

# The Partitioning of Chloride Ions between Aqueous and Microemulsion Phases in the System Water/Cetylpyridinium Chloride/Butanol/Dodecane/NaCl

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The distribution of water and NaCl between aqueous solutions and butanol, butanol + cetylpyridinium chloride (CPC) and butanol + CPC + dodecane solutions in equilibrium with the aqueous solution has been investigated. Addition of CPC increases water and NaCl solubility in the organic phase at low NaCl concentrations, due to the formation of reversed micelles. This effect is strongly reduced at high salt concentrations. The results can be conveniently rationalized in terms of the "pseudophase" model of microemulsion structure, i.e., the partitioning of the components between aqueous, membrane and nonpolar domains in the microemulsion. At high salt concentrations, very little salt partitions into the microemulsion. This implies that if this type of microemulsion is used in applications where it comes into contact with solutions with high salt concentrations, it will not be possible to incorporate water domains with high salt concentrations into the microemulsion.

Extensive research activity has recently been devoted to the enhancement of the recovery of oil from oil wells by injection of micellar solutions and microemulsions.<sup>1,2</sup> After some production of oil, the porous rock formation will usually contain a mixture of an aqueous phase and oil. In the so-called "surfactant flooding" process, injection of a surfactant-containing solution lowers the surface tension ( $\gamma$ ) between the two phases, thereby facilitating the release of oil from the pores. It has been shown that in this respect, microemulsions (i.e., thermodynamically stable solutions containing oil, water, surfactant and in many cases a cosurfactant) are superior to simple micellar solutions. Microemulsions can be formulated in such a way that their interfacial tension towards aqueous as well as hydrocarbon solu-

tions is very low and so that they are able to solubilize (dissolve) large amounts of oil without breaking.<sup>3</sup>

A serious practical problem in the use of microemulsions in this type of application, however, is that several factors that may drastically affect the composition and hence the stability of the solutions have to be controlled. These include: adsorption of surfactant on the rock, distribution equilibria with pore solutions with high electrolyte concentration and gradual dilution with oil and water.

The aim of the investigation described in this paper was to elucidate the second of these problems, viz., the distribution of simple electrolyte between a microemulsion that is of potential interest in enhanced oil recovery and an aqueous phase in equilibrium with the microemulsion, and how the stability of the microemulsion is affected by this distribution. The investigated system was cetylpyridinium chloride (CPC)/water/butanol ( $C_4OH$ )/dodecane ( $C_{12}$ ), with sodium chloride as added electrolyte.

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Dedicated to Professor Per Ekwall on his 90th birthday.

## Experimental

**Chemicals.** 1-butanol ( $C_4H_9OH$ , Kebo, purum), dodecane ( $C_{12}H_{26}$ , Fluka, purum), N-cetylpyridinium chloride monohydrate ( $C_{14}H_{29} \cdot C_4H_4NH \cdot Cl$ ) (Merck AG, pro analysi), sodium chloride and nitrate (Merck AG, pro analysi) were used as delivered. In the determinations of water content pyridine-free solvent for titration from Merck AG was used as reagent.

**Methods.** The samples were prepared by mixing weighed amounts of the components. The two-phase systems formed (microemulsion + aqueous solution) were allowed to equilibrate at constant temperature for at least 24 h. The phases were then separated and analyzed. The chloride concentrations were determined by titration with silver nitrate using potassium chromate as indicator. The water concentrations were determined by Karl Fischer titration using a Mettler DK10 automatic titrator. The concentration of CPC was measured by UV spectroscopy, utilizing the adsorption at 259 nm of the pyridinium ring and using a Pye Unicam SP8-200 spectrometer.

## Results

**Distribution of chloride between butanol and water.** When water and 1-butanol are brought into equilibrium at room temperature, the  $C_4OH$  dissolved 19.5%  $H_2O$ , while the  $H_2O$  dissolved 7.5%  $C_4OH$ .

Fig. 1 shows the partition coefficient of chloride  $K_1 = [Cl^-]_{org}/[Cl^-]_{aq}$  between the aqueous and butanol phases as a function of the total concentration of salt in the aqueous phase. The partition coefficient is clearly *not* concentration independent: it decreases rapidly with increasing salt concentration from about 0.025 for pure water to about 0.001 in saturated NaCl.

