Effect of Temperature upon Electrical Conductivity of Sodium Bis(2-ethylhexyl) Sulfosuccinate + 2,2,4-Trimethylpentane + Water + Phase Transfer Catalyst

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The effects of temperature and the concentration of dibenzo crown ethers (DBCEs) upon the electrical conductivity of the system sodium bis(2-ethylhexyl) sulfosuccinate (AOT) + 2,2,4-trimethylpentane (isooctane) + water has been studied. The DBCEs (phase transfer catalysts) used in the ternary systems were dibenzo-15-crown-5, dibenzo-18-crown-6, dibenzo-21-crown-7, dibenzo-24-crown-8, and dibenzo-30-crown-10. A very characteristic behavior has been detected, and different equations have been used to fit the experimental data with success.

Introduction

Microemulsions are highly dynamic structures whose components rearrange themselves over time and space through interactions or collisions, coalescing, and redispersing. Microemulsions are colloidal aggregates of great interest from the point of view of pure chemistry as well as from that of applied chemistry. They can be used as solubilizers or as nanoreactors. These facts permit an important number of industrial applications.[1] One of the most useful techniques in obtaining information on colloid interactions is electrical conductivity.[2,3] A microemulsion has a very low conductivity (0.001 to 0.1) $\mu S \cdot cm^{-1}$, which is already a significant increase if compared to the conductivity of alkanes (10^{-8} $\mu S \cdot cm^{-1}$). This increase in conductivity is due to the fact that microemulsions carry charges. A well-known phenomenon occurs when temperature is increased keeping the composition constant. At a certain temperature 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 water mole fraction of the microemulsion is increased, keeping a constant temperature. This phenomenon is called percolation and is related to the mass transfer process between droplets. This critical value of temperature or water mole fraction is called the threshold of percolation (temperature of percolation if temperature is changed). 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. On the other hand, the solubilities of the DBCEs both in polar and in apolar solvents and their capacity to include cations, especially those of alkali metal, within their cavities make them potential phase transfer catalysts (PTC).[4]

In this work, we carried out studies about the influence of PTC and temperature upon the percolation phenomenon and the use of different equations to fit the experimental data. The results obtained were compared with previous studies that analyzed the effect of the presence of cryptand complexes,[5] crown ethers,[6] and benzo crown ethers[7] upon the electrical conductivity and then upon the percolation phenomena and the value of the percolation temperature.

Experimental Section

Materials. The mixtures formed by sodium bis(2-ethylhexyl) sulfosuccinate (AOT) + isooctane + water employed in the present paper were prepared by direct mixing of AOT, 2,2,4-trimethylpentane, and water under vigorous stirring. The final solution (microemulsion + additive) were prepared by mass with deviations of less than ± 0.2 % from the desired concentration, using microemulsion as solvent. In all cases, the dibenzo crown ether concentrations have been referred to the water volume in the microemulsion. The water used for a solution was distilled−deionized with low electrical conductivity (0.10 to 0.50 $\mu S \cdot cm^{-1}$). All the materials were supplied by Sigma and Fluka having the maximum purity commercially available (≥ 99 %). AOT was supplied by Sigma (Sigma Ultra, purity 99 %).

Electrical Conductivity Measurements. The experimental procedure has been described in previous papers.[5−7] 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 ($C_{(KCl)} = 0.0100$ mol·L^{-1}, $\kappa =$ 1413 $\mu S \cdot cm^{-1}$ at 25 °C and $C_{(KCl)} = 0.100$ mol·L^{-1}, $\kappa = 12.88$ $mS \cdot cm^{-1}$ at 25 °C). During the measurements of electrical conductivity, 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 ± 0.1 %.

