Effects of Temperature on the Conductivity of Microemulsions: Influence of Sodium Hydroxide and Hydrochloric Acid

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The effect of the temperature on the conductivity of ternary systems sodium bis(2-ethylhexyl)sulfosuccinate + 2,2,4-trimethylpentane + water has been studied. Also the effect exercised by the presence of sodium hydroxide and hydrochloric acid on the conductivity of these ternary systems has been analyzed.

Introduction

Microemulsions are chemical systems of great interest. These systems have potential as solubilizers (Mittal, 1977; Elworthy, 1968; McBain and Hutchison, 1955) and as chemical nanoreactors (García-Rio et al., 1993; García-Rio et al., 1995; García-Rio et al., 1996). In particular microemulsions of sodium bis(2-ethylhexyl)sulfosuccinate + 2,2,4-trimethylpentane + water (AOT/isooctane/water) present a special interest, since they are ternary microemulsion systems where it is not necessary to have a cosurfactant. Upon increasing the temperature, the conductivity of these systems increases gradually up to a certain temperature and increases sharply. This phenomenon is known as electrical percolation, and the temperature at which there is a sharp increase is designated the threshold of percolation or the temperature of percolation. It is well-known that this phenomenon is correlated with the mass transfer between droplets (Jada et al., 1989, 1990) and there are evidences that moderate quantities of additives can modify the value of the threshold of percolation (Mathew et al., 1988; Jada et al., 1989). The aim of this work is to determine the effect of various additives on the electrical conductivity in these systems.

Experimental Section

Aqueous solutions of sodium hydroxide and hydrochloric acid were prepared with distilled−deionized water. All solutes were the highest grade purity available from Merck and Sigma (>99%). All the soutions were prepared by mass with deviations of less than ±0.2% from the desired concentrations. In all of the cases the additive concentration has been referred to the water volume of the microemulsion because all of the additives are soluble only in the water pseudophase of the microemulsion. Microemulsions were prepared by direct mixing of the three components and additives using vigorous stirring.

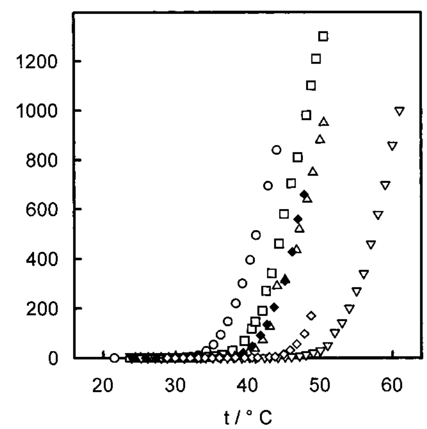

Figure 1. Influence of temperature upon the conductivity of AOT (sodium bis(2-ethylhexyl)sulfosuccinate) + 2,2,4-trimethylpentane + water microemulsions in the presence of different additives ([AOT] = 0.50 mol·dm^{-3}, [H_2O]/[AOT] = 22.2), (○) without additive; (□) [NaOH] = 0.03 mol·dm^{-3}; (△) [NaOH] = 0.06 mol·dm^{-3}; (▽) [NaOH] = 0.24 mol·dm^{-3}; (◆) [HCl] = 0.013 mol·dm^{-3}; (◇) [HCl] = 0.039 mol·dm^{-3}.

The electrical conductivity was measured with a Radiometer CDM3 conductivity meter with a conductivity cell constant of 1 cm mol·dm^{-3}. The cell was calibrated using a solution of KCl. The uncertainty of these measurements was ±0.5%. The temperature was regulated with a precision of ±0.1 °C. In general, each conductivity value reported was an average of 5−10 measurements, where the maximum deviations from the average value were always less than 1.5%. The percolation temperature was determined from the measurements of the electrical conductivity of the microemulsions as a function of temperature.

Results and Discussion

The effect of the nature and the concentration of the additive on the electrical percolation has been studied. The electrical conductivity as a function of temperature was studied in the presence of different concentrations of sodium hydroxide and hydrochloric acid.

