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Polycondensation in tetradecaethoxyhexasiloxane adsorption layers at the methylene chloride/water interface under alkaline conditions: application to the formulation of hollow microcapsules

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Polycondensation in tetradecaethoxyhexasiloxane adsorption layers at the methylene chloride/water boundary under alkaline conditions has been studied by interfacial dilational rheometry in view of the formulation of hollow nano- and microcapsules.

The sol–gel technique is used for the synthesis of functional ceramics, monodisperse dense colloids, zeolites and related molecular sieves, amorphous silicon resins, and molecular crystals composed of cagelike species.[1–4] Less attention was drawn to the formation of polysiloxane films by interfacial adsorption of oligoalkoxysiloxanes followed by the hydrolysis of alkoxy groups and interfacial polycondensation. The aim of this work was to study the kinetics of adsorption of an oligoethoxysiloxane, tetradecaethoxyhexasiloxane (TEOHS), from an organic phase (methylene chloride) at the CH_2Cl_2/water interface, and the consequent formation of a gel-like structure inside the adsorption layer through intermolecular condensation under alkaline conditions in view of the formulation of polysiloxane hollow nano- and microcapsules.†

Figure 1 represents the effect of the variation of the pH on the interfacial tension $\gamma(t)$ and both dilational modules, $E'(t)$ and $E''(t)$, of the adsorption layer of Si_6Et_{14} at the CH_2Cl_2/water interface. At normal pH 7 (before the injection of a NaOH solution into water) the interfacial tension γ decreased slowly during ~1 h according to an exponential law with the characteristic time $\tau_{ads} \cong 10^3$ s. At the same time, storage E' and loss E'' dilational modules gradually increased with relatively low rates. After 1 h of formation, these modules were $E' \cong 8$ mN m^{-1} and $E'' \cong 2$ mN m^{-1}, respectively. At pH 11, after the injection of NaOH into the cell, the module E' sharply increased during 10^2 s up to 30 mN m^{-1} testifying for the gel-like behavior of the adsorption layer, and slowly decreased during the next 2 h of observation. At the same time, the interfacial tension decreased and stabilized at $\gamma \sim 15$ mN m^{-1}. The loss module E'' underwent a slight increase testifying for some liquefaction of the adsorption layer, but after ~1500 s of the storage this module dropped to zero, which is typical of solid-like adsorption layers.[11]

According to the current concepts of alkoxysilane hydrolysis,[12] the alkoxy groups at the silicon atom are replaced by hydroxyl groups:

$$MeSi(OR)_3 + nH_2O \rightarrow Si(OR)_{3-n}(OH)_n + nROH. \quad (1)$$

This replacement does not occur on all alkoxy units at the same time, and under alkaline conditions, the condensation of partially hydrolyzed species may occur prior to complete hydrolysis:

$$\equiv Si–OH + HO–Si\equiv \rightarrow \equiv Si–O–Si\equiv + H_2O, \quad (2)$$

$$\equiv Si–OR + HO–Si\equiv \rightarrow \equiv Si–O–Si\equiv + ROH. \quad (3)$$

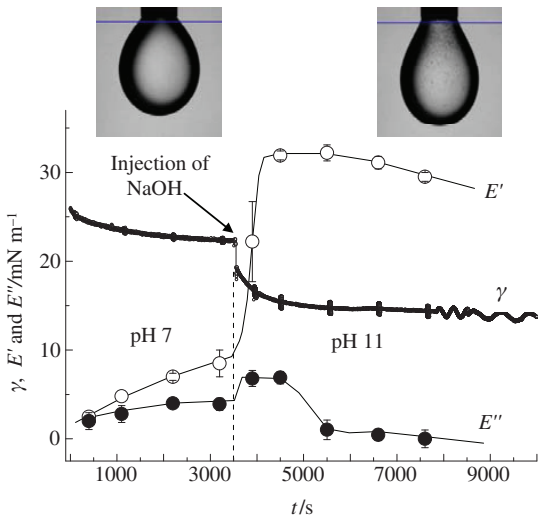

Figure 1 Variation of the interfacial tension and viscoelasticity modules E' and E'' of adsorption layers of Si_6Et_{14} with increasing pH. Concentration of Si_6Et_{14} in CH_2Cl_2 is $C = 0.1$ mol dm^{-3}.