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

Results and Discussion

The electrical conductivity of AOT + 2,2,4-trimethylpentane + water mixtures ($C_{(AOT)} = 0.5$ mol·L^{-1} and $W = C_{water}/C_{AOT}$

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Table 1. Specific Electrical Conductivity κ Values at Different Temperatures for Microemulsions of AOT + Isooctane + Water in the Presence of Dibenzo-15-crown-5 (1)

C_1 =										
$2.69 \cdot 10^{-3}$ mol·L^{-1}		$5.70 \cdot 10^{-3}$ mol·L^{-1}		$1.33 \cdot 10^{-2}$ mol·L^{-1}		$2.00 \cdot 10^{-2}$ mol·L^{-1}		$2.53 \cdot 10^{-2}$ mol·L^{-1}		$3.21 \cdot 10^{-2}$ mol·L^{-1}	
t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
22.3	1.48	23.5	2.24	22.9	1.60	23.2	2.03	22.2	4.02	23.0	2.78
23.2	1.54	25.0	2.48	24.8	1.67	24.0	2.07	23.2	4.36	24.1	2.98
24.6	1.61	26.0	2.61	26.0	1.75	25.2	2.14	24.2	4.81	25.4	3.28
25.2	1.65	27.0	2.78	28.3	1.94	26.1	2.25	25.5	5.58	26.1	3.51
26.2	1.73	28.0	2.96	29.1	2.03	27.0	2.34	26.5	6.30	28.1	4.26
27.2	1.83	29.0	3.19	30.0	2.14	27.8	2.49	27.5	7.18	30.2	5.39
28.2	1.96	30.0	3.50	31.3	2.35	28.8	2.72	28.5	8.45	31.1	6.19
29.5	2.12	31.5	4.07	32.2	2.56	29.8	2.97	30.0	10.90	32.1	7.17
30.7	2.42	32.5	4.65	34.6	3.34	30.9	3.35	31.0	13.30	33.1	8.67
31.6	2.73	34.0	5.90	35.6	3.87	31.8	3.73	32.2	17.13	34.1	10.30
32.6	3.17	35.0	7.22	37.1	5.10	34.1	5.28	33.0	20.3	35.1	12.81
33.9	4.08	36.0	9.03	38.3	6.92	35.0	6.22	34.0	27.5	37.0	20.7
34.5	4.68	37.2	12.50	39.3	9.72	36.0	7.69	36.0	55.1	38.0	32.0
35.5	6.17	38.2	17.72	40.3	15.43	37.0	10.23	37.0	86.5	39.0	49.6
37.0	10.52	39.0	25.2	41.3	27.3	38.6	18.44	38.0	150	40.0	79.4
38.3	20.1	40.0	46.4	42.3	63.7	39.6	30.2	39.0	228	41.1	176.2
39.2	37.2	41.0	85.0	43.3	170	41.3	109.3	40.0	358	42.0	314
40.0	74.5	42.0	167.8	44.8	627	42.3	280	41.0	560	43.0	552
41.2	225	43.0	309	45.8	1200	43.4	643	42.1	988	43.9	850
42.0	440	44.0	576	47.8	3250	45.2	1800	43.0	1299		
43.0	880	45.0	950	48.9	4540	46.5	3250	44.0	1848		
44.0	1598	46.0	1470	49.5	5420	48.9	6580	45.3	2890		
45.6	3110	47.6	2780			49.5	7700	46.0	3530		
46.5	4570	48.3	3260					47.0	4250		
48.0	6580	49.0	3800					48.0	5300		
		50.0	4500					49.0	6200		

Table 2. Specific Electrical Conductivity κ Values at Different Temperatures for Microemulsions of AOT + Isooctane + Water in the Presence of Dibenzo-18-crown-6 (2)

