Effects of Temperature on the Conductivity of Sodium Bis(2-ethylhexyl) Sulfosuccinate + 2,2,4-Trimethylpentane + Water Microemulsions. Influence of Sodium Salts

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The effect of temperature on the conductivity of the ternary systems sodium bis(2-ethylhexyl) sulfosuccinate + 2,2,4-trimethylpentane + water has been studied. Also the effect exercised by the presence of sodium salts—NaCl, NaBr, NaI, $NaNO_3$, $NaClO_4$, NaSCN, and Na_2SO_4—on the conductivity of these ternary systems has been analyzed.

Introduction

Microemulsions are thermodynamically stable and transparent mixtures of water, oil, and surfactant whose behavior has been extensively studied (Aveyard et al., 1989; Clark et al., 1990; Pileni, 1989; Kahlweit et al., 1990). In this work will be studied the microemulsions formed by sodium bis(2-ethylhexyl) sulfosuccinate + 2,2,4-trimethylpentane + water. These systems are frequently used as solubilizators (Elworthy, 1968; Mittal, 1991) or as chemical nanoreactors (García-Rio et al., 1995, 1996) permitting a important number of industrial applications.

When the temperature increases, the conductivity of these systems increases gradually until a detemined temperature is reached from which a sudden increase of conductivity is produced. This phenomenon, namely electrical percolation, is described in a previous paper (Álvarez et al., 1998a), and the temperature at which it is produced is known as the percolation threshold or as the temperature of percolation.

The temperature of percolation can be modified by small quantities of additives that hinder the appearance of electrical percolation or favor it (Mathew et al., 1988). In previous papers (Álvarez et al., 1998a,b) we have studied the effect of the presence of ureas, thioureas, and secondary amines on the percolation threshold of sodium bis(2-ethylhexyl) sulfosuccinate + 2,2,4-trimethylpentane + water microemulsions.

The objective of this work is to measure the electrical conductivity of ternary systems sodium bis(2-ethylhexyl) sulfosuccinate + 2,2,4-trimethylpentane + water with various sodium salts at different temperatures. From these data we are able to get the temperature at which the electrical percolation is produced. Sodium salts have been selected since the AOT is a anionic surfactant that normally is marketed in the form of sodium salt; therefore, the effects of the anions on the electrical percolation will be studied.

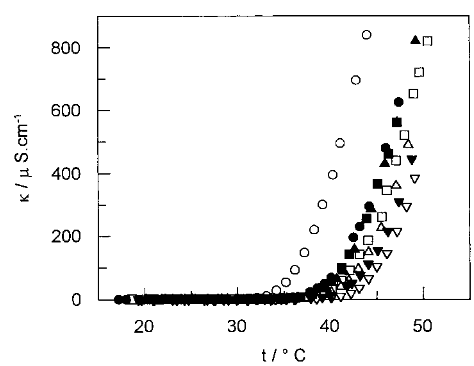

Figure 1. Influence of temperature on the conductivity of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions in the presence of different sodium salts ([AOT] = 0.50 mol·dm^{-3}, [H_2O]/[AOT] = 22.20), (○) without additive, (□) [NaCl] = 0.04 mol·dm^{-3}, (△) [NaBr] = 0.04 mol·dm^{-3}, (▽) [NaI] = 0.04 mol·dm^{-3}, (●) [$NaNO_3$] = 0.04 mol·dm^{-3}, (●) [$NaClO_4$] = 0.04 mol·dm^{-3}, (■) [NaSCN] = 0.04 mol·dm^{-3}, (▲) [Na_2SO_4] = 0.04 mol·dm^{-3}.

Experimental Section

The aqueous solutions of sodium salts—NaCl, NaBr, NaI, $NaNO_3$, $NaClO_4$, NaSCN, and Na_2SO_4—were prepared with

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Table 1. Electrical Conductivity Values at Different Temperatures, without Additive and in the Presence of Different Concentrations of Sodium Salts in Sodium Bis(2-ethylhexyl) Sulfosuccinate (AOT) + 2,2,4-Trimethylpentane + Water Microemulsions

