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

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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. The effect of the presence of secondary amines—morpholine, piperidine, piperazine, pyrrolidine, dimethylamine, and *N*-methylbenzylamine—on the variation of conductivity with the temperature of these ternary systems has also been studied.

Introduction

Microemulsions are chemical systems of great interest from the point of view of pure chemistry as well as from that of the applied chemistry because they have a great potential as solubilizators (Mittal, 1977; Elworthy et al., 1968) or as chemical nanoreactors (García-Rio et al., 1993, 1995, 1996), permitting an important number of industrial applications (Rieger, 1977; Datyner, 1983; Kuhn, 1963). In particular the microemulsions of sodium bis(2-ethylhexyl) sulfosuccinate present a special interest because is not necessary to have the presence of a cosurfactant. In this work will be studied the microemulsions formed by sodium bis(2-ethylhexyl) sulfosuccinate + 2,2,4-trimethylpentane + water (AOT + isooctane + water).

A microemulsion has a very low conductivity (10^{-9}−10^{-7} Ω^{-1} cm^{-1}), which is already a significant increase if compared to the conductivity of alkanes ($\sim 10^{-14}$ Ω^{-1} cm^{-1}) and is due to the fact that microemulsions carry charges. When the temperature increases, the conductivity of these systems increases gradually until a determined temperature is reached from which a sudden increase of conductivity is produced. This phenomenon is known as electrical percolation, and the temperature at which it is produced is known as threshold of percolation or temperature of percolation.

The values of the threshold of percolation can be modified by small quantities of additives (Mathew et al., 1988). In another paper (Álvarez et al., 1998) we have studied the effect of the presence of ureas and thioureas on the temperature of percolation of sodium bis(2-ethylhexyl) sulfosuccinate + 2,2,4-trimethylpentane + water (AOT + isooctane + water) microemulsions.

The aim of this work is to measure the electrical conductivity of these ternary systems with secondary amines at different temperatures and determine the temperature at which the electrical percolation is produced. On the other hand, the presence of amines in these systems generates a great interest owing the important number of chemical processes in those which are involved. Most 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 reaction between CO_2 and aqueous solutions of alkanolamines are frequently used in the absorption processes (Oyervaar et al., 1990).

Experimental Section

The aqueous solutions of morpholine (MOR), piperidine (PIPER), piperazine (PIP), pyrrolidine (PYR), dimethylamine (DMA), and *N*-methylbenzylamine (NMBA) were prepared with distilled−deionized water. All the reactives were supplied by Merck and Sigma, and all of them were of the maximun purity commercial available (>99%). Previously the amines were distilled under argon.

The concentrations of amines considered in this work were inferior to 1 mol/dm^3. In all cases the additive concentration has been referred to the total volume of microemulsion.

The electrical conductivity was measured employing a conductivimeter radiometer CDM 3 with a conductivity cell with a constant of 1 cm^{-1}. The accuracy of these measurements was ±0.5%. During the measurements of conductivity, the temperature was regulated with a precision of

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S0021-9568(97)00232-X CCC: $15.00
Published on Web 04/28/1998

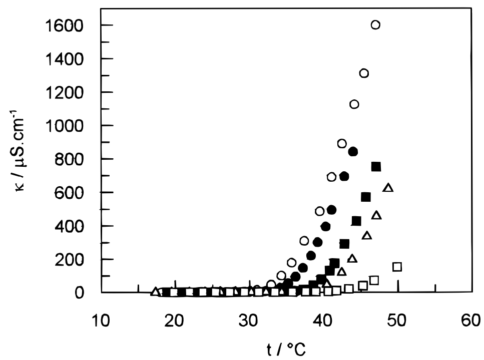

Figure 1. Influence of temperature upon the conductivity of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions in the presence of different secondary amines ([AOT] = 0.50 mol·dm^{-3}, [H_2O]/[AOT] = 22.2): (●) without additive, (○) [MOR] = 0.04 mol·dm^{-3}, (■) [PIP] = 0.04 mol·dm^{-3}, (△) [DMA] = 0.04 mol·dm^{-3}, (□) [PIPER] = 0.04 mol·dm^{-3}.

