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Interfacial Phenomena in the System Water + CO_2 + Alcohol Ethoxylates

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A systematic investigation of alcohol ethoxylates (AEOs) and their use as surfactants in the CO_2 + water system was performed by measuring the interfacial tension (IFT) at 283 K and (5 to 20) MPa. It is the first time that the polydispersity of the AEOs has been studied. The synergistic effect was examined thoroughly. The findings enable the surfactant behavior to be expressed as the hydrophilic−CO_2-philic balance, analogous to the HLB of the tradinional o/w systems, and also permit a relationship to be established between surfactant structure and the behavior at the interface.

1. Introduction

Carbon dioxide in its liquid or supercritical state has been found to be a promising medium for reactions, separations, and cleaning processes. The main advantages are adjustment of solvent properties and the ease of subsequent solvent removal.[1]

However, a cleaning fluid has three tasks to fulfill: it has to remove both soluble and insoluble pollutants and solid particles. If compressed carbon dioxide is used instead of water, lipophilic pollutants are readily dissolved. To remove hydrophilic compounds and particles, detergents have to be employed. Removal comprises roughly three processes: dissolving, dispersing, and transporting. As compressed carbon dioxide has weak transport and dispersion capacities even at liquidlike densities, surfactants are needed to disperse and transport the pollutant away from the substrate.

In recent years an enormous effort has been invested in finding suitable surfactants for compressed CO_2. In 1990 Consani et al.[2] reported the solubility data of over 130 commercial surfactants at 323 K and at pressures up to 50 MPa. The surfactants containing fluorine−carbon bonds invariably tended to dissolve at lower pressures than those for the corresponding hydrogenated substances, if at all. Blasberg et al.[3] tested four ionic and four nonionic industrial surfactants and determined the solubility data up to 50 MPa. They reported the same trends: only the fluorinated surfactants were soluble in the technically applicable pressure and temperature ranges. At the investigated conditions nonfluorinated alcohol ethoxylates (AEOs) were the second choice.

Low surface tension values[4] and microemulsions[5] have been reported for fluorinated ionic surfactants. However, these surfactants are neither cheap nor environmentally benign, and therefore, they are of limited use for the cleaning industry. The use of such surfactants is restricted in Europe: fluorinated compounds may not be released into the environment.

In considering technical process feasibility, the weaker surface activity of the AEOs compared with the fluorinated ionic surfactants is outweighed by the environmentally benign characteristics of this surfactant class: they are classified as readily biodegradable by the OECD 301 A, B, and D tests.

Low interfacial tension values are one prerequisite that a surfactant mixture has to fulfill before it is used in the cleaning industry. Microemulsions can be expected to form more easily at lower interfacial tension (IFT) values, , and these emulsions are the driving force in all models of the washing process.

The reduction of the interfacial tension value of the water + carbon dioxide interface was studied as a screening parameter for the usability of the surfactants. The objective of this study is to utilize new measurements for available technical linear alcohol ethoxylates to support the formulation of detergents for industrial cleaning processes. To use the alcohol ethoxylates as detergents, they have to be fully soluble in CO_2 and they have to lower the interfacial tension of the binary system drastically. To date, no systematic study has reported on interfacial tension measurements for this surfactant system. The underlying two-phase system of carbon dioxide + water is reported elsewhere.[6] A relationship between structure and interfacial tension was derived from the measurements.

2. Experiments

Method and Apparatus. The interfacial tension data were obtained by using a modified high-pressure pendant drop method, the quasi-static method. The method and apparatus used are described in detail elsewhere.[6] Briefly, the system consists of a high-pressure circuit with a gear pump, a viewing cell, and a sample loop. The whole system is installed in a climatic chamber, which allows precise and accurate temperature adjustment to within ±0.2 K. The pressure stability is ±0.02 MPa and the experimental accuracy of the measuring system is above 98%.[6] Isotherms of the interfacial tension are measured using the quasi-static method. This method ensures a time regime where the influence of diffusion and drop aging does not affect the IFT. Two surfactants were measured twice in order to prove that the reproducibility is well above 97%.

