Effects of Temperature on the Conductivity of Sodium Bis(2-ethylhexyl)sulfosuccinate + 2,2,4-Trimethylpentane + Water Microemulsions. Influence of Amides and Ethylene Glycol

E. Alvarez,*,† L. García-Río,‡ J. C. Mejuto,§ and J. M. Navaza‖

Departments of Chemical Engineering and Physical Chemistry and Organic Chemistry, University of Vigo, Vigo 36200, Spain, and Departments of Physical Chemistry and Chemical Engineering, University of Santiago of Compostela, Santiago of Compostela 15706, Spain

The conductivity of ternary systems sodium bis(2-ethylhexyl)sulfosuccinate + 2,2,4-trimethylpentane + water has been studied over a temperature range. In addition the effect of the additives formamide, *N*-methylformamide, *N*,*N*-dimethylformamide, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, and ethylene glycol on the conductivity of these ternary systems was studied.

Introduction

Microemulsions are stable and transparent dispersions of water, oil, and surfactant, with or without a cosurfactant. 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). Because they provide both organic and aqueous environments, microemulsions can simultaneously dissolve both hydrophobic and hydrophilic compounds, each compound being distributed among water, organic solvent, and surfactant film in accordance with its physicochemical nature. Microemulsions have found an important number of scientific and technological applications (Rieger, 1977; Datyner, 1983). They have numerous applications in the fields of solubilization and extraction (Mittal, 1991; Elworthy et al., 1968) or as chemical nanoreactors (García-Rio et al., 1995, 1996). In particular the microemulsions of sodium bis(2-ethylhexyl)-sulfosuccinate are of special interest because it is not necessary to have a cosurfactant present.

These systems have a very low electrical conductivity (10^{-9}−10^{-7} $\Omega^{-1}\cdot cm^{-1}$), that increases gradually with an increase in temperature until a determined temperature is reached when a rapid increase of the conductivity occurs. This phenomenon, namely, electrical percolation, is described in a previous paper (Alvarez et al., 1998a), and the temperature at which it occurs is known as the percolation threshold or the temperature of percolation.

The temperature of percolation can be modified by addition of small quantities of additives that hinder the appearance of electrical percolation or favor it (Mathew et al., 1988). These results together with others (Jada et al., 1989, 1990) indicate that the process of electrical percolation is not associated with the formation of bicontinuous structures in the microemulsion, but the structure keeps discreet droplets. In previous papers (Alvarez et al., 1998a−c) we have studied the effect of the presence of ureas, thioureas, secondary amines, and sodium salts on the percolation threshold of the sodium bis(2-ethylhexyl)-sulfosuccinate + 2,2,4-trimethylpentane + water micro-emulsions.

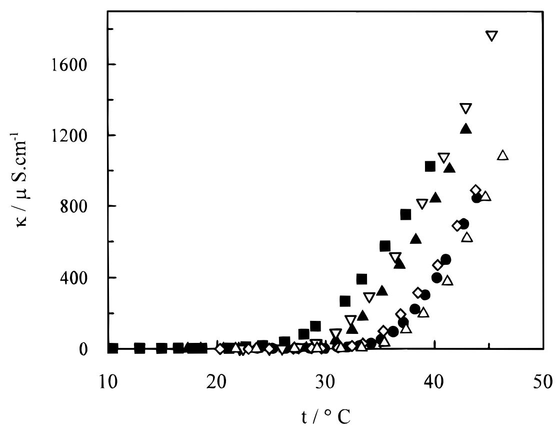

Figure 1. Influence of temperature upon the conductivity of AOT (sodium bis(2-ethylhexyl)sulfosuccinate) + 2,2,4-trimethylpentane + water microemulsions in the presence of different additives ([AOT] = 0.5 mol·dm^{-3}, [H_2O]/[AOT] = 22.2): (●) without additive, (■) [FOR] = 0.040 mol·dm^{-3}, (▲) [MFOR] = 0.040 mol·dm^{-3}, (▽) [DMFOR] = 0.040 mol·dm^{-3}, (◇) [ETGL] = 0.040 mol·dm^{-3}, and (△) [MNTS] = 0.009 mol·dm^{-3}.

The objective of this work is to measure the electrical conductivity of these ternary systems with different amides and ethylene glycol at various temperatures and determine the temperature of percolation. Some of these additives are frequently used in the study of mass transfer processes.

