16—19] except for $[\mathrm{VMo_5O_{19}}]^{3-}$ and α-

$[Mo_8O_{26}]^{4-}$. In this paper we demonstrate a typical process for the determination of $\Delta_O^W\phi^\ominus$ using as examples the transfer of $[VMo_5O_{19}]^{3-}$ and α-$[Mo_8O_{26}]^{4-}$.

Figure 1 shows cyclic voltammograms for the transfer of $[VMo_5O_{19}]^{3-}$ at the NB/W(pH 4.8) interface, which were recorded using five different scan rates. In each voltammetric wave, the anodic (positive-current) peak corresponds to the transfer of the polyanion from NB to W, whereas the cathodic (negative-current) peak corresponds to its transfer back to NB. As can be seen in the figure, the cathodic peak became less prominent upon lowering the scan rate. This may be ascribed to the partial decomposition of the polyanion in the W-phase (cf. Ref. 18). Nevertheless, the midpoint potential $E_{\rm mid}$ ($\equiv(E_{\rm pa}+E_{\rm pc})/2$; $E_{\rm pa}$ and $E_{\rm pc}$ being the anodic and cathodic peak potentials) was practically independent of the scan rate. As shown in Fig. 2, the values of $E_{\rm mid}$ were almost invariant at higher pH-values (>4), though they shifted to positive potentials at lower pH-values due to protonation of the polyanion in the organic-solvent phase.[24] The invariant value of $E_{\rm mid}$ at higher pH-values (viz., 0.201 V) was then considered as the reversible half-wave potential ($E_{1/2}^{\rm rev}$) for the individual-ion transfer accompanying no protonation. The $E_{1/2}^{\rm rev}$ is related to $\Delta_O^W\phi^\ominus$ as[25]

$$E_{1/2}^{\rm rev} = \Delta_O^W\phi_{1/2}^{\rm rev} + \Delta E_{\rm ref} \qquad (1)$$

and

$$\Delta_O^W\phi_{1/2}^{\rm rev} = \Delta_O^W\phi^\ominus + \frac{RT}{zF}\ln\frac{\gamma^O\sqrt{D^W}}{\gamma^W\sqrt{D^O}}, \qquad (2)$$

where z is the ionic valence (here $z=-3$); γ^α and D^α (α=O or W) are the activity coefficient and the diffusion coefficient of the transferred ion in the organic-solvent phase (O) or the water phase (W); F, R, and T have their usual meanings; and $\Delta E_{\rm ref}$ is a constant (0.323 V[26] for cell A) which depends only on the reference-electrode system. The second term of the right-hand side of Eq. 2 is quite small; the contribution was evaluated to be only −0.003 V (for $z=-3$) by assuming $\gamma^O/\gamma^W=1$ and $D^W/D^O=2.07$[27] (Walden rule). Finally, $\Delta_O^W\phi^\ominus$ was determined to be −0.119 V for $[VMo_5O_{19}]^{3-}$. Further, using a well-known relation,[13,15]

$$\Delta G_{\rm tr}^{\ominus,{\rm O}\to{\rm W}} = -zF\Delta_O^W\phi^\ominus, \qquad (3)$$

$\Delta G_{\rm tr}^{\ominus,{\rm O}\to{\rm W}}$ was also determined to be −35 kJ mol^{-1}.

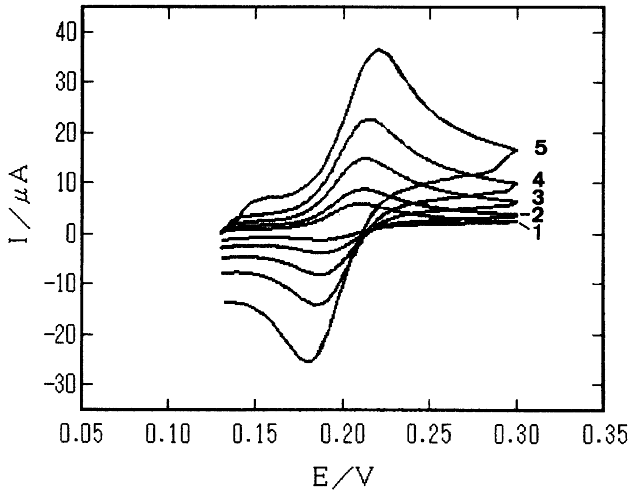

Fig. 1. Cyclic voltammograms of the transfer of $[VMo_5O_{19}]^{3-}$ at the NB/W (pH 4.8) interface. The polyanion was added to the NB-phase as the tetrabutylammonium salt so that the concentration became 0.20 mM. The scan rates were (1) 0.02; (2) 0.05; (3) 0.1; (4) 0.2; (5) 0.5 V s^{-1}. Supporting electrolytes, 0.1 M TPnATPB in NB; 0.05 M $MgCl_2$ + 0.5 M $MgSO_4$ in W.

