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Conductivity of Sodium Bis(2-ethylhexyl)sulfosuccinate/Isooctane/ Water Microemulsions Containing Phase-Transfer Catalysts. 2[†]

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The effects of temperature and crown ether (CE) concentration upon the conductivity of the system Aerosol OT (AOT) + 2,2,4-trimethylpentane (isooctane) + water have been studied. The CEs (phase transfer catalysts) used in the ternary systems were 1,4,7,10-tetraoxacyclododecane (12-crown-4), 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5), and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6). This behavior is compared with the previous one obtained in the presence of kriptand complexes.

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 a great potential as solubilizers (Mittal, 1977; Elworthy et al., 1968) or as nanoreactors (García-Río et al., 1993, 1995, 1996), permitting an important number of industrial applications (Rieger, 1977; Datyner, 1983). Numerous methods have been used to determine the structure and dimension of these systems, including ultrasedimentation, several scattering techniques (Zana, 1987), time-resolved fluorescence, and NMR (Chachaty, 1987). Eastoe (Eastoe et al., 1991) recently reviewed some of the structural studies of AOT-stabilized microemulsions. Conductivity measurements are useful techniques in obtaining information on micellar interactions (Maitra et al., 1990; Hamilton et al., 1990; Mukhopadhyay et al., 1990; Alexandridis et al., 1995; Ray et al., 1993; Hurugen et al., 1991). A microemulsion has a very low conductivity ($0.001-0.1$ μS cm^{-1}), which is already a significant increase if compared to the conductivity of alkanes ($\sim 10^{-8}$ 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. A similar behavior is observed if the temperature is increased keeping the composition constant (see Figure 1). This phenomenon is called percolation. It is usually considered that during percolation the droplets come in contact, ions are transferred by some kind of "hopping" mechanism, and/or channels are formed through which microdroplet contents can be exchanged.

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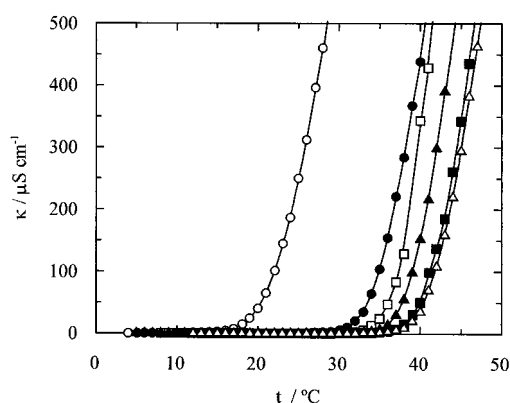
Figure 1. Influence of temperature upon the conductivity of Aerosol OT + 2,2,4-trimethylpentane + water microemulsions in the presence of different concentrations of 12-crown-4: (○) [12-crown-4] = 0.3144 mol dm^{-3}; (●) [12-crown-4] = 0.1257 mol dm^{-3}; (□) [12-crown-4] = 0.0843 mol dm^{-3}; (▲) [12-crown-4] = 0.0629 mol dm^{-3}; (■) [12-crown-4] = 0.0314 mol dm^{-3}; (△) [12-crown-4] = 0.0125 mol dm^{-3}. The solid lines correspond with the fit of the experimental data to eq 1.

On the other hand, the high solubilities of the crown ethers (CEs) (see Chart 1) 1,4,7,10-tetraoxacyclododecane (12-crown-4), 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5), and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) in apolar solvent and their capacity to include cations, in special alkali metal cations, within their cavities confer on them a potential use as phase transfer catalysts (Lehn, 1995).

Chart 1

12-Crown-4   15-Crown-5   18-Crown-6
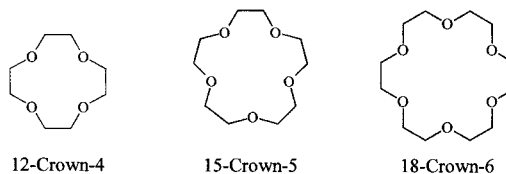
In previous papers it was well established that the values of the threshold of percolation can be modulate by small quantities of additives (Álvarez, 1998a, 1998b, 1998c). In particular the addition of macrocycles as CEs (Schuebel, 1998) to water in oil microemulsions leads to drastic

Table 1. Specific Conductivity Values at Different Temperatures for Aerosol OT + 2,2,4-Trimethylpentane + Water Microemulsions in the Presence of Different Concentrations of 12-Crown-4[a]

