Conductivity of Sodium Bis(2-ethylhexyl)sulfosuccinate + Isooctane + Water Microemulsions Containing Phase-Transfer Catalysts. 3†

Javier Dasilva-Carvalhal,‡ Luis García-Río,§ Diego Gómez-Díaz,*,|| Juan C. Mejuto,‡ and José M. Navaza||

Department of Physical Chemistry, Faculty of Sciences, University of Vigo at Ourense, Ourense, Spain, and Department of Physical Chemistry, Faculty of Chemistry, and Department of Chemical Engineering, ETSE, University of Santiago de Compostela, Santiago de Compostela, Spain

The effects of temperature and benzo crown ether (BCE) concentration upon the conductivity of the system aerosol OT (AOT) + 2,2,4-trimethylpentane (isooctane) + water have been studied. The BCEs (phase-transfer catalysts) used in the ternary systems were 2,3-benzo-1,4,7,10-tetraoxacyclododec-2-ene (benzo-12-crown-4, BC4), 2,3-benzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene (benzo-15-crown-5, BC5), and 2,3-benzo-1,4,7,10,13,16-hexaoxacyclooctadec-2-ene (benzo-18-crown-6, BC6). The behaviors observed were compared with previous ones obtained in the presence of cryptand complexes (CC) and crown ethers (CE) with electrical conductivity.

Introduction

Microemulsions are highly dynamic structures whose components rearrange themselves over time and space through interactions or collisions, coalescing, and redispersing. Microemulsions are chemical systems of great interest from the point of view of pure chemistry as well as from that of applied chemistry because they have great potential as solubilizators or as nanoreactors permitting an important number of industrial applications.[1] Conductivity measurements are useful techniques to use in obtaining information on micellar interactions.[2,3] A microemulsion has a very low conductivity from (0.001−0.1) μS cm^{-1}, which is already a significant increase if compared to the conductivity of alkanes (10^{-8} μS cm^{-1}) and is due to the fact that microemulsions carry charges. A well-known phenomenon occurs when water is added to the system. At a certain volume fraction, the conductivity rises sharply over a narrow range and then remains practically unchanged at a considerably higher value than that before the transition. Similar behavior is observed if the temperature is increased, keeping the composition constant. This phenomenon is called percolation. It is usually considered that during percolation the droplets come in contact with one another, ions are transferred by some kind of "hopping" mechanism, and/or channels are formed through which microdroplet contents can be exchanged.

However, the high solubilities of the BCEs in apolar solvent and their capacity to include cations, especially those of alkali metals, within their cavities make them potential phase-transfer catalysts.[4]

The results obtained were compared with previous studies that analyzed the effect of the presence of cryptand complexes[5] and crown ethers[6] upon the electrical conductivity and then upon the percolation phenomena and the value of the percolation temperature.

Experimental Section

The microemulsions were prepared by directly mixing an AOT solution of 1 M 2,2,4-trimethylpentane, water, and 2,2,4-trimethylpentane under vigorous stirring. The final solution (microemulsion + additive) was prepared by mass with deviations of less than ±0.2% from the desired concentration, using the microemulsion as the solvent. In all cases, the benzo crown ether concentrations have been referred to the water volume in the microemulsion. The water used for a solution was distilled and deionized with low electrical conductivity (0.10 to 0.50 μS cm^{-1}). All materials were supplied by Sigma and Fluka having the maximum purity commercially available (≥99%). AOT was supplied by Sigma (Sigma Ultra, purity 99%).

The experimental procedure has been described in previous papers.[9] The electrical conductivity (κ) was measured with a Crison conductivimeter GLP 32 conductivity meter with an electrical conductivity cell with a constant of 1 cm^{-1}. The conductivity meter was calibrated using two KCl conductivity standard solutions supplied by Crison ($C_{(KCl)}$ = 0.0100 M, κ = 1413 μS·cm^{-1} at 25 °C and $C_{(KCl)}$ = 0.100 M, κ = 12.88 mS·cm^{-1} at 25 °C). During the measurements of electrical conductivity, the temperature was regulated using a thermostat-cryostat Teche TE-8D RB-5 with a precision of ±0.1°C. The uncertainty of these measurements was 0.05 μS cm^{-1}.

The container with the sample was immersed in an ethanol + water bath, and the temperature was measured together with the conductivity inside the sample container. In general, each electrical conductivity value reported was an average of five measurements. The percolation temperature was determined from the variation of the specific conductivity with temperature.

