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Effect of Temperature on the Electrical Conductivity of Sodium Bis(2-ethylhexyl)sulfosuccinate + 2,2,4-Trimethylpentane + Water Microemulsions. Influence of Alkylamines

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The effect of the presence of alkylamines (*n*-propylamine, *n*-butylamine, *n*-pentylamine, *n*-octylamine, *n*-decylamine, *n*-laurylamine, *i*-butylamine, *i*-pentylamine, neopentylamine, *sec*-butylamine, *tert*-butylamine, methyl-*n*-octylamine, dimethylamine, dipropylamine, di-*i*-butylamine, dimethyl-*n*-laurylamine, dimethyl-*n*-octylamine, triethylamine, triethylamine, and diethylmethylamine) on the variation of electrical conductivity with the temperature of the ternary systems sodium bis(2-ethylhexyl)sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water has been studied. Also, the effect of other amines (*N*-methylbenzylamine, dibenzylamine, diphenylamine, morpholine, piperazine, piperidine, and pyrrolidine) on the variation of electrical conductivity with the temperature of these ternary systems has been studied.

Introduction

Microemulsions are transparent isotropic dispersions of an immiscible organic compound in water in the presence of a surfactant (Pileni, 1989). They are thermodynamically stable, and they have been described as consisting of spherical droplets of a disperse phase separated from a continuous phase by a film of surfactant (Pileni, 1989). Microemulsions present a great interest from the point of view of the chemical industry due to the fact that they have great potential as solubilizers and nanoreactors (Mittal, 1977; Elworthy et al., 1968; García-Río et al. 1995, 1996), permitting an important number of industrial applications (Rieger, 1977; Datyner, 1983; Kuhn, 1963). In the present work will be studied microemulsions formed by ternary mixtures of sodium bis(2-ethylhexyl)sulfosuccinate + 2,2,4-trimethylpentane + water. In normal conditions and at room temperature, a microemulsion has a very low electrical conductivity (0.01 to 0.1 $\mu\text{S}\cdot\text{cm}^{-1}$), which is already a significant increase if compared to the electrical conductivity of pure 2,2,4-trimethylpentane (electrical conductivity of alkanes $\sim 10^{-8}$ to 10^{-3} $\mu\text{S}\cdot\text{cm}^{-1}$) and is due to the fact that these ternary systems carry charges. Increasing the temperature, the electrical conductivity of these systems increases gradually at a particular temperature from which there is a marked increase in the variation of the electrical conductivity with temperature (see Figure 1). This phenomenon is known as electrical percolation, and the temperature at which this occurs is known as the threshold of percolation or the temperature of percolation. The values of the threshold of percolation can be modified by small quantities of additives (Mathew et al., 1988).

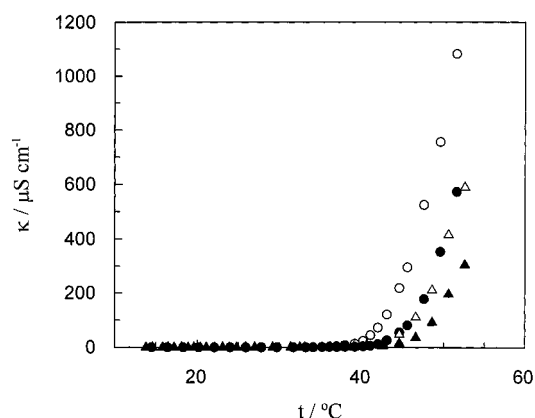


Figure 1. Influence of temperature upon the conductivity of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions in the presence of different linear alkylamines ([additive] = 0.01 mol dm⁻³, [AOT] = 0.5 mol dm⁻³, *w* = [H₂O]/[AOT] = 22.2): (○) *n*-propylamine; (●) *n*-butylamine; (Δ) *n*-pentylamine; (▲) *n*-octylamine.