t/°C	$\kappa/\mu S\ cm^{-1}$	t/°C	$\kappa/\mu S\ cm^{-1}$	t/°C	$\kappa/\mu S\ cm^{-1}$	t/°C	$\kappa/\mu S\ cm^{-1}$	t/°C	$\kappa/\mu S\ cm^{-1}$	t/°C	$\kappa/\mu S\ cm^{-1}$
Without Additive ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/ [AOT] = 22.20)											
23.8	0.37	28.6	0.82	33.1	10.90	36.2	93.00	39.2	300.00	42.8	695.00
25.2	0.43	29.9	1.29	34.2	28.00	37.2	147.00	40.3	395.00	44.0	840.00
26.4	0.51	31.1	2.60	35.2	54.00	38.3	220.00	41.1	495.00	45.1	1000.00
27.5	0.62	32.1	5.00								
Without Additive ([AOT] = 0.264 mol·dm^{-3}; [H_2O]/[AOT] = 49.26)											
24.0	0.20	26.5	0.27	29.0	0.77	30.5	82.00	32.0	275.00	38.0	2350.00
25.0	0.22	27.5	0.28	29.5	5.80	31.5	152.00	34.0	670.00		
[NaCl] = 0.04 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.20)											
18.6	0.26	25.4	0.42	32.3	0.96	37.1	5.80	42.1	91.00	47.1	440.00
19.6	0.28	26.1	0.44	33.4	1.24	38.1	9.80	43.2	142.00	48.0	520.00
20.6	0.30	28.4	0.51	34.7	1.75	39.1	18.00	44.1	195.00	49.0	650.00
21.8	0.31	29.4	0.57	35.1	2.15	40.2	31.50	45.6	260.00	49.6	720.00
22.8	0.33	30.2	0.64	36.2	3.20	41.2	58.00	46.1	345.00	50.5	820.00
23.6	0.35	31.2	0.76								
[NaCl] = 0.08 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.20)											
20.7	0.30	26.2	0.39	30.7	0.53	35.8	0.95	41.2	3.70	45.9	38.50
21.7	0.31	27.1	0.42	31.8	0.59	36.8	1.12	42.1	5.20	46.9	57.50
22.9	0.33	28.2	0.44	32.8	0.64	38.1	1.49	43.1	7.40	47.9	105.00
23.8	0.35	28.9	0.48	33.7	0.69	39.1	1.85	44.0	12.50	48.9	148.00
25.1	0.37	29.8	0.50	34.9	0.82	40.1	2.65	44.9	19.50	49.6	180.00
[NaCl] = 0.0056 mol·dm^{-3} ([AOT] = 0.264 mol·dm^{-3}; [H_2O]/[AOT] = 49.26)											
20.0	0.18	23.5	0.24	26.5	0.39	29.5	1.42	32.5	248.00	37.0	1100.00
21.5	0.20	24.0	0.26	27.5	0.48	30.5	32.75	33.6	460.00	38.0	1650.00
22.5	0.22	25.5	0.32	28.5	0.66	31.5	110.00	36.0	730.00	39.0	1950.00
[NaBr] = 0.02 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.20)											
22.5	0.30	28.3	0.52	34.6	3.21	38.9	58.00	43.1	310.00	47.4	810.00
24.0	0.34	30.3	0.69	36.4	11.80	40.8	150.00	45.3	560.00	49.0	1010.100
26.1	0.40	32.5	1.30								
[NaBr] = 0.04 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.20)											
20.2	0.23	26.8	0.36	32.2	0.67	38.7	8.60	42.0	60.00	45.5	225.00
22.2	0.26	28.3	0.42	34.0	1.00	40.1	22.50	43.0	96.00	47.1	360.00
23.9	0.29	29.9	0.48	35.7	1.70	41.1	40.00	44.1	148.00	48.4	490.00
25.4	0.32	31.4	0.58	37.3	3.50						
[NaBr] = 0.20 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.20)											
26.1	0.33	30.5	0.39	36.3	0.51	44.2	0.92	48.2	1.67	54.8	16.40
27.1	0.34	32.8	0.43	39.5	0.61	46.4	1.18	53.6	8.20	55.3	20.40
28.2	0.36	35.0	0.48	42.9	0.77						
[NaI] = 0.02 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.20)											
19.5	0.26	24.9	0.39	30.5	0.75	36.7	9.30	41.7	230.00	45.7	675.00
21.3	0.30	26.9	0.46	33.1	1.70	38.5	48.00	42.5	325.00	47.5	860.00
23.0	0.32	28.8	0.59	34.5	3.30	40.5	149.00	44.2	490.00	49.3	1155.00
[NaI] = 0.04 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.20)											
19.3	0.21	27.4	0.32	32.1	0.48	36.2	0.98	42.2	19.50	46.1	145.00
20.9	0.23	29.0	0.36	33.6	0.60	38.5	2.20	43.1	36.00	47.2	215.00
23.4	0.26	30.0	0.39	34.1	0.65	40.1	5.80	44.1	66.00	48.2	295.00
24.7	0.28	31.1	0.43	35.2	0.78	41.1	10.90	45.0	104.00	49.1	385.00
26.7	0.31										
[$NaClO_4$] = 0.02 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.20)											
23.1	0.34	27.9	0.54	32.1	1.67	36.1	21.10	40.2	185.00	43.6	475.00
24.5	0.37	28.9	0.64	33.1	2.73	37.3	44.00	41.5	275.00	44.9	620.00
25.7	0.41	30.0	0.86	34.2	5.10	38.5	85.00	42.4	353.00	46.0	760.00
26.8	0.46	31.0	1.10	35.0	9.00	39.3	126.00				
[$NaClO_4$] = 0.04 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.20)											
21.1	0.26	25.4	0.35	30.5	0.72	36.8	7.60	41.2	98.00	45.1	365.00
22.4	0.28	26.6	0.39	32.5	1.08	38.0	17.00	42.1	142.00	46.3	460.00
23.4	0.30	27.0	0.41	34.8	2.50	39.2	36.00	43.9	255.00	47.2	560.00
24.9	0.33	27.9	0.46	35.8	4.10	40.1	57.00				
[$NaClO_4$] = 0.08 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.20)											
23.5	0.31	29.5	0.45	32.8	0.62	36.8	1.40	39.7	3.45	42.9	14.60
25.5	0.35	30.7	0.50	34.4	0.78	37.9	17.0	40.5	4.50	44.7	53.00
26.9	0.39	31.9	0.55	35.7	0.97	39.0	2.55	41.7	7.90	45.4	69.00
28.1	0.42										
[$NaNO_3$] = 0.04 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.20)											
17.2	0.20	23.0	0.28	28.9	0.49	33.3	1.60	38.6	34.50	43.2	230.00
18.0	0.21	23.9	0.30	30.0	0.60	34.7	3.05	39.4	49.00	44.2	295.00
19.4	0.22	25.1	0.33	31.6	0.93	35.0	6.20	40.1	68.00	46.0	480.0
20.8	0.25	26.1	0.36	32.6	1.20	37.8	22.25	42.5	195.00	47.4	625.00
22.0	0.26	27.6	0.42								
[NaSCN] = 0.04 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/ [AOT] = 22.20)											
20.2	0.22	25.1	0.30	29.8	0.53	33.9	1.35	39.6	34.00	44.4	285.00
21.9	0.25	26.8	0.36	31.0	0.65	35.3	2.45	40.7	61.00	45.9	430.0
23.0	0.27	27.9	0.40	31.8	0.76	36.4	4.50	41.4	89.00	47.2	560.00
24.3	0.29	28.9	0.46	33.6	1.18	38.0	13.20	42.6	158.00	49.2	820.00
[$NaSO_4$] = 0.04 mol·dm^{-3} ([AOT] = 0.50 mol·dm^{-3}; [H_2O]/ [AOT] = 22.20)											
19.6	0.22	27.6	0.36	32.0	0.58	36.1	1.70	41.8	43.50	45.1	155.00
21.0	0.24	28.5	0.39	32.9	0.75	37.9	3.95	42.3	51.00	46.2	215.00
23.0	0.27	29.9	0.44	33.7	0.87	39.1	7.60	43.2	76.00	47.4	310.00
24.3	0.29	31.0	0.50	34.7	1.10	40.0	12.20	44.1	112.00	48.8	445.0
26.4	0.33										