MM2 (molecular mechanics) calculations were carried out using a commercial software package (CS ChemBats3D Pro 4.0 supplied by the Cambridge Soft Corporation).

* To whom correspondence should be addressed. E-mail: eqnava1@usc.es.

† Part 1: Álvarez, E.; García-Río, L.; Gómez-Díaz, D.; Mejuto, J. C.; Navaza, J. M.; Pérez-Juste, J. *J. Chem. Eng. Data* **2000**, *45*, 428−432. Part 2: Alvarez, E.; García-Río, L.; Gómez-Díaz, D.; Mejuto, J. C.; Navaza, J. M. *J. Chem. Eng. Data* **2001**, *46*, 526−534.

‡ University of Vigo at Ourense.

§ Department of Physical Chemistry, University of Santiago de Compostela.

|| Department of Chemical Engineering, University of Santiago de Compostela.

10.1021/je049683e CCC: $30.25
Published on Web 01/14/2005

Table 1. Specific Electrical Conductivity κ Values at Different Temperatures for Microemulsions of AOT + Isooctane + Water in the Presence of Benzo-12-crown-4 (1)

$C_1 = 1.56 \times 10^{-3}$ mol·L^{-1}		$C_1 = 5.79 \times 10^{-3}$ mol·L^{-1}		$C_1 = 1.20 \times 10^{-2}$ mol·L^{-1}	
t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
22.8	1.63	28.6	1.35	26.5	1.25
23.8	1.66	29.6	1.4	28.5	1.31
24.8	1.71	30.6	1.45	29.6	1.35
25.8	1.75	31.6	1.52	31.3	1.43
27.4	1.89	32.6	1.6	32.6	1.56
28.6	2.02	33.6	1.75	34.1	1.76
29.4	2.13	34.6	1.92	35.1	1.95
30.5	2.34	35.9	2.29	36.1	2.27
31.7	2.65	36.6	2.6	37.1	2.72
32.5	2.94	39.5	6.45	38.1	3.53
33.5	3.45	40.5	11.06	39.1	4.89
34.5	4.07	41.5	26.1	40.1	7.59
36.5	6.71	42.5	81	41.6	22.4
37.5	9.52	43.5	270	43.0	107
38.5	15.05	44.5	701	43.6	221
39.6	27.05	45.5	1423	44.9	743
40.2	40.6	47.6	3740	46.1	1661
41.0	73.7	48.6	5040	47.3	2880
42.2	193.7	49.5	6320	48.0	3700
43.0	365				
44.0	726				
45.1	1255				
46.1	2002				
47.0	2850				
48.5	4520				
49.5	5650				

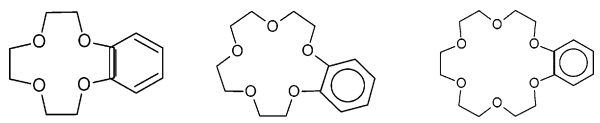
$C_1 = 2.00 \times 10^{-2}$ mol·L^{-1}		$C_1 = 3.40 \times 10^{-2}$ mol·L^{-1}		$C_1 = 4.80 \times 10^{-2}$ mol·L^{-1}	
t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
24.0	1.62	26.0	1.32	26.0	1.47
25.0	1.66	27.1	1.36	27.4	1.53
26.8	1.75	28.3	1.41	28.5	1.60
28.0	1.84	29.0	1.46	29.5	1.72
29.0	1.94	30.0	1.55	32.2	2.30
30.0	2.06	31.0	1.67	33.2	2.62
31.2	2.26	32.5	1.91	34.0	3.00
32.0	2.43	33.5	2.17	35.8	4.68
33.0	2.71	34.5	2.56	36.5	6.05
34.1	3.20	35.7	3.29	37.7	10.6
35.0	3.73	37.0	4.85	38.6	20.3
36.0	4.62	38.0	7.36	39.6	52.2
37.0	6.02	39.0	13.78	40.6	173.4
38.1	8.66	40.0	32	42.0	653
39.1	13.46	41.0	103.5	43.3	1567
40.1	23.7	42.0	319	45.3	3740
41.1	51.1	43.5	1102	46.3	5100
42.1	129.4	46.5	4450	47.6	7140
43.1	300	47.7	6150	48.9	9260
44.1	638	48.7	7830		
45.5	1412				
46.5	2220				
47.5	3170				
48.7	4500				

Results and Discussion

The electrical conductivity of AOT + isooctane + water microemulsions ($C_{(AOT)} = 0.5$ M and $W = C_{water}/C_{AOT} = 22.2$) was measured at different temperatures that include the percolation phenomenon and in the presence of different crown ether concentrations (phase-transfer catalysts). Tables 1, 2, and 3 show the experimental values corresponding to the electrical conductivity at different temperatures for all systems studied and in the presence of different quantities of benzo crown ethers.