In the literature the effect of long chain substrates added to a microemulsion as cosurfactants has been reported (Hou et al., 1988; Giamma et al., 1992). The effects of long chain alcohols upon the percolation phenomenon and upon the structure of microemulsions are quite interesting. Hou et al. (1988) concluded that the radius of the microdroplet increases linearly with water content and that the cosurfactants increased or decreased interactions between droplets according to their structure. They made the distinction between short chain and long chain alcohols: the former increase interactions, while the latter decrease them. A decrease in interactions was also noticed for Arlacel (a long chain nonionic surfactant) (Nazario et al., 1996). When decanol is added to the system, the resulting microemulsion has a higher percolation temperature (Nazario et al., 1996), and at higher concentration of alcohol, larger effects on percolation temperature were observed. In view of the

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Table 1. Specific Conductivity Values at Different Temperatures of Sodium Bis(2-ethylhexyl)sulfosuccinate (AOT) + 2,2,4-Trimethylpentane + Water Microemulsions in the Presence of Amines ([additive] = 0.01 mol dm⁻³, [AOT] = 0.5 mol dm⁻³, *w* = [H₂O]/[AOT] = 22.2)

dimethylamine								<i>n</i> -pentylamine				methyl- <i>n</i> -octylamine			
<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$
4.5	0.46	15.7	0.52	24.6	0.73	35.6	28.70	13.8	0.69	27	0.90	15.8	0.63	36.6	2.21
5.1	0.47	16.1	0.53	25.1	0.78	36.1	38.00	14.6	0.69	29.2	1.00	17.6	0.66	37.6	2.82
6.6	0.48	16.6	0.53	26.1	0.87	36.6	52.70	15.8	0.69	31.4	1.15	19.6	0.69	38.6	3.82
7.8	0.48	17.5	0.53	26.6	0.89	37.1	69.70	16.5	0.69	32.5	1.29	21.6	0.71	39.6	5.07
8.3	0.48	18.1	0.54	27.1	0.93	37.6	89.00	17.2	0.69	33.1	1.42	23.6	0.77	41.1	9.47
9.4	0.48	18.6	0.56	27.6	1.07	38.1	111.90	18.1	0.70	36.2	2.14	25.6	0.83	42.6	15.30
10.1	0.49	19.1	0.56	28.1	1.11	38.6	140.00	18.9	0.70	37.6	3.25	27.6	0.90	44.6	46.50
10.8	0.49	19.6	0.56	28.6	1.18	39.1	165.00	19.6	0.71	39.1	4.27	29.6	1.02	46.6	89.60
11.3	0.50	20.1	0.58	29.1	1.28	39.6	197.10	20.4	0.73	40.6	7.50	31.6	1.23	48.6	226.00
12.1	0.50	21.1	0.59	29.6	1.40	40.1	232.00	21.1	0.74	42.6	15.25	33.6	1.51	50.6	415.00
12.6	0.50	21.6	0.60	30.1	1.59	40.6	268.00	22.1	0.76	44.6	48.00	35.6	1.99		
13.2	0.51	22.1	0.61	30.6	1.90	41.1	306.00	23.1	0.79	46.6	111.60				
13.6	0.51	22.6	0.63	31.6	2.79	41.6	333.00	23.9	0.80	48.6	211.00				
14.2	0.51	23.1	0.65	32.6	4.82	42.1	366.00	24.8	0.83	50.6	416.00				
14.6	0.52	23.6	0.69	33.6	8.36	42.6	406.00	25.9	0.87	52.6	590.00				
15.2	0.52	24.1	0.70	34.6	15.20	43.1	461.00								

diethylmethylamine				trimethylamine				<i>n</i> -butylamine				<i>n</i> -propylamine			
<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$
16.2	0.57	32.6	5.27	16.2	0.58	32.6	4.60	14.5	0.59	36.1	1.65	14.5	0.60	36.1	3.13
17.6	0.59	33.9	7.10	17.6	0.60	33.9	6.34	16.4	0.60	37.0	1.96	16.4	0.62	37.0	4.46
19.1	0.62	35.6	30.40	19.1	0.62	35.6	28.20	18.3	0.62	38.0	2.75	18.3	0.63	38.0	8.38
20.6	0.64	37.1	70.10	20.6	0.65	37.1	67.70	20.2	0.64	39.2	3.40	20.2	0.67	39.2	13.97
22.1	0.70	38.6	137.70	22.1	0.69	38.6	137.10	22.1	0.67	40.2	4.62	22.1	0.70	40.2	24.00
23.6	0.78	40.6	291.00	23.6	0.77	40.6	274.00	24.0	0.70	41.1	6.65	24.0	0.75	41.1	45.40
25.1	0.88	42.6	433.00	25.1	0.84	42.6	410.00	25.9	0.74	42.0	12.60	25.9	0.81	42	73.40
26.6	1.04	44.6	723.00	26.6	0.99	44.6	674.00	27.8	0.78	43.1	26.90	27.8	0.88	43.1	122.00
28.1	1.31	47.6	1109.00	28.1	1.21	47.6	1179.00	29.7	0.87	44.6	56.20	29.7	1.02	44.6	219.00
29.6	1.74	49.3	1375.00	29.6	1.64	49.3	1396.00	31.7	0.99	45.6	81.10	31.7	1.24	45.6	296.00
31.1	2.45			31.1	2.33			33.2	1.15	47.6	178.80	33.2	1.57	47.6	526.00
								34.1	1.26	49.6	354.00	34.1	1.79	49.6	757.00
								35.2	1.48	51.6	574.00	35.2	2.56	51.6	1083.00

