



Article Stability of Detonation Nanodiamond Colloid with Respect to Inorganic Electrolytes and Anionic Surfactants and Solvation of the Particles Surface in DMSO–H₂O Organo-Hydrosols

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Abstract: In this article, the stability of sols of detonated nanodiamonds, DND, with positively charged colloidal particles, is studied in different salt solutions in water–dimethyl sulfoxide (DMSO) binary systems containing 95 vol.% organic solvent. Additionally, several CCC values are determined in 95 vol.% acetonitrile for comparison. The critical coagulation concentrations (CCC) are determined using the dynamic light scattering technique and the Fuchs function. As coagulators, NaCl, NaBr, NaNO₃, NaClO₄, Nan-C₈H₁₇SO₃, and Nan-C₁₂H₂₅OSO₃ are used. Comparison of the CCC values in DMSO–H₂O and CH₃CN–H₂O with those obtained in water allows us to make some conclusions. The variations of these values in different solvents are explained in terms of good and poor interfacial solvation of colloidal particles, "structural" contribution to the interparticle interaction energy, lyotropic series for anions, and more or less pronounced adsorption of surfactants. The study of the stability of DND hydrosol in solutions of anionic surfactants with different hydrocarbon tail length demonstrated the crucial role of adsorption in the coagulation process.

Keywords: nanodiamond; dimethylsulfoxide-water; acetonitrile-water; salts; surfactants; coagulation

1. Introduction

The colloid chemistry of detonated nanodiamonds (DND) has become a topical issue [1–9]. For example, they have found wide application in biomedical research [1–4]. This is due to the fact that these materials are the most harmless among nanocarbon structures. Unique optical properties of nanodiamond suspensions are also the subject of intense research [7]. Bombarding of DND with neutrons and irradiating with γ radiation was also examined [9]. The most studies of the suspensions and sols of DND were carried out in aqueous media [8]. At the same time, DND dispersions in water–organic mixed solvents and entire organic liquids are much less explored. Meanwhile, the colloidal properties in non-aqueous systems are of interest not only in itself, but also allow shedding light on the nature of hydrosols and aqueous suspensions of the same dispersed matter. This was the case, for example, with hydro- and organosols of fullerenes [10,11].

Previously, we studied DND hydrosols with positively charged particles, Nanocarbon Research Institute (Japan) [12–14]. In our recent paper, we also described the influence of ethyl alcohol and acetonitrile on the stability of DND hydrosol with respect to different electrolytes [13]. In particular, these studies revealed that the critical concentration of coagulation, CCC, for NaCl decreases (7.5–9.7)-fold, ongoing from water to 80 vol.% ethanol or acetonitrile.

The question naturally arises: is such an effect characteristic of any organic solvents? Therefore, the present article is devoted to the behavior of DND mainly in dimethyl sulfoxide (DMSO)–water binary solvent. DMSO is a polar cationophilic solvent. For comparison, some experiments were made in mixtures of water with a cationophobic



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). solvent acetonitrile. As the study was based on the dynamic light scattering study by using the Zeta Sizer (Malvern Instruments, Malvern, UK), some limitations concerning the viscosity of solutions were taken into account.

In addition to a set of inorganic coagulating electrolytes in organo-hydrosols, sodium *n*-dodecyl sulfate and sodium *n*-octylsulfonate were also used in this work. Additionally, in order to clarify the driving forces of coagulation influence of these amphiphiles, we performed a comparative study of behavior of DND hydrosols in the presence of a series of sodium sulfate and sulfonates.

2. Experimental

2.1. Materials

The DND hydrosol was used as produced in the NanoCarbon Research Institute, Tokyo, Japan. A detailed description of the synthetic procedure was published previously [15]. Sodium chloride, bromide, and nitrate samples of high purity were used for preparation of solutions for coagulation studies. Sodium perchlorate was synthesized, recrystallized, dried, and kept protected from the atmosphere before preparation of working solutions. Sodium *n*-dodecyl sulfate, hereafter, SDS (99%), was from Merck, Schuchardt OHG, Germany. Other samples of alkyl sulfates and sulfonates were the same as used previously [12]. Organic solvents were purified via conventional procedures. Stock DMSO and acetonitrile solvents contained 0.02 and 0.03 wt.% water, respectively, as determined by coulometric Karl Fischer method.