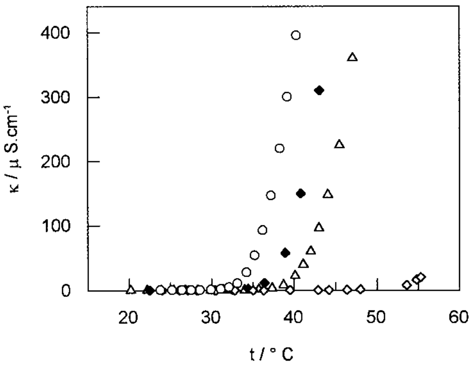

Figure 2. Influence of temperature on the conductivity of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions at different concentrations of sodium bromide, (○) without additive, (◆) [NaBr] = 0.02 mol·dm^{-3}, (△) [NaBr] = 0.04 mol·dm^{-3}, (◇) [NaBr] = 0.20 mol·dm^{-3}

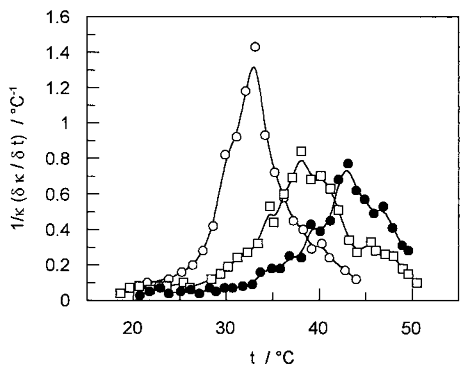

Figure 3. Determination of percolation temperature obtained by the Kim method (Kim and Huang, 1986), for sodium bis(2-ethylhexyl) sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions ([AOT] = 0.50 mol·dm^{-3}, [H_2O]/[AOT] = 22.20), (○) without additive, (□) [NaCl] = 0.04 mol·dm^{-3}, (●) [NaCl] = 0.08 mol·dm^{-3}.

distilled−deionized water. The solutes were supplied by Merck and Sigma, and all of then were of the maximun purity commercial available (>99%). They all were employed without further purifications.