dibenzylamine				<i>n</i> -octylamine				dipropylamine				neopentylamine			
<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$
20.0	0.66	33.6	5.94	13.8	0.70	27.0	0.84	20.0	0.72	33.6	3.49	19.7	0.68	32.6	1.88
21.6	0.71	34.6	9.09	14.6	0.70	29.2	0.91	21.6	0.77	34.6	5.81	20.6	0.68	34.1	2.9
23.6	0.77	35.6	15.22	15.8	0.70	31.4	1.02	23.6	0.83	35.6	8.60	22.1	0.72	35.6	4.69
25.1	0.85	36.6	25.00	16.5	0.70	32.5	1.11	25.1	0.91	36.6	12.15	23.6	0.76	37.6	11.00
26.6	0.94	37.6	50.10	17.2	0.70	33.1	1.19	26.6	1.01	37.6	25.10	24.6	0.8	39.6	23.10
28.1	1.18	38.6	81.60	18.1	0.70	36.2	1.59	28.1	1.21	38.6	39.90	25.6	0.86	41.6	77.00
29.6	1.53	40.6	183.50	18.9	0.70	37.6	2.02	29.6	1.50	40.6	105.60	26.6	0.9	43.6	176.00
30.6	1.76	42.6	340.00	19.6	0.70	39.1	2.49	30.6	1.68	42.6	220.00	27.6	0.98	45.1	280.00
31.6	2.40	45.1	539.00	20.4	0.71	40.6	3.87	31.6	2.09	45.1	380.00	28.6	1.11	46.6	420.00
32.6	3.60			21.1	0.72	42.6	6.30	32.6	2.52			29.6	1.23	48.6	660.00
				22.1	0.73	44.6	15.45					30.6	1.36	49.6	836.00
				23.1	0.75	46.6	36.70					31.6	1.56		
				23.9	0.77	48.6	92.30								
				24.8	0.79	50.6	197.00								
				25.9	0.81	52.6	305.00								

<i>tert</i> -butylamine				<i>n</i> -decylamine				<i>n</i> -laurylamine				<i>sec</i> -butylamine			
<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	<i>t</i> /°C	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$
19.7	0.76	32.6	1.79	22.1	0.75	38.1	1.55	22.1	0.71	40.1	1.97	10.5	0.65	24.2	2.05
20.6	0.77	34.1	2.39	23.1	0.75	39.1	1.63	23.1	0.73	41.2	2.41	12.2	0.66	26.2	3.71
22.1	0.80	35.6	3.55	24.2	0.76	40.1	1.95	24.2	0.79	42.2	3.14	14.2	0.73	27.7	5.21
23.6	0.83	37.6	7.11	25.6	0.78	41.2	2.39	25.6	0.81	43.1	3.89	15.7	0.78	29.2	9.70
24.6	0.89	39.6	12.80	27.6	0.80	42.2	3.09	27.6	0.83	44.6	6.04	17.2	0.85	30.7	18.30
25.6	0.93	41.6	44.20	29.1	0.86	43.1	3.76	29.1	0.90	46.6	11.70	18.7	0.97	32.2	46.50
26.6	0.96	43.6	110.00	30.1	0.90	44.6	5.68	30.1	0.93	49.6	40.20	19.7	1.06	34.2	124.00
27.6	1.01	45.1	172.00	31.1	0.94	46.6	10.83	31.1	0.97	51.6	121.20	21.2	1.22	36.2	232.00
28.6	1.12	46.6	270.00	32.6	0.99	49.6	40.60	32.6	1.03	52.2	157.00	22.7	1.57	38.2	398.00
29.6	1.21	48.6	476.00	33.6	1.04	51.6	128.20	33.6	1.10	52.9	206.00				
30.6	1.32	49.6	652.00	34.6	1.16	54.6	360.00	34.6	1.17	53.3	239.00				
31.6	1.51			35.6	1.23	55.9	596.00	35.6	1.22	54.1	318.00				
				36.4	1.30	56.8	853.00	36.4	1.30	54.6	353.00				
				37.4	1.48			37.4	1.44	55.1	433.00				
								38.1	1.54	55.64	548.00				
								39.1	1.74	56.2	653.00				