2.2. Apparatus

Size distribution of colloidal particles and electrokinetic potential, or zeta-potential, ς , were determined with the help of a Zeta Sizer ZS, Malvern Instruments at 25.0 °C, as described previously [12–15]. The Henry equation was used for ς determinations using the approximation proposed by Ohshima [16]. Equations (1) and (2) were used for calculations:

$$\varsigma = u_e \frac{3\eta}{2\varepsilon_r \varepsilon_0} \times f^{-1} \tag{1}$$

$$f = 1 + 0.5 \left[1 + \frac{2.5}{\kappa r (1 + 2 \exp(-\kappa r))} \right]^{-3}$$
(2)

Here, u_e , η , and ε_r stand for the electrophoretic mobility, viscosity, and relative permittivity, respectively; $\varepsilon_0 = 8.854 \times 10^{-12}$ F m⁻¹, κ is the reciprocal Debye length. For instance, in water, $\kappa = 3.299 I^{1/2} (\text{nm}^{-1})$, I is the ionic strength in M (1 M = 1 mol dm⁻³); r is the radius of the colloidal particles, nm. In 95 vol.% DMSO, $\kappa = 4.098 I^{1/2} (\text{nm}^{-1})$. Previously it was demonstrated that the Cl⁻ ions serve as counterions in the initial DND hydrosol with positive surface charge [12]. Without adding foreign electrolytes, the concentration of the chloride ion in the diluted working solutions is negligible, and the f values approach unity. It means that the ς values should be calculated using the Hückel–Onsager equation (f = 1).

Electronic absorption spectra were run on a Hitachi 2000 instrument at 25.0 °C, cell path length 1.00 cm.

2.3. Procedure

The colloidal solutions were prepared by dilution of the stock 0.236 wt./vol.% DND hydrosol. The concentrations of the sols are expressed in wt./vol.%, and the composition of the binary solvents in vol.%. For instance, "95 vol.% aqueous DMSO" means that 4.75 mL DMSO were mixed with a required volume of aqueous salt solution in a volumetric flask. Then, an aliquot of the DND hydrosol was added; finally, the flask was made up to 5.00 mL with water and thoroughly stirred. Next, the stock DND hydrosol was added only after dilution of the salt in order to avoid high local electrolyte concentrations, which can accelerate the coagulation and thus distort the results. If a salt solution was prepared directly in DMSO, the volume of this stock solution was included in the above-mentioned

4.75 mL. In the case of acetonitrile-based colloidal systems, the procedure was the same. The size was measured using Zetasizer Nano ZS every 30 s during 15 min. One result was the average of three measurements lasting 10 s. Experiments in aqueous solutions were performed as described previously [12–14]. Details of the spectrophotometric procedure are given in Section 3.4.

3. Results and Discussion

3.1. Choice of the Solvent Composition and Characterization of the Systems

Aqueous 95 vol.% DMSO mixed solvent was chosen as a media for studying the colloidal properties of DND. Here, the relative permittivity is $\varepsilon_r = 50.5$, viscosity $\eta = 2.4017$ mPa s [17]. Solutions with lower DMSO content are too viscous and unusable for the DLS experiments with the above-mentioned equipment, e.g., in 80 vol.% DMSO, $\eta \approx 3.8$ mPa s. For comparison, 95 vol.% acetonitrile was also used in some experiment ($\varepsilon_r = 38.1$; $\eta = 0.420$ mPa s) [17]. In water, $\varepsilon_r = 78.4$ at 25 °C.

In Figure 1, the particle size distributions of 0.01 and 0.024 wt./vol.% DND solutions in aqueous 95 vol.% DMSO and 95 vol.% acetonitrile are presented.



Figure 1. Distribution by intensity (1), volume (2), and number (3) of 0.01 wt./vol.% DND colloidal solutions in 95 vol.% DMSO (a) and 95 vol.% acetonitrile (b) and of 0.024 wt./vol.% DND in 95 vol.% DMSO (c).

