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PHYSICOCHEMICAL STUDIES **OF SYSTEMS AND PROCESSES**

Gelation in Extraction Systems with Basic Copper(II) and Neodymium(III) Alkyl Phosphates

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Received February 13, 2002

Abstract—Gelation in extraction systems containing purified or commercial di(2-ethylhexyl) hydrogen phosphate (HDEHP), copper(II) or neodymium(III) hydroxides, hydrocarbon solvent, and water was studied at different ratios of the metal and extractant. The region was determined in which gelation caused by formation of basic neodymium(III) di(2-ethylhexyl) phosphates occurs in decane. Some characteristics of organogels in the HDEHP (commercial)-Cu(OH)2-organic diluent (decane, hexane or toluene)-H2O extraction systems were studied.

Structure formation in extraction systems affects their main characteristics, such as the distribution and separation factors and the rates of extraction and phase separation. Formation of disperse structures like gels, liquid crystals, amorphous and crystalline precipitates in the bulk of both aqueous and organic phases or at the interface are the factors which, as a rule, deteriorate the extraction process. One of the consequences of the structure formation is appearance of so-called meduses, i.e., stable emulsions, precipitates, or gels located between partially separated organic and aqueous phases [1]. Accumulation of meduses can deteriorate extraction to so significant extent that the extraction process must be interrupted [2, 3]. To prevent this detrimental effect, the region of formation of the disperse structures and their features promoting meduse formation should be studied.

The most attention is given to the structure formation in extraction of metals with di(2-ethylhexyl) hydrogen phosphate (HDEHP) and tributyl phosphate (TBP), which are widely used for recovery, separation, and purification of various organic and inorganic compounds including nonferrous, rare-earth, and radioactive metals. These meduses contain species typical of detergent solutions, e.g., liquid crystals and associates of polymeric metal hydroxides.

Formation of liquid crystals by lanthanide di(2ethylhexyl) phosphates in CCl₄ was reported in [4]. Liquid crystals were also found in the HDEHP-NaDEHP-decane-H₂O system at high NaDEHP concentration (>90 wt %) [5].

It was reported [6] that, in organic solutions, metals

can form oligomeric neutral and acidic di(2-ethylhexyl) phosphates consisting of several alkyl phosphate units [6]. The degree of polymerization of neutral Y(III) and La(III) di(2-ethylhexyl) phosphates in organic solvents reaches $10^2 - 10^3$ [7]. High polymeric species poorly dissolve in both aqueous and organic phases. Therefore, polymeric metal alkyl phosphates can form gels and precipitates in both aqueous and organic phases. It was found that, in extraction of zirconium(IV) and hafnium(IV) with HDEHP, both gels and gel films are formed in the aqueous phase near the interface [8].

In our preliminary study of structure formation in extraction systems containing HDEHP, copper(II) or neodymium(III), hydrocarbon solvent, and water at different ratio of the metal and extractant, neither liquid crystals nor gels were found in the aqueous phase.

In this work we studied gelation in the organic phase of the HDEHP-Cu(OH)2-decane-H2O and HDEHP-Nd(OH)₃-decane-H₂O systems at different metal to extractant ratios. In the experiments, both purified and commercial HDEHP were used.

EXPERIMENTAL

In our experiments we used two different HDEHP samples: HDEHP containing >98% main substance (Merck) and commercial grade HDEHP containing 66% di(2-ethylhexyl) hydrogen phosphate and 19.5% mono(2-ethylhexyl) dihydrogen phosphate, produced by Khimprom Volgograd Joint-Stock Company. Mono(2-ethylhexyl) dihydrogen phosphate (H₂MEHP) was first separated from commercial HDEHP as a water-soluble sodium salt and then converted to H₂MEHP by treatment with sulfuric acid [9]. The other chemicals [decane, $CuSO_4 \cdot 5H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$, and NaOH] were of pure grade. Double-distilled water was prepared by the standard technique.

Copper(II) and neodymium(III) hydroxides were precipitated from aqueous solutions of the corresponding salts by addition of NaOH to pH >10 for Cu(II) and pH > 12 for Nd(III). The Cu(OH)₂ precipitate was rapidly separated from the mother liquor by centrifugation and then was washed with double-distilled water to pH 7. The Nd(OH)₃ precipitate was kept under mother liquor for 1 h to complete hydrolysis, separated by centrifugation, and washed with doubledistilled water to pH 7. Then the prescribed amounts of water and extractant were added to the precipitates of neodymium or copper hydroxide. To obtain an organogel, this mixture was carefully shaken for 30 s. In the Nd(III)–HDEHP and Cu(II)–H₂MEHP systems, gelation occured within several minutes, and in the Cu(II)-commercial grade HDEHP system, within several hours and became complete after keeping at 20°C for a day. Emulsions in these systems were prepared by stirring the aqueous and organic phases at their volume ratio of 3 : 2 with a stirrer at 3000 rpm for 2 min with copper(II) and 30 s with neodymium.

