Scientific paper

Dielectric Spectroscopy of Co-Ion Effects on Microemulsion Dynamics and Phase Behaviour

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Dedicated to Professor Josef Barthel on the occasion of his 80th birthday

Abstract

The effect of added cationic co-ions (Li^+, Na^+, Cs^+, $(CH_3)_4N^+$) on the dielectric spectra of didodecyldimethylammonium bromide / water / *n*-dodecane microemulsions is reported. At high water/surfactant mole ratios ($W \approx$ 100–120) small amounts of co-ions drastically change the shape of the dielectric spectra in the 5–500 MHz region whereas for $W \approx 20$ almost no effect is observed. It is shown that the sensitivity of the dielectric spectra towards co-ion addition correlates with the percolation transition of the microemulsion structure from reverse micelles at high *W* to a bicontinuous phase at low *W*.

Keywords: Microemulsions, dielectric spectroscopy, phase behaviour, co-ion effect

1. Introduction

Surfactant systems and their microemulsions play a considerable role in current research activities as they show promise for a broad range of technical applications, including the generation of highly dispersed catalysts and use for drug-delivery systems.[1–4] Microemulsions also appear to be useful model systems for the elucidation of certain biological processes.[5] However, although the numerous investigations of recent years have led to a better understanding of this field,[6] some essential aspects of microemulsions are still unexplained.

The influence of co-ions on the ternary system didodecyldimethylammonium bromide (DDAB) / water (W) / *n*-dodecane (D) is a typical example of this. At room temperature, a homogeneous water-in-oil microemulsion ('L_2') is formed over wide areas of the DDAB/W/D phase diagram (Figure 1), the surfactant cations being located almost entirely at the W/D interface.[7,8] However, adding electrolytes to this system beyond a threshold concentration shrinks the stability region of the microemulsion to a tiny 'island', which remains constant upon further electrolyte addition.[9] The reason for this phenomenon, which can be ascribed entirely to the cation, is obscure,[10] especially since the threshold concentration amounts to only 1% of the total ion concentration in the system. The development of an appropriate mesoscale probe to elucidate this 'co-ion effect' would be a major step towards understanding the co-ion influence on the stability of ionic microemulsions and of polyelectrolyte solutions in general.

Dielectric relaxation spectroscopy (DRS)[11,12] is a useful tool to study co-ion effects in microemulsions. This technique determines the dielectric function $\hat{\eta}(\nu) = \varepsilon'(\nu) - i(\varepsilon''(\nu) + \kappa/2\pi\nu\varepsilon_0)$ for frequencies ν in the microwave region, with κ being the static ($\nu \rightarrow 0$) conductivity of the sample and ε_0 the vacuum permittivity. The spectra of permittivity, $\varepsilon'(\nu)$, and the dielectric loss, $\varepsilon''(\nu)$, are connected with the fluctuations of the macroscopic dipole moment of the sample and provide thus information on associated dynamical processes on the pico- to nanosecond time scale.

The present contribution reports a DR study, covering a frequency range between 5 MHz and 89 GHz, which compares the effect of the co-electrolytes LiBr, NaBr, CsBr and $(CH_3)_4NBr$ on DDAB/W/D microemulsions. The results obtained suggest that the co-electrolyte sensitivity of the dielectric spectra strongly depends on the water/surfactant mole ratio, *W*, and can be correlated with the percolation transition of the microemulsion structure from reverse micelles at high *W* to a bicontinuous phase at low *W*.