Fig. 2 shows that the distribution coefficient of water  $K_2 = [H_2O^-]_{org}/[H_2O]_{aq}$  also changes with increasing salt concentration. The solubility of water in the organic phase decreases rapidly and at the highest salt concentrations it is about half of that of pure water.

**Distribution of chloride between butanol and water containing CPC.** Fig. 3a shows results corresponding to those given in Fig. 1 but with different total concentrations of CPC added to the sys-

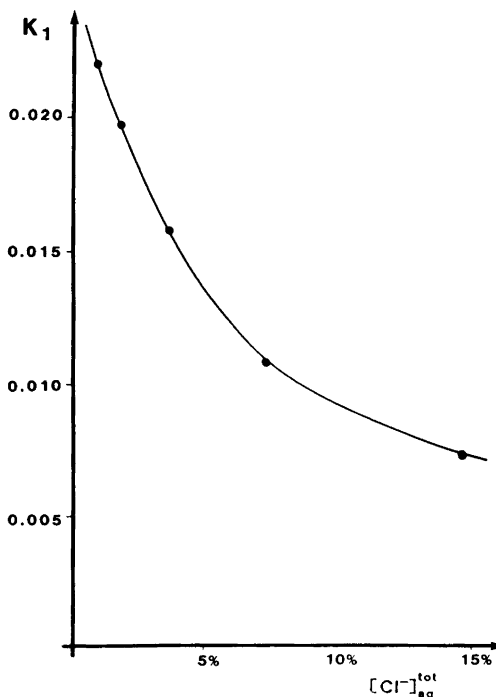


Fig. 1. Binary systems. The partitioning of chloride between the organic and the aqueous phases plotted versus the initial concentration of chloride in the aqueous phase.

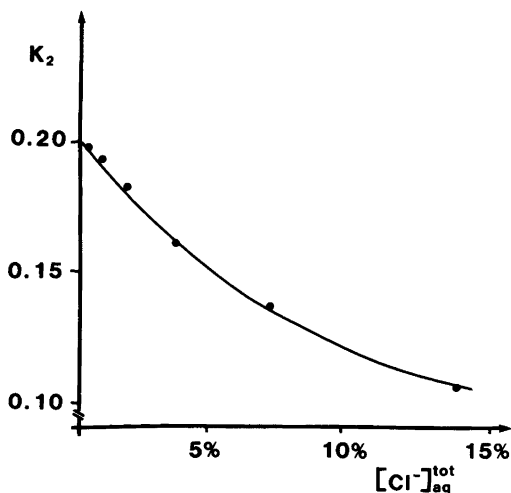


Fig. 2. Binary systems. The partitioning of water between the organic and the aqueous phases plotted versus the total concentration of chloride in the aqueous phase.

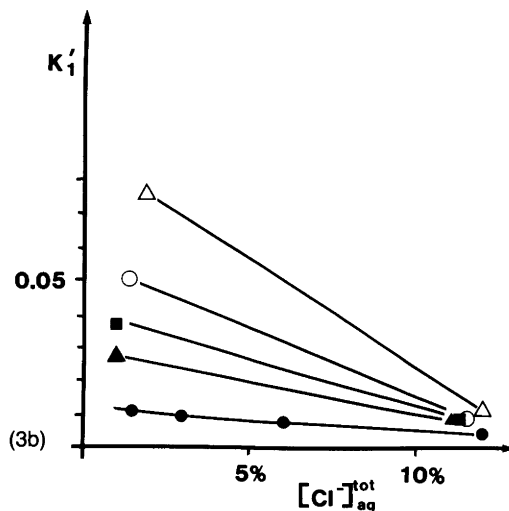
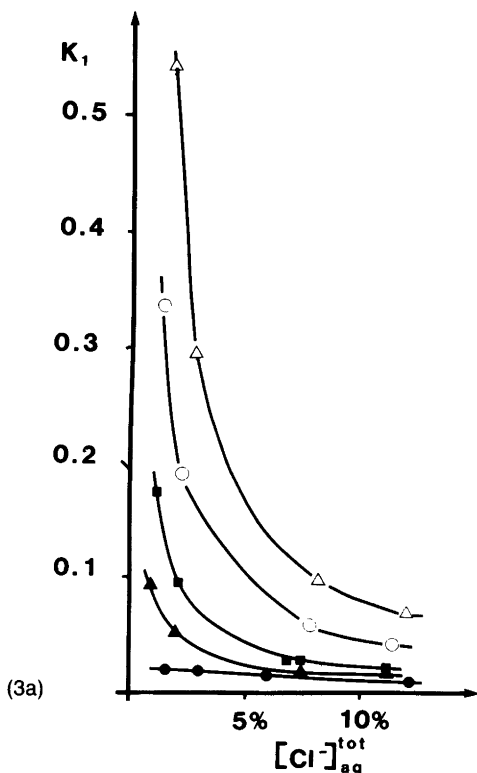