In all cases, the observed behavior was an increase in the electrical conductivity from typical values of organic compounds, such as the alkane employed in the present paper as a microemulsion component, to high values typical of aqueous solutions.[7,8] The observed behavior is characteristic of this kind of colloidal aggregate (microemulsion) and consists of a dramatic increment in the value of the electrical conductivity above a certain temperature. This increment in the value of the electrical conductivity is related to the increase in the mass interchange between water droplets presents in the microemulsion. The zone of temperature in which this dramatic increase in electrical conductivity is produced and then the mass transfer between water pools is called the percolation temperature and was previously discussed.

Figure 2 shows an example of the behavior of AOT + isooctane + water microemulsions in the absence and



Benzo-12-crown-4 *Benzo-15-crown-5* *Benzo-18-crown-6*

Figure 1. Benzo crown ethers employed in the present paper.

Table 2. Specific Electrical Conductivity κ Values at Different Temperatures for Microemulsions of AOT + Isooctane + Water in the Presence of Benzo-15-crown-5 (2)

$C_2 = 2.80 \times 10^{-3}$ mol·L^{-1}		$C_2 = 5.00 \times 10^{-3}$ mol·L^{-1}		$C_2 = 8.05 \times 10^{-3}$ mol·L^{-1}	
t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
25.8	0.84	20.2	1.31	16.9	0.82
27.7	0.94	21.0	1.31	17.2	0.82
29.0	1.02	22.1	1.32	18.0	0.83
30.7	1.15	23.0	1.32	19.1	0.89
31.3	1.21	23.8	1.32	20.0	0.98
32.2	1.36	25.0	1.33	21.0	1.24
33.5	1.63	25.8	1.34	22.2	3.35
34.5	1.99	26.8	1.35	23.5	3.97
35.3	2.34	27.8	1.38	24.9	5.12
35.8	2.75	29.0	1.43	26.6	6.88
37.0	4.33	29.9	1.47	27.6	11.3
37.5	5.78	31.2	1.56	28.9	29.3
38.1	8.75	32.0	2.81	29.9	64.5
38.6	14.97	33.1	3.65	31.1	315
39.1	33.2	33.8	4.48	32.3	548
40.3	142	34.3	6.92	34.1	878
40.8	357	35.3	12.04	34.9	1120
41.3	1151	36.0	23.06		
41.8	1768	36.9	80		
		37.5	256		
		38.3	501		
		39.0	1117		
		39.6	1846		

$C_2 = 1.52 \times 10^{-2}$ mol·L^{-1}		$C_2 = 4.47 \times 10^{-2}$ mol·L^{-1}	
t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
16.0	0.54	14.1	0.65
17.2	0.55	14.9	0.65
18.0	0.55	16.0	0.65
19.1	0.55	17.1	0.68
20.2	0.56	18.2	1.10
21.0	0.56	19.1	1.64
22.1	0.57	20.8	4.33
23.0	0.59	22.7	5.78
24.8	0.61	24.0	8.75
25.5	1.22	25.7	49
26.3	1.82	26.3	108
27.1	3.9	27.2	325
28.0	24.2	28.5	657
29.0	98.4	29.5	1151
30.0	287	30.3	1768
31.0	864		
32.0	1343		
33.4	2220		

presence of different quantities of benzo-12-crown-4. In this Figure (Figure 2), typical behaviors corresponding to the aggregates previously discussed were observed in the system employed in the present paper. In Figure 2, it is possible to observe that a change exists in the slope of the electrical conductivity/temperature data that corresponds to the percolation temperature and is affected by the phase-transfer catalyst concentration in the microemulsion.

The effect produced by the presence of other phase-transfer catalysts such as cryptand complexes and crown ethers[5,6] has been studied and published in previous papers. In both cases, the behavior found for these systems was quiet similar in relation to that of the systems employed in the present paper.