2. Experimental Section

Dielectric spectra were recorded at (25 ± 0.05) °C using the time-domain reflectometer (TDR, $0.005 \leq \nu$ / GHz ≤ 0.2) and two waveguide interferometers ($26.5 \leq \nu$ / GHz ≤ 89) at Regensburg. For intermediate frequencies ($0.2 \leq \nu$ / GHz ≤ 20) a Hewlett-Packard model 85070M dielectric probe system based on an HP 8720D vector network analyzer (VNA) was used at Murdoch University (Australia). The operation of these instruments is described in detail elsewhere.[13–15] Generally, a seamless fit between the data points obtained by the different experimental techniques was observed. Conductivity was determined from the $\nu \rightarrow 0$ limit of the total loss, $\mathrm{Im}(\hat{\eta}(\nu))$.[14] Since the dielectric loss, $\varepsilon''(\nu)$, remains large at the lowest frequencies accessible to us κ is only accurate to ~5%.

All microemulsions were prepared gravimetrically without buoyancy corrections using de-gassed MILLIPORE water and *n*-dodecane (Merck, Germany, > 99%). DDAB (ACROS, Belgium, > 99%, 40 °C), LiBr (Merck, Germany, extra pure > 99%, 100 °C), NaBr (Merck, Germany, suprapure, 80 °C), CsBr (Merck, Germany, suprapure, 80 °C) and $(CH_3)_4NBr$ (Fluka, Switzerland, puriss. > 99%, 50 °C) were used without further purification, but were dried under high vacuum (~10^{-5} bar) for at least 24 h at the indicated temperatures.

3. Results and Discussion

Figure 1 shows the position of the L_2-type microemulsion phase in the DDAB/W/D phase diagram[8] and the composition of the samples investigated in this study. In the current series of measurements, the addition of the co-electrolyte NaBr at concentrations below the breakup of the microemulsion phase was probed for five points along a path characterized by a constant mass fraction of dodecane ($w_D = 0.35$) and a variable water/surfactant mole ratio, $W = n_W / n_{DDAB}$. These points were chosen because they show considerable differences in their sensitivity towards the addition of co-ions. According to the investigations by Sjöblom et al., the L_2 phase already disappears for $c_{NaBr} = 1.36$ mM at $W = 119$, whereas it remains unaffected by the addition of NaBr at $W = 16$.[9]

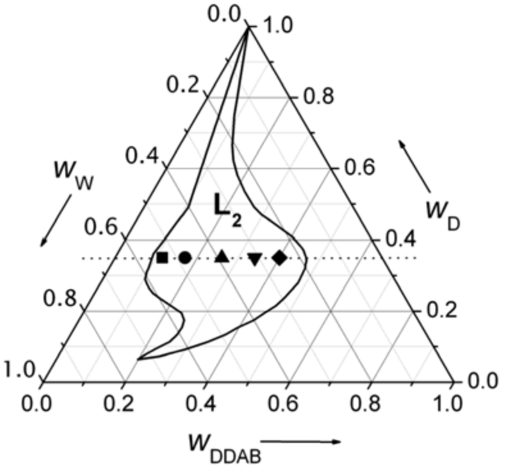

Figure 1. Phase diagram of the system DDAB/W/D at 25 °C[8] showing the microemulsion phase (L_2). Samples investigated in this work were at dodecane mass fraction $w_D = 0.35$ and water/surfactant mole ratios of $W = 119$ (■), 72 (●), 39 (▲), 23 (▼), 16 (◆).

Figures 2 and 3 show the dielectric spectra for DDAB/NaBr(aq)/D at $W = 119$ and $W = 16$, respectively. Two clearly distinct regions can be observed. The large contribution below ~1 GHz is specific to the microemulsion and arises mainly from polarization effects caused by the DDA^+ and Br^- ions at the oil/water interface.[16] The weaker contribution at $\nu \geq 1$ GHz is due to the water in the microemulsion droplets. Comparison of the dielectric loss, ε'' (Figures 2b and 3b), with that of pure water (concentration c_W°), scaled to the appropriate molar concentration c_W, indicates that a large amount of the water in the microemulsions is so strongly bound that its dipoles cannot respond to the applied microwave field any more. Additionally, the relaxation of the detectable H_2O is severely affected since the shapes of the permittivity, $\varepsilon'(\nu)$, and the dielectric loss spectra, $\varepsilon''(\nu)$, are significantly changed.