† TEOHS was supplied by Pentasilicon, Russia. The purity of the TEOHS (99.5%) was determined by the elemental analysis. The molecular mass $M = 900 \pm 50$ was measured by cryoscopy in benzene solutions.[5,6] This compound was conventionally designed as Si_6Et_{14} and its molecular structure was represented as EtO–$[SiO(OEt)_2]_6$–Et (corresponding to 14 terminated reactive ethoxy groups able to hydrolysis and condensation). Methylene chloride of extra pure grade was supplied by Roskhimreaktiv, Russia.

Nano- and microsize hollow capsules have been produced by the emulsification/solvent evaporation method.[7] Scanning electron microscope (SEM) investigations of the capsules have been carried out with digital high resolution SEM LEO-1450VP.

The interfacial tension *versus* time was measured at the CH_2Cl_2/water interface using a dynamic pendant drop method with a drop tensiometer (Teclis – IT Concept, Longessaigne, France).[8] The interfacial tension was determined by analyzing the axial symmetric shape (Laplacian profile) of pendant drops of CH_2Cl_2 solutions of Si_6Et_{14} immersed in water. The area of a drop was submitted to periodic small sinusoidal deformations with the standard frequency $f = 0.1$ Hz to measure continuously the interfacial tension γ and the two-dimensional complex dilational elasticity module $\bar{E}$ of adsorption layers.[9,10]

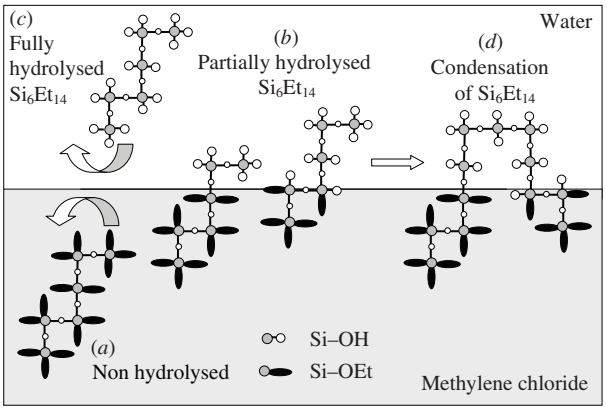

Figure 2 Schematic presentation of the hydrolyzed enhanced adsorption of Si_6Et_{14} and the condensation reaction.

In contrast, hydrolysis in most cases is faster than condensation reaction in an acidic medium.[13]

Non-hydrolyzed Si_6Et_{14} is a nonpolar substance; therefore, its adsorption at the CH_2Cl_2/water interface is energetically unfavorable [Figure 2(*a*)]. Nevertheless, because of a low but finite solubility of water in CH_2Cl_2, Si_6Et_{14} molecules could be partially hydrolyzed near the CH_2Cl_2/water interface in the presence of water traces. Such partially hydrolyzed molecules containing one or more OH groups become amphiphilic and, consequently, surface active [Figure 2(*b*)].

Note that the kinetics of adsorption of partially hydrolyzed Si_6Et_{14} is difficult to predict because of the interplay of numerous physico-chemical processes accompanying the formation of adsorption layers of this compound. These processes are the mutual diffusion of water and CH_2Cl_2 molecules into adjacent phases, the diffusion of Si_6Et_{14} molecules from the bulk of CH_2Cl_2 to the interface, the hydrolysis of Si_6Et_{14} at the interface and in the subsurface layer according to equation (1), the desorption of fully hydrolyzed molecules from the interface to the water phase, intermolecular condensation inside the adsorption layers according to equation (2) and (3), *etc*. With increasing the degree of hydrolysis, the hydrophilic-lipophilic balance (HLB) of Si_6Et_{14} molecules increases to increase their solubility in water [completely hydrolyzed alkoxysiloxanes are readily soluble in water and desorb from the interface, Figure 2(*c*)]. Consequently, the intense formation of a gel-like network at the interface *via* intermolecular condensation is assumed to occur only during the laps of time when the hydrolyzed Si_6Et_{14} molecules are yet localized at the interface [Figure 2(*d*)]. This time is unknown, although it is dependent on the pH of the aqueous solution.