Also, in previous studies developed by our research group related to the electrical conductivity of water in oil microemulsions, an empirical correlation with three adjustable parameters was developed. This correlation allows us to fit the experimental electrical conductivity/temperature data for this kind of system with suitable results for a large body of data.[9−11] A three-term equation (eq 1) has been applied with good results to numerous microemulsions modified with different additives, such as amines, ureas, salts, and so forth, with the conclusion that the A parameter of eq 1 corresponds to the value of the percolation temperature. This conclusion was reached by a comparison of the percolation temperature determined using the Kim and Huang method [12] with the values obtained for the Aparameter by fitting the experimental data of electrical conductivity using eq 1.

$$t = A + B\sqrt{\kappa} + \frac{C}{\kappa} \tag{1}$$

Recently, Hait et al.[13] developed an alternative equation to analyze conductivity/temperature data in terms of the Sigmoidal−Boltzmann equation (SBE)

$$\log \kappa = \log \kappa_f \left[1 + \left(\frac{\log \kappa_i - \log \kappa_f}{\log \kappa_f}\right) \times \{1 + e^{(t - t_p)/\Delta t}\}^{-1}\right] \tag{2}$$

where κ and t represent the conductivity and temperature, respectively; Δt is the constant interval of t; and subscripts i, f, and p stand for initial, final, and percolation zones, respectively.

Figure 3 shows a comparison between electrical conductivity/temperature experimental data in relation to the calculated values using the equation developed by Álvarez et al. and Hait et al. In this Figure (Figure 3), it is possible

Table 3. Specific Electrical Conductivity κ Values at Different Temperatures for Microemulsions of AOT + Isooctane + Water in the Presence of Benzo-18-crown-6 (3)

$C_3 = 6.78 \times 10^{-4}$ mol·L^{-1}		$C_3 = 1.36 \times 10^{-3}$ mol·L^{-1}		$C_3 = 3.37 \times 10^{-3}$ mol·L^{-1}	
t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
24.9	0.25	24.0	0.33	5.5	0.15
25.6	0.28	24.8	0.34	6.1	0.16
26.5	0.29	25.5	0.35	7.8	0.17
28.5	0.30	27.2	0.38	10.1	0.18
29.2	0.32	28.0	0.41	11.3	0.18
29.9	0.33	29.0	0.44	13.0	0.19
31.0	0.34	30.1	0.48	14.5	0.20
32.1	0.38	31.3	0.50	15.8	0.20
32.8	0.40	32.1	0.52	16.7	0.21
33.9	0.43	33.1	0.53	18.3	0.22
34.8	0.46	34.0	0.54	19.8	0.23
35.3	0.53	34.8	0.62	22.5	0.27
36.2	0.78	35.7	0.65	23.7	0.29
37.1	1.81	36.8	0.67	25.0	0.33
37.6	6.71	37.0	0.73	25.6	0.36
38.0	18.82	38.0	0.75	26.6	0.40
38.5	62.0	38.5	0.80	28.2	0.53
39.0	124	39.0	1.24	29.2	0.67
39.7	235	39.3	2.09	30.5	0.98
40.2	366	39.7	3.21	31.1	1.21
40.8	487	40.0	4.98	32.1	1.89
		41.0	7.50	32.6	2.56
				33.4	4.64
				34.3	8.59
				34.9	13.33
				36.5	39.4
				37.3	64.2
				38.2	97.7

$C_3 = 6.75 \times 10^{-3}$ mol·L^{-1}		$C_3 = 1.35 \times 10^{-2}$ mol·L^{-1}	
t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
7.5	0.20	4.5	0.42
8.8	0.21	5.7	0.48
10.0	0.21	6.4	0.50
11.4	0.22	7.0	0.52
12.1	0.23	7.8	0.57
14.5	0.23	9.2	0.68
16.0	0.24	10.0	0.73
17.0	0.25	11.0	0.82
18.2	0.26	12.0	0.93
19.6	0.27	13.0	1.09
20.9	0.28	13.8	1.21
23.4	0.33	15.4	1.60
25.2	0.38	17.0	2.07
25.9	0.41	17.7	2.40
27.0	0.48	18.8	2.97
27.6	0.53	19.6	3.68
28.6	0.62	21.1	5.01
29.6	0.75	22.0	6.71
30.3	0.90	23.0	8.88
31.7	1.37	24.0	11.93
32.4	1.75	24.7	16.31
33.4	2.85	25.8	25.50
33.9	3.74		
34.6	7.51		
35.6	11.87		
36.1	15.83		
38.2	68.10		

to observe that the equation developed by Hait et al. allows us to correlate with the best results the experimental data for the systems analyzed in the present paper. Equation 1 has fit the experimental data for other phase-transfer catalysts (crown ether and cryptand complexes)[5,6] with suitable results with respect to the behavior observed in the presence of benzo crown ethers.