Table 1 (Continued)

di- <i>i</i> -butylamine				<i>i</i> -pentylamine				<i>i</i> -butylamine				diphenylamine			
$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$
17.9	0.68	31.6	3.98	17.6	0.64	33.7	1.60	17.6	0.68	33.7	2.41	14.4	0.59	31.6	2.28
19.6	0.69	33.6	11.34	19.6	0.67	34.6	1.93	19.6	0.70	34.6	3.04	15.6	0.59	32.6	3.10
21.6	0.76	35.1	35.40	21.6	0.71	36.1	2.63	21.6	0.74	36.1	5.03	17.6	0.60	33.6	4.40
23.1	0.83	36.6	73.30	23.1	0.74	37.6	3.79	23.1	0.79	37.6	9.62	19.6	0.63	34.6	7.60
24.6	0.93	38.1	148.00	24.6	0.77	38.1	4.31	24.6	0.83	38.1	12.32	21.1	0.66	35.6	15.00
26.1	1.13	39.6	230.00	26.1	0.84	39.1	5.42	26.1	0.91	39.1	19.70	22.6	0.70	36.6	29.00
27.1	1.31	41.6	420.00	27.1	0.90	40.6	9.08	27.1	1.00	40.6	40.90	24.1	0.77	38.6	76.40
28.6	1.62	43.6	610.00	28.0	0.96	41.6	13.73	28.0	1.08	41.6	70.20	25.6	0.81	40.6	187.00
30.1	2.53	45.6	850.00	29.1	1.05	43.2	27.80	29.1	1.24	43.2	128.40	27.1	1.03	42.6	329.00
				30.1	1.13	44.1	57.00	30.1	1.38	45.6	213.00	28.6	1.18	44.6	555.00
				31.1	1.25	45.6	138.70	31.1	1.59	47.6	372.00	29.6	1.43	46.6	864.00
				32.0	1.35	47.6	354.00	32.0	1.80	50.6	654.00	30.6	1.74		
				33.1	1.49	50.6	709.00	33.1	2.13	51.9	930.00				

triethylamine				dimethyl- <i>n</i> -laurylamine				dimethyl- <i>n</i> -octylamine				<i>N</i> -methylbenzylamine			
$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$
14.4	0.59	31.6	2.64	22.6	0.77	33.6	6.22	22.6	0.80	33.6	5.37	18.2	0.33	33.1	7.80
15.6	0.59	32.6	3.52	24.6	0.82	34.6	11.27	24.6	0.86	34.6	9.15	19.2	0.34	34.8	21.00
17.6	0.60	33.6	5.48	26.1	0.92	35.6	21.10	26.1	0.96	35.6	17.70	21.9	0.43	36.4	37.00
19.6	0.63	34.6	10.66	26.6	0.96	37.6	66.40	26.6	0.99	37.6	53.50	23.7	0.52	38.1	70.00
21.1	0.66	35.6	22.80	27.6	1.07	39.6	160.40	27.6	1.09	39.6	130.10	26.2	0.67	39.6	127.00
22.6	0.69	36.6	43.20	29.1	1.36	41.6	285.00	29.1	1.37	41.6	236.00	28.3	1.19	40.9	197.00
24.1	0.77	38.6	128.00	30.5	1.75	43.6	459.00	30.5	1.71	43.6	432.00	29.8	1.85	42.8	313.00
25.6	0.81	40.6	260.00	31.1	2.27	45.6	755.00	31.1	2.18	45.6	679.00	31.2	3.20	44.4	438.00
27.1	1.02	42.6	429.00	32.6	3.44			32.6	3.19						
28.6	1.20	44.6	682.00												
29.6	1.49	46.6	938.00												
30.6	1.88														