Before measuring the viscosity and evaluating the stability, the emulsions containing copper(II) or neodymium(III) alkyl phosphates were kept for 1 day and 1.5 h, respectively, to ensure completion of structure formation. The period of half-settling of the emulsion in the organic phase was determined by centrifugation at 90g. The emulsion viscosity was measured with a Rheotest-2 rotary viscometer with coaxial cylinders within the shear rate interval of 0.167–16.2 s⁻¹ at 20°C. The photographs of emulsions were obtained with an optical microscope equipped with a photographic attachment.

The neutral copper(II) and neodymium(III) salts are hydrolyzed in aqueous solutions to form basic salts. Therefore, in extraction of these metals with HDEHP, their basic alkyl phosphates can be formed as intermediate species. We studied the structure formation in the HDEHP–Cu(OH)₂–decane–water and HDEHP– Nd(OH)₃–decane–water systems at the ratio of the metal and exractant corresponding to the formation of both neutral and basic alkyl phosphates.

In the organic phase, basic neodymium(III) di(2ethylhexyl) phosphate is present as precipitate and gel.



Fig. 1. Apparent precipitate volume V (% of the organic phase volume) as a function of the ratio of molar concentrations of HDEHP and neodymium hydroxide. [HDEHP] = 0.3 M; the same for Figs. 3 and 5. HDEHP: (1) pure and (2) commercial.

The turbid or opalescent gel-like phases do not flow under their gravity. In additional mechanical loading, the structure of these gels is destroyed. Figure 1 shows that, in the HDEHP(pure)–Nd(OH)₃–decane– water system at [HDEHP]/[Nd(OH)₃] < 2.2, gelation occurs throughout the organic phase. At this ratio of Nd(OH)₃ and HDEHP, both mono- and disubstituted basic neodymium(III) di(2-ethylhexyl) phosphates can be formed. With commercial HDEHP contaminated with H₂MEHP, gelation occurs throughout the organic phase at [HDEHP/Nd(OH)₃] < 1.4. At higher [HDEHP]/[Nd(OH)₃] ratios, either dense precipitate at the water–extract interface or neodymium di(2-ethylhexyl) phosphate solution in decane is formed.

When the concentration of basic neodymium(III) di(2-ethylhexyl) phosphate in organic phase exceeds a certain limit, the gelation in the organic phase starts. At HDEHP concentration > 0.03 M and HDEHP/Nd(OH)₃ = 1, the organic phase is completely converted to the gel.

Optical microscopic study of gel-like organic phases containing basic neodymium(III) di(2-ethylhexyl) phosphates failed to reveal any crystal structure. On removal of the solvent from both the gels and precipitate, an amorphous solid is obtained. It is known that neutral lanthanide di(2-ethylhexyl) phosphates form coordination polymers in the organic phase [4, 7]. We believe that basic poorly soluble lanthanide di(2-ethylhexyl) phosphates present in the organic and aqueous phases are also coordination polymers. These polymers build up the three-dimensional network of the organogel.

In the HDEHP (commercial)– $Cu(OH)_2$ –decane– water system, gelation occurs within the range of [HDEHP]/[CuOH)_2] ratios of 1.0–1.6 (Fig. 2). Under

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Fig. 2. Gelation in the HDEHP (commercial)–decane–water system at 20°C. (c) $Cu(OH)_2$ content. (1) No gelation and (2) gelation occurs.

these conditions, gelation occurs in the organic phase only, while the aqueous phase is free of the gel. At the ratio of the HDEHP and $Cu(OH)_2$ concentrations outside the gelation region (at excess of HDEHP), the copper alkyl phosphate organic solution is in equilibrium with the aqueous phase. At an HDEHP concentration insufficient for gel formation, a dense crystalline precipitate is formed at the interface.

We found that the gel formation in the systems studied is insensitive to the nature of the nonpolar solvent. Substitution of decane by any other nonpolar solvent results in only minor changes in both the minimal HDEHP concentration and the [HDEHP]/[CuOH)₂] ratio corresponding to the gelation region in the phase diagram. The HDEHP minimal concentration and the ratios of HDEHP and Cu(OH)₂ concentrations corresponding to the gelation region in decane, hexane, and toluene are given in the table.