In relation to the variations found in the value of the percolation temperature, in all cases we observed an increase in the percolation temperature of the system as the benzo crown ether concentration increases until a maximum value is reached, from which the percolation temperature decreases. Thus, at high crown ether concentrations the percolation temperature is significantly lower than that observed for the microemulsions without additives. For example, Figure 5 shows the behavior observed in the presence of different benzo crown ethers. As is the case for other macrocycles (crown ethers and cryptand complexes), the observed biphasic behavior in the presence of these additives can be rationalized by taking into account the double nature of these substrates: (i) their capacity to sequester ions,[14] transport them through the interface,[15] and solubilize them in apolar phases and (ii) their ability

Table 4. Temperature of Percolation for AOT + Isooctane + Water Microemulsions in the Presence of Different Quantities of BCEs Obtained by the Kim and Huang Method (KH) and Fitting Parameters from Equations 1 (TTE) and 2 (SBE)

$10^{-3}C_{BCE}$ / mol·L^{-1}	t_p / °C (KH)	t_p / °C (SBE)	Δt_p / °C	A / °C (TTE)	B / °C·μS$^{-0.5}$·cm$^{0.5}$ (TTE)	C / °C·μS·cm^{-1} (TTE)
			Benzo-12-crown-4			
48.0	31.1	31.47	−2.13	40.5	0.12	−26.1
34.0	31.5	31.60	−2.00	42.1	0.09	−16.4
20.0	32.6	32.58	−1.02	37.3	0.19	−18.4
12.0	33.3	33.42	−0.18	34.1	0.26	−13.6
5.70	34.0	34.14	0.54	40.4	0.09	−17.1
1.60	33.8	34.02	0.42	39.4	0.10	−18.1
			Benzo-15-crown-5			
44.7	24.2	23.97	−9.63	23.5	0.18	−5.5
15.2	27.4	28.12	−5.48	28.5	0.10	−4.7
8.00	31.1	30.94	−2.66	26.5	0.26	−7.5
5.00	37.1	36.58	2.98	37.1	0.06	−16.1
2.80	40.7	40.66	7.06	39.5	0.06	−10.7
			Benzo-18-crown-6			
13.5	25.1	25.31	−8.29	17.3	1.95	−6.2
6.74	31.5	30.25	−3.35	36.5	0.06	−5.2
3.37	32.9	32.66	−0.94	35.6	0.18	−4.2
1.36	36.4	36.22	2.66	50.2	−3.58	−7.9
0.678	34.6	34.52	0.92	39.5	0.02	−3.2

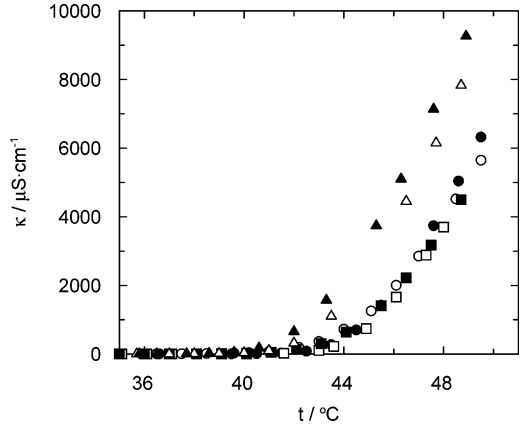


Figure 2. Influence of temperature on the electrical conductivity value at different concentrations of B12-C-4: ○, $C_{B12-C-4} = 1.56 \times 10^{-3}$ M; ●, $C_{B12-C-4} = 5.79 \times 10^{-3}$ M; □, $C_{B12-C-4} = 1.20 \times 10^{-2}$ M; ■, $C_{B12-C-4} = 2.00 \times 10^{-2}$ M; △, $C_{B12-C-4} = 3.40 \times 10^{-2}$ M; ▲, $C_{B12-C-4} = 4.80 \times 10^{-2}$ M.

to associate at the surfactant film, as shown in studies carried out on "normal" micelles.