C_2 =											
$3.88 \cdot 10^{-4}$ mol·L^{-1}		$2.66 \cdot 10^{-3}$ mol·L^{-1}		$5.72 \cdot 10^{-3}$ mol·L^{-1}		$7.27 \cdot 10^{-3}$ mol·L^{-1}		$1.15 \cdot 10^{-2}$ mol·L^{-1}		$1.25 \cdot 10^{-2}$ mol·L^{-1}		$1.43 \cdot 10^{-2}$ mol·L^{-1}	
t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
22.1	0.43	21.3	0.64	21.3	0.96	23.5	0.87	23.0	0.66	22.7	0.51	22.1	0.63
23.2	0.43	22.2	0.65	22.1	0.98	24.5	0.88	24.1	0.68	23.4	0.53	23.5	0.67
24.2	0.44	23.1	0.65	23.5	0.99	25.5	0.89	25.0	0.70	24.4	0.54	24.7	0.72
25.0	0.44	24.1	0.66	24.7	1.00	27.1	0.92	26.7	0.73	25.2	0.56	25.8	0.79
26.1	0.45	25.0	0.65	25.8	1.01	28.2	0.94	28.0	0.78	26.5	0.59	26.7	0.87
27.6	0.45	26.2	0.66	27.0	1.02	29.1	0.96	28.8	0.81	27.5	0.63	27.4	0.97
28.8	0.47	27.0	0.68	28.2	1.04	30.0	1.00	30.1	0.93	28.2	0.68	28.3	1.18
29.4	0.52	28.1	0.69	29.0	1.05	31.0	1.04	30.9	1.04	28.9	0.73	28.9	1.43
30.5	0.57	29.5	0.74	30.2	1.09	32.0	1.14	31.5	1.20	29.5	0.77	29.8	2.08
31.0	0.64	30.5	0.81	31.0	1.12	32.7	1.20	32.3	1.41	30.2	0.84	30.6	4.12
32.5	1.04	31.5	0.92	32.7	1.27	33.6	1.29	33.0	1.81	31.4	1.09	31.2	15.16
33.0	1.67	32.2	1.04	33.5	1.40	34.3	1.56	34.0	3.04	31.8	1.32	32.3	401
33.5	4.97	33.0	1.28	34.3	1.59	35.5	2.00	34.7	5.86	32.5	2.11	33.7	2730
34.0	49.4	33.8	1.72	35.0	1.83	36.0	2.38	35.5	27.7	33.3	4.44	34.2	3950
34.5	265	35.2	5.16	35.5	2.05	36.5	2.86	36.0	112.2	34.1	30.3	35.3	7370
35.0	808	36.1	31.4	36.0	2.38	37.0	3.73	36.5	363	34.6	131.4		
36.7	1937	36.8	260	36.6	2.94	37.5	5.23	37.0	850	35.6	1200		
		37.3	600	37.4	4.40	38.0	8.62	37.5	1630	36.6	2100		
		38.0	1551	38.2	8.48	38.5	17.69	38.0	2360	37.4	3690		
		38.5	2630	38.8	18.59	39.0	45.4	38.5	3450	38.0	4860		
				39.4	55.6	39.5	124.7			38.5	6010		
				40.0	165.8	40.0	330						
				40.5	364	40.6	787						
				41.0	657	41.1	1330						
				41.5	1073	41.6	1910						
				42.0	1492	42.3	3000						
				42.5	2050	43.0	4120						
				43.0	2660								
				41.0	6570								

= 22.2) was measured at different temperatures that includes the percolation phenomenon and in the presence of different dibenzo crown ether concentrations (PTCs). Tables 1 to 5 show the experimental values corresponding to electrical conductivity at different temperatures for all systems studied and in the presence of different quantities of dibenzo crown ethers shown in Figure 1.

In all cases, we observed an increase in electrical conductivity from the typical values for organic compounds, such as the 2,2,4-trimethylpentane, to higher values, typical of aqueous solutions.[8,9] This behavior is characteristic for this kind of colloidal aggregates (microemulsions) and consists of a dramatic increment in the value of electrical conductivity above a certain temperature. This increment on the value of the electrical

Table 3. Specific Electrical Conductivity κ Values at Different Temperatures for Microemulsions of AOT + Isooctane + Water in the Presence of Dibenzo-21-crown-7 (3)