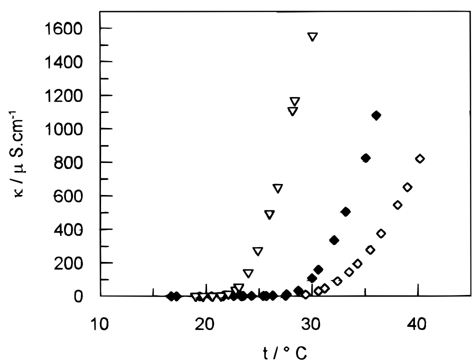

Figure 2. Influence of temperature upon the conductivity of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions at different [H_2O]/[AOT] values ([MOR] = 0.103 mol·dm^{-3}): (◇) [H_2O]/[AOT]=22.20, (◆) [H_2O]/[AOT] = 33.30, (▽) [H_2O]/[AOT] = 47.20.

±0.1 °C. In general, each conductivity value reported was an average of 5 to 10 measurements, where the maximum deviations from the average value were always less than 1.5%. The percolation temperature was determined through the study of the influence of the temperature on the electrical conductivity of the microemulsions.

Results and Discussion

The effect of the nature and additive concentration on the process of electric percolation has been studied. A series of conductivity/temperature data for a group of secondary amines—morpholine (MOR), piperidine (PIPER), piperazine (PIP), pyrrolidine (PYR), dimethylamine (DMA), and *N*-methylbenzylamine (NMBA)—were measured. In these experiments the amine concentration (0.103 mol/dm^3 and 0.040 mol/dm^3) and the quantity of water present in the microemulsion (W = [H_2O]/[AOT] = 22.20 and 47.20) were varied.

Figure 1 shows the effect of amines on the electrical conductivity of sodium bis(2-ethylhexyl) sulfosuccinate + 2,2,4-trimethylpentane + water (AOT/isooctane/H_2O) microemulsions. In this figure it can be observed how moderate additive concentrations produce an important decrease in the percolation temperature. Figure 2 shows the effect of the volume of the disperse phase (volume of water in the microemulsion) on the variation of the electrical conductivity with the temperature.

The values of the electrical conductivity/temperature, κ/T, obtained for different additive concentrations are

Table 1. Electrical Conductivity Values at Different Temperatures, without Additive and in the Presence of Different Concentrations of Amines in Sodium Bis(2-ethylhexyl) Sulfosuccinate (AOT) + 2,2,4-Trimethylpentane + Water Microemulsions ([AOT] = 0.50 mol·dm^{-3})