The average size of particles for 0.024 wt./vol.% DND in 95 vol.% DMSO is $Z_{average} = 63 \pm 2$ nm, $\zeta = +(80 \pm 2)$ mV. Most further experiments are performed with DND working concentration of 0.01 wt./vol.%. At this concentration of DND, the size parameters of the colloidal system in 95 vol.% DMSO are as follows: Z-average = 53.7 ± 1.5 nm, *d* by

intensity, volume, and number are 61.9 ± 4.1 , 41.9 ± 3.3 , and 31.7 ± 2.9 nm, respectively; polydispersity index (PDI) = 0.174 ± 0.016 ; $\zeta = +(74 \pm 3)$ mV.

In 0.01 wt./vol. DND organo-hydrosol in 95 vol.% acetonitrile, the size parameters of the colloidal system are as follows: Z-average = 179 ± 20 nm, *d* by intensity, volume, and number are 152 ± 27 , 100 ± 11 (second fraction: 28 ± 5), and 64 ± 4 nm (second fraction: 29 ± 3 nm), respectively; PDI = 0.36 ± 0.09 ; $\zeta = 46.4 \pm 1.9$ mV.

3.2. Coagulation of the DND Sols

First of all, the CCC value of the DND sol in water is determined. Although this value was already determined by us previously, it is necessary to revisit this issue because of the ageing phenomenon over time described earlier [13–15]. This effect results in variations in the CCC value. Additionally, the CCC values are, to some extent, concentration-dependent. The corresponding data are shown in Figure 2. The salt concentrations are expressed in mM = 0.001 M.



Figure 2. Reciprocal Fuchs function, W^{-1} , or coagulation efficiency coefficient, vs. the logarithm of concentration of NaCl (mM) in DND hydrosol: 0.01% wt./vol. (1) and 0.024% wt./vol. (2).

The CCC values are determined using the Fuchs function [18], as in our previous works [10,11,14,15].

$$W = \frac{k_{\text{rapid}}}{k} = \frac{\left[(\partial r/\partial t)_{t\to 0}\right]_{\text{rapid}}}{(\partial r/\partial t)_{t\to 0}}$$
(3)

Here, *k* and k_{rapid} are the rate constants of slow and rapid coagulation, respectively. The beginning of the plateau (Figure 2) corresponds to the CCC value. For extrapolation of the $\partial r / \partial t$ slopes to zero time, the initial linear parts of the curves are used. The CCC values thus determined are 5.5 and 6.3 mM, respectively.

The next step is the study of DND in 95 vol.% aqueous DMSO. In Figure 3, the colloidal particle size evolution over time at different salt concentrations is exemplified. Am analogous set of curves are obtained for all systems studied here.



Figure 3. Dependence of particle size in 0.01 wt./vol.% DND organo-hydrosol in 95 vol.% DMSO; NaCl concentrations/mM: 0.2 (1); 0.5 (2); 0.8 (3); 0.9 (4); 1.0 (5); 1.5 (6); 2.0 (7); 2.5 (8); 3.0 (9); 4.0 (10); 5.0 (11).

Some dependences of the W^{-1} values on logarithms of salt concentrations are presented in Figures 4 and 5. Uncertainty of the CCC values is around \pm 15%.



Figure 4. Reciprocal Fuchs function vs. the logarithm of sodium perchlorate concentration/mM. The increase in the particle size along with coagulation is shown in the insert.



Figure 5. Reciprocal Fuchs function vs. the logarithm of the electrolyte concentration/mM of 0.01% wt./vol. DND in 95 vol.% DMSO: SDS (1), $NaC_8H_{17}SO_3$ (2), NaCl (3), $NaClO_4$ (4), NaBr (5), and $NaNO_3$ (6); in 95 vol.% CH₃CN: $NaC_8H_{17}SO_3$ (2'), $NaClO_4$ (4').

The results are presented in Table 1. When comparing the CCCs in water–organic media with that in entire water, the above-mentioned ageing phenomenon of the DND hydrosols should be taken into account. As result, the CCC value for NaCl varies within the range of 2.8–6.6 mM [12–15]. Therefore, we either determined the CCC values in water with the same initial aqueous DND solution as for aqueous organic solvents or cited previously published data with appropriate comments.