Figure 1 shows the effect of sodium hydroxide and hydrochloric acid on the electrical conductivity of the microemulsions sodium bis(2-ethylhexyl)sulfosuccinate + 2,2,4-trimethylpentane + water (AOT/isooctane/water). A

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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

[AOT] = 0.50 mol·dm^{-3}, W = 22.20		[AOT] = 0.264 mol·dm^{-3}, W = 49.26		[NaOH] = 0.015 mol·dm^{-3}, [AOT] = 0.50 mol·dm^{-3}, W = 22.20		[NaOH] = 0.03 mol·dm^{-3}, [AOT] = 0.50 mol·dm^{-3}, W = 22.20		[NaOH] = 0.04 mol·dm^{-3}, [AOT] = 0.50 mol·dm^{-3}, W = 22.20	
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}
23.8	0.37	24.0	0.20	23.4	0.35	24.2	0.39	22.6	0.31
25.2	0.43	25.0	0.22	24.5	0.38	24.8	0.41	23.5	0.33
26.4	0.51	26.5	0.27	25.4	0.41	25.9	0.46	24.6	0.36
27.5	0.62	27.5	0.28	26.6	0.48	26.4	0.49	25.5	0.39
28.6	0.82	29.0	0.77	27.1	0.50	27.5	0.55	26.4	0.42
29.9	1.29	29.5	5.80	28.1	0.61	28.6	0.64	27.7	0.48
31.1	2.60	30.5	82.00	28.9	0.72	29.4	0.74	29.3	0.57
32.1	5.00	31.5	152.00	30.1	0.91	30.3	0.88	30.2	0.64
33.1	10.90	32.0	275.00	31.0	1.02	31.8	1.26	31.2	0.83
34.2	28.00	34.0	670.00	32.3	1.48	32.9	1.75	32.0	1.02
35.2	54.00	38.0	2350.00	33.3	2.45	33.6	2.25	33.1	1.34
36.2	93.00			34.0	2.50	34.5	3.80	33.9	1.70
37.2	147.00			35.1	8.00	35.5	7.00	34.5	2.05
38.3	220.00			36.0	13.20	36.4	12.20	35.8	4.35
39.2	300.00			37.0	25.50	37.8	28.50	36.8	7.50
40.3	395.00			38.0	49.50	39.0	68.00	38.0	16.00
41.1	495.00			39.0	89.00	40.0	118.00	39.3	49.00
42.8	695.00			40.2	141.00	41.0	145.00	40.9	110.00
44.0	840.00			42.0	280.00	42.0	190.00	41.4	130.00
45.1	1000.00			43.1	350.00	42.5	270.00	42.3	175.00
				44.0	455.00	43.3	340.00	43.1	215.00
				45.1	560.00	44.3	460.00	44.2	285.00
				46.2	680.00	45.5	580.00	45.2	360.00
				47.3	980.00	46.6	705.00	46.3	455.00
				48.0	1050.00	47.5	810.00	47.1	540.00
				49.0	1210.00	48.8	980.00	48.5	710.00
				50.0	1390.00	49.7	1100.00		
						50.5	1210.00		
						51.0	1300.00		