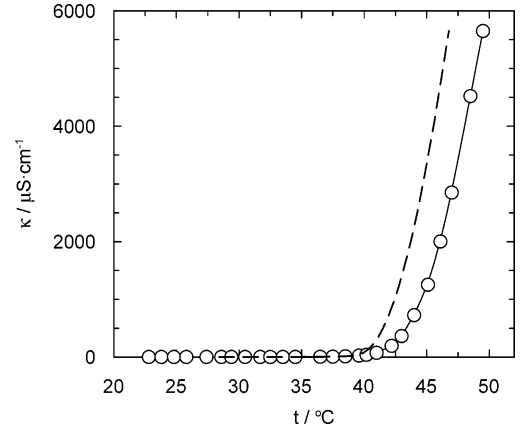


Figure 3. Comparison between experimental and calculated electrical conductivity data for $C_{B12-C-4} = 1.56 \times 10^{-3}$ M: −, SBE; - - -, TTE.

As we observed for cryptand complexes[5] and crown ethers,[6] low macrocycle concentrations hinder the electric percolation phenomena, but medium and high concentrations favor the percolation (Figure 5). At moderate concentrations, they behave similarly to electrolytes. This effect of electrolytes is one of the most widely documented.[16−18]

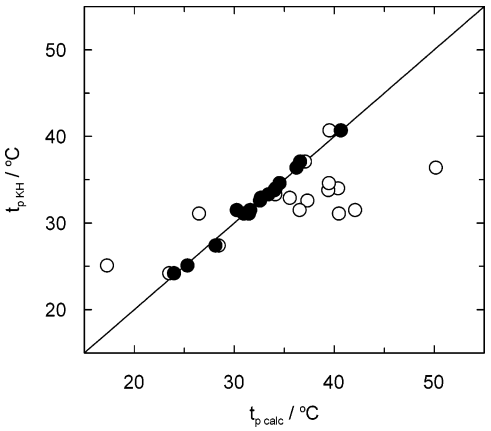


Figure 4. Comparison between percolation temperature values determined by the typical method, $t_{p,KH}$ (Kim and Huang) and the values calculated ($t_{p,calcd}$) using the equations developed by Álvarez et al. (○, TTE) and Hait et al. (●, SBE).

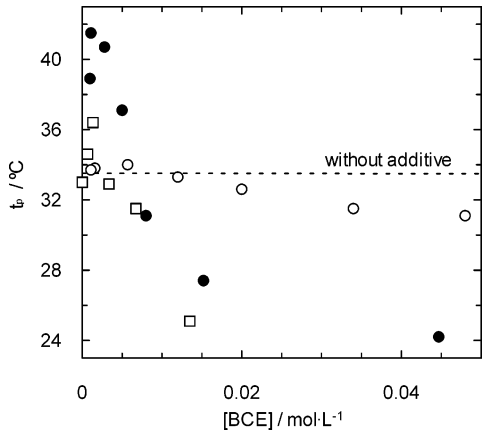


Figure 5. Effect of benzo crown ethers on the percolation temperature for AOT + isooctane + water microemulsions: ○, B12-C-4; ●, B15-C-5; □, B18-C-6.

This effect can be justified by taking into account the complexing ability of the BCEs with respect to the Na^+

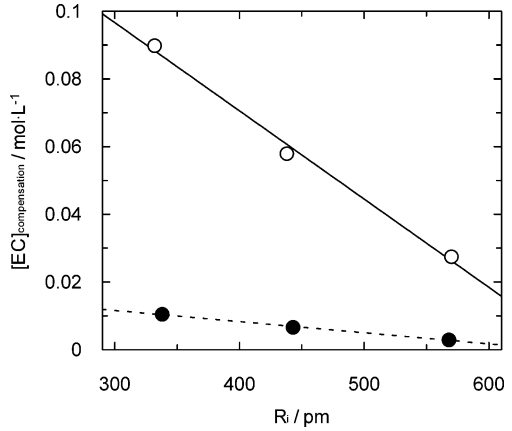


Figure 6. Correlation between the internal radius of the benzo crown ethers with respect to the compensation concentration of these systems: ○, CEs; ●, BCEs.

