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Convective Instability in a Liquid−Liquid System Due to Complexation with a Crown Ether

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Periodic convective instability has been observed in a biphasic system during the complexation reaction of alkali picrate and dicyclohexano-18-crown-6 which undergoes mass transfer from the hexane phase into the aqueous phase. The convection was visualized by means of precipitated crystals that are formed in both phases by the complexation reaction. The fluid motion was observed with an optical microscope and further analyzed with the particle image velocimetry (PIV) technique. The partition at the extraction of cesium into the organic phase was followed by means of the radioactive isotope ^{137}Cs. The type of the hydrodynamic instability is governed by the alkali metal expressed via its stability constants for the complex formed. More stable complexes trigger a higher precipitation, thereby favoring a Raleigh−Taylor instability. Complexes with a lower stability constant induce Marangoni cells which show a pulsating character in a cubic container. Depending on the confinement of the experiment cell the fluid motion can also follow a back-and-forth movement. Possible mechanisms for the occurring oscillations are discussed.

1. Introduction

Interfacial tension-driven convection, known as Marangoni convection, is widely observed in systems submitted to heat or mass transfer.[1–3] Its accelerating effect on extraction processes has attracted numerous studies in engineering science.[4,5] If the convective instability appears only transiently, and the system switches periodically between two transport regimes (a slower and a faster one), then an oscillation will occur.[6]

Periodic oscillations of the interfacial tension and the electrical potential difference across the oil/water interface were observed when the water and oil phases, each containing an ionic solute (one of which is a surfactant), were brought in contact and the solutes began to transfer in the opposite directions through the interface.[7,8] More regular and well-shaped oscillations develop when solute transfer occurs between two water layers through an interposed oil layer.[9,10]

According to theory,[6] auto-oscillation of the surface tension is the result of Marangoni instability periodically arising and fading. As an example, the instability could fade due to the interaction of the longitudinal wave, generated by instability, with the vessel wall.[11] For instance, this is observed in systems in which mass transfer is coupled to a chemical reaction. On the basis of the well-known CTAB/picric acid system, several authors[9,10] have reported oscillatory behavior of the interfacial surface tension or electrical potential when a surfactant, initially solubilized in a water phase, is brought into contact with an organic phase containing either a hydrophilic acid or a base. The reaction involved is the formation of ion pairs resulting from counterion exchange in the water phase. These ion pairs are rather hydrophobic and similar to those involved in phase transfer catalysis.

Another way to produce spontaneous oscillation at the liquid interface is the use of only one transferred solute from the surfactant source in the bulk. Auto-oscillation of the surface tension was observed by dissolution of a surfactant droplet under the water surface.[12,13] Oscillation of the interfacial tension and of the electrical potential through the water/nitrobenzene interface occurs by gradual injection of an ionic surfactant into the bulk water.[14] The peculiarity of all the systems considered is their nonlinearity. The appearance of the oscillations cannot be explained in the frame of the existing theory based on the linear stability analysis as proposed by Sternling and Scriven.[15] Although the correlations between the physicochemical and hydrodynamic processes underlying the behavior of these systems are not quite clear to date it has been established that chemical processes between transferred solutes are crucial for oscillations.

In reaction systems with crown ethers the formation of ion pairs occur if an adequate cation is added. Crown ethers are commonly used for the extraction of alkali metal ions from aqueous solutions. Hydrodynamic instabilities during the extraction process can occur if suitable conditions are chosen such as the type of crown ether and the solvents. Here, as organic solvent for the crown ether is used hexane which is uncommon in extraction systems but known to be used in systems that produce instabilities like reported in former works that consider simple neutralization reactions as reported by Eckert et al.[16] and Bratsun and De Wit.[17] Here, in difference, a complexation reaction with an alkali metal cation is investigated which leads to a new kind of oscillating Marangoni convection.

2. Experimental Setup

2.1. Chemicals. All chemicals used were of at least analytical grade and used as purchased. Picric acid, sodium nitrate, potassium nitrate, cesium nitrate, and dicyclohexano-18-crown-6 were purchased from Sigma-Aldrich. Hexane and water were of HPLC grade and purchased from Fluka. For most experiments the following concentration in the aqueous phase was used: 5 mM alkali nitrate (sodium, potassium, or cesium), 5 mM picric acid. Because of partial dissociation of picric acid the pH value of the solutions was 2.35. For a control experiment a solution with cesium picrate was prepared by precipitation of cesium nitrate with picric acid. The yellow needles which formed were washed with ethanol and recrystallized from water but not dried

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TABLE 1: Stability Constants of Dicyclohexano-18-crown-6 Complexes in Water

cation	log K_C
sodium	1.52
potassium	1.90
rubidium	1.19
cesium	1.04
ammonium	1.08

TABLE 2: Equilibrium Constants of Dicyclohexano-18-crown-6 Complexes in Picrate Extractions[a]

cation	extraction solvent	log K_E	log K_D	log K_C	log P_E	log P_C
K^+	CH_2Cl_2	6.32	7.57	2.06	−3.59	7.95
K^+	$CFCl_2CF_2Cl$	4.27	<6	2	−1.15	3.43
K^+	n-C_6H_{14}	3.57	<6	2	−0.82	2.4
Na^+	CH_2Cl_2	4.18	8	1.6	−3.59	6.17

[a] Ref 19.

and then dissolved in water to give a saturated solution. Dicyclohexano-18-crown-6 was dissolved in hexane with concentrations of 50 and 100 mM (for the radioanalytical measurements between 10 and 50 mM).