$C_3 =$										
$1.60 \cdot 10^{-4}$ mol·L^{-1}		$2.22 \cdot 10^{-4}$ mol·L^{-1}		$6.43 \cdot 10^{-4}$ mol·L^{-1}		$1.24 \cdot 10^{-3}$ mol·L^{-1}		$2.10 \cdot 10^{-3}$ mol·L^{-1}		$5.44 \cdot 10^{-3}$ mol·L^{-1}	
t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
26.4	2.73	25.5	1.84	25.5	2.35	25.1	3.43	25.5	2.85	24.8	2.85
27.4	3.13	26.6	2.04	26.9	2.78	26.2	3.70	26.6	3.26	26.7	3.62
28.7	4.26	27.6	2.26	28.1	3.14	27.0	4.13	27.5	3.70	28.4	4.76
29.6	5.70	28.5	2.57	29.3	3.82	28.3	4.83	28.5	4.30	29.3	5.70
31.1	9.73	29.9	3.23	30.1	4.46	30.3	7.77	29.5	5.29	30.8	8.15
32.1	17.90	31.0	4.09	31.0	5.48	32.3	14.74	31.0	7.42	31.7	10.70
33.3	41.3	31.9	5.18	32.0	7.07	33.4	23.9	32.0	9.92	32.7	15.17
34.3	88.4	33.0	7.38	33.0	9.24	35.0	51.1	33.0	14.3	33.7	23.6
35.5	260	34.0	11.03	34.1	14.14	36.0	97.3	34.0	21.4	35.7	74.7
37.0	670	35.4	25.1	35.0	22.5	37.0	184.6	35.5	46.6	37.1	204
38.0	1256	36.4	51.1	36.3	46.9	38.0	350	36.6	93.2	38.1	400
39.5	2340	37.8	170	37.7	125.6	39.0	586	37.6	181.3	39.0	678
40.5	3420	39.5	626	39.4	396	41.7	1616	38.5	315	40.0	1090
41.6	4750	40.5	1160	40.5	750	42.7	2310	39.6	560	41.0	1677
42.9	6630	42.6	2870	41.7	1345	44.0	3580	40.6	934	43.6	3920
44.1	8210	43.4	3770	43.3	2230	45.2	4600	42.0	1630	44.8	5260
		44.4	4980	44.3	3030	46.1	5500	43.0	2300	46.1	6880
				45.3	3920			44.0	3030		

Table 4. Specific Electrical Conductivity κ Values at Different Temperatures for Microemulsions of AOT + Isooctane + Water in the Presence of Dibenzo-24-crown-8 (4)

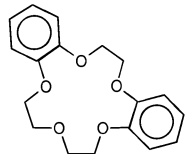
$C_4 =$									
$1.60 \cdot 10^{-4}$ mol·L^{-1}		$2.22 \cdot 10^{-4}$ mol·L^{-1}		$6.43 \cdot 10^{-4}$ mol·L^{-1}		$3.00 \cdot 10^{-3}$ mol·L^{-1}		$6.40 \cdot 10^{-3}$ mol·L^{-1}	
t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
24.0	4.00	24.0	1.78	25.4	2.66	26.0	4.84	27.0	7.13
25.5	4.96	25.6	2.09	26.6	3.18	27.1	5.45	28.0	9.14
26.2	6.10	26.9	2.48	27.5	3.70	28.1	6.28	29.0	12.12
28.0	8.82	28.4	3.19	28.9	5.05	29.0	7.43	30.2	18.94
29.5	13.46	29.8	4.50	30.5	8.17	30.5	10.88	31.0	26.5
31.0	21.4	30.9	6.26	31.5	11.85	32.4	24.3	32.1	47.7
32.0	41.7	32.1	10.18	33.2	29.7	33.1	36.5	33.1	81.3
33.0	80.3	33.1	17.39	34.3	64.4	34.9	139.9	34.0	148.1
34.0	157	34.1	33.6	35.4	143.1	36.3	400	35.0	270
35.0	380	35.3	90.9	36.8	376	37.1	681	36.0	466
36.2	1005	36.3	228	37.8	654	38.1	1090	37.0	710
37.2	1735	37.3	472	39.0	1165	39.3	1922	38.0	1050
39.0	4060	39.2	1393	40.3	1950	41.8	4500	39.0	1500
40.8	6200	40.4	2410	42.0	3390	43.6	6800	40.0	2050
41.9	8460	41.6	3640	43.1	4460			41.0	2870
41.9	8460							42.0	3890

Table 5. Specific Electrical Conductivity κ Values at Different Temperatures for Microemulsions of AOT + Isooctane + Water in the Presence of Dibenzo-30-crown-10 (5)

