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Formation of nanomicelle-like associates in water-saturated organic solutions of strong acids

Evgenii S. Stoyanov* and Vsevolod N. Kolomiichuk

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 383 235 5766; e-mail: stoyanov@catalysis.nsk.ru

SAXS investigations have shown that proton hydratosolvates in organic solutions of strong acids HAn form nanomicelle-like associates; the dependence of the size of the 'nanomicelle' (35–60 Å), their degree of shape distortion and tendency towards further aggregation on HAn concentration, the nature of An^- and solvent basicity are discussed.

The proton H^+ in the organic extracts of strong acids is highly hydrated forming associated hydrosolvates $H^+(H_2O)_nL_m{\cdot}An^-$ of variable composition, depending on HAn concentration and the nature of the basic organic molecules L.[1] A study of the composition and structure of $H^+(H_2O)_nL_m{\cdot}An^-$ **1** associates is important for ascertaining the features of the state of the hydrated proton in solution, including aqueous solution. There is evidence to believe that the structure of associates **1** is similar to that of a reverse micelle of nearly spherical shape.[2,3] For this reason we named them, by convention, as 'nanomicelles'. The present work presents direct proof of formation of that kind of species by strong acids in tributylphosphate (TBP) and butylacetate (BA) solutions equilibrated with water, by means of small-angle X-ray scattering (SAXS).

The organic extract was obtained by shaking equal volumes of TBP or BA (both purity grade) and water solutions of HAn for 10 min followed by centrifuge and separation from the water phase. The HAn concentrations were determined by titration with NaOH. TBP was preliminarily washed with 5% Na_2CO_3 solution to remove traces of dibutylphosphoric acid.

Small-angle X-ray scattering $I(\theta)$ was measured at an interval of angles 2θ 7′–2° using a four-slit camera KPM-1 (CoK radiation with Fe-filter and pulse-height analyser). $D_n(R)$ – the size distribution of the species' diameters – is determined by the integral equation

$$I(\theta) \quad D_n(R)i_0(hR)R^6\mathrm{d}R,$$

where $h = (4 \ \sin\theta)/\lambda$ and $i_0(hR)$ is the characteristic function of individual particle scattering, which for spherical particles is equal to

$$3 \ \frac{\sin hR - hR\cos hR}{h^3R^3} \ ^2.$$

The slope of the rectilinear portion of the plots of ln *I versus* ln θ for an ideal sphere is 4. Out-of-sphericity reduces this slope to the range from 4 to 3. This is typical only of experimental curves (Figure 1). Use of the spherical form-factor in the case of prolate ellipsoids of axial ratio no more than 2–3 retains the general view of $D_n(R)$-curves and produces a small modification to the descent of this curve toward increased values of *R*. In this case $D_n(R)$ refers to diameters of cross-section.[4,5]

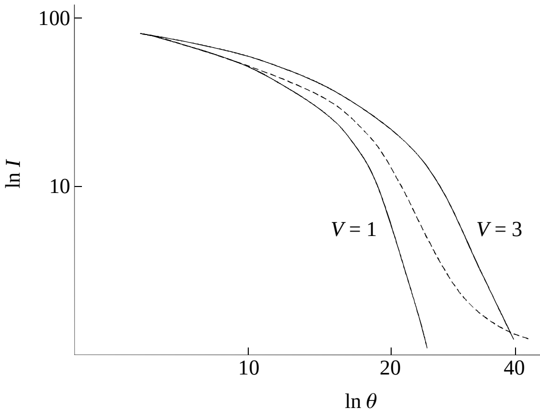

Figure 1 A comparison of the slit corrected curve (representative) for nanomicelles (dashed line) with theoretical scattering curves for prolate ellipsoids of revolution (eccentricity *V* = 1 and 2).

TBP and BA saturated with water contain hydrated associates of varying content. The more basic TBP includes mainly nanomicelle-like associates $(TBP{\cdot}2H_2O)_m$ **2** with $m >> 2$,[6] whereas less basic BA includes $BA{\cdot}H_2O$ and $2BA{\cdot}H_2O$ compounds as well as associates similar to **2** $(BA{\cdot}kH_2O)_m$ **3** with $m >> 1$.[7] By means of the SAXS method only **2** and **3** associates are detectable.

It follows from the curves for particle size distribution (Figure 2) that there are three forms of **2** and **3** in existence: A, B and C. A discontinuous distribution of sizes allows us to assume (this will be confirmed below) that form A belongs to the class of single 'nanomicelles'. Forms B and C possibly represent assemblies of such 'nanomicelles', *e.g.* their clusters.

It is of interest that 'nanomicelles' A, both **2** and **3**, are very similar in size, in spite of the different nature of the solvent (Figure 2).