$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$
					[12-Crown-4] = 0.3144 mol dm^{-3}						
4.0	0.34	9.0	0.67	13.0	1.56	17.0	7.72	21.0	65.50	25.0	250.00
5.1	0.38	10.0	0.83	14.0	2.27	18.1	15.18	22.1	101.70	26.0	312.00
6.0	0.41	11.0	1.00	15.0	3.07	19.0	25.10	23.1	145.10	27.1	396.00
7.0	0.47	12.0	1.26	16.0	4.63	20.0	40.80	24.0	187.00	28.0	460.00
8.0	0.57										
					[12-Crown-4] = 0.1257 mol dm^{-3}						
8.0	0.22	14.0	0.28	20.0	0.44	26.0	1.29	31.0	10.67	36.0	154.50
9.0	0.23	15.0	0.30	21.0	0.48	27.0	1.58	32.0	21.20	37.0	221.00
10.1	0.24	16.0	0.31	22.0	0.57	28.0	2.54	33.0	35.70	38.0	284.00
11.0	0.25	17.0	0.33	23.0	0.67	29.0	3.48	34.0	64.70	39.0	367.00
12.0	0.25	18.0	0.36	24.0	0.80	30.1	6.23	35.0	104.20	40.0	438.00
13.0	0.26	19.0	0.39	25.0	0.95						
					[12-Crown-4] = 0.0943 mol dm^{-3}						
8.1	0.19	14.0	0.23	20.0	0.31	26.0	0.55	31.0	2.10	36.0	47.60
9.0	0.19	15.0	0.24	21.0	0.33	27.0	0.66	32.0	3.18	37.0	83.60
10.0	0.20	16.0	0.25	22.0	0.35	28.0	0.86	33.0	5.75	38.0	128.80
11.1	0.20	17.1	0.26	23.0	0.38	29.0	1.02	34.0	13.36	40.0	343.00
12.0	0.21	18.0	0.27	24.0	0.43	30.0	1.42	35.0	24.80	41.0	428.00
13.1	0.22	19.0	0.29	25.0	0.49						
					[12-Crown-4] = 0.0629 mol dm^{-3}						
5.0	0.22	12.0	0.24	19.0	0.30	26.0	0.49	32.1	1.82	38.0	55.40
6.0	0.22	13.0	0.25	20.0	0.32	27.0	0.55	33.1	2.70	39.0	98.80
7.0	0.22	14.0	0.25	21.0	0.33	28.0	0.64	34.0	3.99	40.0	152.30
8.0	0.22	15.0	0.26	22.0	0.35	29.0	0.77	35.0	7.06	41.0	216.00
9.0	0.23	16.0	0.27	23.1	0.37	30.0	0.94	36.0	14.32	42.0	298.00
10.0	0.23	17.0	0.28	24.0	0.40	31.0	1.21	37.0	30.10	43.0	390.00
11.0	0.24	18.0	0.29	25.0	0.45						
					[12-Crown-4] = 0.0314 mol dm^{-3}						
10.0	0.22	17.1	0.25	23.0	0.31	29.0	0.54	35.0	2.58	41.1	98.80
11.0	0.23	18.0	0.26	24.0	0.33	30.1	0.65	36.0	4.13	42.0	137.00
12.0	0.23	19.0	0.27	25.0	0.35	31.0	0.75	37.0	7.71	43.0	185.00
13.0	0.24	20.1	0.28	26.0	0.38	32.0	0.91	38.0	15.18	44.0	261.00
14.0	0.24	21.0	0.29	27.0	0.43	33.0	1.21	39.1	30.80	45.0	342.00
14.9	0.25	22.0	0.30	28.0	0.47	34.0	1.67	40.0	50.50	46.0	435.00
16.0	0.25										
					[12-Crown-4] = 0.0125 mol dm^{-3}						
12.0	0.22	18.0	0.26	24.0	0.32	30.0	0.58	36.0	3.03	42.0	107.98
13.0	0.24	19.0	0.27	25.0	0.34	31.0	0.69	37.0	5.69	43.0	158.90
14.0	0.25	20.0	0.28	26.0	0.36	32.0	0.80	38.0	9.37	44.0	220.00
15.0	0.25	21.0	0.29	27.0	0.39	33.0	1.01	39.0	20.50	45.0	294.00
16.0	0.25	22.0	0.30	28.0	0.45	34.0	1.55	40.0	35.40	46.0	382.00
17.0	0.26	23.0	0.31	29.0	0.51	35.0	1.99	41.0	69.50	47.0	462.00
					[12-Crown-4] = 0.0063 mol dm^{-3}						
21.0	0.34	26.0	0.55	31.0	1.63	36.0	17.13	40.0	106.80	44.0	251.00
22.1	0.37	27.0	0.65	32.1	2.45	37.0	30.80	41.0	142.50	45.0	292.00
23.0	0.39	28.1	0.79	33.0	3.53	37.5	42.80	42.0	180.00	46.0	322.00
24.0	0.43	29.0	0.96	34.0	5.72	39.0	74.10	43.1	220.00	47.0	350.00
25.0	0.49	30.0	1.22	35.0	9.76						
					[12-Crown-4] = 0.0013 mol dm^{-3}						
20.0	0.32	25.0	0.39	30.0	0.66	35.2	2.80	40.1	47.00	44.0	200.20
21.1	0.32	26.0	0.42	31.0	0.78	36.0	3.89	41.0	74.40	45.0	249.00
22.0	0.33	27.0	0.46	32.0	0.95	37.2	8.02	42.0	113.20	46.1	299.00
23.0	0.35	28.0	0.51	33.0	1.22	38.0	13.60	43.3	173.10	47.0	323.00
24.0	0.37	29.0	0.58	34.0	1.66	39.0	24.60				

[a] [Aerosol OT] = 0.5 mol dm^{-3}, w = 22.2.

rheological changes. For example, a mixture of a 20 wt % solution of CE in water with an oil stock solution of Aerosol OT (sodium bis(2-ethylhexyl)sulfosuccinate (AOT)) is biphasic but can be transformed into a homogeneous, transparent, and viscoelastic solution by simple shaking. This gelly phase demixes again after hours up to several days. In addition, anomalous properties (García-Río et al., 1997; Schuebel, 1998) were found for mixtures containing small amounts of CE. These anomalous properties were found for different kriptand complexes (4,7,13,16,21,24-hyxaoxa-1,10-diazabicyclo[8,8,8]hexacosane (C222), 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8,8,5]tricosane (C221), and 4,7,-13,18-tetraoxa-1,10-diazabicyclo[8,5,5]eicosane (C211)) (Alvarez et al., 2000).

The aim of this work is to measure the specific conductivity (κ) of these ternary systems with three different crown ethers (12-crown-4, 15-crown-5, and 18-crown-6) at varying concentrations, temperatures, and microemulsion compositions to determine the threshold of percolation in these systems.

Experimental Section

The microemulsions were prepared by direct mixing of a 1 M Aerosol OT solution in 2,2,4-trimethylpentane with

Table 2. Specific Conductivity Values at Different Temperatures for Aerosol OT + 2,2,4-Trimethylpentane + Water Microemulsions in the Presence of Different Concentrations of 15-Crown-5[a]