Experimental Section

The aqueous solutions of formamide (FOR), *N*-methylformamide (MFOR), *N*,*N*-dimethylformamide (DMFOR), ethylene glycol (ETGL), and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) were prepared with distilled−

* To whom correspondence should be addressed. E-mail: ealvarez@uvigo.es.
† Department of Chemical Engineering, ETSEI, University of Vigo.
‡ Department of Physical Chemistry, University of Santiago of Compostela.
§ Department of Physical Chemistry and Organic Chemistry, University of Vigo.
‖ Department of Chemical Engineering, University of Santiago of Compostela.

10.1021/je980129c CCC: $18.00
Published on Web 03/10/1999

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

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: [AOT] = 0.5 mol·dm^{-3}; [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
Without Additive: [AOT] = 0.264 mol·dm^{-3}; [H_2O]/[AOT] = 49.26							
24.0	0.20	27.5	0.28	30.5	82.00	34.0	670.00
25.0	0.22	29.0	0.77	31.5	152.00	38.0	2350.00
26.5	0.27	29.5	5.80	32.0	275.00		
With [Formamide] = 0.04 mol·dm^{-3}: [AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.2							
10.5	0.22	18.6	0.65	26.3	37.00	33.4	387.00
12.9	0.27	21.1	1.50	28.0	81.00	35.5	570.00
15.0	0.34	22.7	4.05	29.1	124.00	37.4	750.00
16.5	0.43	24.2	11.20	31.8	262.00	39.7	1020.00
17.8	0.54						
With [Formamide] = 0.16 mol·dm^{-3}: [AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.2							
4.3	0.18	14.7	4.42	22.0	177.00	29.3	720.00
7.4	0.26	16.0	11.80	23.7	275.00	31.3	910.00
10.9	0.53	17.8	37.50	25.3	385.00	33.3	1110.00
11.6	0.66	19.6	89.00	27.5	560.00	35.5	1380.00
13.6	1.65						
With [*N*-Methylformamide] = 0.04 mol·dm^{-3}: [AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.2							
17.1	0.19	26.6	1.35	32.4	106.00	38.3	610.00
18.5	0.22	27.5	2.47	33.4	180.00	40.1	840.00
20.4	0.27	28.4	5.20	35.4	320.00	41.4	1010.00
22.1	0.35	29.5	15.50	36.9	470.00	42.9	1230.00
24.2	0.52	30.9	47.00				
With [*N*-Methylformamide] = 0.08 mol·dm^{-3}: [AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.2							
18.3	0.31	24.2	6.20	30.1	250.00	35.9	860.00
18.9	0.35	25.3	19.00	30.7	305.00	36.7	970.00
20.4	0.51	26.7	58.00	32.3	442.00	38.5	1240.00
22.4	1.23	27.8	109.00	33.5	560.00	40.2	1490.00
23.3	2.33	29.0	170.00	34.7	710.00	40.8	1575.00
With [*N*,*N*-Dimethylformamide] = 0.04 mol·dm^{-3}: [AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.2							
22.1	0.56	27.5	9.80	34.0	295.00	40.9	1080.00
22.4	0.61	29.1	33.70	36.4	520.00	42.8	1360.00
24.8	1.34	30.9	92.00	38.9	820.00	45.1	1770.00
26.4	3.10	32.3	167.00				
With [*N*,*N*-Dimethylformamide] = 0.08 mol·dm^{-3}: [AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.2							
8.6	0.18	18.6	0.64	28.6	210.00	37.0	1140.00
10.5	0.21	21.2	1.72	31.3	430.00	38.5	1417.00
11.6	0.23	23.2	8.40	33.0	620.00	41.3	1800.00
13.6	0.28	25.1	40.70	35.1	860.00	43.1	2170.00
16.4	0.42	27.2	124.00				
With [*N*,*N*-Dimethylformamide] = 0.16 mol·dm^{-3}: [AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.2							
6.0	0.20	16.3	7.00	23.0	290.00	30.1	1070.00
9.6	0.32	18.1	33.20	25.1	460.00	31.4	1260.00
12.0	0.52	19.9	92.00	26.6	630.00	33.6	1625.00
15.4	2.70	21.7	197.00	28.2	820.00		
With [*N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide] = 0.009 mol·dm^{-3}: [AOT] = 0.50 mol·dm^{-3} ; [H_2O]/[AOT] = 22.2							
21.70	0.30	31.40	2.00	37.40	108.00	43.00	620.00
23.60	0.35	33.30	7.20	39.00	197.00	44.70	850.00
27.10	0.53	35.40	34.30	41.20	377.00	46.30	1080.00
29.20	0.78						
With [*N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide] = 0.003 mol·dm^{-3}: [AOT] = 0.50 mol·dm^{-3} ; [H_2O]/[AOT] = 33.3							
18.30	0.22	24.80	0.51	29.50	14.90	33.60	410.00
20.60	0.27	26.90	1.15	31.00	86.00	35.10	685.00
22.60	0.36	28.40	3.95	32.30	215.00	36.50	1020.00
With [Ethylene Glycol] = 0.0402 mol·dm^{-3}: [AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.2							
20.30	0.30	28.70	1.58	33.40	30.50	40.30	470.00
22.90	0.39	29.60	2.50	35.30	101.00	42.10	690.00
24.80	0.52	31.10	6.70	36.90	195.00	43.80	890.00
27.00	0.84	32.40	16.70	38.50	315.00		
With [Ethylene Glycol] = 0.0804 mol·dm^{-3}: [AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.2							
22.00	0.38	27.20	1.09	32.30	26.50	39.00	432.00
23.50	0.45	28.40	1.70	34.00	79.00	40.90	640.00
24.70	0.55	29.80	4.17	35.70	167.00	43.50	980.00
25.70	0.70	31.10	10.10	37.40	292.00		