Fig. 3. The system water/CPC/butanol/NaCl. (a) The partitioning of chloride (from both NaCl and CPC) between the organic and the aqueous phases as a function of the total initial concentration of chloride in the aqueous phase. (b) The partitioning of chloride (only from NaCl) between the organic and the aqueous phases as a function of the total initial concentration of chloride in the aqueous phase in the same system.  $\Delta$ : 5% CPC.  $\circ$ : 2.5% CPC.  $\blacksquare$ : 1% CPC.  $\blacktriangle$ : 0.5% CPC.  $\bullet$ : 0% CPC.

tem. Analysis of the concentrations of CPC in the butanol and water phases shows that the partition coefficient of CPC depends on the total concentration of CPC. However, the CPC is always strongly distributed into the butanol phase at low total concentrations ( $[\text{CPC}]_{\text{org}}/[\text{CPC}]_{\text{aq}} \approx 10^3$ ). In this investigation, we were primarily interested in the effect of CPC on the distribution of electrolyte. Fig. 3b shows the distribution of  $\text{Cl}^-$  in excess of the  $\text{Cl}^-$  that was added as the counterion of the cetyl pyridinium ion, i.e.,  $K'_1 = ([\text{Cl}^-]_{\text{org}} - [\text{CPC}]_{\text{org}})/[\text{Cl}^-]_{\text{aq}}$  and ( $[\text{CPC}]_{\text{aq}} \ll [\text{Cl}^-]_{\text{aq}}$ ). At low concentrations of  $\text{Cl}^-$ ,  $K'_1$  was strongly increased by adding CPC. At total concentrations of  $\text{Cl}^-$  exceeding 10%,  $K'_1$  was rather independent of the amount of surfactant in the system.

Fig. 4 shows the water concentration in the butanol phase as a function of the concentration of CPC in the butanol phase and at different total concentrations of NaCl in the aqueous phase. The water concentrations are given relative to the solubility of water in pure  $\text{C}_4\text{OH}$  ( $[\text{H}_2\text{O}]^{\circ}_{\text{org}}$ ). The salt had little effect on the solubility at low

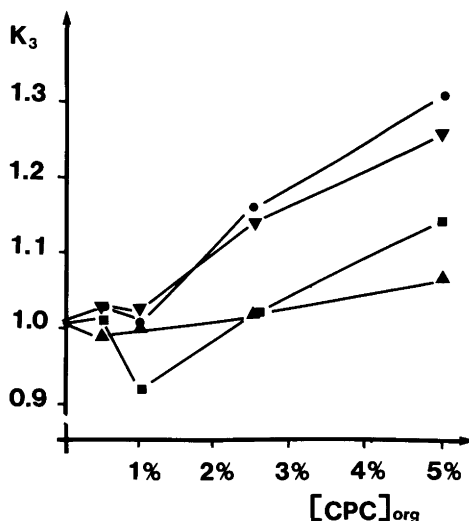


Fig. 4. The relative concentration of water in a butanol solution in equilibrium with aqueous solution as a function of the concentration of CPC and at different concentrations of NaCl.  $\bullet$ : 0.75% NaCl.  $\blacktriangledown$ : 1.5% NaCl.  $\blacksquare$ : 6% NaCl.  $\blacktriangle$ : 9% NaCl.