$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$
[15-Crown-5] = 0.2022 mol dm^{-3}											
5.1	0.48	9.0	1.08	13.0	4.74	17.0	40.80	20.0	126.90	23.1	275.00
6.0	0.55	10.0	1.34	14.0	8.11	18.1	63.70	21.0	172.10	24.1	350.00
7.0	0.67	11.0	2.11	15.0	14.61	19.1	95.60	22.0	223.00	25.1	418.00
8.2	0.88	12.0	3.00	16.0	23.40						
[15-Crown-5] = 0.0919 mol dm^{-3}											
12.0	0.37	17.0	0.64	22.0	1.81	26.0	7.32	30.1	58.90	34.0	230.00
13.0	0.40	18.0	0.75	23.0	2.38	27.0	12.91	31.0	80.10	35.0	284.00
14.1	0.45	19.0	0.95	24.0	3.24	28.0	20.10	32.1	129.00	36.0	363.00
15.0	0.49	20.0	1.08	25.1	5.54	29.0	34.30	33.0	164.60	37.0	432.00
16.0	0.57	21.0	1.35								
[15-Crown-5] = 0.0705 mol dm^{-3}											
15.0	0.36	20.1	0.58	25.1	1.33	29.0	4.51	33.0	34.50	37.0	199.80
16.1	0.39	21.0	0.65	26.0	1.62	30.0	7.25	34.2	65.40	38.0	257.00
17.0	0.42	22.0	0.74	27.0	2.14	31.3	12.49	35.1	95.20	39.0	332.00
18.0	0.45	23.0	0.87	28.0	3.03	32.0	20.02	36.0	132.70	40.0	403.00
19.1	0.49	24.0	1.08								
[15-Crown-5] = 0.0481 mol dm^{-3}											
16.0	0.34	21.0	0.47	26.0	0.85	31.0	2.84	36.1	38.70	40.2	223.00
17.0	0.36	22.0	0.51	27.2	1.00	32.0	4.14	37.0	58.90	41.2	298.00
18.0	0.38	23.0	0.56	28.1	1.23	33.0	6.40	38.0	96.20	42.0	354.00
19.0	0.40	24.2	0.64	29.0	1.58	34.1	12.49	39.0	146.90	43.0	448.00
20.0	0.44	25.5	0.76	30.1	2.07	35.2	22.10				
[15-Crown-5] = 0.0247 mol dm^{-3}											
19.0	0.31	24.0	0.44	29.0	0.79	34.0	2.81	38.0	26.30	42.0	168.50
20.0	0.34	25.0	0.48	30.0	0.94	35.2	5.14	39.0	46.90	43.0	227.00
21.0	0.36	26.0	0.53	31.0	1.15	36.0	7.53	40.5	97.00	44.0	293.00
22.0	0.38	27.1	0.61	32.0	1.45	37.0	13.88	41.0	117.00	45.0	362.00
23.0	0.41	28.2	0.69	33.1	2.08						
[15-Crown-5] = 0.0100 mol dm^{-3}											
14.0	0.28	20.0	0.34	26.0	0.50	32.0	1.18	38.0	15.63	43.0	159.20
15.0	0.29	21.0	0.36	27.0	0.54	33.2	1.68	39.0	28.60	44.0	212.00
16.0	0.30	22.1	0.38	28.0	0.61	34.0	2.10	40.0	49.50	45.0	266.00
17.0	0.31	23.0	0.40	29.0	0.70	35.0	3.10	41.0	77.30	46.0	330.00
18.0	0.32	24.0	0.42	30.0	0.82	35.9	4.66	42.2	127.10	47.0	420.00
19.0	0.33	25.1	0.46	31.0	0.99	37.4	11.21				
[15-Crown-5] = 0.0050 mol dm^{-3}											
14.0	0.26	20.0	0.32	26.0	0.42	32.0	0.90	37.0	5.19	42.0	87.00
15.0	0.27	21.2	0.34	27.0	0.46	33.0	1.14	38.1	10.57	43.0	126.30
16.0	0.28	22.0	0.35	28.0	0.51	34.0	1.49	39.0	18.52	44.0	211.00
17.0	0.29	23.0	0.36	29.1	0.58	35.0	2.10	40.0	31.90	45.0	285.00
18.0	0.30	24.0	0.38	30.0	0.64	36.0	3.15	41.0	56.60	46.0	351.00
19.0	0.31	25.1	0.40	31.0	0.76						
[15-Crown-5] = 0.0010 mol dm^{-3}											
14.0	0.26	20.0	0.29	26.0	0.39	32.2	0.72	38.0	5.02	43.0	50.40
15.0	0.27	21.0	0.30	27.0	0.41	33.0	0.84	39.0	9.01	44.0	62.00
16.0	0.27	22.0	0.32	28.1	0.44	34.0	1.02	39.7	14.83	45.1	80.00
17.0	0.27	23.1	0.33	29.0	0.48	35.0	1.34	41.2	28.30	46.8	114.00
18.0	0.28	24.0	0.35	30.0	0.54	36.0	1.87	42.0	38.30	49.5	173.00
19.0	0.28	25.0	0.37	31.0	0.61	37.1	3.11				

[a] [Aerosol OT] = 0.5 mol dm^{-3}, w = 22.2.

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

The experimental procedure has been described in previous papers (Álvarez, 1999a, 1999b). 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 ([KCl] = 0.0100 mol dm^{-3}, κ = 1413 μS cm^{-1} at 25 °C and [KCl] = 0.100 mol dm^{-3}, κ = 12.88 mS cm^{-1} at 25 °C). The inaccuracy of these measurements was ±0.5%. During the measurements of electrical conductivity the temperature was regulated using a thermostat−cryostat Teche TE-8D RB-5, with a precisión of ±0.1 °C. 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 5 to 10 samples, where the maximum deviations from the average value were always <1.5%. The percolation temperature was determined from the variation of the specific conductivity with the temperature.

Table 3. Specific Conductivity Values at Different Temperatures for Aerosol OT + 2,2,4-Trimethylpentane + Water Microemulsions in the Presence of Different Concentrations of 18-Crown-6[a]