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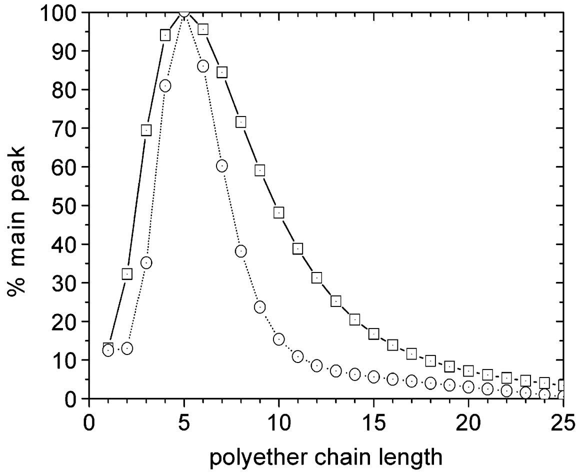

Figure 1. Distribution function of the polyether chain: ⊡, normal; ⊙, narrow distribution.

Because the surfactants were mixtures, they were homogenized prior to any experiment. At the start of a measurement, a small water drop was formed at the tip of the measuring capillary (T20C10, Valco, GAT, Bremerhaven, Germany; 1.6 mm o.d., 0.25 mm i.d.). The surfactant was fed into the system via a calibrated sample loop ($V = (2.73 \pm 0.02\ \mu L)$); the concentration by volume was the same for all surfactants despite small differences in density and molar masses. The molar concentration for all surfactants was (0.041 ± 0.001) mg of surfactant/g of CO_2 at temperature and pressure values near 283 K and 5 MPa. Afterward the system was agitated vigorously with the gear pump. The drop was then enlarged by adding water. The system was allowed to relax, and then the measuring procedure was started. The mixing was needed in order to equilibrate the surfactant concentration in the system between the water and carbon dioxide phases. Three successive measurements at 5 MPa were performed to determine the thermodynamic equilibrium. If there was no change within the limits of the reproducibility, the pressure was raised by adding CO_2 up to a maximum of 20 MPa. This procedure limits the range of measurable surfactants because only liquid substances can be added to the system via the sample loop.

Substances. CO_2 of quality 99.9999% (Messer Griesheim, Karlsruhe, Germany) and Milli-Qplus water were used. The surfactants were supplied by Kreussler (Chemische Fabrik Kreussler & Co. GmbH, Wiesbaden, Germany) and used without further cleaning.

The alcohol ethoxylates are nonionic surfactants. The alkyl chain makes the surfactant soluble in CO_2 and therefore enhances the CO_2-philicity. The ethoxylate chain originates from polymerization of ethylene oxide. Thus, the resulting surfactant is a polydisperse mixture. The distribution in polyether chain length (EO no.) approximates a Poisson distribution. The nomenclature of the surfactants is based on the main peak. The systematic name reads C_x-EO_y. Four surfactants were synthesized with two distributions: normal and narrow. The narrowly distributed surfactants have the prefix nr- added to their name, for example, nr-C_8EO_5. The difference in the distribution is given in Figure 1. Table 1 shows a list of the surfactants tested.

Table 1. Table of the Experimental Interfacial Tension of Water + CO_2 + Surfactant, as a Function of Temperature and Pressure[a]