Flashealysta	CCC, mM			
Electrolyte	in 95 vol.% DMSO	in H ₂ O	in 95 vol.% CH ₃ CN	
NaC ₁₂ H ₂₅ OSO ₃	0.90	0.010 ^a	_	
NaC ₈ H ₁₇ SO ₃	1.8	0.080 ^b	0.18	
NaCl	4.0	5.5	0.68 (80 vol.% CH ₃ CN) ^c	
NaBr	7.5	4.9 ^d	_	
NaNO ₃	9.0	3.5	0.6	
NaClO ₄	5.5	3.5 ^e	0.55	

Table 1. Critical concentrations of coagulation of DND organo-hydro- and hydrosols (25 °C).

Note: ^a Determined in this work, see below. A much higher value of 0.039 mM was determined earlier using a (simplified) procedure of spectrophotometric, i.e., turbidimetric, titration [12]. ^b A value of 0.15 mM was determined by spectrophotometric titration [12]; discussion of the discrepancies see below. ^c From ref. [15], higher fractions of acetonitrile were not used in the experiments with NaCl because of solubility limitations. ^d In ref. [12], where the stability of the 0.19% DND sample was characterized by the CCC value for NaCl of 2.8 mM, this CCC value was 2.5. ^e In ref. [12], where the stability of the 0.19% DND sample was characterized by the CCC value for NaCl of 2.8 mM, this CCC value was 1.8.

In Table 2, the ζ values of the colloidal particles in 95 vol.% DMSO are presented. Equations (1) and (2) were used for calculations. The values obtained according to Smoluchowski correspond to f = 1.5. As is more adequate, the values ζ according to Ohshima should be considered.

Salt/mM	ζ-Potential/mV; Smoluchovski	f	ζ-Potential/mV; Ohshima	
0	49.3 ± 3.1	1.00	74.0	
NaCl				
0.5	28.6 ± 1.0	1.077	39.8	
0.9	24.0 ± 0.2	1.101	32.7	
5.0	20.6 ± 0.6	1.218	25.4	
NaBr				
3.0	28.4 ± 1.0	1.178	36.2	
5.0	25.1 ± 1.4	1.218	30.9	
7.5	19.7 ± 1.2	1.249	23.6	
NaNO ₃				
5.0	31.3 ± 1.5	1.218	38.5	
NaC ₈ H ₁₇ SO ₃				
0.5	23.6 ± 2.0	1.077	32.9	
NaC ₁₂ H ₂₅ OSO ₃				
0.0075	38.9 ± 1.5	1.006	58.0	
0.075	25.2 ± 2.7	1.033	36.6	
0.50	17.9 ± 1.9	1.077	24.9	

Table 2. The values of the electrokinetic potential of 0.01 wt./vol.% DND in 95 vol.% DMSO.

Note: In 95 vol.% acetonitrile, the ζ value of 0.01 wt./vol.% DND sol is 46.4 \pm 1.9 mV. In 0.5 mM NaCl solution, ζ = 25.8 \pm 0.4 mV (by Ohshima).

The decrease in the ζ value can be caused by screening of the interfacial charge of colloidal particles by the electrolyte and adsorption of anions. The last effect becomes obvious by comparing the ζ values at NaCl, NaC₈H₁₇SO₃, and NaC₁₂H₂₅OSO₃ concentration of 0.50 mM: ζ = 40, 33, and 25 mV, respectively.

3.3. Analysis of the CCC Values

The data obtained, although not numerous, still allow us to draw some conclusions. First, the CCCs in DMSO and water should be compared. Because some of the CCC values in water were determined previously with another DND sample, a following correction can be made. For the present sample, CCC(NaCl) = 5.5 mM, while with the previously studied sample, CCC(NaCl) = 2.8 mM [12]. Therefore, as rough approximation, the "old" CCC values for other salts should be multiplied by 2.0 (see Note to Table 1). Thus, corrected values in water are still lower than those in DMSO. This can be explained by the additional stabilization of positively charged colloidal DND particles owing to the solvation by a cationophilic solvent DMSO (Donor Number, DN = 29.8 [19]). The sole exception is NaCl; in this case, the reason is the poor solvation of the relatively small Cl⁻ ion by a non-HBD solvent DMSO. In this case, one can even assume adsorption of Cl⁻ ions on the surface of DND particles. Better solvated anions with more delocalized charge, Br⁻, NO₃⁻, and ClO₄⁻ display weaker coagulation impact. The picture is reversed as compared to the aqueous media, where the coagulation power of the anions in hydrosols with positively charged particles is reversed, according to the Hofmeister or lyotropic series.