$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$	$t/°C$	$\kappa/\mu S \cdot cm^{-1}$
{18-Crown-6} = 0.1140 mol dm⁻³											
6.4	0.20	11.5	0.28	16.2	0.59	19.9	2.85	23.6	43.00	26.2	146.00
7.5	0.20	12.3	0.31	17.1	0.70	20.8	5.40	24.2	60.00	27.1	200.00
8.6	0.21	13.7	0.38	17.9	1.07	21.5	9.20	24.8	82.00	27.8	245.00
9.6	0.23	14.5	0.43	18.3	1.26	22.2	15.80	25.6	116.00	28.7	310.00
10.4	0.25	15.2	0.49	19.2	2.00	22.7	23.00				
{18-Crown-6} = 0.0570 mol dm⁻³											
15.0	0.25	19.4	0.36	24.2	0.88	27.7	3.80	29.9	18.40	31.9	70.00
15.3	0.26	20.3	0.40	25.1	1.13	28.2	5.30	30.5	29.00	33.0	118.00
16.2	0.27	21.3	0.46	26.1	1.54	28.8	7.80	31.0	40.10	33.9	170.00
17.4	0.30	22.2	0.54	27.1	2.60	29.5	13.20	31.6	58.00	34.4	200.00
18.6	0.33	23.2	0.64								
{18-Crown-6} = 0.0142 mol dm⁻³											
15.6	0.22	21.2	0.28	26.0	0.38	29.9	0.70	32.3	1.57	34.4	5.00
16.1	0.23	22.1	0.29	26.8	0.42	30.6	0.85	32.9	2.10	35.0	4.40
17.2	0.24	22.9	0.30	27.5	0.52	31.2	1.02	33.3	2.50	35.6	13.70
18.2	0.25	24.0	0.32	28.2	0.52	31.7	1.20	33.9	3.60	36.4	26.50
20.2	0.26	25.0	0.35	29.1	0.61						
{18-Crown-6} = 0.0085 mol dm⁻³											
15.2	0.25	23.4	0.33	30.1	0.65	33.8	2.17	37.9	38.50	41.5	250.00
17.1	0.26	24.7	0.36	31.1	0.83	34.8	3.77	38.6	62.50	42.3	327.00
18.8	0.28	26.2	0.40	31.9	1.03	35.9	8.65	39.5	105.00	43.3	425.00
20.4	0.29	27.5	0.45	33.0	1.54	36.9	19.50	40.5	160.00	44.3	543.00
21.8	0.31	28.7	0.52								
{18-Crown-6} = 0.0050 mol dm⁻³											
14.8	0.25	28.1	0.47	31.9	0.98	34.0	2.50	36.5	11.60	39.2	81.00
16.3	0.26	28.5	0.49	32.3	1.08	34.5	3.05	36.7	13.40	39.6	105.00
18.4	0.26	29.0	0.59	32.6	1.17	34.8	3.05	36.9	16.00	40.1	130.00
19.1	0.28	30.0	0.63	32.9	1.30	35.1	3.75	37.3	21.00	40.6	170.00
20.8	0.30	30.4	0.67	33.3	1.48	35.4	4.40	37.7	28.50	41.1	205.00
22.7	0.31	30.6	0.72	33.4	1.60	35.6	5.40	38.0	38.00	41.6	250.00
23.8	0.34	31.1	0.80	33.6	1.75	35.8	6.60	38.4	49.00	42.0	285.00
25.4	0.38	31.5	0.88	33.8	1.95	36.3	8.80	38.9	65.00	42.4	330.00
26.6	0.44										
{18-Crown-6} = 0.0043 mol dm⁻³											
14.5	0.22	20.4	0.29	29.1	0.51	35.0	3.50	37.8	34.25	41.8	220.00
15.9	0.25	21.9	0.30	30.2	0.61	35.8	5.90	38.2	43.00	42.6	285.00
16.8	0.26	23.5	0.32	31.0	0.73	36.4	11.15	39.3	86.00	43.5	335.00
17.7	0.27	24.7	0.34	32.0	0.92	36.9	17.00	40.1	120.00	44.1	405.00
18.6	0.27	26.7	0.39	33.0	1.27	37.4	25.50	41.1	170.00		
19.6	0.28	28.1	0.45	34.0	2.01						440.00
{18-Crown-6} = 0.0010 mol dm⁻³											
20.6	0.29	29.2	0.52	34.7	2.35	36.5	6.80	37.9	19.25	40.4	100.00
21.2	0.30	30.0	0.58	34.9	2.65	36.6	7.40	38.2	24.75	40.7	116.00
22.1	0.31	30.8	0.67	35.2	3.00	36.7	8.00	38.4	27.50	41.1	134.00
23.1	0.32	31.5	0.77	35.4	3.30	36.9	9.30	38.5	30.00	41.5	160.00
24.2	0.34	32.5	0.99	35.6	3.75	37.2	11.80	38.9	41.50	41.9	180.00
25.1	0.35	33.2	1.22	35.8	4.25	37.4	13.50	39.3	52.00	42.5	215.00
25.6	0.36	33.9	1.72	36.0	4.85	37.6	15.40	39.6	63.00	42.8	240.00
26.5	0.39	34.4	2.10	36.2	5.80	37.8	17.25	40.1	87.00	43.0	255.00
27.9	0.44										
{18-Crown-6} = 0.0005 mol dm⁻³											
21.6	0.29	26.9	0.38	30.4	0.56	33.7	1.34	37.1	13.50	39.6	80.00
23.4	0.32	28.0	0.41	31.3	0.67	34.6	2.03	37.9	26.00	40.2	112.00
24.8	0.33	28.8	0.46	32.0	0.80	35.5	3.90	38.8	46.00	40.7	139.00
25.9	0.36	29.4	0.49	33.0	1.25	36.5	7.80				
{18-Crown-6} = 0.0001 mol dm⁻³											
22.2	0.34	27.0	0.48	31.1	1.02	34.4	4.00	37.4	30.50	40.5	145.00
23.0	0.35	28.0	0.54	32.0	1.35	35.2	6.45	38.5	56.25	41.4	195.00
24.6	0.38	28.9	0.62	32.8	1.85	36.0	11.40	39.2	89.00	42.2	250.00
25.7	0.42	29.9	0.65	33.6	2.75	36.6	17.25				

[a] [Aerosol OT] = 0.5 mol dm⁻³, w = 22.2.

The maximum water solubilization capacity of the microemulsions (with or without additive) was studied by adding an appropriate volume of water (or water + additive) to samples containing known amounts of AOT and isooctane under continuous stirring until permanent turbidity was observed. The samples thus prepared were stored at 25 °C for several weeks. The phases resolved were studied by using the dyes Sudan IV (soluble in the organic phase) and Methylene Blue (water-soluble) according to reported procedures (Hou and Shah, 1987). Liquid crystal phases were observed by using cross-polarizers.