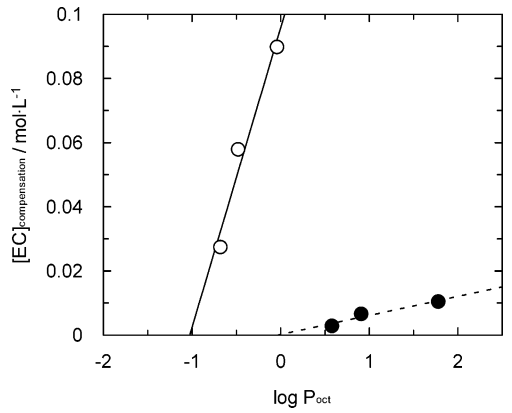


Figure 7. Correlation between the logarithm of the partition coefficient of the benzo crown ethers between water and 1-octanol with respect to the compensation concentration of these systems: △, CEs; ▲, BCEs.

counterion of aerosol OT ions and their transfer to the AOT film and the 2,2,4-trimethylpentane continuous phase. The electrical conductivity of microemulsions is due to the passage of cations through transient channels formed between droplets that have collided, creating local regions of positive curvature. The less naturally prone the surfactant is to adopt positive curvatures, the more difficult the mass-transfer process and hence electrical conduction will be. In this respect, the capacity of BCEs to change the screening electrostatic repulsion between charged headgroups increases the natural negative curvature of the surfactant, thus hindering the channel opening required for mass transfer among droplets and hence electrical percolation.

At moderate and high concentration of the BCEs, the percolation temperature is lowered to such a degree that the high-conductivity region can be reached at unusually low temperatures. It is possible to follow similar reasoning to that used in the literature[19] to explain the behavior of other organic substances. The studies by Kang et al.[20] on the effect of various organic molecules on frozen vesicles suggest that the addition of moderate concentrations of such molecules "opens" the interface and facilitates water penetration into the vesicle structure.

The observed phenomenon, taking into account the nature and properties of benzo crown ethers as phase-transfer catalysts and as organic substrates, is consistent with those of other additives previously studied.[9−11]

However, we can estimate the crown ether concentration at which the temperature of percolation is the same as that without additives; in this case, there are two different effects: the ability of crown ethers to bind Na^+ and the compensation for their organic nature. The compensation temperature has been successfully correlated with respect to the internal radius that was estimated using MM2 calculations. This correlation is shown in Figure 6 and compared with the results obtained for crown ethers (CEs). A satisfactory relationship was also found between the logarithm of partition coefficient of BCEs between water and 1-octanol.[21] The partition coefficient is the more common parameter used to measure the hydrophobicity of a substrate (Figure 7).