In the case of a cationophobic non-HBD solvent acetonitrile, the CCCs are an order of magnitude lower than in DMSO. If the sol in aqueous acetonitrile is taken as a reference point, where specific solvation of the colloidal particles is weakened, the CCC values should be arranged in a row: aqueous acetonitrile $\{DN_{CH3CN} = 14.1 [19]\} <$ aqueous DMSO $\{DN_{DMSO} = 29.8\} \approx$ water $\{DN = 24.3,$ conventionally [19]}. An additional proof of the poor solvation of DND by acetonitrile is the substantially larger size of the colloidal particles in 95 vol.% CH₃CN, three-fold higher than that in the 95 vol.% DMSO and in water (see above).

Therefore, it is reasonable to suspect an existence of some stabilizing factors just in water and in aqueous DMSO. Here, the concept of structural (solvation, hydration) contribution to the inter-particle interaction energy introduced by Churaev and Derjaguin is applicable [20]. This contribution is a function of the distance, *h*, between two plates immersed into a solution, Equation (4).

$$V_{\rm s} = K l \exp(-h/l) \tag{4}$$

Here, *K* and *l* are constants. For hydrophilic (solvophilic) and hydrophobic (solvophobic) surfaces, K > 0 (structural repulsion) and K < 0 (structural attraction), respectively. For two spherical particles with radius *r*, the Derjaguin's integration leads to Equation (5).

$$U_{\rm s} = K l^2 \pi r \exp(-h/l) \tag{5}$$

Therefore, for the energy of interaction between two spherical colloidal particles, in addition to the energy of electrical repulsion, U_{el} , and molecular attraction, U_{attr} , caused by dispersion forces, a corresponding contribution should be included, Equation (6).

$$U = U_{\rm el} + U_{\rm attr} + U_{\rm s} \tag{6}$$

Here $U_{el} > 0$, $U_{attr} < 0$. All items in the rhs are functions of *h*. U_{el} also depends on *r*, ionic strength, relative permittivity, and the electrostatic surface potential, Ψ , and U_{attr} is dependent on the Hamaker constant A^*_{DSD} of the nanodiamond particles interaction in the solution. As for the *f* and φ functions, various expressions have been proposed in the literature. In a general form, Equation (6) may be represented as follows:

$$U = f(\Psi, I, \varepsilon_r, r, h) - A^*_{\text{DSD}}\varphi(h, r) + Kl^2\pi r \exp(-h/l)$$
(7)

Here $A_{\text{DSD}}^* = (A_{\text{DD}}^{1/2} - A_{\text{SS}}^{1/2})^2$; A_{DD} and A_{SS} are Hamaker constants of diamonddiamond and solvent-solvent interactions. According to the literature data, $A_{\text{DD}} = (28.4-29.6) \times 10^{-20}$ J [12]; the A_{SS} for solvents under study are about (2.5–5.5) $\times 10^{-20}$ J.

This deals with some hydrophilic interaction of the nanodiamond with water, and solvophilic interaction with DMSO. As opposite systems, aqueous acetonitrile (Table 1) and aqueous ethanol [15] can be considered. There, the *K* values are probably negative, or at least much lower compared with those in water and aqueous DMSO.

A special case is SDS. Here, the CCC in DMSO ca. 90-fold higher than in water, despite poor solvation of the SO_3^- group by DMSO. The obvious reason for such a difference is the extremely low CCC value in water as a result of pronounced adsorption of the amphiphilic surface-active anions on the surface of the colloidal particles. The latter effect leads to the neutralization of the positive surface charge of colloidal particles and thus to coagulation. Contrary to it, the solvation of the hydrocarbon chain by organic solvents leads to the near disappearance of hydrophobic hydration, which was the driving force of the diphilic anions adsorption. A sharp increase in the CCC values of an anionic surfactant upon going from water to organic media was convincingly proved in the present work with DND sols. For SDS as coagulator, the CCCs in water, 80 vol.% aqueous ethanol, and 95 vol.% DMSO are 0.010, 0.37, [14] and 0.90 mM, respectively.