2.2. Complexation Reactions. All reactions were performed in measuring cells made of quartz glass (Hellma, Müllheim, Germany). The measuring cells mostly used have a gap of 2 mm and a width of 10 mm. Alternatively, cubic cells with a cross section of 30 × 30 mm^2 were used. All cells had a height of 45 mm. The reactions were monitored by a microscope connected to a high-resolution camera (Dalsa, Waterloo, Ontario, Canada) enabled to record movies. The movies were recorded with a frame rate of 10 frames/s with a commercial software (Stemmer Imaging, Puchheim, Germany) and analyzed with the free ImageJ package. Particle image velocimetry was performed with commercial software using cross-correlation of successive images (PivTec, Göttingen, Germany). Surface tensions were measured with the KSV Sigma 70 system using the Wilhemy plate method (LOT Oriel, Darmstadt, Germany). In several experiments, the metal concentration after the incubation time was detected using radioanalysis in both phases by γ-radiation of ^{137}Cs in a NaI (TI) scintillation counter (Cobra II/Canberra-Packard). The instabilities were observed in an undisturbed system, i.e., it was not shaken.

3. Characteristics of the Complexation of Alkali Picrate with Dicyclohexano-18-crown-6

One of the specific characteristics of crown compounds is the ability to selectively form complexes by capturing cations with an ionic diameter fitted to the cavity size of the crown compound, i.e., alkali metal cations form complexes with dicyclohexano-18-crown-6. In comparison to sodium or potassium, which form 1:1 complexes, cesium forms a 2:1 complex in which two crown ether molecules enclose one cesium ion.[18] The complexation reactions of crown ethers and inorganic salts in water (subscript aq) are an equilibrium reaction as shown in eq 1:

$$M^+_{aq} + L_{aq} \rightleftharpoons ML^+_{aq} \qquad K_C = \frac{[ML^+]}{[M^+][L]}_{aq} \tag{1}$$

Here M is an alkali cation and L is the ligand (herein the crown ether). The equilibrium constant K_C indicates the degree of complex formation and the stability of the resulting complex in the solution. With dicyclohexano-18-crown-6 as ligand some equilibrium constants K_C for water are listed for the sake of comparability (see Table 1).[18]

Because crown ethers facilitate the complexation of inorganic cations, it is possible to use organic solvents, containing crown ether, to extract inorganic cations from aqueous solutions which then form soluble complexes in the organic phase. The extraction is achieved more effectively with cations that have bulky and highly polarized anions, such as picrates. Picrate ion is used for quantitative studies on complexation because of its good extraction capability and its simple analysis due to the strong absorption at 360 nm. Cations are extracted by crown ether according to the extraction equilibrium in eq 2 and the dissociation equilibrium in eq 3:

$$M^+_{aq} + A^-_{aq} + L_{org} \rightleftharpoons LMA_{org} \qquad K_E = \frac{[LMA_{org}]}{[M^+_{aq}][A^-_{aq}][L_{org}]} \tag{2}$$

$$LMA_{org} \rightleftharpoons LM^+_{org} + A^-_{org} \qquad K_D = \frac{[LM^+][A^-]}{[LMA]}_{org} \tag{3}$$

In addition to the definitions above, A is the picric anion and the subscripts aq and org means in the aqueous or in the organic phase. Table 2 presents the extraction equilibrium constant K_E and the dissociation equilibrium constant K_D for several solvent systems as reported by Frensdorff[19] and recently complemented by Kikuchi and Sakamoto for extractions with 1,2-dichloroethane.[20] The value K_E depends on the stability constant K_C of the complex in aqueous solution and the distribution constants of the crown ether P_E and the complex P_C. The selectivity of crown ethers for solvent extraction of metal ions clearly results from the relationship between ionic diameter and cavity size of the crown ring. The highest selectivity was observed with potassium, whose ionic diameter is nearest to the cavity of the 18-crown ring. The overall extraction equilibrium K_E in eq 2 is too complex to allow the specific molecular effects to be unravelled. One can analyze K_E in terms of eq 1 and two additional equilibria:

$$L_{org} \rightleftharpoons L_{aq} \qquad P_E = \frac{[L_{aq}]}{[L_{org}]} \tag{4}$$

$$ML^+_{aq} + A^-_{aq} \rightleftharpoons LMA_{org} \qquad P_C = \frac{[LMA_{org}]}{[ML^+_{aq}][A^-_{aq}]} \tag{5}$$