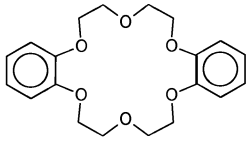
$C_5 =$									
$6.15 \cdot 10^{-4}$ mol·L^{-1}		$8.01 \cdot 10^{-4}$ mol·L^{-1}		$9.13 \cdot 10^{-4}$ mol·L^{-1}		$1.30 \cdot 10^{-3}$ mol·L^{-1}		$4.47 \cdot 10^{-3}$ mol·L^{-1}	
t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
24.0	1.77	26.5	2.50	24.0	0.33	23.0	3.67	24.5	6.81
25.3	1.87	27.4	2.69	25.3	0.36	24.4	3.90	26.0	9.00
26.3	2.00	29.1	3.22	26.3	0.40	25.9	4.39	27.0	10.03
27.9	2.27	30.1	3.75	27.9	0.46	27.3	5.17	28.0	12.00
29.3	2.71	31.7	5.07	29.3	0.58	28.8	6.44	29.0	16.88
30.5	3.31	33.0	6.98	30.5	0.70	30.2	8.48	30.0	25.7
31.7	4.26	34.6	12.05	31.7	0.94	31.5	11.25	31.0	33.8
33.3	6.48	35.4	17.58	33.3	1.57	33.2	19.69	32.1	67.8
35.5	19.02	36.5	31.7	35.5	5.04	34.7	44.7	34.0	208
37.0	47.9	37.7	63.2	37.0	14.99	36.4	130.8	35.5	591
38.5	166.2	38.7	126.7	38.5	50.6	38.0	463	36.5	1091
40.0	651	39.8	298	40.0	133.2	39.6	1365	37.6	1880
42.0	2120	40.8	511	42.0	341	41.5	3080	39.0	3690
43.5	3300	42.6	1141	43.5	520	42.5	4500	40.8	5560
45.0	5500	43.8	1815	45.0	780	44.0	6480		
46.0	7030	44.8	2670	46.0	946				

conductivity is related to the increase in the mass interchange between water droplets present 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.

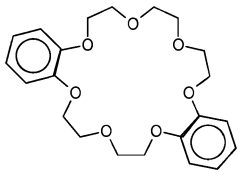
Figure 2 shows the values obtained for the electrical conductivity of AOT + 2,2,4-trimethylpentane + water mixtures in the absence and presence of different quantities of dibenzo-15-crown-5. In Figure 2, it is possible to observe that a clear change in the slope of electrical conductivity/temperature data



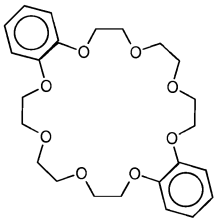
DB15C5
Dibenzo[b,h][1,4,7,10,13]pentaoxacyclopentadecin,
6,7,9,10,17,18-hexahydro- (8CI,9CI)



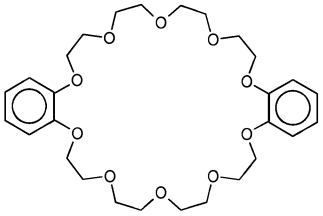
DB18C6
Dibenzo[b,k][1,4,7,10,13,16]hexaoxacyclooctadecin,
6,7,9,10,17,18,20,21-octahydro- (8CI,9CI)



DB21C7
Dibenzo[b,k][1,4,7,10,13,16,19]heptaoxacycloheneicosin,
6,7,9,10,12,13,20,21,23,24-decahydro- (8CI,9CI)



DB24C8
Dibenz[b,n][1,4,7,10,13,16,19,22]octaoxacyclotetracosin,
6,7,9,10,12,13,20,21,23,24,26,27-dodecahydro- (8CI,9CI)



DB30C10
Dibenzo[b,q][1,4,7,10,13,16,19,22,25,28]decaoxacyclotriacontin,
6,7,9,10,12,13,15,16,23,24,26,27,29,30,32,33-hexadecahydro- (8CI,9CI)

Figure 1. Structures of the dibenzo crown ethers employed in this study.

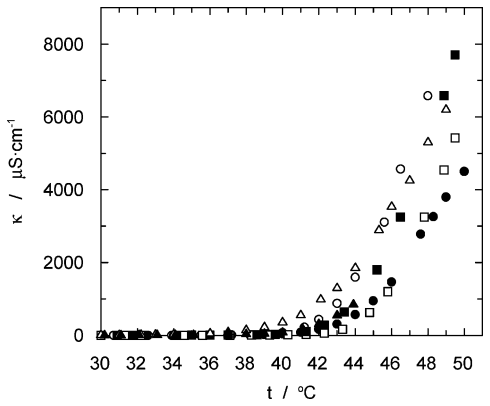


Figure 2. Influence of temperature upon electrical conductivity AOT + 2,2,4-trimethylpentane + water + PTC mixtures at different concentration of DB15-C-5. ○, $C_{DB15-C-5} = 2.69 \cdot 10^{-3}$ mol·L^{-1}; ●, $C_{DB15-C-5} = 5.70 \cdot 10^{-3}$ mol·L^{-1}; □, $C_{DB15-C-5} = 1.33 \cdot 10^{-2}$ mol·L^{-1}; ■, $C_{DB15-C-5} = 2.00 \cdot 10^{-2}$ mol·L^{-1}; △, $C_{DB15-C-5} = 3.21 \cdot 10^{-2}$ mol·L^{-1}; ▲, $C_{DB15-C-5} = 2.53 \cdot 10^{-2}$ mol·L^{-1}.