When moving to TBP–HAn–H_2O systems all three types of macromolecular states A, B and C remained. However, one can observe some important changes as well.

Let us consider at first the solutions with C°_{HAn} 14 mol dm^{-3}, when the nanomicelle core incorporates only one proton.[2,3] It follows from the data listed in Table 1 that two types of nanomicelle are formed in solution, depending on the nature of the anion, An^-. The first involves poorly hydrated $An^- = ClO_4^-$, $FeCl_4^-$, $BiCl_4^-$ or NO_3^- and the second involves highly-hydrated Cl^- or SO_4^{2-} anions. The sizes of the first type of nanomicelle A and their clusters B and C are practically independent of the nature of An^-, and A $\leftrightarrow$ B $\leftrightarrow$ C equilibria are almost fully shifted to the left, in comparison with the system TBP–H_2O. The sizes of the second type of nanomicelles A, as well as of the cluster content B and C in solutions, are correspondingly greater than those of the first type. Probably, the reason is that Cl^- anion is incorporated in the core of nanomicelle A,[2] increasing its size (possibly, so does the SO_4^{2-} anion). The anion-disturbing influence on the solvating shell of the micelle core decreases simultaneously. As a result, the A $\leftrightarrow$ B $\leftrightarrow$ C equilibrium closely approaches that for the two-component system TBP–H_2O (Figure 2).

As C°_{HAn} increases (> 14 mol dm^{-3}) and nanomicelles with more than one H^+ in its core are formed, the size distribution curves for nanomicelles of the second type strongly change, approximating to those for the first type (Figure 2).

There are some differences between the nanomicelles of the first type as well. Thus, the parameters of the size distribution curves for nanomicelles of the first type, formed by $HFeCl_4$, are constant for $C^{\circ}_{\mathrm{HFeCl_4}}$ 0.1–0.4 mol dm^{-3}. In the case of $HClO_4$, in contrast, they are changed at interval of $C^{\circ}_{\mathrm{HClO_4}}$ 0.1–1.65 mol dm^{-3}. In fact, if we plot the dependences of the half-width and asymmetry of peak A and the size of clusters B $C^{\circ}_{\mathrm{HClO_4}}$ using the data of Table 1, we shall see that these plots have a clear-cut extremum at $C^{\circ}_{\mathrm{HClO_4}} = 0.78$ mol dm^{-3},

Table 1 Peak A, B and C parameters of the size distribution curves for the species formed by the strong acids HAn in TBP or BA solutions equilibrated with water (nanomicelles of the second type are italicised).

Solvent	HAn	C°_{HAn}/mol dm^{-3}	Position of maxima (in Å) and intensities of peaks A, B, C (in brackets in conventional units)			Half-width[a] of A peak/Å	Asymm.[b] of peak
			A	B	C		
TBP	–	0	48 (0.17)	126 (1)	220 (1)	12	0.71
	HNO_3	0.116	36 (1)	105 (0.04)	–	23.5	0.81
	$HBiCl_4$	0.10	37 (1)	108 (0.05)	162 (0.01)	28	0.72
	$HFeCl_4$	0.0991	37 (1)	110 (0.06)	–	26.1	0.79
	$HFeCl_4$	0.388	37 (1)	110 (0.05)	–	26.0	0.79
	HCl	*0.10*	*54 (0.69)*	*128 (0.72)*	*220 (1)*	*12*	*0.71*
	HCl	1.55	37 (1)	107 (0.07)	163 (0.02)	245	0.75
	H_2SO_4	*0.0665*	*44 (1)*	*105 (0.31)*	*157 (0.22)* *200 (0.40)*	*25.5*	*1.0*
	H_2SO_4	0.304	36 (1)	99 (0.09)	145 (0.01)	22.5	0.87
	$HClO_4$	0.103	37 (1)	110 (0.06)	162 (0.01)	25.5	0.64
		0.435	36 (1)	107 (0.07)	162 (0.02)	24.5	0.75
		0.774	35 (1)	98 (0.11)	150 (0.04)	22	0.83
		1.09	36 (1)	100 (0.10)	160 (0.04)	24	0.846
		1.65	37 (1)	105 (0.07)	162 (0.02)	24.5	0.846
BA	–	0	47 (1)	110 (0.30)	163 (0.16)	28.5	1.00
	$HFeCl_4$	0.066	56.5 (1)	114 (0.50)	172 (0.43)	21.5	0.954
	$HClO_4$	0.112	59 (1)	117 (0.50)	174 (0.42)	19.5	1.0

[a]The band width at half-height. [b]Defined as a ratio a/b, see Figure 2.

which exactly coincides with the extremum observed for the dependence of $C^\circ_{H_2O}$ on $C^\circ_{HClO_4}$ caused by the change in the composition of associates **1**.[8] Hence, the half-width and asymmetry of peak A are functions of composition and shape of micelles A, respectively, and the position of peak B is more sensitive to the size of the nanomicelle A than peak A itself, *i.e.*, the sizes of A and B are interconnected. This indicates that the number of nanomicelles A which are a constituent element of cluster B is approximately the same over a rather wide range of HAn concentrations. Furthermore, it was found that the degree of asymmetry of peaks A changes in parallel with the deviation of the straight part of the $\ln I$–$\ln \vartheta$ plot from 4. This indicates a correlation between the degree of asymmetry of peak A and the size of the shape deviation of nanomicelles from an ideal sphere.