Literature Cited

(1) Datyner, A. *Surfactant in Textile Processing*; Marcel Dekker: New York, 1983.
(2) Garcia-Rio, L.; Leis, J. R.; Mejuto, J. C.; Pena, M. E.; Iglesias, E. Effects of Additives on the Internal Dynamics and Properties of Water/AOT/Isooctane Microemulsions. *Langmuir* **1994**, *10*, 1676−1683.
(3) Hait, S. K.; Sanyal, A.; Moulik, S. P. Physicochemical Studies on Microemulsions. 8. The Effects of Aromatic Methoxy Hydrotropes on Droplet Clustering and Understanding of the Dynamics of Conductance Percolation in Water/Oil Microemulsion System. *J. Phys. Chem. B* **2002**, *106*, 12642−12650.
(4) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, Germany, 1995.
(5) Álvarez, E.; García-Río, L.; Gómez-Díaz, D.; Mejuto, J. C.; Navaza, J. M.; Pérez-Juste, J.; Conductivity of AOT/Isooctane/Water Microemulsions Containing Phase Transfer Catalysts. 1. *J. Chem. Eng. Data* **2000**, *45*, 428−432.
(6) Álvarez, E.; García-Río, L.; Gómez-Díaz, D.; Mejuto, J. C.; Navaza, J. M. Conductivity of AOT/Isooctane/Water Microemulsions Containing Phase-Transfer Catalysts. 2. *J. Chem. Eng. Data* **2001**, *46*, 526−534.
(7) Álvarez, E.; García-Río, L.; Mejuto, J. C.; Navaza, J. M.; Pérez-Juste, J.; Rodríguez-Dafonte, P. Effect of Temperature on the Electrical Conductivity of Sodium Bis(2-ethylhexyl) Sulfosuccinate + 2,2,4-Trimethylpentane + Water Microemulsions. Influence of Alkylamines. *J. Chem. Eng. Data* **1999**, *44*, 1286−1290.
(8) Ray, S.; Bisal, S. R.; Moulik, S. P. Structure and dynamics of microemulsions. 1. Effect of additives on percolation of conductance and energetics of clustering in water-AOT-heptane microemulsions. *J. Chem. Soc., Faraday Trans* **1993**, *89*, 3277−3282.
(9) Álvarez, E.; García-Río, L.; Leis, J. R.; Mejuto, J. C.; Navaza, J. M. Effects of Temperature on the Conductivity of Sodium Bis(2-ethylhexyl)sulfosuccinate + 2,2,4-Trimethylpentane + Water Microemulsions in the Presence of Ureas and Thioureas. *J. Chem. Eng. Data* **1998**, *43*, 123−127.
(10) Álvarez, E.; García-Río, L.; Mejuto, J. C.; Navaza, J. M. Effects of Temperature on the Conductivity of Sodium Bis(2-ethylhexyl)-sulfosuccinate + 2,2,4-Trimethylpentane + Water Microemulsions. Influence of Amines. *J. Chem. Eng. Data* **1998**, *43*, 433−435.
(11) Álvarez, E.; García-Río, L.; Mejuto, J. C.; Navaza, J. M. Effects of Temperature on the Conductivity of Sodium Bis(2-ethylhexyl)-sulfosuccinate + 2,2,4-Trimethylpentane + Water Microemulsions. Influence of Amides and Ethylene Glycol. *J. Chem. Eng. Data* **1999**, *44*, 484−487.12.
(12) Kim, M. W.; Huang, J. S. Percolation like Phenomena in Oil-conitunous Microemulsions. *Phys. Rev. A* **1986**, *34*, 719−722.
(13) Hait, S. K.; Moulik, S. P.; Palepu, R. Refined Method of Assessment of Parameters of Micellization of Surfactants and Percolation of W/O Microemulsions. *Langmuir* **2002**, *18*, 2471−2476.
(14) Lehn, J. M.; Sauvage, J. P. Cryptates. XVI. [2]-Cryptates. Stability and Selectivity of Alkali and Alkaline-Earth Macrobicyclic Complexes. *J. Am. Chem. Soc.* **1975**, *97*, 6700−6707.
(15) Lamb, J. D.; Christensen, J. J.; Oscarson, J. L.; Nielsen, B. L.; Asay, B. W.; Izatt, R. M. The Relationship between Complex Stability Constants and Rates of Cation Transport through Liquid Membranes by Macrocyclic Carriers. *J. Am. Chem. Soc.* **1980**, *102*, 6820−6824.
(16) Álvarez, E.; García-Río, L.; Mejuto, J. C.; Navaza, J. M. Effects of Temperature on the Conductivity of Sodium Bis(2-ethylhexyl)-sulfosuccinate + 2,2,4-Trimethylpentane + Water Microemulsions. Influence of Sodium Salts. *J. Chem. Eng. Data* **1998**, *43*, 519−522.
(17) Álvarez, E.; García-Río, L.; Mejuto, J. C.; Navaza, J. M.; Pérez-Juste, J. Effects of Temperature on the Conductivity of Microemulsions. Influence of Sodium Hydroxide and Hydrochloric Acid. *J. Chem. Eng. Data* **1999**, *44*, 846−849.

(18) Álvarez, E.; García-Río, L.; Mejuto, J. C.; Navaza, J. M.; Pérez-Juste, J. Effects of Temperature on the Conductivity of AOT/Isooctane/Water Microemulsions. Influence of Salts. *J. Chem. Eng. Data* **1999**, *44*, 850−853.
(19) García-Río, L.; Leis, J. R.; Mejuto, J. C.; Peña, M. E.; Iglesias, E. Effect of Additives upon the Internal Dynamics and Properties of Water/AOT/Isooctane Microemulsions. *Langmuir* **1994**, *10*, 1676−1683.
(20) Kang, Y. S.; MdManus, H. J. D.; Kevan, L. An Electron Magnetic Resonance Study on the Photoionization of *N*-Alkilphenothiazines in Dioctadecyldimethylammonium Chloride Frozen Vesicles: The Effect of Urea, 1,3-Dimethylurea, 1,3-Diethylurea, and 1,1′,3,3′-Tetramethylurea. *J. Phys. Chem.* **1992**, *96*, 10055−10060.
(21) Stolwijk, T. B.; Vos, L. C.; Sudhölter, E. J. R.; Reinhoudt, D. N. Partition coefficients of crown ethers. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 103−108.

Received for review September 3, 2004. Accepted November 9, 2004. Financial support from the regional government (Xunta de Galicia) (PGIDIT03TAM20902PR) is gratefully acknowledged.

JE049683E