3.4. Peculiarities of Coagulation by Anionic Surfactants in Water

Adsorption of surfactants on the surface of DND colloidal species is described in detail in the literature [12,21–26]. Vervald et al. [23–25] examined the behavior of both positively and negatively charged DND colloidal particles in water in the presence of sodium octanoate. Soboleva et al. [21,22] proved the adsorption of the cationic surfactants on the surface of negatively charged DND particles. Badun et al. [26] reported their results of detailed study of cationic surfactants adsorption on the DND surface. In the case of negatively charged particles. As result of adsorption is 26–37 times higher than for the positively charged particles. As result of adsorption, the ς values became less negative or more positive. The specific surface area for these two types of DND was determined by the BET procedure: 286 and 250 m²/g [26]. For our DND sample, this value is 178 m²/g,

as determined using the adsorption of an anionic polymethine dye [27]. Gibson et al. [28] determined a value of $175 \text{ m}^2/\text{g}$ for a sample of DND with negatively charged particles using a cationic dye. Therefore, the key role of surfactant adsorption in aqueous solutions of DND is evident.

It seemed worth to perform some experiments in order to shed additional light on the DND–water–surfactant system. The CCC values were determined for a set of anionic surfactants with hydrocarbon chains of different length in a DND hydrosol either via the DLS method using the Zetasizer apparatus or by spectrophotometric titrations using the wavelength 525 nm as an analytical position; the procedure was described by us earlier [12]. The last procedure demands an increase in the hydrosol concentration; 0.13 wt./vol.% is used for the working solutions. Figures 6 and 7 demonstrate some differences of properties of such concentrated and ten-fold diluted colloidal solutions.



Figure 6. Size distribution of colloidal species in 0.13% (**a**) and 0.013% (**b**) DND hydrosols: by number (**1**); by volume (**2**); by intensity (**3**). Z-average = 54.6 ± 1.2 and 54.3 ± 1.0 nm; PDI = 0.236 ± 0.006 and 0.153 ± 0.022 , respectively.



Figure 7. Zeta potential distribution of the nanodiamond solutions, obtained on Zetasizer Nano ZS, for (1): 0.013% nanodiamond solution, (2): 0.13% nanodiamond solution; = 20.3 ± 1.1 and 45.3 ± 1.2 mV (by Smoluchovski) and 30.4 and 68.0 mV (by Hückel–Onsager equation; f = 1).

To 2.00 mL of DND hydrosol in an optical cell, 0.03 mL of aqueous solutions of sodium sulfate or sulfonate is successively added. After each portion is added, the absorbance is measured (Figure 8). The CCC corresponds to the electrolyte concentration, which corresponds to a 15% increase in absorbance compared to the initial value [12]; dilution of the solution during titration was taken into account. Alternatively, for two surfactants, NaC₆H₁₃SO₃ and NaC₁₆H₃₃OSO₃, another technique is used [12]. To avoid high local electrolyte concentrations, a series of DND solutions with different surfactant concentrations are prepared; 2.00 mL of DND hydrosol is mixed with 1.00 mL of surfactant solution with proper concentration. The spectra are measured for 40 min and time dependences at 525 nm are drawn [12]. Results of both methods coincide.



Figure 8. Spectrophotometric titration of 0.13 wt./vol.% DND hydrosols by sodium sulfate or sulfonate solutions.

The determination of the CCC values by the standard procedure using the Zetasizer instrument is exemplified in Figure 9.



Figure 9. Reciprocal Fuchs function vs. the logarithm of the electrolyte concentration (mM) of 0.13% wt./vol. DND in water: $NaC_{14}H_{29}OSO_3$ (1), $NaC_{12}H_{25}OSO_3$ (2).

The results are presented in Table 3. First of all, it should be stated that the values determined by spectrophotometric measurements, which is in fact a kind of turbidimetry, strongly differ from those determined previously for some of the surfactants [12] (see the notes to Table 1). Obviously, this is caused by the ageing of the DND hydrosols. Therefore, the comparison of the two methods of CCC determination should be made for simultaneously determined data.