The blue transparent gels initially formed in the HDEHP (commercial)– $Cu(OH)_2$ –organic solvent–water system become turbid and whitish on long-term keeping. An optical microscopic study of mature gels

Boundaries of gelation region in the HDEHP (commercial)–Nd(OH)₃–organic solvent–water system

Organic solvent	c _{HDEHP} *	[HDEHP]/[Cu(OH) ₂], mol/mol		
		lower boundary	upper boundary	
Decane Hexane Toluene	0.025 0.010 0.050	1.0 1.2 1.2	1.6 1.8 2.2	

* Minimal HDEHP concentration at which gelation occurred.

showed that their structure is built of fine crystals. On keeping the organogel for several days at 20°C, it becomes turbid owing to increase in the crystal size. The mean size of gel particles in the HDEHP–Cu(OH)₂– decane–water system {[HDEHP]/[Cu(OH)₂] = 1.2, [HDEHP] = 0.3 M, $T = 20^{\circ}$ C} was determined with an optical microscope at 160-fold magnification. These data are given below:

τ,	days	1	2	3	4
d,	μm	9.4 ± 1.3	18.9 ± 2.5	31.1 ± 4.4	34.9 ± 3.8

On heating above 75°C, the gel is destroyed owing to dissolution of alkyl phosphate crystals. Upon cooling, the structure of the organogel is restored. On mechanical loading, the organogels in the HDEHP (commercial)–Cu(OH)₂–decane–water system are irreversibly destroyed.

We found that gelation does not occur in systems containing both commercial HDEHP preliminarily purified as described in [10] and pure HDEHP (Merck) containing more than 98% main substance. In this case, at [HDEHP]/[Cu(OH)₂] < 1.8, a dense crystalline substance is precipitated at the interface, which dissolves at [HDEHP]/[Cu(OH)₂] = 2.0. These experiments showed that gelation of alkyl phosphates is caused by impurities present in commercial HDEHP.

The main organic impurities present in commercial HDEHP are mono(2-ethylhexyl) dihydrogen phosphate H_2MEHP and 2-ethylhexanol. We found that, on addition of aliphatic alcohols (from butanol to decanol) to pure HDEHP, no gel is formed in the systems concerned. Turbid faintly blue organogels are formed in the H_2MEHP –Cu(OH)₂–decane–water systems containing 0.3 M H₂MEHP at [H₂MEHP]/[Cu(OH)₂] < 2. Taking into account that H₂MEHP is dibasic acid, both neutral and acidic copper(II) alkyl phosphates can be formed under these conditions. In the region of formation of acidic copper alkyl phosphates, [H₂MEHP]/[Cu(OH)₂] > 2.0, two homogeneous liquid phases (aqueous and organic) are formed.

In industrial production of HDEHP, the raw product is washed with NaOH or Na_2CO_3 aqueous solutions to remove H_2MEHP . We found that, after single scrubbing of commercial HDEHP in an organic solvent (0.3 M) with aqueous NaOH, the gelation region is narrowed, and gelation occurs at [HDEHP]/[Cu(OH)_2] 1.6–1.8.

In extraction, a contact between aqueous and organic phases, as a rule, is attained by emulsification of the extraction system at vigorous stirring. We studied

the effect of gel formation on the emulsion stability in the HDEHP (commercial)-Cu(OH)2-decane-water and HDEHP (commercial)-Nd(OH)₃-decane-water systems. In these systems, emulsions were produced by stirring Cu(OH)₂ and Nd(OH)₃ precipitates suspended in water with an HDEHP solution in decane. Figure 3 shows how the half-separation time of the emulsion (time of the half-settling of the emulsified organic phase) in the HDEHP-Nd(OH)₃-decanewater system depends on the HDEHP/Nd(OH)₃ ratio in centrifugation at 90g. This figure shows that emulsions are stable only at [HDEHP]/[Nd(OH)₂] ratios corresponding to the gelation region. Agitation of the system concerned drastically affects its phase behavior. While no stirring, the gelation occurs in the organic phase only, and in vigorous stirring of the aqueous and organic phases at 3000 rpm, a stable emulsion is formed.

When lanthanide hydroxides suspended in water are stirred with an HDEHP solution in decane, stable emulsions are formed with all the lanthanides. For example, we obtained stable emulsions in the $RE(OH)_3$ -HDEHP-decane-water systems (RE = Sm, Dy, Ho, and Yb) at [HDEHP]/[Ln(OH)_3] = 1.6 and [HDEHP] = 0.3 M.

In the HDEHP (commercial)– $Cu(OH)_2$ –decane– water system, stable emulsions are formed in the range of metal and extractant ratio corresponding to organogel formation. At [HDEHP/[Cu(OH)₂] ratios beyond the gelation region (below 1.0 and above 1.6), the emulsions are separated into aqueous and organic phases within 1–2 min.