morpholine				piperazine				piperidine				pyrrolidine			
$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$t/^{\circ}\text{C}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$
17.4	0.22	35.5	32.50	14.9	0.22	33.5	6.80	8.2	0.27	32.2	3.34	12.0	0.30	28.0	1.39
18.5	0.23	36.1	48.10	16.3	0.27	34.8	17.70	9.6	0.31	33.9	5.90	15.0	0.35	30.1	2.16
19.6	0.25	37.3	91.00	18.2	0.29	36.1	40.00	11.5	0.34	35.0	9.60	16.8	0.41	32.4	4.20
21.1	0.27	38.4	151.00	20.4	0.32	37.2	79.00	13.1	0.41	36.7	19.90	18.9	0.49	34.6	8.10
22.9	0.28	39.2	198.00	21.9	0.35	38.3	130.00	15.2	0.46	38.6	42.00	21.1	0.56	36.8	26.00
25.3	0.36	40.4	281.00	24.0	0.40	39.0	174.00	17.0	0.51	40.1	72.00	22.1	0.61	38.9	66.00
26.7	0.44	41.4	385.00	25.6	0.47	40.2	291.00	18.7	0.57	42.2	143.00	23.6	0.74	41.0	154.00
28.4	0.58	43.0	555.00	27.4	0.60	41.6	431.00	20.6	0.65	43.1	194.00	26.0	1.02	42.0	215.00
30.6	0.95	43.9	661.00	28.9	0.72	42.8	585.00	21.6	0.69	44.9	318.00				
32.4	2.10	45.1	832.00	30.7	1.45	44.2	790.00	22.6	0.73	46.0	445.00				
34.3	10.40	47.3	1151.00	32.1	2.80	45.6	1021.00	24.5	0.91	48.0	793.00				
								26.7	1.16	49.8	1110.00				
								29.1	1.66	51.2	1410.00				
								30.9	2.43	52.5	1740.00				

percolation temperatures, long chain alcohols make the interface more rigid and hence aggregation occurs, and consequently percolation is more difficult.

On the other hand, the presence of amines in these ternary systems generates a great interest owing to the important number of chemical processes in which they are involved. In particular, commercial processes for the removal of CO_2 or H_2S from industrial gaseous streams involve the use of amines (Hagewiesche et al., 1995), and the reactions between CO_2 and aqueous solutions of alkanolamines are frequently used in the absorption processes (Oyervaar et al., 1990).

The aim of this work is to measure the electrical conductivity (κ) of these ternary systems with different amines at different temperatures. These measurements allow us to determine the temperature of percolation.

Experimental Section

The aqueous solutions of amines were prepared with distilled-deionized water ($\kappa = 0.10\text{--}0.50 \mu\text{S}/\text{cm}$). All the materials were supplied by Merck and Sigma, having the maximum purity commercially available (>99%). The amines were previously distilled under argon.

All the solutions were prepared by mass with deviations of less than $\pm 0.2\%$ from the desired concentrations. In all of the cases, the amine concentrations have been referred to the total volume of the microemulsion, due to the solubility of the amines. They will not be restricted to the water microdroplet and can be present in the three pseudophases of the system (water, surfactant film, and 2,2,4-trimethylpentane). The solutions (microemulsion + additive) were prepared by direct mixing under vigorous stirring.

The electrical conductivity (κ) was measured with a radiometer CDM 3 conductivity meter with an electrical conductivity cell with a constant of 1 cm^{-1} . The conductivity meter was calibrated using a $0.01 \text{ mol}\cdot\text{dm}^{-3}$ KCl solution. The inaccuracy of these measurements was $\pm 0.5\%$. During the measurements of electrical conductivity, the temperature was regulated using a thermostat-cryostat with a precision of $\pm 0.1^{\circ}\text{C}$. The container with the sample was immersed in the 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

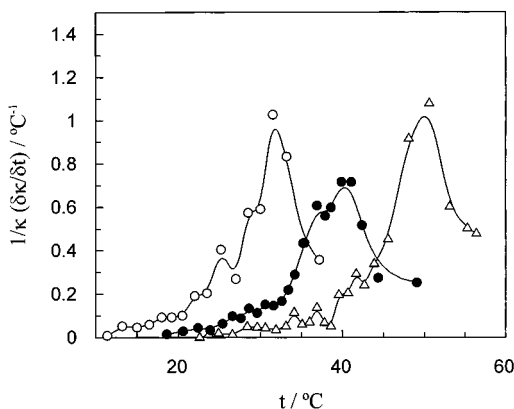


Figure 2. Determination of percolation temperature obtained by the Kim method (Kim and Huang, 1986) for sodium bis(2-ethylhexyl)sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions in the presence of different amines ([additive] = 0.01 mol dm⁻³, [AOT] = 0.5 mol dm⁻³, $w = [\text{H}_2\text{O}]/[\text{AOT}] = 22.2$): (○) *sec*-butylamine; (●) *i*-butylamine; (△) *n*-decylamine.