MM2 (molecular mechanics) calculations were carried out using a commercial software package (CS Chem3D Pro 4.0 supplied by Cambridge Soft Corporation). MM2-

Table 4. Specific Conductivity Values at Different Temperatures for Aerosol OT + 2,2,4-Trimethylpentane + Water Microemulsions in the Presence of [12-Crown-4] = 0.3144 mol dm^{-3} at Different Water Contents[a]

t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
				$w = 11.10$			
5.0	0.70	15.1	2.00	23.9	14.96	36.2	104.30
6.0	0.75	16.0	2.30	24.4	17.00	37.3	116.69
7.0	0.81	16.9	2.70	25.1	20.00	37.8	122.55
8.0	0.88	17.2	2.90	26.0	24.00	39.5	143.59
9.0	0.96	18.3	3.70	27.0	29.00	40.9	162.18
10.0	1.10	19.2	4.60	28.1	35.00	41.5	170.51
11.0	1.20	20.0	6.60	29.5	44.00	42.2	180.49
12.2	1.30	21.0	7.80	31.1	56.00	43.0	192.25
13.0	1.50	21.8	9.80	33.0	72.00	44.2	210.59
13.8	1.60	22.3	11.00	34.2	84.00	46.3	245.00
14.7	1.90	23.3	12.98	35.0	92.00	50.8	326.00
				$w = 15.54$			
5.0	0.52	12.3	1.20	20.1	13.00	29.3	135.00
6.0	0.56	13.5	1.40	21.3	20.00	30.6	165.00
7.2	0.61	14.9	1.90	22.5	30.00	31.1	176.00
8.0	0.67	15.3	2.10	23.4	39.00	33.5	240.00
9.0	0.74	16.4	2.90	24.9	58.00	34.9	282.00
10.9	0.95	17.6	4.40	26.6	84.00	36.7	340.00
11.7	1.10	18.8	7.20	28.2	113.00		
				$w = 28.86$			
4.0	0.27	10.0	0.67	14.1	5.20	20.1	257.00
5.1	0.31	11.0	0.88	14.9	12.00	22.6	496.00
6.3	0.35	11.9	1.40	15.4	21.00	23.7	626.00
6.9	0.38	12.5	1.71	16.3	44.00	24.8	771.00
7.4	0.41	12.9	2.00	17.5	92.00	25.9	931.00
8.1	0.46	13.6	3.20	18.9	170.00	27.3	1156.00
9.2	0.56						
				$w = 35.52$			
2.0	0.33	8.1	0.89	13.1	42.00	18.4	600.00
3.0	0.37	9.0	1.20	14.1	95.00	19.2	743.00
4.0	0.41	10.1	1.90	14.9	156.00	20.1	922.00
5.0	0.48	11.0	3.63	15.1	173.00	20.9	1097.00
6.1	0.57	12.1	13.00	16.3	298.00	21.8	1312.00
7.2	0.71	12.9	34.00	17.2	415.00		

[a] [Aerosol OT] = 0.5 mol dm^{-3}.

Table 5. Specific Conductivity Values at Different Temperatures for Aerosol OT + 2,2,4-Trimethylpentane + Water Microemulsions in the Presence of [15-Crown-5] = 0.2022 mol dm^{-3} at Different Water Contents[a]

t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
				$w = 11.10$			
5.0	0.83	13.0	2.20	21.1	14.00	34.0	104.00
6.1	0.92	14.1	2.60	22.3	19.00	35.0	115.00
7.0	1.00	15.1	3.00	24.0	26.00	36.0	126.00
8.0	1.10	15.7	3.72	25.0	31.00	37.0	138.00
9.0	1.20	17.2	5.20	26.1	37.00	40.0	178.00
10.0	1.40	18.1	6.70	29.0	58.00	42.0	207.00
11.0	1.60	19.1	8.60	30.0	66.00	43.0	222.00
12.2	1.90	20.2	11.00	31.0	75.00	44.2	241.00
				$w = 15.54$			
5.0	0.63	12.0	1.80	17.1	11.00	24.1	84.00
6.0	0.70	13.1	2.40	18.2	17.00	25.3	105.00
7.1	0.79	14.1	3.30	19.5	27.00	26.1	120.00
8.1	0.90	14.7	4.10	20.5	36.00	27.0	139.00
9.0	1.02	15.0	4.90	21.4	46.00	29.1	186.00
10.1	1.22	16.2	8.00	22.6	62.00	31.5	249.00
11.1	1.50						
				$w = 28.86$			
3.0	0.32	8.0	0.79	13.5	42.00	19.1	401.00
3.7	0.35	9.0	1.10	14.2	66.00	20.0	493.00
4.2	0.37	9.9	1.70	15.1	106.00	22.0	733.00
5.1	0.42	10.3	2.10	16.0	156.00	23.0	871.00
6.1	0.50	11.7	7.70	17.1	222.00	24.1	1037.00
7.1	0.62	12.9	26.00	18.0	301.00		
				$w = 35.52$			
1.0	0.39	4.9	0.78	9.1	9.50	13.5	279.00
1.7	0.43	5.3	0.87	9.6	17.90	14.3	375.00
2.2	0.47	6.2	1.20	10.0	28.60	15.9	609.00
2.7	0.50	7.3	1.90	11.5	102.00	17.0	804.00
3.1	0.54	7.9	2.80	12.4	171.00	18.5	1112.00
4.1	0.65	8.4	4.20				

[a] [Aerosol OT] = 0.5 mol dm^{-3}.

Chem3D uses a modified version of the MM2 Allinger force field (Allinger et al., 1982).

Results and Discussion

In the present work the effect of concentration of three CEs (12-crown-4, 15-crown-5, and 18-crown-6) on the process of electric percolation has been studied. A series of conductivity/temperature data for different ether concentrations were measured. In these experiments the crown ether concentration was varied between [CE] = 1.00×10^{-4} mol dm^{-3} and [CE] = 0.3144 mol dm^{-3} while the microemulsion composition was kept constant and equal to [Aerosol OT] = 0.500 mol dm^{-3} and w = [water]/[Aerosol OT] = 22.2.

The influence of microemulsion composition was also measured. The concentration of surfactant was kept constant and equal to [Aerosol OT] = 0.500 mol dm^3. The concentrations of additives were [12-crown-4] = 0.3114 mol dm^{-3}, [15-crown-5] = 0.2022 mol dm^{-3}, and [18-crown-6] = 0.1140 mol dm^{-3}. The water content of the microemulsion, w, was varied between 11.1 and 35.5.