CPC concentrations (<1 %). At higher CPC concentrations, the water solubility increased, probably due to the formation of reversed micelles or other, less well defined association structures. Addition of salt strongly reduced the solubility of water, probably due to screening of the electrostatic charges of the cetylpyridinium ions which reduces the tendency to form swollen reversed micelles. Similar effects have been observed in the potassium oleate/pentanol/water system.<sup>4</sup>

*Distribution of chloride between organic and aqueous phase in the system  $H_2O/C_4OH/CPC/C_{12}$ .* Fig. 5 gives the partition coefficient  $K'_1$  for  $Cl^-$  between the aqueous and organic phases as a function of  $[CPC]_{org}$  for two different NaCl concentrations (1.5 and 6 weight %) and three different  $C_{12}$  concentrations (10, 20 and 40 weight %). For 10 and 20 %  $C_{12}$  the addition of CPC increased the distribution of  $Cl^-$  towards the organic phase. At 40 %  $C_{12}$ , the amount of  $Cl^-$  in the organic phase was very small.

Fig. 6 gives corresponding results for the partitioning of water. In all cases, addition of salt reduced the partitioning of water into the organic phase. It was also reduced when the amount of  $C_{12}$  was increased. Addition of CPC increased the

partitioning into the organic phase (except for 10 % dodecane and low water and CPC concentrations).

## Discussion

*Partitioning of chloride ions and the structure of microemulsions.* The structure of four-component ionic microemulsions (isotropic thermodynamically stable solutions containing water, oil and surfactant<sup>5</sup>) has been studied intensely in recent years. In particular, recent diffusion measurements by the Fourier-Transform-Pulse Gradient Spin Echo NMR method have shown that many microemulsions containing comparable volumes of water and oil are effectively bicontinuous, i.e. they contain water and oil domains that are characterized by properties similar to those of "pure aqueous solution" and "pure apolar solutions".<sup>6-9</sup> At lower water concentrations (and not too low concentrations of surfactant + cosurfactant in the hydrocarbon) the aggregates occurring in the microemulsions can be described as reversed micelles with rather well defined geometries.<sup>10-13</sup> In such solutions, diffusion and other solution properties are those expected if water is confined to slowly diffusing large aggregates.

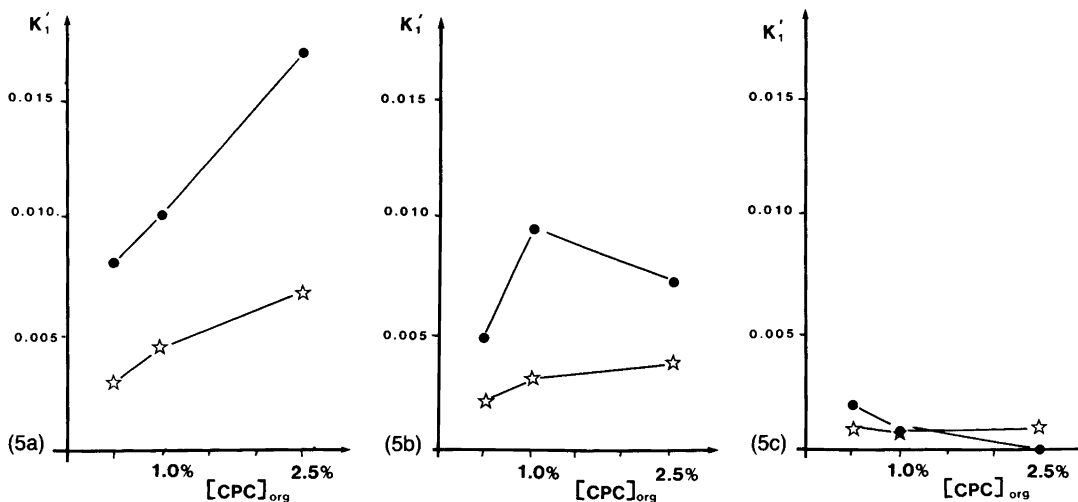


Fig. 5. The partitioning of chloride between the organic and the aqueous phases as a function of the total concentration of CPC in the system water/CPC/butanol/dodecane. ●: 1.5 % NaCl, ☆: 6 % NaCl. (a) 10 % dodecane, (b) 20 % dodecane, (c) 40 % dodecane.