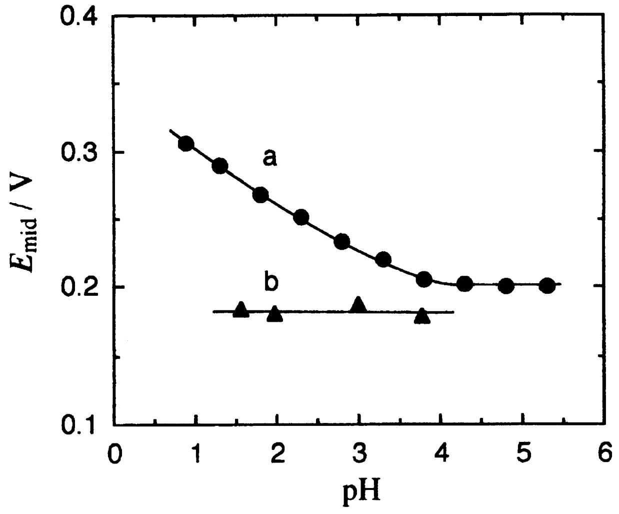

Fig. 2. pH dependences of the midpoint potentials of the cyclic voltammograms for the transfer of (a) $[VMo_5O_{19}]^{3-}$ and (b) α-$[Mo_8O_{26}]^{4-}$ at the NB/W interface.

For the transfer of α-$[Mo_8O_{26}]^{4-}$, it was rather difficult to obtain a reproducible voltammogram at ordinary scan rates, due to the appearance of a maximum which might be related to a quite rapid decomposition or transformation of the complex anion (possibly, into β-isomer) in the W-phase. Nevertheless, a well-defined cyclic voltammogram (not shown) could be obtained most readily by using higher scan rates (e.g., 1.0 V s^{-1}). As shown in Fig. 2, $E_{\rm mid}$ is virtually constant (0.183±0.004 V) over the 1.6 to 3.8 pH range, indicating no participation of protonation in the transfer process. In a similar manner as $[VMo_5O_{19}]^{3-}$ mentioned above, $\Delta_O^W\phi^\ominus$ and $\Delta G_{\rm tr}^{\ominus,{\rm O}\to{\rm W}}$ for α-$[Mo_8O_{26}]^{4-}$ were evaluated based on the pH-independent $E_{\rm mid}$.

As illustrated by the transfer of the two polyanions, the values of $\Delta_O^W\phi^\ominus$ and $\Delta G_{\rm tr}^{\ominus,{\rm O}\to{\rm W}}$ for other kinds of polyanions were likewise determined. The results are summarized in Table 1. For further details, see each reference noted in the table.

In Table 2 the values of $\Delta_O^W\phi^\ominus$ determined using dif-

Table 1. Standard Potentials and Standard Gibbs Free Energies of Transfer of Heteropoly- and Isopolyanions at the Nitrobenzene/Water Interface (25°C)

No.	Anion	Form	$\lvert z\rvert/n^{2/3}$	$\dfrac{\Delta_O^W\phi^\ominus}{V}$	$\dfrac{\Delta G_{tr}^{\ominus,O\to W}}{kJ\,mol^{-1}}$	Ref.
1	$[SiMo_{12}O_{40}]^{4-}$	α	0.342	0.066	26	16, 17
		β	0.342	0.067	27	17
2	$[GeMo_{12}O_{40}]^{4-}$	α	0.342	0.064	26	17
		β	0.342	0.066	26	17
3	$[PMo_{12}O_{40}]^{3-}$	α	0.256	0.248[a]	72[a]	17
		β	0.256	0.248[a]	72[a]	17
4	$[AsMo_{12}O_{40}]^{3-}$	α	0.256	0.243[a]	71[a]	17
5	$[SiW_{12}O_{40}]^{4-}$	α	0.342	0.071	28	17
6	$[PW_{12}O_{40}]^{3-}$	α	0.256	0.253[a]	74[a]	17
7	$[P_2Mo_{18}O_{62}]^{6-}$	α	0.383	0.005	3	19
8	$[As_2Mo_{18}O_{62}]^{6-}$	α	0.383	0.005	3	19
9	$[S_2Mo_{18}O_{62}]^{4-}$	α	0.255	0.269[a]	104[a]	19
10	$[S_2VMo_{17}O_{62}]^{5-}$		0.319	0.085	41	19
11	$[P_2Mo_{18}O_{61}]^{4-}$		0.258	0.239[a]	92[a]	19
12	$[Mo_6O_{19}]^{2-}$		0.281	0.164	32	18
13	$[VMo_5O_{19}]^{3-}$		0.421	−0.119	−35	This study
14	$[Mo_8O_{26}]^{4-}$	α	0.460	−0.137	−53	This study

a) Approximate values estimated from the foot of the voltammetric wave.