The three equilibrium constants are K_C, the aqueous stability constant of the cation complex in eq 1, P_E, the partition coefficient of the crown ether in eq 4, and P_C, the partition coefficient of the resulting complex in eq 5. Thus, the overall extraction equilibrium constant is given by

$$K_E = K_C P_E P_C \tag{6}$$

Substances dissolved in water usually lower the interfacial tension of water by placing molecules at the interface. The interfacial activity of the reactants is quantified with measurements of the interfacial tension performed with the Wilhelmy plate method (see Table 3). Classic surface active agents such as sodium dodecyl sulfate lower the interfacial tension/γ of water down to 30 mN/m, whereas cesium picrate lowers the interfacial tension only to 62.2 mN/m because it does not have the amphiphilic character of sodium dodecyl sulfate. Nevertheless, the flat picric ions show interface activity to some extent due to specific stacking arrangements in water.[21] Dicyclohexano-18-crown-6 lowers the interfacial tension of the hexane/air interface to 13.5 mN/m. Since the extraction is located at the

TABLE 3: Surface Tensions of the Cesium Picrate−Dicyclohexano-18-crown-6 system at 25 °C

system	surface tension γ in mN/m
water/air	72.9
hexane/air	20.5
water/hexane	50.3
cesium nitrate and picric acid in water (5 mM)/air	62.2
cesium nitrate and picric acid in water (5 mM)/hexane	40.5
dicyclohexano-18-crown-6 in hexane (100 mM)/air	13.5
water/dicyclohexano-18-crown-6 in hexane (100 mM)	23.2

water/hexane interface the interfacial activities of the compounds involved are crucial for an understanding of the underlying mechanism. The pure hexane/water system shows a interfacial tension of 50.3 mN/m as known from literature.[22] Dicyclohexano-18-crown-6 (0.15 mmol/kg or 10^{-4} M) reduces the interfacial tension at the hexane/water interface to 37.1 mN/m as shown by Azizian et al.[23] On the basis of eq 7 we find $d\gamma/dc|_L = 134$ N/(m·mol/L). For the aqueous phase containing 5 mM cesium nitrate and 5 mM picric acid the gradient is estimated from values presented in Table 3 finding $d\gamma/dc|_{MA} = 1.96$ N/(m·mol/L). Hence, the crown ether, L, is about 70 times more effective in reducing the interfacial tension than the alkali picrate, MA. This is an approximate comparison of the substance activities as the gradient $d\gamma/dc$ depends on the concentration.

$$\gamma_{org/aq}|_L = \frac{d\gamma}{dc}_L \Delta c_L \qquad \gamma_{org/aq}|_{MA} = \frac{d\gamma}{dc}_{MA} \Delta c_{MA} \qquad (7)$$

4. Convection Due to Complexation Reaction

In the following considerations a hexane phase is superimposed over a water phase. One of the three metal nitrates (sodium, potassium, or cesium) and picric acid are dissolved in the water phase. Dicyclohexano-18-crown-6 is dissolved in the hexane phase. Then, the complexation reaction of the two dissolved species from the two phases takes place at the interface. Because of the different solubility of the resulting complexes each alkali metal cation also leads to a different unstable process with its particular characteristics.

4.1. Potassium Picrate System. The solubility of the complexes is strongly related to their stability constants in water (see Table 1). Potassium ions form the most stable complex in water which precipitates in the water phase in the form of particles of 2−15 μm in size being observable with a microscope. The top views in Figure 1 reveal a thickening of the present pattern which was formed in very beginning of the experiment by change. The thickening continues until the whole interface is filled with precipitates. Viewing from the side, the precipitated particles sediment through the water phase (see Figure 2). The particles forms so-called plumes, structures like slow falling drops of honey which are poured in water. By continuity, this movement is simultaneously accompanied by a convection in the opposite direction toward the interface. After 5 min most of the aqueous phase is filled with precipitated particles which are still moving around after 1 h because the complexation reaction at the interface continues for several hours.

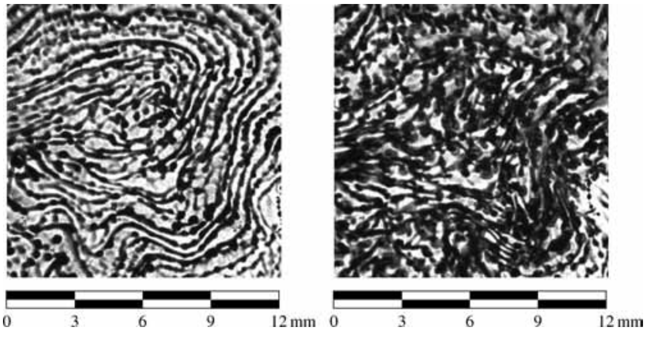

Figure 1. Top views of the potassium picrate system after 60 s (left) and 66 s (right) in a 30 × 30 mm^2 cuvette.