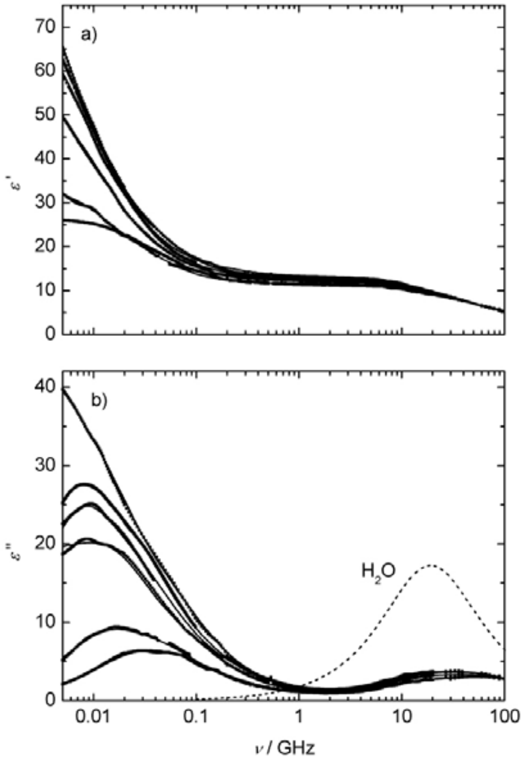

Figure 2. Dielectric permittivity, $\varepsilon'(\nu)$ (a), and loss, $\varepsilon''(\nu)$ (b), spectra for DDAB/NaBr(aq)/D microemulsions at *n*-dodecane mass fraction $w_D = 0.35$ with water / surfactant mole ratio $W = 119$. NaBr concentrations: c/mM = 0, 0.05, 0.10, 0.50, 0.80, 1.0 (top to bottom). Also included in (b) is the dielectric loss spectrum of pure water, scaled to its concentration in the microemulsion system ($c_W \cdot \varepsilon'' / c_W^\circ$).

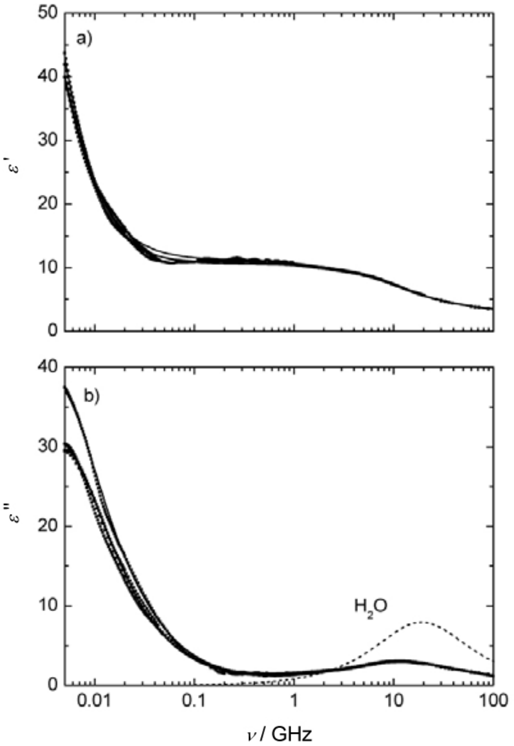

Figure 3. Dielectric permittivity, $\varepsilon'(\nu)$ (a), and loss, $\varepsilon''(\nu)$ (b), spectra for DDAB/NaBr(aq)/D microemulsions at *n*-dodecane mass fraction $w_D = 0.35$ with water / surfactant mole ratio $W = 15.9$. NaBr concentrations: c/mM = 0, 1.0, 25 (top to bottom). Also included in (b) is the dielectric loss spectrum of pure water, scaled to its concentration in the microemulsion system ($c_W \cdot \varepsilon''/ c_W°$).