p/MPa	T/K	IFT[b]/$mN \cdot m^{-1}$	surfactant	alkyl length	EO no.[b]	HCB,[b] eq 2	HCB range
5.02	282.5	21.4	C_6E_3	6	3	7.8	4.8−16.6
5.01	282.8	23.7	nr-C_6E_3	6	3	7.8	6.0−16.6
5.03	283.4	19.8	C_6E_4	6	4	6.5	3.9−16.6
5.06	283.0	18.0	C_6E_5	6	5	5.5	3.2−16.6
5.16	283.1	19.1	nr-C_6E_5	6	5	5.5	4.1−16.6
4.99	283.1	17.2	C_6E_6	6	6	4.8	2.7−16.6
5.00	283.2	17.9	C_8E_3	8	3	9.2	6.0−17.4
5.05	283.4	22.6	nr-C_8E_3	8	3	9.2	7.2−17.4
5.38	282.9	16.2	C_8E_4	8	4	7.8	4.8−17.4
5.25	283.0	15.8	C_8E_5	8	5	6.7	4.1−17.4
5.10	283.1	19.0	nr-C_8E_5	8	5	6.7	5.1−17.4
5.06	282.9	15.1	C_8E_6	8	6	6.0	3.5−17.4
5.16	283.1	16.4	$C_{10}E_3$	10	3	10.3	6.9−17.8
5.00	283.0	12.5	$C_{11}E_3$	11	3	10.8	7.4−18.0
5.14	283.4	6.8	$C_{12}E_9$	12	9	6.0	3.5−18.2
5.28	283.0	14.9	$C_{11-15}E_5$	13	5	9.1	5.9−18.3
5.06	283.0	13.3	$C_{13-15}E_3$	14	3	12.0	8.5−18.4
4.95	283.3	7.0	$C_{13-15}E_7$	14	7	7.8	4.8−18.4
			303 K, $C_{12}E_9$				
7.66	302.9	3.6	$C_{12}E_9$	12	9	6.0	3.5−18.2
7.93	303.0	3.6	$C_{12}E_9$	12	9	6.0	3.5−18.2
8.52	302.7	3.9	$C_{12}E_9$	12	9	6.0	3.5−18.2
10.19	302.9	3.6	$C_{12}E_9$	12	9	6.0	3.5−18.2
10.78	303.2	3.7	$C_{12}E_9$	12	9	6.0	3.5−18.2
11.79	303.2	3.7	$C_{12}E_9$	12	9	6.0	3.5−18.2
13.14	303.2	3.6	$C_{12}E_9$	12	9	6.0	3.5−18.2
14.48	303.2	3.7	$C_{12}E_9$	12	9	6.0	3.5−18.2
16.45	303.2	3.7	$C_{12}E_9$	12	9	6.0	3.5−18.2
18.11	303.2	3.6	$C_{12}E_9$	12	9	6.0	3.5−18.2
20.16	303.2	3.4	$C_{12}E_9$	12	9	6.0	3.5−18.2
			303 K, $C_{13-15}E_3$				
7.46	303.6	14.8	$C_{13-15}E_3$	14	3	12.0	8.5−18.4
7.56	303.7	14.8	$C_{13-15}E_3$	14	3	12.0	8.5−18.4
8.54	303.6	17.1	$C_{13-15}E_3$	14	3	12.0	8.5−18.4
9.91	303.6	18.3	$C_{13-15}E_3$	14	3	12.0	8.5−18.4
12.75	303.5	19.6	$C_{13-15}E_3$	14	3	12.0	8.5−18.4
14.80	303.5	19.9	$C_{13-15}E_3$	14	3	12.0	8.5−18.4
17.82	303.4	20.0	$C_{13-15}E_3$	14	3	12.0	8.5−18.4
20.14	303.4	20.0	$C_{13-15}E_3$	14	3	12.0	8.5−18.4
			303 K, $C_{13-15}E_7$				
7.64	302.6	7.3	$C_{13-15}E_7$	14	7	7.8	4.8−18.4
7.64	302.8	7.3	$C_{13-15}E_7$	14	7	7.8	4.8−18.4
8.69	303.0	8.0	$C_{13-15}E_7$	14	7	7.8	4.8−18.4
9.99	303.1	8.8	$C_{13-15}E_7$	14	7	7.8	4.8−18.4
12.38	303.2	9.9	$C_{13-15}E_7$	14	7	7.8	4.8−18.4
14.89	303.2	10.8	$C_{13-15}E_7$	14	7	7.8	4.8−18.4
19.55	303.3	11.8	$C_{13-15}E_7$	14	7	7.8	4.8−18.4

[a] The data are averages of at least three measurements. [b] IFT = interfacial tension; EO no. = ethylene oxide number; HCB = hydrophilic−CO_2-philic balance.