t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}	t/°C	κ/μS·cm^{-1}
Without Additive ([H_2O]/[AOT] = 22.2)							
23.8	0.37	29.9	1.29	35.2	54.00	40.3	395.00
25.2	0.43	31.1	2.60	36.2	93.00	41.1	495.00
26.4	0.51	32.1	5.00	37.2	147.00	42.8	695.00
27.5	0.62	33.1	10.90	38.3	220.00	44.0	840.00
28.6	0.82	34.2	28.00	39.2	300.00	45.1	1000.00
[Morpholine] = 0.103 mol·dm^{-3} ([H_2O]/[AOT] = 22.2)							
23.5	0.58	30.6	31.50	34.3	195.00	38.1	545.00
25.7	0.96	31.2	47.50	35.5	277.00	39.0	650.00
27.5	2.06	32.4	90.00	36.5	375.00	40.2	820.00
29.4	10.30	33.5	146.00				
[Morpholine] = 0.103 mol·dm^{-3} ([H_2O]/[AOT] = 33.3)							
16.7	0.27	22.6	0.59	27.6	11.00	32.1	335.00
17.2	0.28	23.3	0.68	28.7	33.30	33.2	505.00
19.4	0.36	24.3	0.96	30.0	108.00	34.9	825.00
20.5	0.42	25.4	1.65	30.6	160.00	36.1	1080.00
21.6	0.49	26.3	3.07				
[Morpholine] = 0.103 mol·dm^{-3} ([H_2O]/[AOT] = 47.2)							
19.0	0.85	22.1	15.00	24.9	275.00	28.2	1110.00
19.7	1.16	22.8	37.00	26.0	495.00	28.4	1170.00
20.6	2.01	23.1	57.00	26.8	650.00	30.1	1555.00
21.4	4.46	24.0	142.00				
[Morpholine] = 0.04 mol·dm^{-3} ([H_2O]/[AOT] = 22.2)							
18.1	0.28	26.3	0.86	32.9	46.50	41.1	690.00
19.5	0.32	28.1	1.65	34.3	100.00	42.5	890.00
21.9	0.40	29.2	3.01	35.7	177.00	44.2	1125.00
24.9	0.62	30.1	6.02	37.4	310.00	45.5	1310.00
25.5	0.71	31.0	12.80	39.5	485.00	47.1	1600.00
[Piperidine] = 0.103 mol·dm^{-3} ([H_2O]/[AOT] = 22.2)							
20.7	0.47	24.9	0.60	31.7	1.14	41.1	22.40
21.0	0.48	26.0	0.65	32.9	1.35	42.8	36.30
21.7	0.50	27.2	0.71	34.5	1.76	43.6	46.40
22.4	0.52	28.2	0.78	36.6	2.80	45.2	79.00
23.3	0.54	29.4	0.88	38.5	5.70	46.9	127.00
23.8	0.56	30.7	1.01	39.6	10.20	48.6	170.00
[Piperidine] = 0.04 mol·dm^{-3} ([H_2O]/[AOT] = 22.2)							
19.8	0.42	29.3	0.74	37.6	2.42	43.4	19.70
21.9	0.46	31.2	0.90	38.9	3.32	45.3	38.50
23.7	0.51	33.4	1.15	40.6	5.80	46.8	71.00
25.4	0.56	35.8	1.65	41.7	9.50	48.9	152.00
27.3	0.64						
[Pyrrolidine] = 0.04 mol·dm^{-3} ([H_2O]/[AOT] = 22.2)							
19.1	0.31	28.3	0.57	35.3	1.38	44.1	24.70
22.1	0.36	29.3	0.60	37.4	2.15	46.2	65.00
24.0	0.41	30.9	0.73	39.7	4.10	48.3	149.00
26.1	0.48	33.2	1.02	41.9	9.00	49.3	205.00
[Piperazine] = 0.04 mol·dm^{-3} ([H_2O]/[AOT] = 22.2)							
18.8	0.27	28.1	0.46	36.0	6.60	41.5	175.00
20.7	0.29	29.9	0.59	37.3	16.70	42.7	290.00
22.9	0.31	31.4	0.70	38.6	42.00	44.1	427.00
24.4	0.34	33.2	1.43	39.7	78.00	45.3	570.00
26.5	0.39	34.6	2.70	40.8	129.00	46.7	750.00
[Piperazine] = 0.04 mol·dm^{-3} ([H_2O]/[AOT] = 33.3)							
17.9	0.21	23.6	0.29	31.5	2.15	38.9	480.00
18.4	0.22	24.5	0.32	32.9	6.40	40.2	720.00
19.4	0.23	26.0	0.38	34.4	30.00	42.0	1090.00
21.1	0.25	27.8	0.51	35.5	78.00	43.0	1340.00
22.3	0.26	29.8	0.92	37.0	210.00		
[Dimethylamine] = 0.04 mol·dm^{-3} ([H_2O]/[AOT] = 22.2)							
17.3	0.27	28.1	0.55	36.0	4.23	43.8	197.00
19.5	0.29	30.2	0.77	38.3	13.30	45.8	335.00
21.9	0.33	32.2	1.19	40.4	47.00	47.1	457.00
24.0	0.37	34.3	2.00	42.4	118.00	48.7	620.00
26.1	0.45						
[*N*-Methylbenzylamine] = 0.04 mol·dm^{-3} ([H_2O]/[AOT] = 22.2)							
19.9	0.33	27.9	0.67	34.8	7.80	41.3	127.00
20.9	0.34	30.0	1.19	36.5	20.70	42.6	197.00
23.6	0.43	31.5	1.85	38.1	36.50	44.5	300.00
25.4	0.52	32.9	3.20	39.8	70.00	46.1	433.00