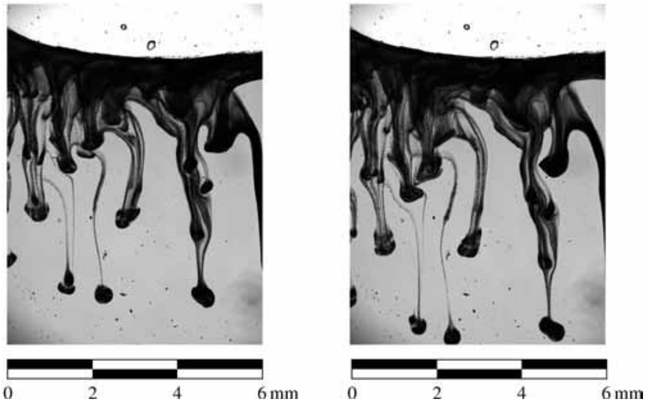

Figure 2. Side views of the potassium picrate system after 60 s (left) and 66 s (right) in a 10 × 2 mm^2 cuvette.

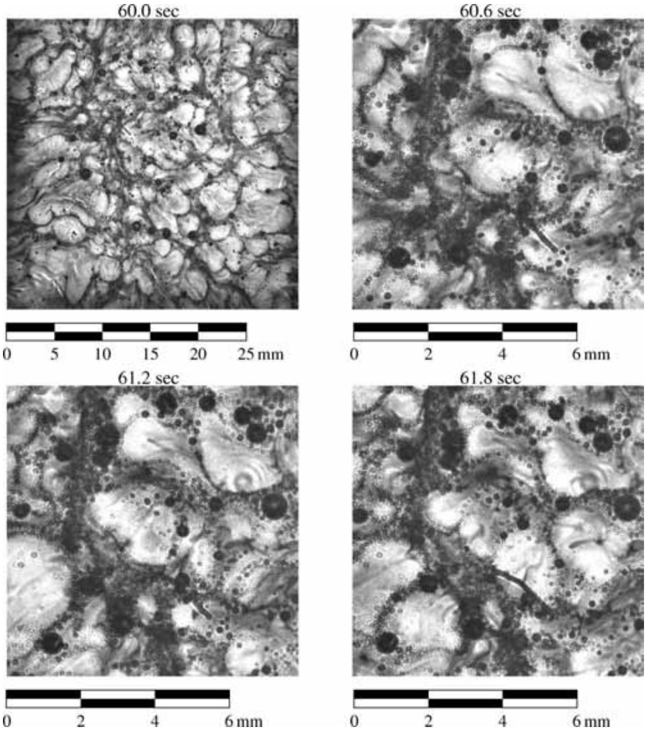

Figure 3. Top views of the sodium picrate system in a 30 × 30 mm^2 cuvette.

4.2. Sodium Picrate System. Sodium ions form a less stable complex than potassium ions do. The precipitation of the complex in the water phase occurs as in the potassium picrate system. Some of the precipitated particles vanish after a few seconds if they intrude deeper into the aqueous phase. The precipitation is shaped in particles of 2−15 μm in size (see Figure 3), similarly to section 4.1. Here, precipitated particles also occur in the upper hexane phase, assuming that the dissolved product first crosses the interface and then is

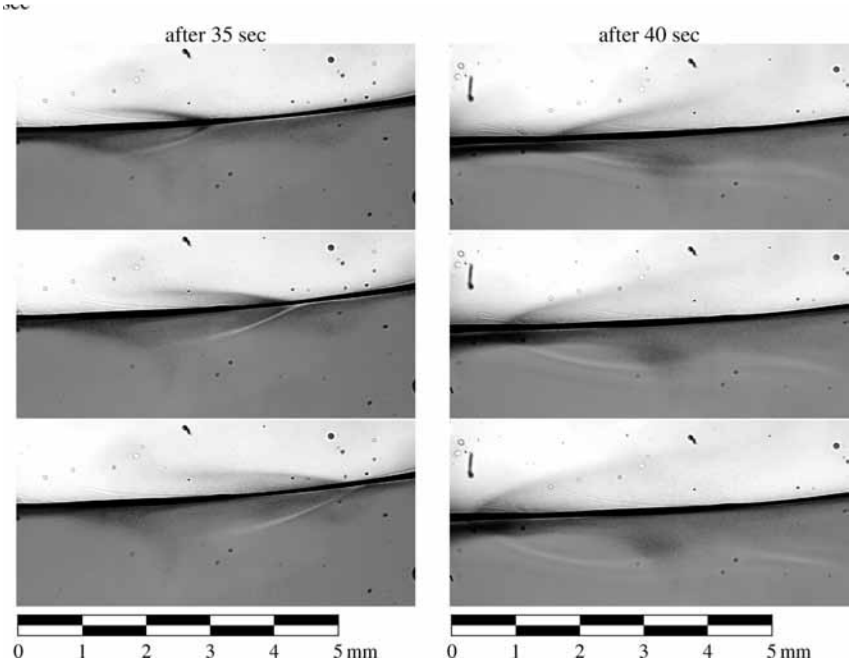

Figure 4. Side views in the sodium picrate system showing successive images with a time gap of 0.2 s.