Figure 4 demonstrates the flow curves of emulsions stabilized with organogels in the HDEHP (commercial)-Cu(OH)2-decane-water and HDEHP (commercial)–Nd(OH)₃–decane–water systems. Curves 1 and 2 show that the emulsion viscosity considerably decreases with increasing shear rate. With the subsequently decreasing shear rate (curves 1' and 2'), the viscosity of the liquefied emulsions does not return to the initial values, i.e., the initial emulsion structure is not restored. We found that, in mechanically destroyed emulsions, the initial structure is not restored even on keeping for several days. The irreversible breakdown of emulsions under mechanical loading indicates that they are nonthixotropic. Such a behavior correlates with that of organogels of copper(II) and neodymium(III) alkyl phosphates.

The structural features of the emulsions were judged from their viscosity, optical microscopic patterns, and electrolytic conductivity. The miscibility of emulsions with aqueous and organic phases was also



Fig. 3. Time of half-settling of the emulsified organic phase, $\tau_{1/2}$, as a function of the HDEHP and neodymium hydroxide molar ratio in the HDEHP (commercial)–Nd(OH)₃-decane-water system.



Fig. 4. Effective viscosity η of emulsions stabilized with copper(II) and neodymium(III) organogels as a function of the shear rate γ' . [HDEHP] = 0.3 M, [HDEHP]/[Nd(OH)₃] = 1.2 and [HDEHP]/[Cu(OH)₂] = 1.2; commercial HDEHP. The viscosity was measured in the course of (*1*, 2) increasing and (*I'*, 2') decreasing the shear rate.

examined. These studies showed that the stability of the emulsion structure is ensured by the organogel network. The photomicrographs of emulsified HDEHP (commercial)–Cu(OH)₂–decane–water and HDEHP (commercial)–Nd(OH)₃–decane–water mixtures contain light droplets of the liquid phase and darker areas between them. The dark areas correspond to turbid organogels formed by copper(II) mono(2-ethylhexyl) phosphates and basic neodymium(III) di(2-ethylhexyl) phosphates (Figs. 5a, 5b).

Our data on gelation and emulsification in extraction systems containing copper and lanthanide alkyl phosphates allow us to make certain recommendations to prevent the detrimental effect of structure formation. Taking into account that both organogels and stabilized emulsions are irreversibly destroyed under mechanical loading, the mechanical impact can be used for brekdown and removal of meduses.

The removal of H_2MEHP from commercial HDEHP by scrubbing with NaOH aqueous solution

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Fig. 5. Photomicrographs of (a) emulsified HDEHP (commercial)–Cu(OH)₂–decane–water system with [HDEHP]/[Cu(OH)₂] = 1.0 and (b) emulsified HDEHP (commercial)–Nd(OH)₃–decane–water system with [HDEHP]/[Nd(OH)₃] = 1.0. Scale: 16 mm = 100 μ m.

sharply narrows the gelation region in the extraction systems containing copper(II) alkyl phosphates. As a result, purification of the extractant to remove H₂MEHP decreases the probability of meduse formation in the extraction. Under the industrial conditions, the meduse formation is prevented by scrubbing a commercial extractant with Na₂CO₃ aqueous solution. In going from commercial to pure HDEHP, the gelation region of basic neodymium(III) di(2-ethylhexyl) phosphates expands (Fig. 1). Therefore, unlike the cases when, in extraction of metals with commercial HDEHP, gel formation is promoted by organic impurities and, therefore, can be prevented by their removal, in extraction of lanthanides(III) with HDEHP, its purification to remove impurities does not prevent the structure formation.

Our experiments showed that gel formation in the organic phase is caused by basic alkyl phosphates formed at HDEHP deficiency. At sufficiently high acidity suppressing the metal hydrolysis, the meduse formation can be prevented. At low metal concentration and large excess of the extractant, the probability of meduse formation also decreases.

CONCLUSIONS

(1) Conditions of gelation in the basic neodymium di(2-ethylhexyl) phosphate-decane-water system were

determined for pure and commercial HDEHP.

(2) The gelation region in the di(2-ethylhexyl) hydrogen phosphate– $Cu(OH)_2$ –(decane, hexane or toluene)–water systems was determined at 20°C. A three-dimensional network of organogels is built up by copper(II) mono(2-ethylhexyl) phosphate crystals.

(3) Organogels based on copper(II) mono(2-etylhexyl) phosphate or basic neodymium(III) di(2-ethylhexyl) phosphate promote emulsification in extraction systems.

(4) Different approaches to elimination of the detrimental effect of structure formation in extraction systems containing copper(II) or lanthanide(III) di(2-ethylhexyl) phosphates (e.g., meduse formation) are analyzed.

ACKNOWLEDGMENTS

This work was financially supported in part by the Integration Special Federal Program (project no. A0078/3,5).

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