<1.5%. The percolation temperature was determined from the variation of the specific conductivity with the temperature.

Results and Discussion

The effect of the nature of the additive on the process of electric percolation has been studied (Figure 1). A series of electrical conductivity/temperature data for a group of amines were measured. In these experiments the amine concentration was 0.01 mol dm⁻³, the composition of the microemulsion was [AOT] = 0.5 mol dm⁻³, and $w = [\text{water}]/[\text{AOT}] = 22.2$.

The values of the specific conductivity–temperature, obtained for different additives are shown in Table 1. The temperatures of percolation t_p (listed in Table 2) were obtained using the method described elsewhere (Álvarez et al., 1998a) (Figure 2).

The amines studied are listed in Table 2. *n*-Alkylamines increase the temperature of percolation, and this increase is correlated with the length of the alkyl chain (Figure 3). The presence of substituents in the alkyl chain decreases the effect observed on the percolation behavior as compared with that for linear *n*-alkylamines (viz. *n*-butylamine > *i*-pentylamine and di-*n*-propylamine > di-*i*-butylamine). On the other hand, the presence of different substituents on the nitrogen atom decreases the effect on the temperature of percolation as compared with the effect observed for *n*-alkylamines (viz. *n*-octylamine > methyl-*n*-octylamine > dimethyl-*n*-octylamine and *n*-dodecylamine > dimethyl-*n*-dodecylamine).

Most of the amines increase the temperature of percolation, whereas morpholine and *sec*-butylamine decrease the temperature of percolation. This behavior would be justified by their capacity of association to the surfactant film (García-Río et al., 1993). Morpholine association to the surfactant film favors the formation of structures with positive curvature, facilitating the mass exchange between droplets. An analogous explanation can be assumed for *sec*-butylamine. The apparently contradictory behavior of others amines (they increase t_p) corresponds with the partial dissociation of amine into ammonium and hydroxide ions (García-Río et al., 1994). It is well-known that the presence of electrolytes in the microemulsions increases the temperature of percolation (Álvarez et al., 1998b, 1999a, and 1999b).

Table 2. Fitting Parameters (Eq 1) and Percolation Temperature t_p Obtained by the Kim Method (Kim and Huang, 1986) for Sodium Bis(2-ethylhexyl)sulfosuccinate (AOT) + 2,2,4-Trimethylpentane + Water Microemulsions ([AOT] = 0.5 mol dm⁻³, $w = [\text{H}_2\text{O}]/[\text{AOT}] = 22.2$)