exists that corresponds to the percolation threshold and is affected by the presence of PTCs. Table 6 shows the value determined for percolation temperature corresponding to different PTCs nature and concentration.

Our research group has studied the effect produced upon electrical conductivity behavior by the presence of different PTCs such as cryptand complexes[5] and, crown and benzo crown ethers.[6,7] All cases have shown similar behavior to that observed in this paper. In previous studies in respect to electrical conductivity of water in oil microemulsions, an empirical correlation with three adjustable parameters was developed. This correlation allows fitting the experimental electrical conductivity/temperature data for this kind of system with results suitable for a great number of data.[10−12] This correlation (three-term equation, TTE) has been applied with good results to numerous microemulsions modified with different additives such as amines, ureas, salts, etc, with the conclusion that the *A* parameter of eq 1 corresponds to the value of the percolation temperature. This conclusion was reached by comparison of the percolation temperature determined by the Kim and Huang method[13] and the values obtained for the *A* parameter by fitting experimental data of electrical conductivity using eq 1:

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

Recently, Hait et al.[14] have 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 conductivity and temperature, respectively; Δt is the constant interval of t; and the i, f, and p subscripts stand for initial, final, and percolation zones, respectively.

A comparison between electrical conductivity/temperature experimental data in relation with the calculated values using the equation developed by our research group and Hait et al.[14] is shown in Figure 3 and in Table 6. Figure 3 indicates that there is an acceptable correlation between these two equations and experimental data for the systems studied in this paper.

Regarding the variations found in the value of the percolation temperature, in all cases, we observed an increase in the

Table 6. Temperature of Percolation for AOT + Isooctane + Water Microemulsions in the Presence of Different Quantities of DBCEs Obtained by Kim and Huang Method (KH) and Fitting Parameters from Equations 1 (TTE) and 2 (SBE)

C_{DBCE}/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)
			Dibenzo-15-crown-5			
0.0027	35.8	36.1	2.5	39.5	0.11	−23.8
0.0057	36.8	36.3	2.7	40.0	0.15	−37.1
0.0133	35.1	35.2	2.0	42.0	0.10	−26.6
0.0200	32.1	32.0	−0.9	40.2	0.11	−31.8
0.0253	31.6	31.5	−2.1	38.0	0.18	−60.1
0.0321	28.5	28.0	−5.6	36.0	0.22	−43.3
			Dibenzo-18-crown-6			
0.0004	33.8	34.0	0.4	34.3	0.04	−2.8
0.0027	36.5	37.0	3.4	37.0	0.02	−6.3
0.0057	39.4	39.5	5.9	41.0	0.02	−14.4
0.0073	39.3	38.1	4.5	39.9	0.04	−11.1
0.0115	35.8	35.5	1.9	36.1	0.04	−6.4
0.0125	35.1	34.9	1.3	35.0	0.04	−5.3
0.0143	31.7	31.5	−2.1	32.1	0.03	−5.4
			Dibenzo-21-crown-7			
0.0001	33.9	34.0	0.4	33.3	0.14	−30.9
0.0002	34.1	34.2	0.6	35.7	0.17	−29.3
0.0006	35.5	35.7	2.1	35.6	0.16	−34.4
0.0012	34.5	35.1	1.5	34.7	0.16	−25.2
0.0021	34.1	34.3	0.7	35.0	0.13	−19.3
0.0054	33.4	32.1	−0.4	34.8	0.12	−19.9
			Dibenzo-24-crown-8			
0.0003	34.1	35.2	1.6	32.5	0.10	−37.2
0.0008	35.5	35.9	2.3	33.9	0.14	−18.1
0.0010	34.5	35.0	1.4	33.5	0.15	−23.1
0.0030	33.4	33.3	−0.3	33.8	0.12	−38.4
0.0006	33.4	32.9	−0.7	32.3	0.16	−44.4
			Dibenzo-30-crown-10			
0.0006	33.6	34.1	0.5	36.8	0.11	−21.7
0.0008	33.4	33.4	−0.2	36.6	0.17	−25.9
0.0009	33.1	33.2	−0.4	35.8	0.34	−31.9
0.00130	32.6	32.5	−1.1	35.3	0.11	−44.0
0.0045	30.3	30.1	−3.5	32.2	0.12	−57.1