precipitated. The pattern inside the cubic cell is unsteady and shows a low degree of order (see Figure 3). It is characterized by pulsating Marangoni cells whose shape is not regular and tends more to be round instead of being polygonal as reported for a Bénard–Marangoni convection.[2] No substructures in the form of smaller cells are visible inside most of the cells.[24]

In the small, thin cuvette details can be resolved, particularly in the normal direction with respect to the interface (see Figure 4). Because of local gradients in the interfacial tension the reaction is forced to move back and forth along the interface leading to an oscillating movement of the formed particles. In detail, an arrow-like structure occurs which moves along the interfaces at an angle of approximately 30° in relation to the interface. Approaching the opposite wall of the cuvette fades out the convection for 5 s in order to restart in the reverse flow direction. Numerous such cycles were observed taking place as long as the complexation reaction occurred (at least 1 h). The particular shape of the convection structure becomes visible due to a combination of a Schliere in the aqueous phase with an enrichment of precipitates in the upper hexane phase. The speed of the moving particles can reach up to 200 μm/s as analyzed by particle imaging velocimetry (PIV).

4.3. Cesium Picrate System. Cesium ions form the least stable complex of the alkali cations shown in Table 1. Precipitates of the complex formed occur temporarily for a few seconds. They dissolve later in the course of the reaction. The size of the precipitated particles is here again in the range of 2–15 μm. In addition, cesium has the advantage of having an easily available radioactive isotope. Hence, the extraction of cesium into the hexane phase can precisely be investigated by measuring the radioactive activity in the hexane and aqueous phase. The partition of cesium between the hexane and aqueous phase is around 0.5% (see Figure 5) which is also the extraction limit for shaken phases as generally used in extraction studies. Thus, only a small amount of cesium is extracted into the hexane phase, and the extraction obeys the expected time and concentration dependencies. The extraction is speeded up with increasing concentration of the crown ether, and the concentration of cesium reaches a plateau after a certain time. With this partition coefficient most of the complexation reaction take place at the interface of the aqueous phase.

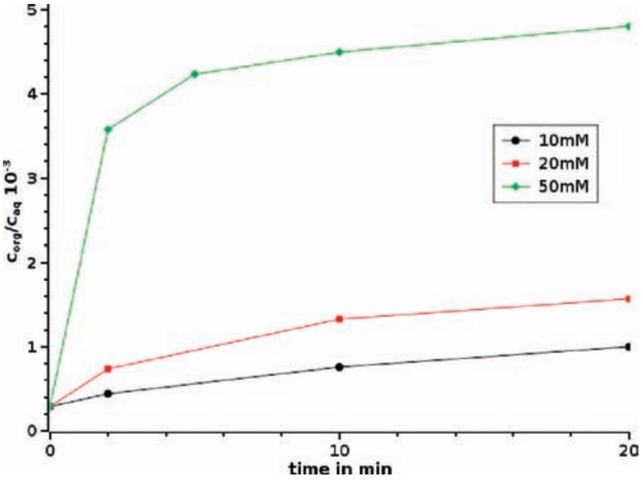

Figure 5. Partition of cesium into the hexane phase due to dicyclohexano-18-crown-6.

The cesium picrate system (with 100 mM dicyclohexano-18-crown-6) also generates oscillating convection in the aqueous phase as the sodium picrate system does. Looking from above into a rectangular measuring cell of 30 × 30 mm^2 even structured and oscillating particle assemblies occur moving periodically (see Figure 6). The oscillation typically occurs at periods of about 5 s and starts after a short induction time of approximately 10 s (see Figure 7). The speed of the precipitated particles can reach up to 40 μm/s as analyzed by PIV. Lower amounts of dicyclohexano-18-crown-6 (50 mM) dissolved in the hexane phase lead to a longer induction time of approximately 10 s while oscillation periods stay nearly unchanged. Several confinements were tested to investigate the influence of the spatial arrangement on the observed convection. In cuvettes with a larger gap (10 mm instead of 2 mm) oscillations occur in the same manner.

Changes in the concentration of dicyclohexano-18-crown-6 in hexane are limited by its solubility (maximum of 120 mM).