	CCC, mM			
Surfactant	Determined by Spectrophotometric Titrations ^a		Determined with Zetasizer Instrument Using the Fuchs	
	15%-Criterion	50%-Criterion	Function	
NaC ₆ H ₁₃ SO ₃	0.025	0.10	0.100	
NaC ₈ H ₁₇ SO ₃	0.014	0.078	0.080	
NaC ₉ H ₁₉ SO ₃	0.0085	0.050	-	
$NaC_{10}H_{21}SO_3$	0.0051	0.037	0.050	
NaC ₁₀ H ₂₁ OSO ₃	0.0039	0.024	-	
NaC ₁₂ H ₂₅ OSO ₃	0.0021	0.011	0.010	
NaC ₁₄ H ₂₉ OSO ₃	0.0014	0.006	0.006	
NaC ₁₆ H ₃₃ OSO ₃	0.00031	0.001	-	

Table 3. The CCC values of the 0.13 wt./vol.% DND hydrosol in surfactant solutions.

Note: ^a Uncertainty about $\pm 15-20\%$.

In any case, the increasing in the length of the hydrocarbon chain decreases the CCC. Similar effects were observed in the above-mentioned studies on negatively charged DND particles with cationic surfactants [22] and for negatively and positively charged silver iodide hydrosols coagulated by cationic [29] and anionic surfactants [30], respectively.

Inspection of Table 3 clearly demonstrates that the measurements of the absorbance results in substantially lower CCC, determined based on the "15%" criterion as compared with the DLS measurements and W^{-1} dependence on the electrolyte concentration. Qualitatively, the same effects were described by Ottewill and Watanabe as early as 1960 for

coagulation of the positive AgI hydrosol by anionic surfactants [30]. In our case, the lower CCC values are caused by the titration procedure. Indeed, gradually adding the electrolyte by small portions leads to the effect, well-known in colloid chemistry, "negative adaptation". However, the coincidence of the results with those obtained by preparation of a set of independent solutions (see above) allows ruling out this assumption. Therefore, considering the data obtained using the Fuchs function as more reliable, we revealed that the same CCCs correspond to the 50% increase in the absorbance. These values are also included in Table 3.

The 15% criterion was chosen earlier [12] because such changes of absorbance obviously exceed the measurement errors. However, comparison with the DLS data indicate that under such conditions, the regime of rapid coagulation is still not reached.

The real concentration of an amphiphilic anion is obviously less than the determined CCC because of adsorption of these anions on the positively charged colloidal species of DND. Indeed, the inspection of Table 4 demonstrates the decreasing in the ζ values. The concentrations of the surfactants are too small to substantially screen the interfacial charge. Hence, the alterations are caused by neutralization of the positive charges due to the adsorption of surfactant anions on the surface. The most pronounced changes can be seen for NaC₁₂H₂₅OSO₃: on going from 0.001 to 0.004 mM, a drop of ζ from 62 to 28 mV is observed; the CCC is 0.010 mM. Additionally, a change of ς from 60 to 24 mV for DND colloids in NaC₁₄H₂₉OSO₃ solutions on going from 0.001 to 0.002 mM of the surfactant corresponds to beginning of the rapid coagulation (see curves 2 and 3 in Figure 8). This, in turn, supports the idea of the decisive role of adsorption in the coagulation process in the system of interest. At the same time, the size of colloidal particles is almost unaffected by the surfactant adsorption at concentrations below the CCC value (Table 4).

Surfactant	<i>C</i> , mM	ζ-Potential/mV; Smoluchovski	f	ζ-Potential/mV; Ohshima
None ^a	0	48.3 ± 0.7	1.0000	72.4
NaC ₆ H ₁₃ SO ₃ ^b	0.030	45.3 ± 1.2	1.0409	65.3
NaC ₁₀ H ₂₁ SO ₃ ^c	0.006	44.7 ± 0.8	1.0032	66.8
NaC ₁₂ H ₂₅ OSO ₃ ^d	0.001	41.2 ± 3.2	1.0004	61.8
NaC ₁₂ H ₂₅ OSO ₃	0.004	18.5 ± 0.5	1.0066	27.6
NaC ₁₄ H ₂₉ OSO ₃ ^e	0.001	40.0 ± 0.5	1.0004	60.0
NaC ₁₄ H ₂₉ OSO ₃	0.002	16.0 ± 0.6	1.0009	24.0

Table 4. The ζ -potential values of 0.13 wt./vol.% DND hydrosol in surfactant solutions.