Table 2. Standard Ion-Transfer Potentials of Some Typical Polyanions at the Nitrobenzene/Water Interface Determined Using Three Different Supporting-Electrolyte Systems (25°C)

Anion	$\Delta_O^W\phi^\ominus$/V		
	System 1[a]	System 2[b]	System 3[c]
α-$[SiMo_{12}O_{40}]^{4-}$	0.071	0.066[16,17]	0.073
α-$[GeMo_{12}O_{40}]^{4-}$	0.068	0.064[17]	0.072
α-$[P_2Mo_{18}O_{62}]^{6-}$	0.005[19]	0.005	0.023
$[Mo_6O_{19}]^{2-}$	0.172	0.164[18]	0.170

a) 0.1 M TPnATPB (NB)/0.05 M $MgCl_2$ + 0.5 M $MgSO_4$ (W).[18] b) 0.1 M TBATPB (NB)/0.5 M $MgCl_2$ (W).[16] c) 0.1 M TBATPB (NB)/0.1 M LiCl (W).[25]

ferent supporting-electrolyte systems are compared for some typical polyanions. The divergences are almost within the experimental errors (±0.005 V), except for α-$[P_2Mo_{18}O_{62}]^{6-}$, which shows a slight deviation. This result implies that the ion association in either NB or in W has no significant influence on the transfer potential of a polyanion. It should also be noted that the $\Delta_O^W\phi^\ominus$-values given in Table 1 were determined using some different supporting-electrolyte systems. If the effect of ion association was not negligible, such a clear correlation as shown below (Fig. 3) could not been obtained.

Discussion

In Table 1, anions **1**—**6** have the Keggin-type structure, whereas anions **7**—**11** have the Dawson-type structure (or a related structure for **11**).[28] In either structure, anions of the same ionic charge have nearly equal values of $\Delta_O^W\phi^\ominus$ and $\Delta G_{tr}^{\ominus,O\to W}$, independent of the central heteroatoms. Further, there is no difference in the transfer potential and energy between the α- and β-isomers, in which one M_3O_{13} (M=Mo or W) group is rotated by $\pi/3$.[1] These results seem to support the hypothesis that the surface charge of such a polyanion is nonlocalized.

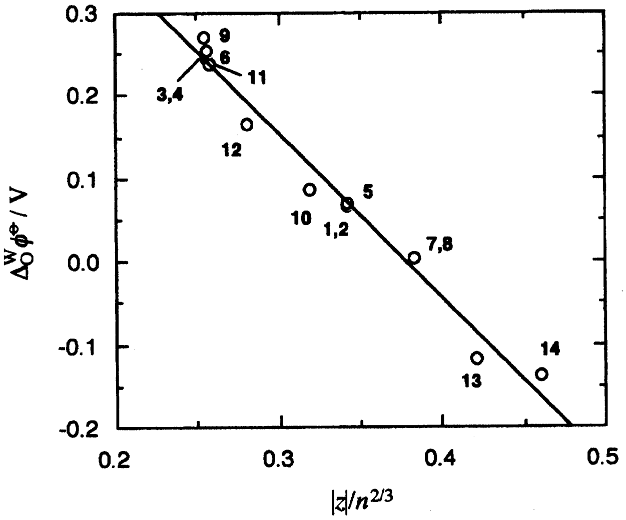

Fig. 3. Plot of the standard ion-transfer potentials of heteropoly- and isopolyanions at the NB/W interface against $\lvert z\rvert/n^{2/3}$ (z, ionic valence; n, number of oxygen atoms). Numbers **1**—**14** correspond to the polyanions listed in Table 1.