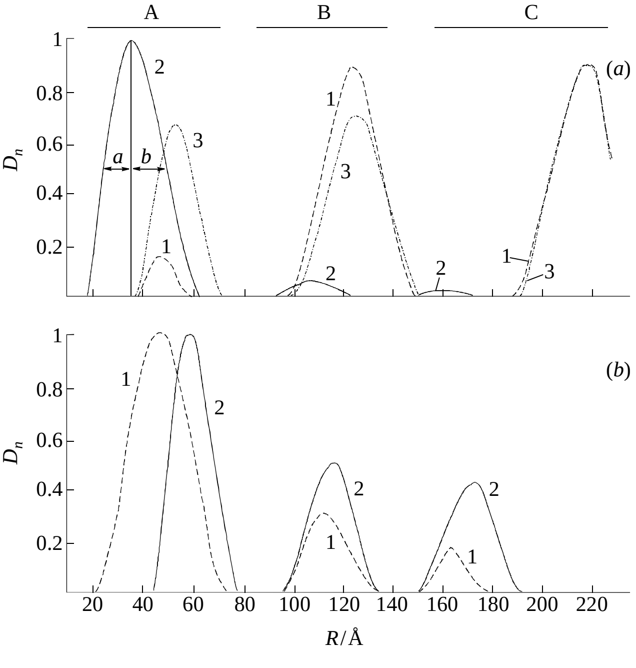

Figure 2 The size distribution function for species formed in TBP (*a*) and BA (*b*) equilibrated with water without (1) and with acids: $HClO_4$ of 0.103 M in TBP (2) or 0.112 M in BA (2) and 0.10 M HCl in TBP (3). The *a* to *b* ratio at half-height represents the asymmetry of band A.

Butyl acetate extracts only two detectable acids, $HFeCl_4$ and $HClO_4$. The sizes of nanomicelles A or clusters B and C in systems BA–HAn–H_2O as well as distribution A ↔ B ↔ C are practically unchanged when passing from $HFeCl_4$ to $HClO_4$, but differ significantly from those for TBP–HAn–H_2O systems with comparable C°_{HAn} (Table 1). The sizes of nanomicelles A in BA are 1.6 times larger than that for TBP in accordance with the tendency of growing degree of hydration of H^+ with decreasing solvent basicity.[9] The content of clusters B and C increases as well, *e.g.* the degree of aggregation of the nanomicelles. The size increase of nanomicelles A in BA is accompanied by an increase in their symmetry shape (Table 1).

All the data obtained allow us to draw the following conclusions:

1. It is common for strong mineral acids in organic solutions equilibrated with water to form nanomicelle-like associates of *ca.* 35–60 Å in size when C°_{HAn} ranges from very small values to at least 1–1.5 mol dm^{-3}. These species are capable of further aggregation, forming clusters of a distinct size.

2. In TBP solutions at low C°_{HAn} (0.14 mol dm^{-3}) the nanomicelles are formed with only one H^+ present in its core.[2,3] One can subdivide them into two types depending on the nature of the anion, An^-. The first type is with poorly hydrated anions $FeCl_4^-$, ClO_4^-, $BiCl_4^-$ or NO_3^-, located outside the core. Therefore, these nanomicelles are asymmetric with sizes approximately equal to ~37 Å, depending only on the molecular state of the proton. Their aggregation is low. The second type involves highly hydrated anions (Cl^-, SO_4^{2-}) incorporated in the core. As a result, the size of the latter increases (~44–60 Å), depending on the nature of anion, and its shape is more spherical. The self-association possibilities of this type of nanomicelle are greater.

3. With increasing C°_{HAn} up to 1–1.5 mol dm^{-3}, the nanomicelles vary in size according to changes in their composition, but for nanomicelles of the second type variations are more significant (~30%) than for the first (~5.5%). The sizes of both types of nanomicelle come closer together, as well as their aggregation abilities, and the shape tends to be more spherical.

4. When passing from TBP to a less basic BA solvent, the nanomicelle sizes, their sphericity and aggregation ability increase.

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