The values of the specific conductivity/temperature, obtained for different crown ether concentrations, are shown in Tables 1–6. From these data it is possible to obtain the percolation temperature (t_p). This temperature has been obtained from the conductivity/temperature data using the method described elsewhere (Álvarez et al., 1998a) and illustrated in Figure 2. In Table 7, t_p values

induced in the standard microemulsion by crown ether concentrations used in this study are listed. An alternative analysis can be carried out by the fit of an empirical equation to the experimental data (see for example Álvarez et al., 1998c):

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

The fit of κ/t values was satisfactory (Figure 1) in all cases studied, and the parameters A, B, and C are shown in Table 7. Equation 1 reproduces the experimental conductivity data with a deviation of less than 4%. The value of parameter A corresponds to the temperature of percolation, and the values of B and C seem to be associated with the nature of the additive and the composition of the microemulsion.

As we observed for kriptand complexes (Álvarez et al., 2000), low macrocycle concentrations hinder the electric percolation phenomena but medium and high concentrations favor the percolation (see Figure 3). At moderate concentrations, they behave similarly to electrolytes. This effect of electrolytes is one of the most widely documented (Cabos and Delord, 1980; Lang et al., 1988; Rouviere et al., 1979). This effect can be justified by taking into account the complexing ability of the CE with respect to the Na$^+$ counterion of Aerosol OT ions and its transfer to the AOT film and the 2,2,4-trimethylpentane continuous phase (García-Río et al., 1997). Changes in the Na$^+$ in the Aerosol OT headgroup vicinity imply changes in the effective polar area of surfactants by changes in the screening electrostatic repulsion (Finer et al., 1972). Electrical conductivity of microemulsions is due to the passage of cations through

Table 6. Specific Conductivity Values at Different Temperatures for Aerosol OT + 2,2,4-Trimethylpentane + Water Microemulsions in the Presence of [18-Crown-6] = 0.1140 mol dm^{-3} at Different Water Contents[a]

t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
				$w = 11.10$			
10.0	0.49	17.0	0.99	24.0	4.80	31.3	40.00
11.0	0.53	18.1	1.20	25.1	7.03	32.5	50.60
12.0	0.58	19.1	1.37	26.1	9.90	33.9	64.70
13.0	0.63	20.1	1.66	27.1	13.70	34.7	73.50
14.0	0.70	21.2	2.13	28.2	19.00	35.9	87.90
15.0	0.77	22.1	2.68	29.1	24.13	37.0	102.00
16.0	0.87	23.1	3.60	30.1	30.80	38.0	116.00
				$w = 15.54$			
10.0	0.34	18.0	0.94	23.0	6.18	29.0	75.40
12.0	0.41	19.0	1.19	24.0	10.90	31.0	120.00
13.0	0.45	20.0	1.58	25.0	18.30	35.0	241.00
15.0	0.57	21.0	2.27	26.0	28.50	36.0	278.00
16.0	0.66	22.0	3.58	28.0	57.10	37.0	318.00
17.0	0.78						
				$w = 28.86$			
10.0	0.22	15.0	0.39	19.0	6.50	22.0	127.00
11.0	0.23	16.0	0.53	19.5	14.00	24.0	307.00
12.0	0.24	17.0	0.83	20.0	26.70	25.0	426.00
13.0	0.25	18.0	1.71	21.0	67.00	28.0	900.00
14.0	0.31						
				$w = 35.52$			
7.0	0.23	11.0	0.41	15.1	1.74	19.0	172.00
7.4	0.24	11.9	0.49	16.0	4.37	20.0	304.00
8.0	0.26	12.2	0.53	16.6	11.60	21.0	473.00
9.0	0.30	13.1	0.68	17.0	22.60	23.0	927.00
10.0	0.34	14.1	0.99	18.0	77.70		

[a] [Aerosol OT] = 0.5 mol dm^{-3}.

transient channels formed between droplets that have collided. As noted in the literature (Fletcher et al., 1987), the opening of surfactant films (to form transient channels) involves large activation energies related to the creation of local regions of positive curvature. The less naturally prone the surfactant is to adopt positive curvatures, the more difficult will be the mass transfer process and hence electrical conduction. In this respect, the capacity of a CE to change the screening electrostatic repulsion between charged headgroups will (by the capture of Na$^+$) lead to a more markedly trapezoidal Aersol OT shape and increase 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 concentrations of the CE, the percolation temperature is lowered to such a degree that the high-conductivity region can be reached at unusually low temperature (see comparative results with usual organic additives and electrolytes in Table 8). It is possible to follow a similar reasoning to that used in the literature (García-Río et al., 1994) to explain the behavior of other organic substances. If additives associated to the surfactant film could increase disorder in the interfacial zone, they could thereby increase the film rigidity and increase its deformability, favoring the channel opening required for mass transfer among droplets and hence electrical percolation. In this respect, it is interesting to ascertain whether the role of these additives in the interfacial region is to replace water molecules. The studies by Kang et al. (Kang et al., 1992) 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. However, at high concentrations the additive replaces water molecules at the interface, thereby playing a direct role in the solvation of headgroups. Light scattering
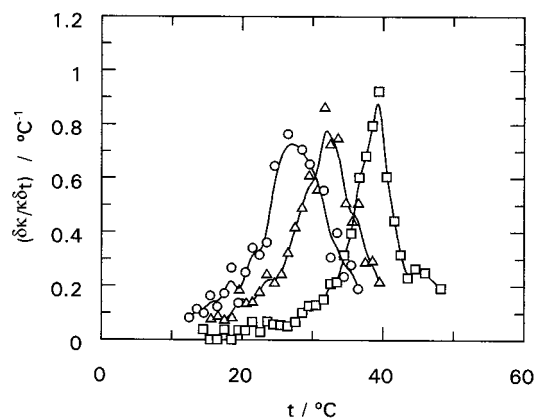

Figure 2. Determination of the percolation temperature obtained by the Kim method (Kim and Huang, 1986) for Aerosol OT + 2,2,4-trimethylpentane + water microemulsions in the presence of different concentrations of 15-crown-5: (○) [15-crown-5] = 0.0919 mol dm^{-3}; (△) [15-crown-5] = 0.0705 mol dm^{-3}; (□) [15-crown-5] = 0.0010 mol dm^{-3}.
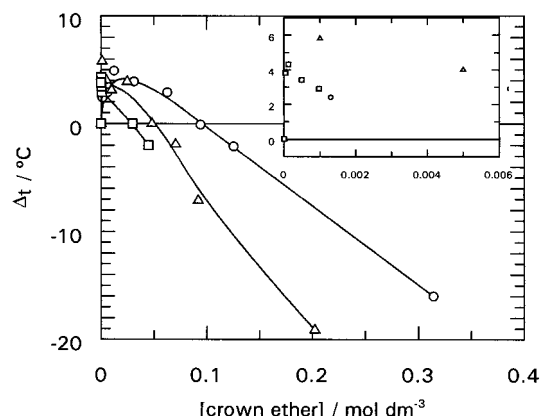
Figure 3. Variation of $\Delta t_p = [t_p(\text{with crown}) - t_p(\text{without crown})]$ with crown ether concentration: (○) 12-crown-4; (△) 15-crown-5; (□) 18-crown-6.

experiments support this reasoning. This increase in the disorder is also the origin of the decreased maximum water solubilizing capacity of the microemulsions (Table 9).