Relatively low adsorption kinetics of Si_6Et_{14} at pH 7 (Figure 1) is explained by the low rate of hydrolysis of this compound in contact with the water phase.[12,13] The characteristic time τ_{ads} of adsorption by diffusion (under assumption of the absence of simultaneous desorption) can be estimated according to the Ward and Tordai equation[14]

$$\Gamma(t) = 2C\sqrt{\frac{D}{\pi}t}, \qquad (4)$$

where $D \cong 10^{-11}$ m^2 s^{-1} is the diffusion coefficient, and C = = 0.1 mol dm^{-3} is the Si_6Et_{14} concentration. Even for a hypothetical case of maximal adsorption amount $\Gamma_{max} \cong 10^{-5}$ mol m^{-2} ($\Gamma_{max} = 1/N_A a_1$, N_A is the Avogadro number, $a_1 \cong 0.5$ nm^2 is the area per one Si_6Et_{14} molecule), one obtains for the characteristic time of diffusion controlled adsorption a very low value of the order of $\tau_{ads} \cong \Gamma_{max}^2/C^2D \cong 1$ ms. This value is much lower with regard to the experimentally found characteristic time of adsorption $\tau_{ads} \cong 10^3$ s [curve $\gamma(t)$ (Figure 1)]. Consequently, we conclude that the decrease of the interfacial tension is due to the adsorption of partially hydrolyzed Si_6Et_{14} molecules, but this hydrolysis occurs mainly during the laps of time when alkoxysiloxane molecules stay at the interface.

When the pH of the aqueous phase was increased up to pH 11, the kinetics of hydrolysis sharply increased to result in a sharp increase in the adsorption kinetics [curve $\gamma(t)$ in Figure 1]. A simultaneous sharp increase of the storage module E' testifies for the condensation reaction between hydrolyzed OH groups. Meantime, the loss module E'' underwent a slight increase up to ~7 mN m^{-1} during ~1500 s after injection of the alkali into the cell. The increase of E'' is attributed to the excess of free hydrophilic OH groups, which easily and abundantly adsorb and desorb during dilational deformation of the drop area and produce the effect of the apparent liquefaction of the adsorption layer.[15] Later on, the module E'' dropped to zero; this is interpreted as the disappearance of free adsorbing groups near the interface apparently because of the condensation reaction inside the adsorption layer and the formation of a gel-like structure.

Figure 3 represents the isotherms $E'(C)$ and $E''(C)$ for the adsorption layers of Si_6Et_{14} formed in contact with an alkaline solution (pH 11) during the conventionally chosen standard time $t_f = 10^3$ s. The difference between these series of experiments and those represented in Figure 1 consists in that the formation of drops of CH_2Cl_2 solutions occurred directly in the alkaline solution (Figure 3), whereas in the previous case (Figure 1) the drops were initially formed in water at pH 7 and afterward the pH was increased up to 11 by injection of an alkali. The characteristic time of diffusion controlled adsorption τ_{ads} was always much lower with regard to the standard storage time t_f [for example, for the minimal concentration $C = 10^{-3}$ mol dm^{-3}, the time τ_{ads} estimated according to equation (4) was about 10 s]. This signifies that the formation of adsorption layers was never limited by diffusion but exclusively by the kinetics of hydrolysis and condensation at the interface.

It seems surprising that the sharp increase of the storage module E' begins after critical concentration $C^* \cong 0.04$ mol dm^{-3} corresponding to chosen physico-chemical conditions: $t_f = 10^3$ s and pH 11. Below this critical concentration threshold C^*, the modules E' and E'' are zero, but at $C > C^*$ the module E' remarkably increases up to ~30 mN m^{-1} when the concentration C increases from 0.04 to 0.1 mol dm^{-3}. In this concentration range, the viscoelastic film begins to form around the drop surface. The existence of this viscoelastic film enveloping the drop is easily demonstrated by decreasing the volume of the drop (Figure 3). Below the critical concentration $C < C^*$, the size