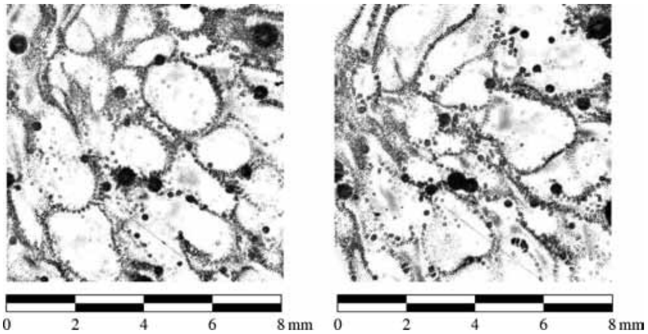

Figure 6. Top views of the cesium picrate system after 30 s (left) and 33 s (right) in a 30 × 30 mm^2 cuvette.

The amount of visible precipitated particles decreases with lower concentrations until no precipitates can be seen at all. The minimum concentration to produce precipitates is different for each alkali cation used (approximately 5−20 mM). The concentration of crown ether has no considerable influence on the speed and the frequency of the periodic movements. In fact, the convection shows a distribution of speeds which are not significantly different for concentrations of the crown ether in the range of 20−100 mM.

If the experiment is solely performed with cesium and picrate ions in the aqueous phase (5 mM and pH = 2.35) precipitates also appear in the aqueous phase, but no oscillating convection at the interface were observed. Instead of that, typical finger instabilities could be seen. As a second control experiment 5 mM of cesium nitrate was solely dissolved in water (pH = 5.19). With the help of shadowgraph optics periodically moving reaction fronts were made visible, but no precipitates occur in this case.

5. Discussion

Two different types of convection have been identified depending on the metal cation present in the aqueous phase: potassium ions induce a Rayleigh−Taylor instability represented by finger-like plumes consisted of precipitates invading into the aqueous phase (see Figure 2). By contrast, in the systems with sodium or cesium as the cation, so-called Marangoni cells are formed at the interface (see Figures 4 and 7) appearing as oscillations which are an intrinsic product of the complexation reaction presented in section 4.3. If no complexing alkali metal cation is present no oscillations will appear.

Oscillations at the liquid/liquid interface with involvement of a surfactant are influenced by the partition coefficient of the surfactant between two liquid phases, which can vary in very wide ranges. Its increase leads to an essential decrease of the oscillation amplitude.[25] The partition coefficient of the crown ether is $\log P_E = -0.82$. This indicates a strong preference for the hexane phase but corroborates the presence of the crown ether in the aqueous phase,[19] too. Hence, a mass transfer takes place, starting from the excess of crown ether in the hexane phase (in the beginning 3.7 g in 100 mL) into the aqueous phase. Here, the solubility of dicyclohexano-18-crown-6 amounts to 0.6 g in 100 mL water (see p 30 in ref 26).

Before discussing possible mechanisms we summarize the main processes taking place during the reaction of the crown ether with the alkali picrate. Alkali metal and picrate ions are not able to pass over from the aqueous phase into the hexane phase. Reaching the aqueous phase the crown ether reacts with the alkali metal cation (for which we take cesium as an example) located in the vicinity of the interface. The partition ratio of the complex formed is less than 0.5% (see Figure 5), and therefore the complex is enabled to extract only a small portion of the present cesium to the organic side.

Several equilibria are involved in the extraction process. The complexation is dependent on the size of the alkali metal cation which is to be extracted. Potassium cations fit optimally into the cavity of the crown ether which belongs to the family of 18-crown-6 polyethers. In contrast, the sodium ion is smaller, causing a looser binding. Cesium is the biggest alkali metal investigated and binds two crown ether molecules for the cost of a looser binding, too. Beside the formation of the alkali metal cation−crown ether complex there is also the solubility product of the salt consisting of the latter complex and the picrate anion. This solubility product is beyond its critical value so that the salt precipitates, forming crystals in the shape of particles of 5−20 μm in size. The salt formation near the interface shifts the equilibrium of the complexation reaction even more on the side of the products. If the crystals reach a critical size they stay stable and are not dissolved again as known from the classic nucleation theory.

In the cesium system the water content in hexane is crucial for the location where the precipitate occurs. If water-saturated hexane (≈0.05%[27]) is used, the precipitate occurs in the hexane phase instead of the aqueous phase. In the sodium system, precipitated particles also appear in the hexane phase pointing to a salt precipitation on this side by the neutral sodium crown ether complex with picrate as the counteracting anion crossing the interface.

Information about the complexation reaction is scarce. Kinetic data for the complexation reaction is only available for the gas phase.[28] This study about the cation transfer from 18-crown-6 to dicyclohexano-18-crown-6 has shown that the rate constants decrease monotonically with increasing alkali cation size. In contrast to that, the diffusivities of the alkali metal ions in water are, at around 2×10^{-9} m^2 s^{-1}, in the same magnitude of order. Previous studies concerning the alkali transfer across a liquid organic membrane have shown that the complexation reaction is fast compared to diffusion. The mass transfer is therefore controlled here by diffusion.[29,30] Therefore we consider our system also to be limited by diffusion of the solutes.