The observed phenomenon, taking into account the nature and properties of crown ethers as phase transfer catalysts and as organic substrates, is consistent with those of other additives previously studied (Álvarez et al., 1998a–c; Álvarez et al., 1999a–c; García-Río et al., 1994)

On the other hand, we can estimate the concentration of crown ether at which the temperature of percolation is the same as that without additive; in this case the two different effects—the ability of crown ethers to bind Na$^+$, and their organic nature—are compensated. The values of [12-crown-4]$_{comp}$, [15-crown-5]$_{comp}$, and [18-crown-6]$_{comp}$ were listed in Table 4. These concentration values seem to be correlated with the binding constant of Na$^+$ and the size of the crown ether cavity (i.e. number of O atoms in the crown ether). MM2, molecular mechanics, calculations (Allinger et al., 1982) were carried out to determine the internal diameter (d_{min}) and external diameter (d_{max}) of crown ethers. The values of d_{min} and d_{max} are listed in Table 10. In Figure 4 the correlation between internal diameter (d_{min}) and the [CE]$_{comp}$ is shown. This relationship is in accord with the assumption that the net effect of the CE is a combination of the two above-describe effects: alter screening of headgroups and alter surfactant film structure by the inclusion of CE in the AOT film.

Table 7. Temperature of Percolation for Aerosol OT + 2,2,4-Trimethylpentane + Water Microemulsions in the Presence of Different CEs Obtained by the Kim Method (Kim and Huang, 1986) and Fitting Parameters (Eq 1) Obtained for Aerosol OT + 2,2,4-Trimethylpentane + Water Microemulsions in the Presence of Different CEs[a]

Crown Ether	[CE] / mol·dm⁻³	w	[AOT] / mol·dm⁻³	t_p / °C	A	B	C
without additive *	-	-	-	33.6	32.6	0.39	-3.30
12-Crown-4	0.3144	22.2	0.500	17.0	15.5	0.61	-4.25
(1,4,7,10-Tetraoxacyclododecane)	0.1257	22.2	0.500	30.0	29.7	0.50	-4.58
	0.0943	22.2	0.500	33.0	33.7	0.35	-4.58
	0.0629	22.2	0.500	36.0	36.5	0.30	-5.94
	0.0314	22.2	0.500	37.0	37.9	0.37	-5.43
	0.0125	22.2	0.500	38.0	38.2	0.39	-5.33
	0.0063	22.2	0.500	37.0	38.0	0.42	-4.08
	0.0013	22.2	0.500	36.0	36.3	0.56	-4.80
	0.3144	11.1	0.500	19.2	17.4	1.85	-9.78
	0.3144	15.5	0.500	18.8	16.8	1.08	-6.50
	0.3144	28.9	0.500	14.1	13.7	0.40	-2.65
	0.3144	35.5	0.500	11.0	11.3	0.29	-3.10
15-Crown-5	0.2022	22.2	0.500	14.5	12.7	0.63	-4.08
(1,4,7,10,13-Penta-oxacyclopentadecane)	0.0919	22.2	0.500	26.5	24.7	0.62	-5.06
	0.0705	22.2	0.500	31.7	29.1	0.57	-5.30
	0.0481	22.2	0.500	35.7	32.5	0.51	-5.66
	0.0247	22.2	0.500	37.5	35.2	0.53	-5.15
	0.0100	22.2	0.500	38.5	36.6	0.51	-5.86
	0.0050	22.2	0.500	37.6	38.0	0.42	-5.79
	0.0010	22.2	0.500	39.4	38.5	0.74	-5.52
	0.2022	11.1	0.500	15.1	14.6	1.91	-9.46
	0.2022	15.5	0.500	14.7	14.0	1.11	-6.27
	0.2022	28.9	0.500	11.7	10.9	0.41	-2.57
	0.2022	35.5	0.500	8.4	8.5	0.30	-3.03
	0.1140	22.2	0.500	21.1	20.2	0.49	-2.58
18-Crown-6	0.0570	22.2	0.500	29.1	27.8	0.48	-3.21
(1,4,7,10,13,16-Hexaoxacyclooctadecane)	0.0142	22.2	0.500	35.3	35.4	0.10	-4.08
	0.0085	22.2	0.500	36.4	36.1	0.34	-4.65
	0.0050	22.2	0.500	36.4	36.3	0.33	-4.38
	0.0043	22.2	0.500	36.1	36.5	0.33	-4.70
	0.0010	22.2	0.500	38.7	36.1	0.43	-4.17
	0.0005	22.2	0.500	36.8	36.3	0.37	-3.86
	0.0001	22.2	0.500	36.6	34.7	0.48	-4.04
	0.1140	11.1	0.500	24.0	22.1	1.48	-6.47
	0.1140	15.5	0.500	23.0	21.5	0.87	-4.10
	0.1140	28.9	0.500	18.0	18.4	0.32	-1.39
	0.1140	35.5	0.500	16.0	16.0	0.23	-2.13

[a] [Aerosol OT] = 0.5 mol dm⁻³.