Hydrophilic−Lipophilic Balance Concept. The solubility in the continuous phases is used to determine the surfactant behavior. Griffin has defined the hydrophilic−lipophilic balance (HLB)[7] (eq 1)

$$\mathrm{HLB} = 20\frac{M_\mathrm{h}}{M} \tag{1}$$

for alcohol ethoxylates in the water regime. Water in oil emulsifiers have HLB = 3 to 6, wetting agents have HLB = 7 to 9, and o/w emulsifiers have HLB = 8 to 18. Because carbon dioxide is used here as a continuous phase, the calculation of the HLB has to be altered. The corresponding hydrophilic−CO_2-philic balance (HCB) (eq 2),

$$\mathrm{HCB} = 20\frac{M_{\mathrm{CO_2}}}{M} \tag{2}$$

analogous to the HLB of the traditional oil−water systems, is obtained. Here, for example, w/o emulsifiers have HCB

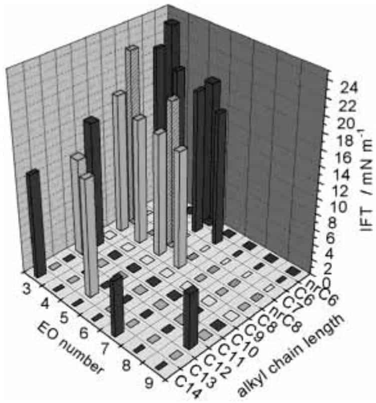

Figure 2. Reduction of IFT as a function of alkyl chain length as well as EO number.

$= 3$ to 6. Instead of the hydrophilic molar mass (M_h), as for the HLB, the CO_2-philic molar mass (M_{CO_2}) is used to calculate the HCB. M denotes the molar mass of the total molecule. The calculated HCB values for the surfactants tested are displayed in Table 1.

Lee et al.[8] defined an HCB for ammonium carboxylated perfluoropolyethers, which are ionic surfactants. But they used the ratio of surfactant molar concentrations at equilibrium in the bulk phases, which means the partition coefficients. These quantities could not be determined with the system described above.

The HCB range of one technical surfactant in Table 1 is estimated: as a measure for the highest ethoxylated alcohol in the mixture, two times the maximum of the distribution is used for normally distributed surfactant and 1.5 times the maximum for narrowly distributed surfactant. This ethylene oxide chain length matches the low HCB values. The high HCB value corresponds to the unreacted alcohol. The surfactants studied here cover the range from medium to high HCB. This range is found even within one surfactant due to the polymerization reaction.

3. Results

The IFT values of 17 technical surfactants at 5 MPa and 283 K are listed in Table 1. The underlying binary water + carbon dioxide system has an IFT value of 28.4 $mN \cdot m^{-1}$ under these conditions.[6] Figure 2 shows the reduction in the IFT as a function of polyether as well as alkyl chain length. The y axis denotes the reduction of the IFT which is achieved by the surfactants. Different IFT values at the same abscissa correspond to different surfactant mixtures. In general, the higher the EO number and the longer the alkyl chain, the more active is the surfactant.

At 303 K the pressure dependence of the IFT for three different surfactants, $C_{13-15}E_3$, $C_{13-15}E_7$, and $C_{12}E_9$, is compared in the range (7 to 20) MPa. To quantify the ability of the surfactant to reduce the interfacial tension, the binary isotherm water + CO_2 is presented as well (Figure 3). Over the whole pressure range, $C_{13-15}E_3$ exhibits the highest IFT values. The reduction is more pronounced as the polyether chain length increases; the best surfactant in this row is $C_{12}E_9$. All measured surfactants exhibit the same trend: with increasing pressure the measured interfacial tension value increases, while that of the binary water + CO_2 system is decreasing. Thus, the ability to reduce the IFT decreases.