However, irrespective of the detailed structure of the microemulsion its properties can in many cases be conveniently described in terms of the so-called "pseudophase" model.<sup>14-16</sup> In this model, the components of the microemulsion are considered to be distributed in equilibrium among three different types of domains in the so-

lution: an aqueous domain containing some of cosurfactant (alcohol); a hydrocarbon domain containing all of the nonpolar hydrocarbon, some cosurfactant (which self-associates in the domain) and water in proportion to the amount of cosurfactant; and a membrane domain that separates the aqueous and hydrocarbon domains and contains all of the surfactant and some cosurfactant. It has been shown experimentally that this model can be used to approximately predict microemulsion properties (e.g., chemical potentials of water and cosurfactant) within rather widely varying concentration intervals.<sup>14-17</sup>

According to this model, added salt will primarily dissolve in the aqueous domains and reduce the repulsion between the ionic end groups of the surfactant in the membrane domains. Figs. 1 and 5 show that very small relative amounts of salt will dissolve in a butanol or butanol + hydrocarbon solution in equilibrium with an aqueous salt solution. In the pseudophase model, this implies that it may be assumed that all of the salt dissolved in a microemulsion is located in the aqueous domains.

The results in Figs. 3 and 4 are entirely consistent with this picture. On adding CPC, the solubility of water in the microemulsion increases,

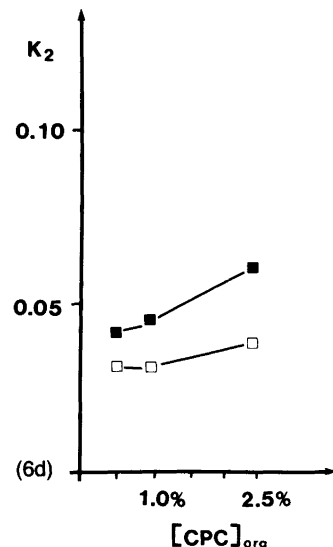
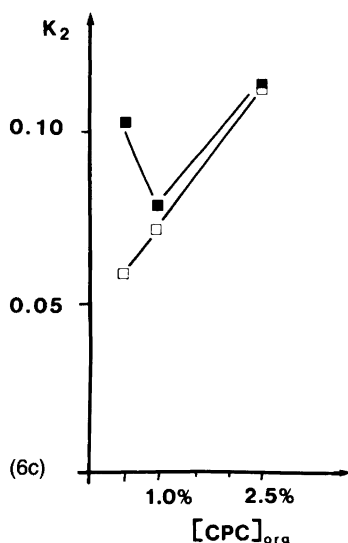
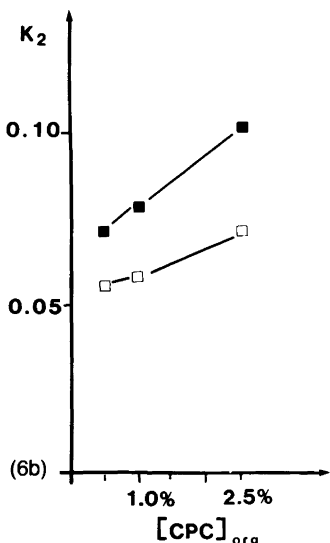
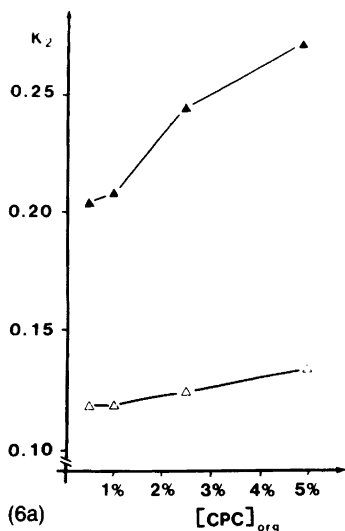


Fig. 6. The partitioning of water between the organic and the aqueous phase as a function of the total concentration of CPC in the system water/CPC/butanol/dodecane. ▲■, 1.5% NaCl, △□, 6% NaCl. (a) 0% dodecane, (b) 10% dodecane, (c) 20% dodecane, (d) 40% dodecane.

i.e., it becomes possible to form aqueous domains (in this case probably true reversed micelles) in the microemulsions. Salt may be dissolved in these domains. Adding electrolyte will lower the chemical potential of the water with the result that water is transferred from the nonpolar into the aqueous domains. As a consequence, the dielectric constant of the nonpolar domains increases<sup>18</sup> and the total amount of water that can be dissolved in the microemulsion decreases, as is shown by Figs. 3 and 4: when the total amount of NaCl increases from 0 to 9% the amount of water in the nonpolar phase is reduced by 25%.