Since the focus of the discussion is on Marangoni convection only a brief comment is given on the Rayleigh−Taylor instability favored in presence of strong precipitation as observed in potassium system or in the absence of picric acid in the sodium and cesium systems. The boundary layer in the aqueous phase containing the product, i.e., the precipitates, is heavier than the underlying aqueous phase. As a result, it is unstable and gives rise to an instability, or equivalently to a density fingering.[31] It manifests itself in downward-sinking reacted fluid, organized in the form of fingers which are visible to the naked eye due to the precipitates. In parallel a counterflow of fresh reactants toward the interface sets in.

The key findings of the experiments with respect to Marangoni convection can be summarized as follows:

(1) The occurrence of Marangoni convection is coupled to the stability constant, K_C, of the complex produced. The potassium system, with a high K_C (see Table 1), produces a Rayleigh−Taylor instability accompanied by a distinct precipitation.

(2) The Marangoni cell pattern is not stationary but shows a pulsating character. Single cells grow abruptly until reaching a final size and decay later on.

(3) The images obtained in the cuvette can be seen to some extent as a two-dimensional section through a particular cell inside the three-dimensional pattern of Figures 3 and 6. Instead

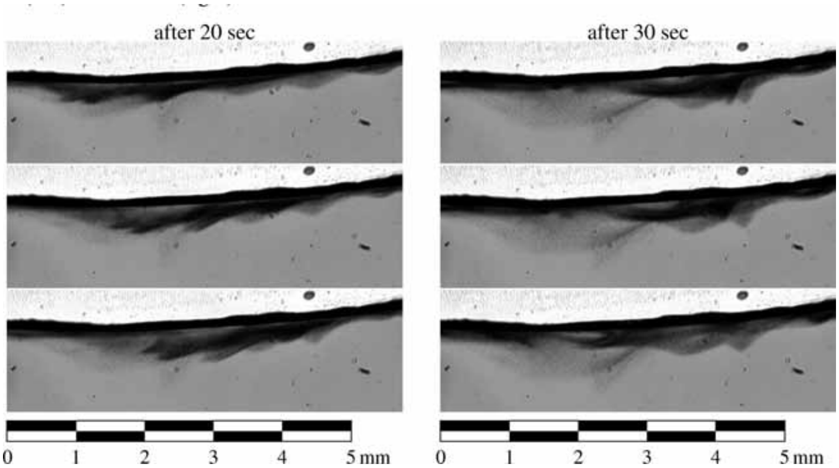

Figure 7. Side views in the cesium picrate system showing successive images with a time gap of 1 s (left) and 0.2 s (right) in cuvette of 2 × 10 × 45 mm^3.

of showing complete Marangoni cells, a periodically reversing motion with a wavelength of about 5 mm occurs in the cuvette along the interface. This typical length can also observed in the top view of the bigger 30 × 30 mm^2 cell.

(4) The amount of the product undergoing a mass transfer from the aqueous to the organic phase is very small. It is in the order of 0.5% for cesium (as shown by the radiochemical measurements in Figure 5). In parallel, we note that the speed of the Marangoni convection is an order of magnitude higher in the sodium system.

(5) If the aqueous phase does not contain picric acid

(a) the Marangoni convection is suppressed in favor of a Rayleigh–Taylor instability when only cesium picrate is present.

(b) In contrast, the Marangoni convection persists without any precipitates when cesium nitrate is present alone.

(6) The alkali metal picrate, the crown ether, and most likely the salt, an intermediate consisting of crown ether and metal picrate, are able to decrease the surface tension in order to create interfacial tension gradients as a precondition for the Marangoni convection.

The Marangoni convection vanishes when the salt is drawn away in the form of precipitates from the interface. This occurs for the potassium system, which has the highest stability constant, K_C in the row of alkali metals (see result 1). The normal concentration gradients due to the permanent precipitation are in this case obviously below the critical values for an onset of the Marangoni convection. Sodium shows a more intensive Marangoni convection than cesium (see result 4) although having the higher K_C. The reaction rate for sodium is assumed to be higher than for cesium since the latter needs two crown ether molecules to form a complex.[28]

The Marangoni convection can be seen as a sort of relaxation oscillation (see result 2)[10] which is known to occur at low interfacial tension gradients, where the inflow of the surfactant is sufficient to trigger the convection but not to sustain it. This assumption that there is a small interfacial gradient corresponds with the absence of a complete Marangoni cell in the small cuvette (i.e., no closed circulation in Figure 2) and with lacking substructures in the form of smaller cells inside the pulsating Marangoni cells of Figures 3 and 6. The pulsating character of the Marangoni cell pattern could be described by a subcritical oscillatory instability governed by a feedback control based on the system linear growth rate and the maximum of the amplitude of the emerging pattern. A control of this type can suppress the ballooning and result in the formation of spatially localized pulses similar to oscillons.[32] The behavior of oscillations in a two-phase system depends considerably on the confinement. Changes in the frequency and pattern of the oscillation are often reported[33] and are also seen in the experiments presented to some extent. In the big cubic cell the oscillation occur in all transversal directions, whereas in small ones the oscillation is forced to align in favor of the largest dimension.