Even more interesting are the pronounced differences in the co-ion sensitivity revealed by the microemulsion part of the dielectric spectra (below ~1 GHz). At the leftmost phase point in Figure 1, with its large water/surfactant mole ratio of $W = 119$, addition of small amounts of NaBr ($c \leq 1$ mM) evokes a pronounced decrease in both ε' and ε'' (Figures 2a, b). This is an extraordinary effect, given that DR spectra of aqueous electrolyte solutions can hardly be distinguished from that of pure water for $c \leq 50$ mM[17] and that the concentration of the added Na$^+$ ions reaches not more than 1% of the total Br$^-$ concentration. However, with decreasing W/DDAB ratios, the sensitivity of the dielectric spectra towards co-ion addition decreased gradually. For $W = 16$ addition of 1 mM NaBr produced only a slight reduction of $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ at $\leq \nu$ 1 GHz, and almost no difference can be observed any more between $c_{NaBr} = 1$ mM and $c_{NaBr} = 25$ mM (Figures 3a, b).

To compare these results obtained for NaBr with the effects of other co-electrolytes, the measurements were repeated using LiBr, CsBr and (CH$_3$)$_4$NBr instead of NaBr at two phase points: at $W = 38.5$, where the effect of the co-electrolyte NaBr was already very small, and at $W = 119$, showing the extraordinarily high sensitivity towards NaBr discussed above. Because of time and of the high cost of DDAB, the remaining three points of Figure 1 were not included in this set of experiments. For the sake of simplicity, only bromide salts have been used as co-electrolytes: As the surfactant counterion Br$^-$ is already abundant in the system, the observed changes in the dielectric spectra can be reasonably assumed to be merely a cationic effect. The results obtained for (CH$_3$)$_4$NBr (Figures 4 and 5) were very similar to NaBr despite their differences in terms of size (and thus charge density) and polarizability. Almost identical results were also obtained for LiBr and CsBr (Table 1).

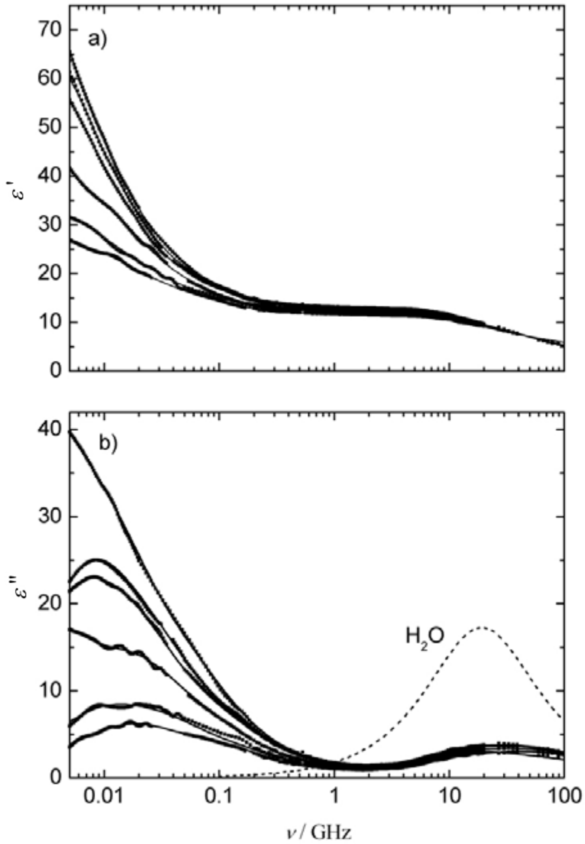

Figure 4. Dielectric permittivity, $\varepsilon'(\nu)$ (a), and loss, $\varepsilon''(\nu)$ (b), spectra for DDAB/(CH$_3$)$_4$NBr(aq)/D microemulsions at *n*-dodecane mass fraction $w_D = 0.35$ with water / surfactant mole ratio $W = 119$. (CH$_3$)$_4$NBr concentrations: c/mM = 0, 0.05, 0.18, 0.50, 0.80, 1.0 (top to bottom). Also included in (b) is the dielectric loss spectrum of pure water, scaled to its concentration in the microemulsion system ($c_W \cdot \varepsilon''/ c_W°$).