percolation temperature of the system as the dibenzo crown ether concentration increased until a maximum value was reached, from which the percolation temperature then decreased. Thus, at high crown ether concentrations the percolation temperature is significantly lower than that observed for the microemulsions without additive. Figure 4 shows the behavior observed in the presence of one dibenzo crown ether. Like other PTCs previously studied (crown ethers, benzo 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 due to (i) their capacity to sequester ions,[15] transport them through the interface,[16] and solubilize them in apolar phases and (ii) their ability to associate at the surfactant film, as shown in studies carried out on "normal" micelles.

As we observed for other PTCs,[5−7] low additive concentrations hinder the electric percolation phenomena, but medium and high concentrations favor the percolation. At moderate concentrations, they behave similarly to electrolytes.[17−19] The temperature of percolation increases with the concentration of DBCE. This effect of electrolytes is one of the most widely documented[17−19] and can be justified by taking into account the complexing ability of the DBCEs with respect to the Na^+ counterion of the AOT ions and their transfer to the AOT film and the continuous phase (2,2,4-trimethylpentane).

At moderate and high concentration of the DBCEs, 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 a similar reasoning to that

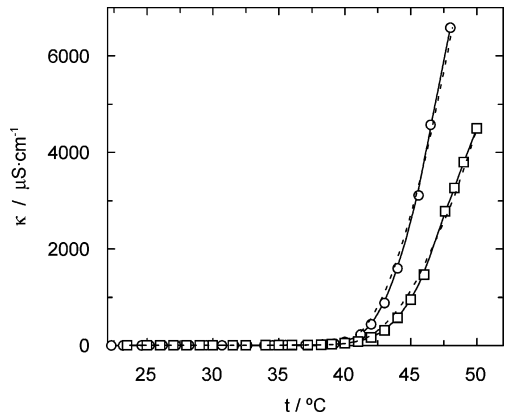


Figure 3. Experimental and calculated data of electrical conductivity for ○, $C_{DB15-C-5} = 2.69 \cdot 10^{-3}$ mol·L^{-1}; □, $C_{DB15-C-5} = 5.70 \cdot 10^{-3}$ mol·L^{-1}. —, SBE; - - -, TTE.

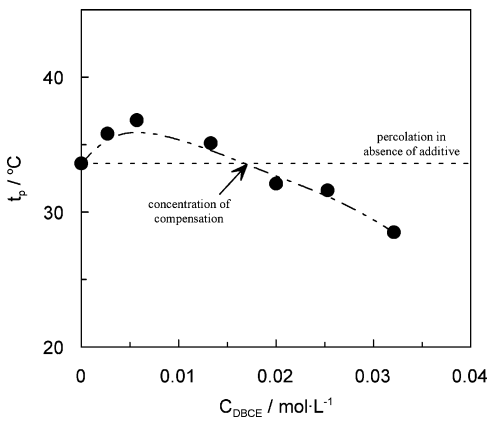


Figure 4. Effect of dibenzo crown ethers upon the percolation temperature (t_p) for AOT + isooctane + water microemulsions. ●, DB15C5.

used in the literature[20] to explain the behavior of other organic substances.

On the other hand, we can estimate the concentration of DBCE, which has a temperature of percolation that is the same as without additive. In this case, the two different effects, the ability of crown ethers to bind Na^+ and their organic nature, are compensated.

Conclusions

The experimental results presented in this study indicate that the effect caused by dibenzo crown ethers are similar to those previously studied for other PTCs. Thus, the increased percolation temperature observed at low concentrations of the dibenzo crown ethers studied could be due to counterions sequestered by the PTC while the effect observed on addition of high concentrations of these substances to the microemulsions was a decrease in the percolation temperature. Also, the equations employed in this study (TTE and SBE) allow calculation of values of electrical conductivity for this kind of complex mixtures with good agreement with experimental results.

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