additive	[additive]/ mol dm ⁻³	A	B	C	$t_p/^\circ\text{C}$
none ^a		32.60	0.39	-3.30	33.0
methylbenzylamine	0.01	32.21	0.61	-4.62	34.0
methylbenzylamine ^a	0.04	33.80	0.62	-4.63	35.0
trimethylamine	0.01	34.58	0.38	-9.50	34.8
<i>i</i> -butylamine	0.01	38.07	0.47	-12.42	40.5
diethylmethylamine	0.01	34.21	0.40	-9.32	35.0
<i>sec</i> -butylamine	0.01	30.02	0.45	-11.37	31.5
<i>n</i> -propylamine	0.01	39.87	0.34	-13.10	40.7
<i>n</i> -butylamine	0.01	43.29	0.30	-14.66	43.0
<i>tert</i> -butylamine	0.01	39.55	0.41	-13.75	40.6
triethylamine	0.01	35.19	0.36	-10.13	35.2
dimethylamine	0.01	35.04	0.34	-9.95	35.1
dimethylamine ^a	0.04	36.90	0.46	-5.05	38.0
dipropylamine	0.01	35.97	0.46	-10.83	37.1
dibenzylamine	0.01	35.65	0.44	-9.02	37.0
diphenylamine	0.01	34.83	0.36	-10.59	35.1
di- <i>i</i> -butylamine	0.01	33.37	0.41	-9.44	34.4
dimethyl- <i>n</i> -laurylamine	0.01	34.73	0.42	-8.20	36.6
dimethyl- <i>n</i> -octylamine	0.01	34.63	0.43	-8.86	36.5
<i>i</i> -pentylamine	0.01	41.52	0.34	-14.02	41.7
methyl- <i>n</i> -octylamine	0.01	42.68	0.39	-15.55	43.6
morpholine	0.01	33.66	0.40	-3.42	33.4
morpholine ^a	0.04	30.16	0.42	-3.47	31.0
<i>n</i> -decylamine	0.01	48.33	0.30	-17.41	50.5
neopentylamine	0.01	38.07	0.41	-11.49	40.6
<i>n</i> -laurylamine	0.01	48.42	0.32	-17.61	50.6
<i>n</i> -octylamine	0.01	49.82	0.27	-19.34	47.6
<i>n</i> -pentylamine	0.01	43.42	0.34	-17.61	43.6
piperazine	0.01	33.76	0.38	-4.33	34.2
piperazine ^a	0.04	35.80	0.44	-4.08	36.0
piperidine	0.01	34.26	0.48	-8.16	35.8
piperidine ^a	0.04	40.62	0.75	-8.93	43.0
pyrrolidine	0.01	33.72	0.71	-6.48	35.7
pyrrolidine ^a	0.04	39.86	0.71	-6.62	42.0

^a Álvarez et al., 1998c.

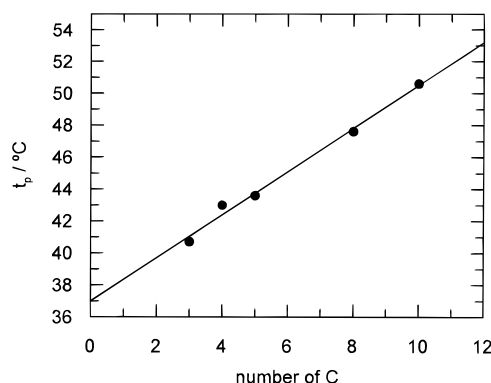


Figure 3. Relationship between the length of the hydrocarbon chain of *n*-alkylamines and the temperature of percolation of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions ([additive] = 0.01 mol dm⁻³, [AOT] = 0.5 mol dm⁻³, $w = [\text{H}_2\text{O}]/[\text{AOT}] = 22.2$).

The variation of electrical conductivity with temperature can be expressed by an empirical equation (Álvarez et al. 1998b):

$$t = A + B\sqrt{\kappa} + \frac{C}{\kappa} \quad (1)$$

The fit of κ/t values was satisfactory (Figure 4) in all the cases studied, and the parameters A , B , and C are given in Table 2. The deviations of A , B , and C obtained from

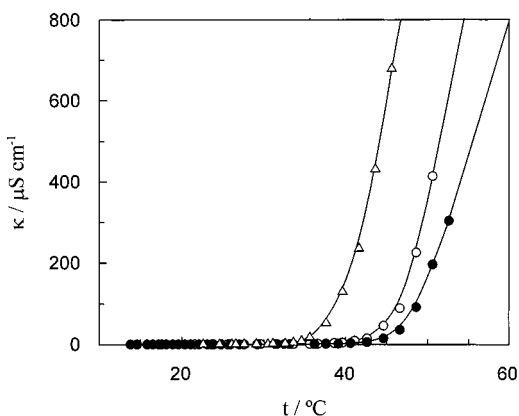


Figure 4. Fit of temperature–conductivity of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions in the absence and in the presence of amines ([additive] = 0.01 mol dm⁻³, [AOT] = 0.5 mol dm⁻³, $w = [\text{H}_2\text{O}]/[\text{AOT}] = 22.2$): (○) methyl-*n*-octylamine; (●) *n*-octylamine; (Δ) dimethyl-*n*-octylamine.

the fit program were always <1%. The value of parameter A corresponds with the temperature of percolation. Small differences were found between the temperatures of percolation calculated by eq 1 and Kim's method; nevertheless, the determination of t_p by Kim's method has a large error (almost ± 1 °C). Taking into account these errors in t_p , the values obtained by eq 1 and Kim's method are compatible.

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