4. Discussion

Concentration Effect. If the surfactant is soluble in CO_2 at the measuring conditions, three adsorption sites are available: water phase, interface, and carbon dioxide phase. All sites are in equilibrium with each other. The solubility is usually a function of surfactant structure and fluid density. The higher the molecular weight of a surfactant and the higher its number of polar groups, the lower is its solubility in carbon dioxide.[9] However, in our system the measured surfactants themselves exhibit a complex solubility characteristic according to their composition. Each component of the surfactant has its own HCB and solubility density in CO_2. The solubility density specifies the minimum density needed to dissolve noticeable amounts of this component. For this reason, the equilibrium shifts due to the pressure (density) increase within an isotherm toward the CO_2 phase. Dimitrov et al.[10] showed the density influence nicely. They extracted different molar mass distributions at different densities. The higher the density, the closer is the extracted distribution to the original one. For most surfactants tested, this density is in the range (400 to 500) $kg \cdot m^{-3}$.

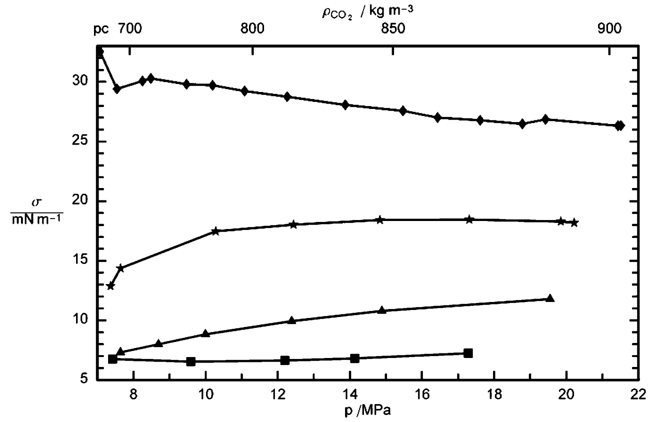

Figure 3. Surfactant solubility graph: ◆, IFT data of the binary water + CO_2 system; ★, binary + $C_{13-15}E_3$; ▲, binary + $C_{13-15}E_7$; ■, binary + $C_{13-15}E_9$ at 303 K. The molar concentration for all surfactants was nearly 0.04 mg of surfactant/g of CO_2 at 5 MPa.

In the following discussion only a selection of tested surfactants is used, and their isotherms are presented in Figure 3. Nevertheless, all surfactants display the trends discussed, but the selection clarifies the effects.

At each data point along an isotherm there is a different composition of the mixture within the viewing cell due to the measuring procedure: first the pressure is increased by adding CO_2; second water is added in order to keep the drop shape. In addition, the solvent power of compressed CO_2 increases with increasing density. Therefore, an isotherm exhibits a complex superimposition of different effects: Adding water and CO_2 decreases the surfactant concentration, expressed in milligrams of surfactant per gram of CO_2 in the system. The increase in solvent power of the CO_2 phase lowers the surfactant concentration at the interface or in the water phase. As a result, the surfactant concentration at the interface is reduced as pressure increases. Consequently, the measured IFT value increases with increasing pressure, despite the reduction in IFT of the binary system (see Figure 3 (the upper x-axis denotes density) and Figure 4).

Owing to the fact that the surfactants are mixtures, they dissolve in a density range rather than at a fixed density. The solubility density is the density at which the surfactant is dissolved. In general, the highest IFT reduction is obtained at this solubility density. The carbon dioxide density at higher temperatures was sometimes lower than the solubility density. Where this was the case, a decrease in IFT with increasing density was observed until the

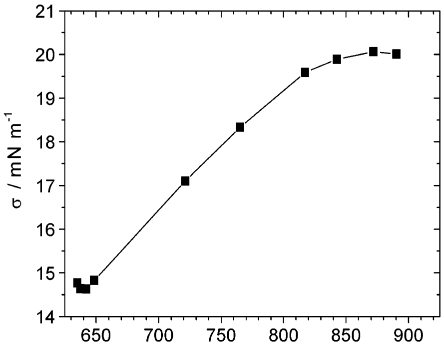

Figure 4. Interfacial tension of $C_{13-15}E_3$ at 303 K as a function of the density.

solubility density was reached. Thereafter, an incline was measured for IFT (see Figure 4). In the case of liquid CO_2, the starting density is higher than the required solubility density and the system exhibits the lowest IFT value already at the lowest measured pressure, owing to the influence of concentration on the interfacial tension (see the discussion above).