[NaOH] = 0.06 mol·dm^{-3}, [AOT] = 0.50 mol·dm^{-3}, W = 22.20		[NaOH] = 0.24 mol·dm^{-3}, [AOT] = 0.50 mol·dm^{-3}, W = 22.20		[NaOH] = 0.0021 mol·dm^{-3}, [AOT] = 0.264 mol·dm^{-3}, W = 49.26		[NaOH] = 0.0105 mol·dm^{-3}, [AOT] = 0.264 mol·dm^{-3}, W = 49.26		[HCl] = 0.0065 mol·dm^{-3}, [AOT] = 0.50 mol·dm^{-3}, W = 22.20	
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}
25.0	0.35	23.7	0.32	24.3	0.20	20.0	0.14	26.50	0.46
25.4	0.36	25.2	0.35	24.9	0.21	21.0	0.15	27.90	0.58
26.4	0.39	26.1	0.36	25.5	0.22	22.7	0.18	29.00	0.75
26.9	0.41	27.1	0.37	27.0	0.25	23.9	0.20	29.90	0.94
28.0	0.43	28.4	0.41	28.4	0.29	24.8	0.22	31.20	1.48
29.0	0.48	28.8	0.42	29.5	0.33	25.5	0.23	32.40	2.60
29.9	0.53	29.9	0.44	31.0	0.39	26.5	0.26	33.50	5.60
31.0	0.61	31.2	0.48	31.7	0.42	27.1	0.28	34.90	14.60
32.1	0.72	32.5	0.50	32.3	0.46	28.5	0.36	35.80	27.00
33.0	0.86	33.4	0.54	33.2	0.53	29.5	0.42	36.70	47.00
34.2	1.28	34.1	0.56	34.1	0.62	30.1	0.48	37.90	92.00
35.0	1.55	35.1	0.61	35.0	0.88	31.0	0.68	38.80	134.00
36.0	2.15	36.2	0.68	37.0	3.55	33.5	3.70	39.70	185.00
37.3	3.75	37.1	0.73	38.3	27.50	34.5	21.50	40.60	270.00
38.1	5.30	38.0	0.81	40.4	235.00	35.5	108.50	41.60	355.00
39.2	12.20	39.1	0.94	41.7	475.00	36.9	285.50	42.90	480.00
40.0	20.10	40.2	1.08	42.4	680.00	38.0	520.00	44.00	595.00
40.9	38.00	41.0	1.30	43.7	1050.00	39.0	750.00	45.10	720.00
42.0	72.00	42.3	1.65	44.8	1450.00	40.0	1030.00	46.00	840.00
43.0	127.00	43.0	1.95	45.3	1650.00	41.5	1490.00	47.10	1120.00
44.0	290.00	44.1	2.50	46.4	2100.00	42.0	1750.00		
45.3	315.00	45.1	3.60	47.0	2400.00	42.5	1950.00		
46.7	435.00	46.0	4.90	48.0	2650.00	43.5	2200.00		
47.5	520.00	47.1	7.60	49.0	3000.00	44.5	2550.00		
48.5	640.00	48.0	12.80	50.0	3350.00	45.5	2900.00		
49.5	750.00	49.0	20.00			46.0	3250.00		
51.0	820.00	50.0	30.00			46.5	3550.00		
52.0	950.00	51.0	50.00			47.0	3900.00		
		52.0	102.00						
		53.0	142.00						
		54.0	200.00						
		55.0	270.00						
		56.0	340.00						
		57.0	460.00						
		59.0	580.00						
		60.0	700.00						
		61.0	860.00						
		62.0	1000.00						

Table 1 (Continued)

[HCl] = 0.0130 mol·dm^{-3} [AOT] = 0.50 mol·dm^{-3} W = 22.20		[HCl] = 0.0195 mol·dm^{-3} [AOT] = 0.50 mol·dm^{-3} W = 22.20		[HCl] = 0.026 mol·dm^{-3} [AOT] = 0.50 mol·dm^{-3} W = 22.20		[HCl] = 0.039 mol·dm^{-3} [AOT] = 0.50 mol·dm^{-3} W = 22.20	
t/°C	κ/μS cm^{-1}	t/°C	κ/μS cm^{-1}	t/°C	κ/μS cm^{-1}	t/°C	κ/μS cm^{-1}
24.00	0.34	24.50	0.37	23.70	0.35	28.80	0.50
25.80	0.38	26.10	0.40	24.90	0.37	29.90	0.54
27.30	0.43	27.30	0.44	26.00	0.40	31.00	0.57
28.50	0.49	28.30	0.47	27.20	0.43	32.00	0.61
29.30	0.54	29.60	0.52	28.40	0.45	33.10	0.66
30.90	0.67	31.10	0.62	30.70	0.53	34.00	0.71
32.10	0.74	32.20	0.72	31.60	0.57	35.00	0.77
33.10	1.07	33.50	0.88	32.60	0.63	36.00	0.85
34.70	1.80	35.10	1.21	34.10	0.72	37.10	0.96
35.80	2.80	36.30	1.75	35.00	0.81	38.20	1.11
36.10	5.20	37.50	2.85	36.00	0.96	39.50	1.50
38.40	10.90	38.70	5.30	37.20	1.16	40.50	1.85
39.30	20.50	39.70	9.10	38.40	1.56	41.30	2.25
40.50	47.50	40.70	18.50	39.60	2.25	42.90	3.70
41.70	91.00	41.60	31.50	40.50	3.60	43.70	5.20
42.60	134.00	42.60	56.00	41.40	4.75	44.90	15.00
43.60	205.00	43.70	98.00	42.60	11.70	45.80	32.00
45.10	310.00	44.70	155.00	43.70	22.00	46.70	56.00
46.10	427.00	45.80	230.00	44.70	41.00	47.80	97.00
46.90	560.00	46.80	340.00	45.60	66.00	48.70	170.00
47.80	660.00	47.80	470.00	46.50	102.00		
		49.10	640.00	47.70	175.00		
				48.90	290.00		