The mechanism of the observed convection patterns is definitely connected with the mass transfer of the crown ether that generates respective concentration gradients perpendicular to the interface. The complexation reaction in the aqueous phase, followed by precipitation, consumes the reactants near the interface, namely, the crown ether and the alkali metal cation picrates. By contrast, an enrichment of the products occurs competing, with the convective transfer toward the bulk phase due to the unstable product stratification (Rayleigh–Taylor instability).

Several species have to be considered as driving ingredient for the present Marangoni instability: the crown ether as the ligand L, the alkali metal picrate as the substrate MA, the alkali metal–crown ether complex as an intermediate LM$^+$, and the precipitated salt as the product LMA (compare eqs 4–6).

We assume that the alkali metal–crown ether complex LM$^+$ causes the onset of the Marangoni convection, because it has a higher interfacial activity than the picrate ion. Thermal fluctuations are sufficient to cause local concentration differences of LM$^+$ at the interface resulting in a drop in the interfacial tension. As a consequence of this a shear stress is created which drags the fluid at the interface to places with higher interfacial tension. This process is continued until the meniscus region (small cuvette) or a second expanding Marangoni cell (large cuvette) is encountered. Then, the motion starts again in the opposite direction (see Figure 8). In this way oscillations lasting for 5–10 s are produced. Different processes can be responsible for the reversal of the convection direction:

(1) Diffusion limitation: The reactants consumed, and subsequently also the complex produced, are not replaced fast enough to prevent a depletion at places of initially higher LMA concentration. Thus, the gradient $\partial\gamma/\partial x$ cannot be sustained any more and the Marangoni convection breaks down temporarily.

(2) The crown ether is transferred preferably into the meniscus region at the wall, leading to a locally higher LMA concentration. Thus, the arrow-like motion may experience a γ-gradient in the opposite direction close to the wall, which

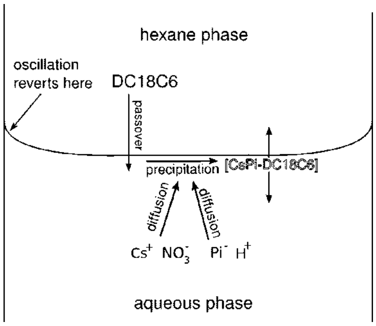

Figure 8. Scheme of the process.

might cease the motion. After an induction period, the onset of motion in opposite direction is triggered by the same gradient.

(3) The Rayleigh−Taylor instability can compete with the Marangoni instability. A starting plume conveys fluid of higher LMA concentration toward the bulk, thereby decreasing the LMA concentration at the interface and hence increasing the interfacial tension there. As a result the direction of the γ-gradient changes.

(4) Finally, the system involves several steps and equilibria related to species of different interfacial activity. The interplay between them might also create the restoring force necessary for the reversal.[6,34]

Analyzing studies on Marangoni convection based on concentration gradients shows that none of them really corresponds to the presented system. In the CTAB system mentioned before mass transfer goes from the aqueous phase to the organic phase.[9] In comparison, in our system the mass transfer is directed in the opposite way. It is considered that in practice, only the mass transfer of a single solute occurs. In a case of this kind the occurrence of Marangoni instability can be predicted by the viscosity of the phases if the transfer is diffusion-controlled.[35] In the presented system the mass transfer occurs from the organic phase with lower viscosity to the aqueous phase with higher viscosity. Hennenberg et al.[36] also predicts oscillatory instability in cases not provided by Sternling and Scriven[15] if the following necessary condition is fulfilled.

$$\frac{D_1 \nu_2}{D_2 \nu_1} > 1 \tag{8}$$

However, the application of their theory, formulated to the pure mass transfer without chemical reactions, has to be done carefully (see Mendes-Tatsis and Perez de Ortiz[37] and von Gottberg et al.[38]).

With the use of a crown ether as the nonionic surfactant, the solvent restriction discussed by Nakache et al.[34] can be circumvented and the oscillations are observable even in hexane. Nakache et al. stated that no oscillations were obtained by using hexane as the organic phase if ionic surfactants are used. There, oscillations are only possible if the dielectric constants of the liquid phases are so high that the ionic surfactant is dissociated in both phases.

To conclude, with the complexation reaction of an alkali metal ion with a crown ether we have presented an alternative system to all foregoing ones[7–10] which is able to display a sort of oscillating Marangoni convection. The appearance of oscillations due to surfactant transfer confirms that these oscillations are the result of Marangoni instability arising and fading periodically. Although a number of key features were identified, such as the sort of pattern formation and its dependence on the stability constant of the complex formed or its partition ratio, a comprehensive exploration of the underlying mechanisms deserves further studies.

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