Note: ^a Z-average = 54.6 ± 1.2 nm; PDI = 0.237 ± 0.006 . ^b Z-average = 52.5 ± 0.5 nm; PDI = 0.223 ± 0.005 . ^c Z-average = 51.4 ± 0.6 nm; PDI = 0.213 ± 0.016 . ^d Z-average = 53.2 ± 1.1 nm; PDI = 0.233 ± 0.013 . ^e Z-average = 57.8 ± 0.9 nm; PDI = 0.236 ± 0.006 .

Using the above-mentioned value of the specific surface area, $178 \text{ m}^2/\text{g}$ [27], it can be estimated that in 0.13 wt./vol.% DND, the total surface of the colloidal particles is about $2.3 \times 10^{20} \text{ nm}^2$. Accordingly, in 0.1 mM NaC₆H₁₃SO₃ for one surfactant anion, there are 3.8 nm² as potential area of adsorption. In 0.01 mM SDS, such potential places for adsorption correspond to 38 nm². Hence, there are enough places for formation of an absorption monolayer.

It should be noted that although adsorption plays a key role in the coagulation process, CCC values do not fall as sharply as the classical Duclaux–Traube rule predicts. Indeed, according to this rule, the CCC of the C₁₂ surfactant must be \approx 1000 fold lower than that of C₆, while the experimentally obtained effect is 100 times smaller, etc. This is in line with the idea of transfer of a substantial part of diphilic ions from solution to the surface of colloidal particles. Similar conclusions can be made from the data published by Tamamushi and Tamaki [29], who determined the CCC values of a series of alkylammonium chlorides, C_nH_{2n+1}NH₃Cl, in solutions of AgI hydrosols with negatively charged particles. In all these cases, the real concentration of the surfactant in the solution, and therefore the CCC, is less than the analytical one due to adsorption.

Although the adsorption of sodium *n*-dodecylsulfate also results in pronounced decrease in the ζ value in 95 vol.% DMSO, it takes place at much higher surfactant concentrations than in water. As a result, the CCC value for this surfactant in aqueous DMSO is 90-fold higher as compared with water. A more detailed comparison is inexpediently because of substantially different DND concentrations in these two systems.

4. Conclusions

Comparison of the CCC values for DND colloids in mixed solvents, mainly containing 95 vol.% organic solvent, with those obtained in water allows us to make some conclusions. Sodium chloride, bromide, nitrate, perchlorate, *n*-octylsulfonate, and *n*-dodecylsulfate are used as coagulators. The CCC values of main electrolytes in 95 vol.% DMSO are higher than those in water, while CCCs in 95 vol.% acetonitrile are even smaller. This is explained by the interfacial solvation and thus stabilization of positively charged colloidal particles by a cationophilic solvent DMSO, contrary to poor solvation by a cationophobic acetonitrile. The consideration in terms of the "structural" contribution to the interaction energy (Churaev and Derjaguin) allows for the deduction of an additional stabilizing factor in DND hydrosols as well.

In some cases, the sequence of anions in the common lyotropic series makes itself felt. Therefore, the CCC of NaCl in 95 vol.% DMSO is not only the lowest among other inorganic salts, but even lower than in water, because of poor solvation of small anion Cl⁻ by DMSO. The CCCs for anionic surfactants in aqueous DMSO are substantially higher than in water, but still much lower than for all other salts in the above mixed solvent. On the one hand, the reason is a poor solvation of sulfate and sulfonate anionic groups. On the other hand, the reason of extremely low CCC values for these anions in water is the adsorption of the diphilic ions and neutralization of the surface charge of colloidal particles. In the presence of organic solvents, the hydrocarbon chains are well solvated, which removes the driving forces of adsorption.

Behavior of the DND hydrosols in the presence of a series of anionic surfactants firmly proves the crucial role of adsorption in the coagulation process. In particular, the 90-fold increase in the CCC for sodium *n*-dodecylsulfate on going from water to 95 vol.% DMSO illustrates this convincingly. In DND hydrosols, the CCCs of sodium sulfates and sulfonates decrease as the length of the hydrocarbon tail increases. However, the effect is less pronounced than the Duclaux–Traube rule predicts. The reason is the adsorption of anions on colloidal particles, which increases the true concentrations in the aqueous phase.

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