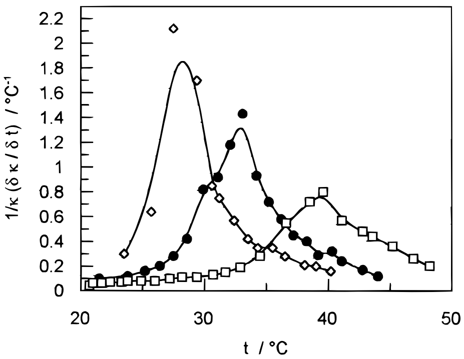

Figure 3. Determination of percolation temperature obtained by the Kim method (Kim and Huang, 1986), for sodium bis(2-ethylhexyl) sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions ([AOT] = 0.50 mol·dm^{-3}, [H_2O]/[AOT] = 22.20): (●) without additive, (◇) [MOR] = 0.103 mol·dm^{-3}, (□) [PIPER] = 0.103 mol·dm^{-3}.

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] = 0.50 mol·dm^{-3})

additive	[H_2O]/[AOT]	*C*/mol·dm^{-3}	*A*	*B*	*C*	t_p
none	22.2		32.60	0.39	−3.30	33
pyrrolidine	22.2	0.040	39.86	0.71	−6.62	42
piperidine	22.2	0.040	40.62	0.75	−8.93	43
piperidine	22.2	0.103	38.76	0.68	−8.68	40
dimethylamine	22.2	0.040	36.90	0.46	−5.05	38
N-methylbenzylamine	22.2	0.040	33.80	0.62	−4.63	35
piperazine	22.2	0.040	35.80	0.44	−4.08	36
piperazine	33.3	0.040	33.12	0.28	−3.02	34
morpholine	22.2	0.040	30.16	0.42	−3.47	31
morpholine	22.2	0.103	28.84	0.39	−3.23	30
morpholine	33.3	0.103	27.18	0.28	−2.86	28
morpholine	47.2	0.103	21.83	0.20	−2.48	23

shown in Table 1. From these data it is possible to obtain the temperature of percolation, t_p. This temperature has been obtained from the κ/T data using the method described elsewhere (Álvarez et al., 1998) and illustrated in Figure 3. In Table 2 are shown differents values for the percolation temperatures in the presence of different amines and of concentrations for various compositions of microemulsion. Most of the amines hinder the electrical percolation; only morpholine advances the point of percolation. This behavior would be justified by their capacity of association to the surfactant film (García-Rio et al., 1993). Morpholine association to the surfactant film favors the formation of structures with positive curvature facilitating the mass exchange between droplets. The apparently contradictory behavior of others amines (they increase t_p) would correspond with a increase of the partial dissociation of amine into ammonium and hydroxide ions (García-Rio et al., 1994).

The variation of conductivity in these systems can be rationalized through an empirical equation (Alvarez et al., 1998) that 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 fit of the κ/T values was satisfactory (Figure 4) in all the cases studied, and the parameters *A*, *B*, and *C* are shown in Table 2. The values of the parameter *A* (that in all cases is slightly less than the value of the percolation threshold obtained by bibliographical method, vide supra) will correspond with the moment in which the phenomenon of percolation is produced.

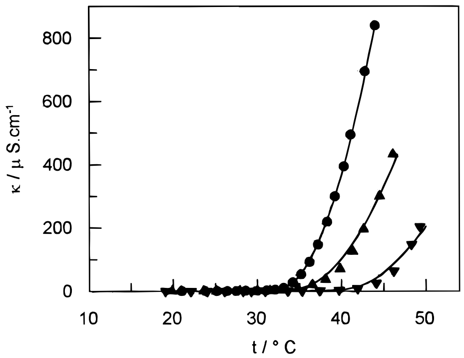

Figure 4. Fit of temperature−conductivity of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions to eq 1 in the presence of different additive concentrations ([AOT] = 0.50 mol·dm^{-3}, [H_2O]/[AOT] = 22.20): (—) calculated from eq 1, (●) without additive, (▲) [NMBA] = 0.04 mol·dm^{-3}, (▼) [PYR] = 0.040 mol·dm^{-3}

Figure 4 shows the experimental data in comparison with those calculated by eq 1. This equation reproduces the experimental data with a deviation less than 4%.

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Received for review October 3, 1997. Accepted February 18, 1998.

JE970232M