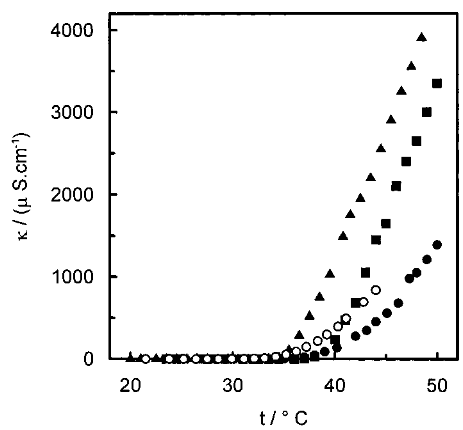

Figure 2. Influence of temperature upon the conductivity of AOT (sodium bis(2-ethylhexyl)sulfosuccinate) + 2,2,4-trimethylpentane + water microemulsions with different concentrations; (○) without additive, [AOT] = 0.50 mol·dm^{-3}; (●) [NaOH] = 0.015 mol·dm^{-3}, [AOT] = 0.50 mol·dm^{-3}; (■) [NaOH] = 0.0021 mol·dm^{-3}, [AOT] = 0.264 mol·dm^{-3}; (▲) [NaOH] = 0.0105 mol·dm^{-3}, [AOT] = 0.264 mol·dm^{-3}.

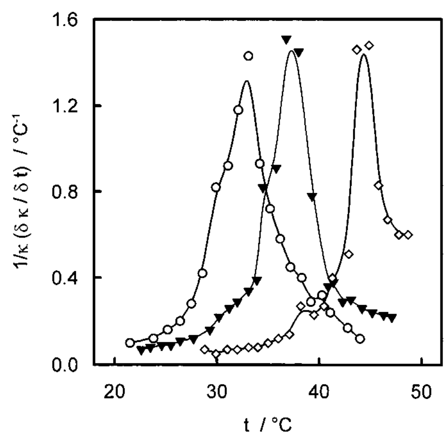

Figure 3. Determination of the percolation temperature obtained by the Kim method (Kim and Huang, 1986), for AOT (sodium bis-(2-ethylhexyl)sulfosuccinate) + 2,2,4-trimethylpentane + water microemulsions ([AOT] = 0.50 mol·dm^{-3}, [H_2O]/[AOT] = 22.2): (○) without additive; (▼) [NaOH] = 0.04 mol·dm^{-3}; (◇) [HCl] = 0.039 mol·dm^{-3}.

small additive concentration gives a meaningful variation in the temperature of percolation. Figure 2 shows the effect of increasing the acid or base concentration.

The experimental values of κ as a function of t obtained for the different additive concentrations are shown in Table 1. The threshold of percolation t_p has been calculated using the Kim method (Kim and Huang, 1986), which has been described in a previous paper (Álvarez et al., 1998a) (see Figure 3). Table 2 shows the calculated temperatures of percolation for the different additive concentrations.

In all cases, the additives give rise to an increase of the temperature of percolation. This behavior is analogous to what is observed for the sodium salts (Alvarez et al., 1998b; García-Rio et al., 1994), and it would be justified by their capacity of favoring the opening of channels to facilitate the mass transfer between droplets (García-Rio et al., 1994).