The salt concentration added has been varied between 0.0056 and 0.200 mol·dm^{-3}, and in all the cases has been referred to the water volume.

The electrical conductivity was measured employing a conductivimeter Radiometer CDM 3 with a conductivity cell with a constant of 1 cm^{-1}. The detailed experimental procedure has been described elsewhere (Alvarez et al., 1998a). The precision of the temperature control was ±0.1 °C, and the accuracy of the measurements was ±0.5%.

Results and Discussion

Figure 1 shows the effect of sodium salts on the electrical conductivity of microemulsions sodium bis(2-ethylhexyl) sulfosuccinate + 2,2,4-trimethylpentane + water (AOT/isooctane/water). In this figure it can be observed that a moderate additive concentration produces a meaningful variation in the temperature of electrical percolation. On the other hand, Figure 2 shows the effect of increasing the additive concentration on the behavior of the system. In this case we can observe how as the additive concentration is increased an important decrease in the temperature of percolation is produced.

The values of electrical conductivity/temperature, κ/T, obtained for the different additive concentrations are shown in Table 1. The percolation threshold, t_p, has been determined from the data κ/T using the Kim method (Kim and Huang, 1986), which has been described in a previous paper (Álvarez et al., 1998a), see Figure 3. The calculated percolation temperatures in the presence of different additives and of different concentrations for various compositions of the microemulsion are shown in Table 2.

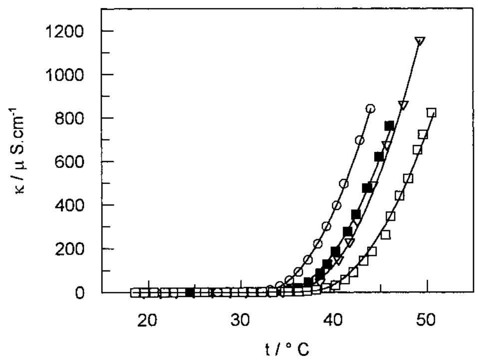

Figure 4. Fit of temperature−conductivity of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions to eq 1 in the presence of different additive concentrations ([AOT] = 0.50 mol·dm^{-3}, [H_2O]/[AOT] = 22.20), (−) calculated from eq 1, (○) without additive, (□) [NaCl] = 0.04 mol·dm^{-3}, (▽) [NaI] = 0.02 mol·dm^{-3}, (■) [$NaClO_4$] = 0.02 mol·dm^{-3}

Table 2. Fitting Parameters (Eq 1) and Percolation Temperature, t_p, Obtained by Kim Method, for Sodium Bis(2-ethylhexyl) Sulfosuccinate (AOT) + 2,2,4-Trimethylpentane + Water Microemulsions

additive	[H_2O]/[AOT]	C/mol·dm^{-3}	A	B	C	t_p
none	22.20		32.60	0.39	−3.30	33
none	49.26		29.45	0.17	−0.92	30
NaCl	22.20	0.040	37.35	0.47	−4.99	38
NaCl	22.20	0.080	42.46	0.55	−6.56	45
NaCl	49.26	0.0056	30.30	0.20	−1.80	31
NaBr	22.20	0.020	35.37	0.43	−3.90	36
NaBr	22.20	0.040	38.10	0.48	−4.20	39
NaBr	22.20	0.200	53.40	0.26	−9.00	∼54
NaI	22.20	0.020	35.70	0.40	−4.28	36
NaI	22.20	0.040	40.73	0.44	−4.53	39
NaNO3	22.20	0.040	35.60	0.49	−3.69	37
NaClO4	22.20	0.020	34.17	0.44	−3.74	35
NaClO4	22.20	0.040	35.97	0.49	−3.87	38
NaClO4	22.20	0.080	40.68	0.59	−5.41	41
NaSCN	22.20	0.040	36.64	0.45	−3.66	37
Na_2SO_4	22.20	0.040	38.55	0.51	−4.20	40

The temperature of percolation is practically independent of the sodium salt taken, but for each salt we observed a delay in the process of percolation as compared to that without additive. This behavior is opposite to that observed for the ureas and thioureas (Alvarez et al., 1998a; García-Rio et al., 1994), and it would be justified by the capacity of these additives of favoring the opening of channels between the microdroplets to facilitate the mass transfer.

Finally, the conductivity of these systems was correlated with temperature by the following expression (Alvarez et al., in 1998a), which permits us to predict the values of conductivity at temperatures after and before the threshold of percolation

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

The values of the parameters A, B, and C are shown in Table 2, and, as can be observed in this table, the value of the parameter A corresponds to the temperature of percolation. In all the cases studied eq 1 reproduces the experimental data with a deviation less than 4% (Figure 4).

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