To confirm the occurrence of these two types of behavior, the maximum water solubization capacity in the presence of these additives compares with the maximum water solubilization capacity in the presence of kriptand complexes, electrolytes, and organic substances (Table 9). In the absence of additives, the maximum water solubilization was found at the mole ratio $w = 56$, consistent with literature results (Huruguen et al., 1991). However, the presence in the aqueous phase of a moderate concentration of organic additives (Table 9) decreased the solubilization capacity and led to phase separation at w values in the range $w = 41-47$. Breakage of the microemulsion led to the formation of a liquid crystal (LC) phase in every case. Consistent with previous results (Wong et al., 1977; Maitra, 1984), the presence of electrolytes significantly reduced the

maximum water solubilization capacity of AOT microemulsions (in the range $w = 30-42$ for the studied electrolytes). In all cases, breakage of the microemulsion and its resolution into different phases led to a heavier aqueous phase containing excess salt, in equilibrium with the microemulsion. Unlikely with organic substances, a liquid crystal phase was formed (Table 9).

The presence of moderate concentrations of CE and/or kryptand complexes further decreased the maximum water solubilization capacity of theses systems (Table 9). The effect was much more pronounced than that observed with the organic substances, which required higher concentrations to have a similar effect. By contrast, the effect was much weaker than that observed in the presence of electrolytes, which led to a much greater decrease in

Table 8. Comparison of Observed Δt_p for Different Additives

additive	[additive]/mol dm^{-3}	$\Delta t_p{}^a$/°C
12-crown-4	1.3×10^{-3}	2.4
	1.257×10^{-1}	−3.6
15-crown-5	1.0×10^{-3}	5.8
	9.19×10^{-2}	−7.1
18-crown-6	1.0×10^{-3}	5.1
	1.14×10^{-1}	−12.5
C222^b	1.22×10^{-4}	3.5
	4.48×10^{-2}	−5.6
C211^b	1.4×10^{-4}	1.4
	1.4×10^{-2}	−0.6
C221^b	4.21×10^{-4}	4.4
	8.42×10^{-3}	−1.6
urea^c	2.34×10^{-1}	−22.6
methylurea^c	2.0×10^{-1}	−6.6
1,1-dimethylurea^c	2.0×10^{-1}	−7.6
1,3-dimethylurea^c	2.0×10^{-1}	−11.6
tetramethylurea^c	2.0×10^{-1}	−12.6
thiourea^c	2.0×10^{-1}	−8.6
1,3-dimethylthiourea^c	2.0×10^{-1}	−13.6
tetramethylthiourea^c	2.0×10^{-1}	−10.6
NaCl^d	4.0×10^{-2}	4.4
NaBr^d	4.0×10^{-2}	5.4
NaI^d	4.0×10^{-2}	5.4
NaNO$_3{}^d$	4.0×10^{-2}	3.4
NaClO$_4{}^d$	4.0×10^{-2}	4.4
NaSCN^d	4.0×10^{-2}	3.4
Na$_2$SO$_4{}^d$	4.0×10^{-2}	6.4

^{a} $\Delta t_p = t_p$(with additive) $- t_p$(without additive). [Aerosol OT] $=$ 0.5 mol dm^{-3}; $w = 22.2$. ^{b} Álvarez et al., 2000. ^{c} Álvarez et al., 1998a. ^{d} Álvarez et al., 1999a.

Table 9. Characteristics of Microemulsions, $w_{breakage}$, and Originated Phase(s) in the Presence of Different Additives

additive	[additive]/mol dm^{-3}	$w_{breakage}$	phases^a
without	0	55.5	LC
12-crown-4	0.08	48.9	LC
15-crown-5	0.08	48.6	LC
18-crown-6	0.08	48.5	LC
C222	0.08	47.2	LC
C221	0.08	47.7	LC
C211	0.08	47.1	LC
tetramethylurea	0.2	44.1	LC
tetramethylthiourea	0.2	44.4	LC
1,3-dimethylurea	0.2	41.6	LC
1.3-dimethylthiourea	0.2	44.4	LC
methylurea	0.2	44.6	LC
methylthiourea	0.2	47.2	LC
urea	0.2	45.9	LC
thiourea	0.2	47.2	LC
NaCl	0.08	38.8	ME + WE
NH$_4$Cl	0.08	36.1	ME + WE
NaBr	0.08	38.9	ME + WE
Na$_2$SO$_4$	0.08	30.5	ME + WE
NaClO$_4$	0.08	41.6	ME + WE

^{a} LC = liquid crystal; WE = water excess; ME = microemulsion; [Aerosol OT] = 0.5 mol dm^{-3}; $w = 22.2$.

Table 10. Geometric Characteristics, d_{min} and d_{max}, of Crown Ethers Used in the Present Work

additive	no. of O	[additive]$_{com}$/10^{-2} mol dm^3	d_{max}/Å	d_{min}/Å
12-crown-4	4	9.01	7.107	3.754
15-crown-5	5	6.04	7.978	4.388
18-crown-6	6	2.84	9.050	5.717

maximum water solubilization capacity at the same concentrations as those for the crown ether and kryptand (Table 9). Beyond the maximum water solubilization capacity, the transition to the liquid crystal phase was observed (similarly as with organic additives). This sug-
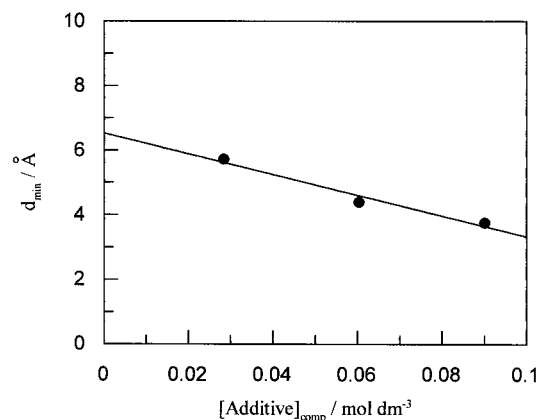
Figure 4. Relationship between [crown ether]$_{\Delta t_p=0}$ and the diameter of the crown ether cavity estimated by MM2 calculations.

gests that the organic nature of the additives is the prevailing factor in the two opposing effects observed.

At constant crown ether content, the increase in w implies a decrease in the value of the percolation temperature (Table 7). This behavior is parallel to the observed behavior in the absence of additive. The w molar ratio is proportional to the hydrodynamic radii of the water pool. An increase of w (and hence an increase in the volume of the microdroplet) increases the probability of collision between droplets because w is directly related with the radius of the water droplet (Pileni, 1989). A high probability of collision implies more probability of channel formation between droplets to allow the passage of cations.

Acknowledgment

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