However, it is suggested that the principal observed effect is primarily to change the sodium concentration in

Table 2. Fitting Parameters (Eq 1) and Percolation Temperature t_p Obtained by the Kim Method (Kim and Huang, 1986), for AOT (Sodium Bis(2-ethylhexyl)sulfosuccinate) + 2,2,4-Trimethylpentane + Water Microemulsions ([AOT] = 0.50 mol·dm^{-3} and [AOT] = 0.264 mol·dm^{-3})

additive	[H_2O]/[AOT]	C/mol·dm^{-3}	A	B	C	t_p/°C
none	22.20		32.60	0.39	−3.30	33
none	49.26		29.45	0.17	−0.92	30
NaOH	22.20	0.0150	34.91	0.42	−4.16	35
NaOH	22.20	0.0300	35.31	0.43	−4.36	36
NaOH	22.20	0.0400	36.41	0.46	−4.48	37
NaOH	22.20	0.0600	37.88	0.48	−4.59	39
NaOH	22.20	0.2400	46.97	0.51	−7.62	48
NaOH	49.26	0.0021	37.80	0.20	−2.68	39
NaOH	49.26	0.0105	33.86	0.22	−2.00	35
HCl	22.20	0.0065	33.53	0.43	−3.54	34
HCl	22.20	0.0130	37.15	0.42	−4.45	38
HCl	22.20	0.0195	39.23	0.41	−5.38	40
HCl	22.20	0.0260	42.28	0.39	−6.53	43
HCl	22.20	0.0390	44.53	0.36	−7.87	45

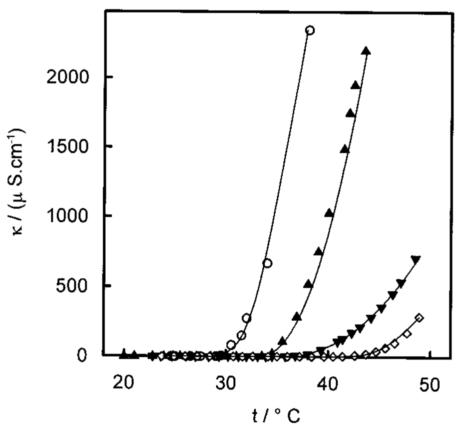

Figure 4. Fit of temperature−conductivity of AOT (sodium bis-(2-ethylhexyl)sulfosuccinate) + 2,2,4-trimethylpentane + water microemulsions to eq 1 in the presence of different additive concentrations: (−) calculated from eq 1; (○) without additive, [AOT] = 0.264 mol·dm^{-3}; (▼) [NaOH] = 0.0400 mol·dm^{-3}, [AOT] = 0.500 mol·dm^{-3}; (▲) [NaOH] = 0.0105 mol·dm^{-3}, [AOT] = 0.264 mol·dm^{-3}; (◇) [HCl] = 0.0260 mol·dm^{-3}, [AOT] = 0.500 mol·dm^{-3}.

the interface; for similar concentrations of the different *halides of sodium* variations of the temperature at which the percolation of NaCl is produced are not observed (Alvarez et al., 1998; García-Rio et al., 1994). This would support the hypothesis that an increase of sodium ions in the proximity of the head of the surfactant will increase the *screening* of the electric charge of the AOT hydrophilic head. This effect will favor the formation of negative curvature structures. A similar explanation can be made for hydrochloric acid. In this case, protons in part replace the sodium ions. This change in the composition of the counterions in the interface changes the screening of the electric charge of the hydrophilic head group of the AOT, favoring the negative curvature and the mass-transfer interchange. On the other hand, anions are concentrated in the aqueous *core* of the microdroplet.

The electrical conductivity of these systems was correlated with temperature by an empirical equation (Alvarez et al., 1998a) that permits us to calculate temperatures before and after the threshold of percolation as a function of microemulsion composition

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

The fit of the conductivity as a function of temperature values was satisfactory (Figure 4), and the parameters *A*, *B*, and *C* are given in Table 2. The value for the parameter *A* corresponds to the temperature of percolation. Equation 1 reproduces the temperature with a deviation less than 4% (Figure 4).

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