To quantify the sensitivity of the DR spectra towards the co-ions, the relative change of the dielectric loss maximum upon co-electrolyte addition, $\delta\varepsilon'' = \mathrm{d}\,\varepsilon_{max}'' / \mathrm{d}\,c$

Table 1. Sensitivity, $\delta\varepsilon'' = \mathrm{d}\,\varepsilon_{max}'' / \mathrm{d}\,c$ (in 10^3 L mol^{-1}), of the maximum of the dielectric loss spectrum upon co-electrolyte addition at two different water/surfactant mole ratios, *W*.

W	LiBr	NaBr	CsBr	(CH$_3$)$_4$NBr
38.5	0.56 ± 0.20	0.39 ± 0.10	0.67 ± 0.15	0.56 ± 0.20
119	21 ± 2	24 ± 4	22 ± 2	20 ± 2

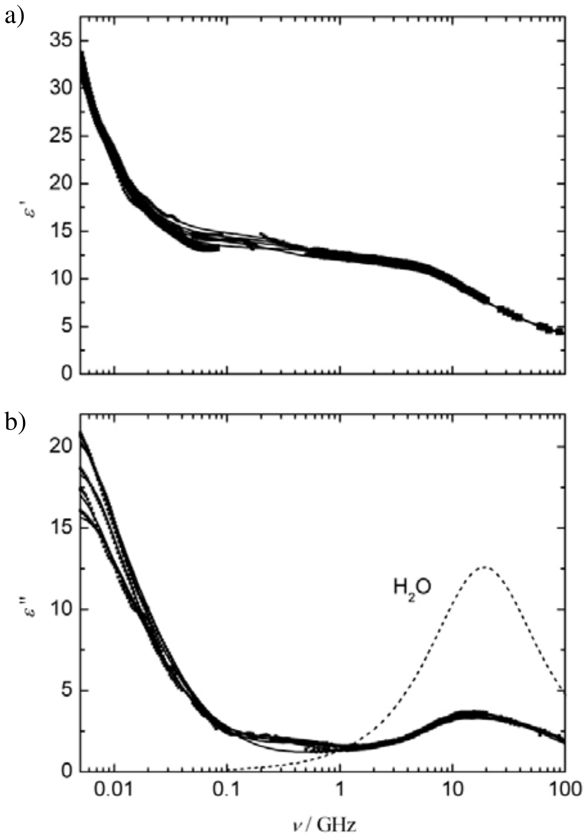

Figure 5. Dielectric permittivity, $\varepsilon'(\nu)$ (a), and loss, $\varepsilon''(\nu)$ (b), spectra for DDAB/$(CH_3)_4NBr(aq)$/D microemulsions at *n*-dodecane mass fraction $w_D = 0.35$ with water / surfactant mole ratio $W = 38.5$. $(CH_3)_4NBr$ concentrations: c/mM = 0, 1.0, 5.0, 7.0, 10 (top to bottom). Also included in (b) is the dielectric loss spectrum of pure water, scaled to its concentration in the microemulsion system ($c_W \cdot \varepsilon''/ c_W^\circ$).

was determined (Table 1). The obtained values of $\delta\varepsilon''$ for $W = 38.5$ and 119 differ by a factor of ~40. Within error limits the sensitivities do not depend on the co-electrolyte, although some trend in the order $Na^+ < Li^+ \approx (CH_3)_4N^+ < Cs^+$ may possibly be seen for $W = 38.5$.