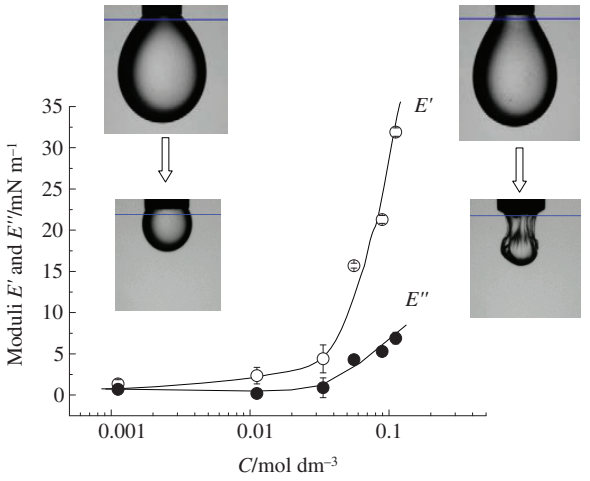

Figure 3 Effect of the bulk concentration C of Si_6Et_{14} in CH_2Cl_2 on the dilational modules E' and E'' of adsorption layers, storaged in contact with the aqueous phase at pH 11 during the standard time t = 1000 s.

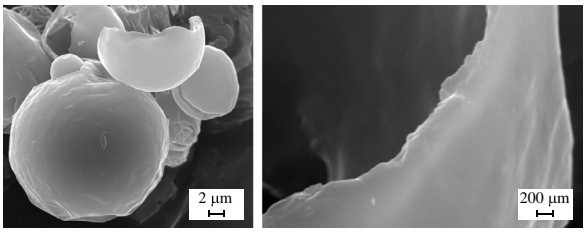

Figure 4 SEM photographs of hollow microcapsules obtained from the mixture Si_6Et_{14}/ε-PCL = 4:1 according to the published method.[7]

of the drop decreases and its shape becomes more and more spherical, which is typical of liquids. Whereas at $C > C^*$ the drop looks as a scrotum containing a liquid core in the interior.

Note that at $C = 0.1$ mol dm^{-3} the dilational storage module E' acquires the same value of ~30 mN m^{-1} as in the case represented in Figure 1 after the injection of NaOH in the aqueous phase. With increasing the storage time up to $t_f = 4000$ s, the module E' does not significantly vary, $E' \sim 30$ mN m^{-1} (this feature correlates with the dependence $E'(t)$ after injection of the alkali represented in Figure 1). It seems that after initial formation of a gel-like layer, the further hydrolysis and condensation of newly arrived Si_6Et_{14} molecules from the bulk of the CH_2Cl_2 solution to the interface do not alter the viscoelasticity of this gel-like layer. An explanation of this feature may be the formation of branched and hyperbranched structures, which are attached to the already formed gel-like layer without affecting significantly its viscoelasticity. Surprisingly, at pH 11 but at lower bulk concentration $C = 0.001$ mol dm^{-3} the module E' which was ~2 mN m^{-1} for the standard storage time $t_f = 1000$ s (Figure 3), does not increase significantly with the time of contact with an alkaline solution. For example, the module E' slightly increases up to ~4 mN m^{-1} for the storage time $t_f = 4000$ s and never exceeds 5 mN m^{-1} for more prolonged time. Thus, the interfacial gel-like structure could be formed by Si_6Et_{14} only when the bulk concentration of the compound exceeds the threshold value $C^* \cong 0.04$ mol dm^{-3} for pH 11.

The emulsification of a methylene chloride solution of Si_6Et_{14} in water at pH 11 and $C > C^*$ leads to the formation of hollow microcapsules *via* polycondensation at the surface of oil droplets. Although the microcapsule walls are viscoelastic at the chosen concentration $C_0 \sim 10\%$ of Si_6Et_{14} in CH_2Cl_2 (Figure 3); nevertheless, the thickness and the strength of these walls seem insufficient for the separation of these microcapsules from the aqueous solution in a powder form. Effectively, the expected maximal thickness h of a microcapsule wall after complete condensation of the polysiloxane matter from CH_2Cl_2 to the interface could be estimated according to the relationship

$$h = 1/3RC_0/C_h, \quad (5)$$

where R is the radius of droplets (capsule), C_h is the concentration of the polysiloxane matter in the capsule wall. Assuming the concentration $C_h > 90$ wt%, we obtain $h \leq R/30$. Thus, the nanocapsules with $R = 0.3$ μm should have the wall thickness $h \cong 10$ nm, whereas this thickness should be $h \cong 1$ μm for microcapsules with $R = 30$ μm. The nano- and microcapsules with such low thickness and viscoelasticity of walls could exist as aqueous dispersions. But these capsules would aggregate to form a sponge-like matter after their concentration by sedimentation or filtration as it is usually made to concentrate and separate solid-like nano- and microcapsules and beads.[7]