Structure Effect Mechanism. From three isotherms the solubility characteristics of this nonionic surfactant class were derived previously.[11] As more data have become available, these findings have been refined. Solubility as well as interface activity is also affected by the structure of the surfactant used. The longer the alkyl chain length, the more soluble is the surfactant in CO_2. Next, the surfactant has to favor the interface to reduce the interfacial tension. The isotherms in Figure 3 are good examples of the influence of polyether chain length: the longer the chain, the greater is the surfactant affinity toward the interface and the more surface active the surfactant will be. A structure effect mechanism was derived from these findings (see Figure 2): long alkyl as well as short polyether chains are needed to make the surfactant CO_2-philic. Long polyether chains increase the affinity toward the interface. The longer both the alkyl and polyether chain lengths were, the lower were the IFTs. $C_{12}E_9$ is the best surfactant measured. As it liquefies at 300 K, the heavier compounds are not feasible for cleaning purposes, as solids are difficult to insert into the system.

This mechanism was verified using two approaches: first that of different distributions and second by calculation of the HCB. Four surfactants with a normal and narrow distribution are reported in Table 1. For the difference in the distribution see Figure 1. As the narrow range surfactants have a lower amount of highly ethoxylated compounds, the resulting reduction in IFT should be lower compared with the case of the normal distribution. This is exactly what we found (see Table 1). Moreover, the reduction in IFT between the normal and narrow distributions displays the general trend, within the limits of experimental error: nr-C_6E_3 < nr-C_8E_3 < C_6E_3 < nr-C_6E_5 ≈ nr-C_8E_5 < C_6E_5 < C_8E_3 < C_8E_5.

The HCB determines whether the component behaves more like a cosolvent or more like a surfactant. Cosolvents exhibit low to zero direct influence on the IFT value, but they increase the solubility of components, which may be highly surface active. If a group of surfactants with the same alkyl chain length is compared, those with the longest polyether chain exhibit the lowest HCB. Even the HCB range reproduces this structure effect mechanism. Highly ethoxylated alcohols have a low HCB and are highly interface active, but they are badly soluble in CO_2. Long alkyl chains on the other hand refer to high HCB, and the result is a highly CO_2-philic compound. This acts as a solubilizer for highly ethoxylated alcohols and is increasing their solubility in CO_2. Shinoda et al.[12] have demonstrated that macroemulsions made with nonionic surfactants that have been purified to a single poly(ethylene oxide) chain length are generally less stable than macroemulsions made with polydisperse commercial surfactants of the same average EO number. These findings were explained by different dissolving powers. We observed the same trend within our system: The broad distribution (HCB range) leads to the best surfactant.

5. Conclusion

In conventional water + surfactant systems, the synergistic effect of different components in a surfactant mixture is well-known.[13,14] With CO_2 as a continuous phase there is a synergistic effect, as well. This effect results in a relationship between surfactant structure and behavior: broad distribution functions of the polyether chain are favorable. The lower ethoxylated alcohol behaves as cosolvent for the heavy ethoxylated highly surface active components. This relationship was verified by measurements of narrowly versus normally distributed AEOs as well as by HCB considerations. The HCB value was introduced similarly to the HLB value for the AEOs in water based systems.

Due to the high accuracy of the measuring method, it was possible to take the influence of the distribution function of the AEOs into account to explain the different IFT data. This structure effect mechanism is needed to produce commercial CO_2 detergents.

Note Added after ASAP Posting. This article was released ASAP on 8/29/2003. In that posting the entry in Table 1, column 4, row 16, which is now $C_{11-15}E_5$, was $C_{13}E_5$. The entry was corrected to indicate that, for this surfactant C_xE_y, $x = 11-15$ with the average being 13. The paper was reposted on 9/8/2003.

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