In addition, adding electrolyte will also reduce the repulsion between the ionic end groups of the cetyl pyridinium ions, which will reduce the mean area per polar group in the membrane phase and, hence, the capacity to dissolve water or electrolyte in the aqueous domains. This is clearly seen in Figs. 3 and 4: at high electrolyte concentrations in the equilibrated aqueous phase, addition of CPC no longer increases the capacity of the nonpolar phase to dissolve electrolyte and has a very small effect on water solubility. In these experiments, as well as in the four-component systems, the CPC concentrations have been kept quite low. Higher concentrations result in the precipitation of a lamellar liquid crystalline phase. No such precipitation could be detected in any of the systems described here. Thus, they all represent two-phase equilibria between micellar and reversed micellar solutions.

In the four-component systems, the effects of CPC and NaCl on the distribution of the components between the pseudophases are even more pronounced. Addition of hydrocarbon will result in a distribution of the cosurfactant from the membrane domains into the hydrocarbon domains with the result that the membrane becomes more close packed and acts as a more effective diffusion barrier for water.<sup>19</sup> Addition of hydrocarbon will also lower the dielectric constant of the nonpolar domains. Both effects result in a reduced solubility of water in the microemulsions as can be seen by comparing Figs. 6a-d at constant concentration of CPC. When the concentration of CPC is increased, the solubility of water increases, since it becomes possible to form a larger membrane area between the aqueous and nonpolar domains.

At the lowest hydrocarbon concentration (Fig. 6b), addition of salt does not affect the distribution of water into the microemulsion very much, but the tendency to dissolve sodium chloride is strongly reduced (Fig. 5a), probably due to the lowered dielectric constant of the nonpolar pseudophase. At higher hydrocarbon concentration, the amounts of cosurfactant in the membrane domains will be strongly reduced and very little will be dissolved from an equilibrium aqueous solution into the probably quite small aggregates present in these systems.

*Application of the results to enhanced oil recovery.* Microemulsions used as injection fluids in different enhanced oil recovery processes come into contact with the aqueous solutions present in the rock formation. These may contain large concentrations of ions (this is, for example, the case in North Sea wells). Our results show that high salt concentrations in the aqueous solution result in a migration of water from the microemulsion into the water (Figs. 4 and 6), i.e. the microemulsion will no longer have a high solubilizing capacity for both water and oil and probably will no longer be effective in reducing the interfacial tensions that prevent effective displacement of oil by water in the formation. The remedy probably is to use an even shorter alcohol (propanol or isopropanol) instead of butanol as the cosurfactant. This will result in nonpolar domains with higher dielectric constants in the concentration and, as a consequence, a more favourable distribution of water into the microemulsions.

In one frequently used procedure to stimulate oil wells in limestone, hydrochloric acid or a mixture of hydrochloric and hydrofluoric acid is injected into the production well in order to open up the pores by acid etching. The disadvantage of using simple aqueous solutions is the very rapid reaction between the acid and the limestone. It has been suggested that this limitation could be overcome by using acid dissolved in the water domains of a microemulsion. This would strongly reduce the self-diffusion coefficient of  $H^+$  and hence, since the reaction rate between  $H^+$  and limestone is mass transport controlled, the rate of reaction in the rock formation would be lowered.

From our results, it can be concluded that if a microemulsion of the type investigated is brought into contact with the salt solution in the formation, the electrolyte in the microemulsion will un-

der these conditions partition strongly into the aqueous phase. Assuming that strong acids partition in the same way as NaCl, it is possible to conclude from Figs. 4–6 that only minor concentrations of acid will be retained in the microemulsion. Thus, microemulsions will be effective as reaction retardants only if they can be formulated in such a way that the partitioning of the electrolyte between aqueous and microemulsion phase can be reduced.

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