In order to make the capsule walls more rigid and to examine the hollow-like structure of these capsules by SEM, we strengthened the siloxane wall by polycaprolactone (PCL) nanoparticles in sort of obtaining a nanocomposite material. For this sake we prepared microcapsules with a mean size of 1–30 μm on the basis of the mixed CH_2Cl_2 solution of Si_6Et_{14} and ε-PCL. Note that individual ε-PCL never gives hollow capsules but exclusively sponge-like or monolith beads.[7,16–18] The microcapsules obtained from the mixed Si_6Et_{14}–PCL solution have an obvious hollow-like structure (these microcapsules were squashed in liquid nitrogen to estimate the wall thickness, Figure 4). This thickness perfectly corresponds to the estimations made using equation (5).

Thus, this study illustrates the principal possibility of the formulation of hollow polysiloxane nano- and microcapsules by interfacial polycondensation of oligoalkoxysilanes.

References

1 C. J. Brinker and G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, San Diego, 1990.
2 J. L. Blin, R. Bleta, J. Ghanbaja and M. J. Stebe, *Microporous Mesoporous Mater.*, 2006, **94**, 74.
3 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1999, **359**, 710.
4 L. Dewimille, B. Bresson and L. Bokobza, *Polymer*, 2005, **46**, 4135.
5 K. A. Andrianov, *Kremniiorganicheskie soedineniya* (*Organosilicon Compounds*), GNTI Khimicheskoi literatury, Moscow, 1955 (in Russian).
6 A. P. Kreshkov, V. A. Bork, E. A. Bondarevskaya, L. V. Myshlyaeva, S. V. Syavtsillo and V. T. Shemyatenkova, *Prakticheskoe rukovodstvo po analizu monomernykh i polimernykh kremniiorganicheskikh soedinenii* (*Manual on the Analysis of Monomeric and Polymeric Organosilicon Compounds*), ed. A. P. Kreshkova, GNTI Khimicheskoi literatury, 1962 (in Russian).
7 V. Hoffart, N. Ubrich, C. Simonin, V. Babak, C. Vigneron, M. Hoffman, T. Lecompte and P. Maincent, *Drug Dev. Ind. Pharm.*, 2002, **28**, 1091.
8 P. Saulnier, F. Boury, A. Malzert, B. Heurtault, T. Ivanova, A. Cagna, I. Panaiotov and J. E. Proust, *Langmuir*, 2001, **17**, 8104.
9 V. G. Babak, R. Auzely, M. Rinaudo and A. R. Khokhlov, *Mendeleev Commun.*, 2005, 239.
10 V. G. Babak, R. Auzely and M. Rinaudo, *J. Phys. Chem. B*, 2007, **111**, 9519.
11 V. G. Babak and J. Desbrieres, *Mendeleev Commun.*, 2005, 190.
12 H. Jiang, Z. Zheng, Z. Li and X. Wang, *Ind. Eng. Chem. Res.*, 2006, **45**, 8617.
13 S. Altmann and J. Pfeiffer, *Monatsh. Chem.*, 2003, **134**, 1081.
14 A. F. H. Ward and L. Tordai, *J. Chem. Phys.*, 1946, **14**, 453.
15 V. G. Babak, J. Desbrieres and V. E. Tikhonov, *Colloid. Surf. A: Phys. Eng. Asp.*, 2005, **255**, 119.
16 Yu. V. Chernysheva, V. G. Babak, N. R. Kildeeva, F. Boury, J. P. Benoit, N. Ubrich and P. Maincent, *Mendeleev Commun.*, 2003, 65.
17 V. G. Babak, Yu. V. Chernysheva, N. R. Kildeeva, V. E. Tikhonov, F. Baros, D. Dumas, N. Ubrich and P. Maincent, *XII International Workshop on Bioencapsulation*, Vittoria, Spain, 2004, p. 41.
18 V. G. Babak, F. Baros, O. Boulanouar, F. Boury, M. Fromm, N. R.Kildeeva, N. Ubrich and P. Maincent, *Colloids Surf. B: Biointerfaces*, 2007, **59**, 194.

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