In the following we discuss the dependence of $\Delta_O^W\phi^\ominus$ on the surface charge density of a polyanion. Unfortunately, however, there is only one available value of the ionic radii, viz., r=0.56 nm for $[\mathrm{SiW_{12}O_{40}}]^{4-}$.[29] Accordingly, the surface charge density of a polyanion was estimated as follows: Because all of the space of the polyanion structure is taken up by the bulky oxygen atoms, which are virtually close-packed,[1] the ionic volume can be determined solely based on the number of oxygen atoms (n). If we assume that the polyanion is a hard sphere with a uniform surface charge, r should be proportional to $n^{1/3}$. Consequently, the surface charge density, $ze/4\pi r^2$ (e, the elementary charge), can be regarded as being proportional to $|z|/n^{2/3}$. Against this quantity, the $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^{\ominus}$-values for the polyanions are plotted in Fig. 3. Despite the large differences in sizes, charges, and even structures, all of the data surprisingly lay on a straight line,

$$\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^{\ominus}(\mathrm{V}) = -1.981\left(|z|/n^{2/3}\right) + 0.749. \qquad (4)$$

Such a simple relationship was not observed between $\Delta G_{\mathrm{tr}}^{\ominus,\mathrm{O}\to\mathrm{W}}$ and $|z|/n^{2/3}$. It should be also noted that a similar linear plot was obtained for polyanion transfer at another ITIES, viz., the 1,2-dichloroethane/water interface.[30]

The standard transfer potentials of ions provide useful criteria for predicting their "hydrophobic" behaviors in such processes as liquid–liquid extraction[31—35] and liquid-membrane transport.[36] Thus, the transfer potentials can be used as a scale for the hydrophobicity of ions. For the polyanions of interest, however, the quantity $|z|/n^{2/3}$ (the values being shown in Table 1) may be conveniently employed as an alternative to $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^{\ominus}$, since a linear relationship exists between the two quantities (Fig. 3).

According to the $|z|/n^{2/3}$-values, polyanions may be classified as being either hydrophobic or hydrophilic. As a whole, polyanions with $|z|/n^{2/3}$ values smaller than 0.3 (e.g., the anions **3**, **4**, **6**, **9**, **11**, **12**) are unstable in aqueous solutions, and are classified as being "hydrophobic"; they are known to be highly stabilized by the addition of water-miscible organic solvents. Most of the new heteropolyanions prepared from mixed aqueous solvents[12] belong to this class. On the other hand, "hydrophilic" polyanions with $|z|/n^{2/3}$-values larger than 0.3 are relatively stable in aqueous solutions. Thus, the values of $|z|/n^{2/3}$ are useful for evaluating the stability of polyanions in solutions. As shown in our recent study,[17,18] the Keggin-type molybdophosphate anion $[\mathrm{PMo_{12}O_{40}}]^{3-}$, being classified as hydrophobic ($|z|/n^{2/3}$=0.256), does not exist stably in an aqueous solution; as a result relatively hydrophilic, lacunary anions, such as $[\mathrm{H_3PMo_{11}O_{39}}]^{4-}$ ($|z|/n^{2/3}$=0.348), are formed.

Furthermore, the $|z|/n^{2/3}$-value may provide useful criteria for evaluating the extractability of polyanions into organic solvents. It appears that polyanions with smaller $|z|/n^{2/3}$-values are preferentially extracted into organic solvents. For the Keggin-type molybdates, the trivalent anions (**3** and **4** with $|z|/n^{2/3}$=0.256) tend to be extracted more readily, i.e., at lower acid concentrations than the tetravalent anions (**1** and **2** with $|z|/n^{2/3}$=0.342).[37—39]

In conclusion, the value of $|z|/n^{2/3}$ seems to be promising for a hydrophobicity scale of polyanions.

Finally, we would like to add that the linear plot of $\Delta_{\mathrm{O}}^{\mathrm{W}}\phi^{\ominus}$ vs. $|z|/n^{2/3}$ in Fig. 3 is of interest concerning a study of ion solvation[40] as well. The plot means that the standard transfer energy ($\Delta G_{\mathrm{tr}}^{\ominus,\mathrm{O}\to\mathrm{W}}$), namely the difference in the solvation energies of the polyanion in O and W, depends linearly on $1/n^{2/3}$ (cf. Eq. 3), which is proportional to $1/r^2$. Note that this dependence cannot be accounted for by the Born-type electrostatic solvation energy,[41] which should depend on $1/r$. Such a non-Bornian solvation energy may be interpreted by taking into account the so-called short-range interactions[42] of an ion with solvent molecules in its immediate vicinity (i.e., donor–acceptor effects or hydrogen bonds). However, it seems that a new basic theory would be necessary for a thorough understanding of the present result.

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