How can the dependence of the co-ion sensitivity on the water/surfactant mole ratio be explained? For the present system it has been suggested that L_2 exhibits different microstructures, depending on the W/DDAB ratio[7,18–20] Specifically, it has been proposed that microemulsions of water-rich samples consist of separated water droplets embedded in oil, whereas a bicontinuous system of interpenetrating oil and water channels prevails for surfactant-rich systems. The latter structure has been confirmed by interfacial tension measurements, which revealed strong long-range van der Waals forces that are characteristic of a dielectric of high permittivity and cylindrical shape interacting across a medium of low dielectric constant.[18]

Our conductivity data (Figure 6) are consistent with a microemulsion structure dominated by reverse micelles at large W and a continuous water sub-phase at low ratios DDAB/NaBr(aq)/D. Moreover, given that κ increases gradually with decreasing W, we can infer that the structural transition of the DDAB/W/D system is through a smooth increase in percolation, i.e. the transition from separated water droplets to a bicontinuous network is gradual. This interpretation is supported by freeze-fracture electron microscopy showing the formation of water channels between neighboring water droplets even for water-rich samples.[20]

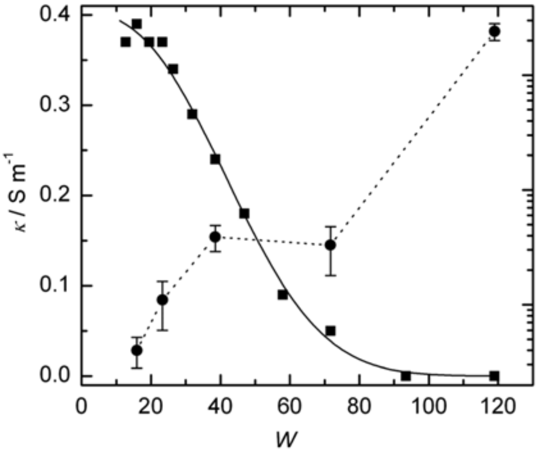

Figure 6. Conductivity, κ(■), of DDAB/W/D microemulsions as a function of the water/surfactant ratio, W, at $w_D = 0.35$ and 25 °C. Also plotted is the sensitivity of the dielectric loss peak upon NaBr addition, $\delta\varepsilon'' = d\,\varepsilon_{max}'' / d\,c$ (●). Lines are only given as a visual aid.

Figure 6 suggests that the change in the sensitivity of ε'' towards co-ion addition is directly related to the transition in the microstructure. Thus, $\delta\varepsilon''$ remains small for water/surfactant mole ratios of $W \leq 70$ where water channels prevail (thus $\kappa > 0$). However, for the non-percolating system with isolated water droplets (thus $\kappa \approx 0$) not only the co-ion sensitivity, $\delta\varepsilon''$, becomes very large. As shown by the pronounced high-frequency shift of the loss peak, also the cooperative microemulsion dynamics are considerably altered well before the breakup of the L_2 phase, indicating that the Na^+ ions directly interact with the interface film. To gain further insights, extended series of samples with various co-ions have been investigated.[16] Currently, work is in progress which will provide more detailed information through the quantitative analysis of the dielectric spectra in terms of a superposition of various relaxation processes. First results suggest that the co-ions are located near the interface and modify its geometry.

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Povzetek

Raziskovali smo vpliv različnih protiionov (Li^+, Na^+, Cs^+, $(CH_3)_4N^+$) na spekter dielektrične relaksacije mikroemulzij didodecil-dimetilamonijev bromid/voda/*n*-dodekan. Ugotovili smo, da v mikroemulzijah z visokim razmerjem vode in surfaktanta ($W \approx$ 100–120) že majhen dodatek protiionov drastično spremeni obliko spektra v območju 5–500 MHz, medtem ko pri manjših razmerjih ($W \approx 20$) vpliv protiionov ni opazen. Izkazalo se je, da je vpliv dodanih protiionov na obliko spektra v korelaciji z območjem prekolacijskega prehoda, kjer struktura mikroemulzij preide iz inverznih micel pri visokih vrednostih *W* v bikontinuirno fazo pri nizkih *W*.