Table 1 (Continued)

t/°C	κ/(μS cm^{-1})	t/°C	κ/(μS cm^{-1})	t/°C	κ/(μS cm^{-1})	t/°C	κ/(μS cm^{-1})
With [Ethylene Glycol] = 0.161 mol·dm^{-3}: [AOT] = 0.50 mol·dm^{-3}; [H_2O]/[AOT] = 22.2							
15.60	0.25	24.30	0.72	32.20	63.50	38.10	520.00
17.00	0.28	26.20	1.42	34.00	144.00	40.60	790.00
19.40	0.34	27.80	3.25	35.40	257.00	42.10	980.00
20.60	0.39	29.00	7.30	37.00	405.00	44.00	1250.00
22.90	0.53	30.60	24.00				

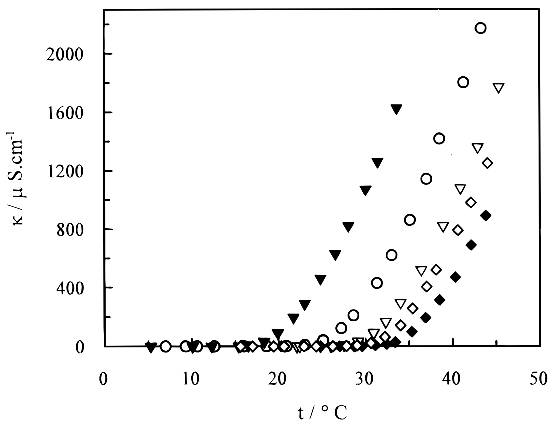

Figure 2. Influence of temperature upon the conductivity of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions at different concentrations of *N*,*N*-dimethylformamide and ethylene glycol: (▽) [DMFOR] = 0.040 mol·dm^{-3}, (○) [DMFOR] = 0.080 mol·dm^{-3}, (▼) [DMFOR] = 0.160 mol·dm^{-3}, (◇) [ETGL] = 0.040 mol·dm^{-3}, and (♦) [ETGL] = 0.161 mol·dm^{-3}.

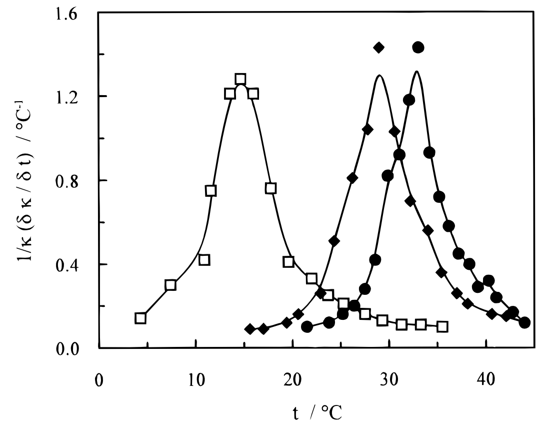

Figure 3. Determination of percolation temperature obtained by the Kim method (Kim and Huang, 1986), for sodium bis(2-ethylhexyl)sulfosuccinate (AOT) + 2,2,4-trimethyl-pentane + water microemulsions ([AOT] = 0.5 mol·dm^{-3}, [H_2O]/[AOT] = 22.2): (●) without additive, (□) with [FOR] = 0.160 mol·dm^{-3}, and (♦) with [ETGL] = 0.161 mol·dm^{-3}.

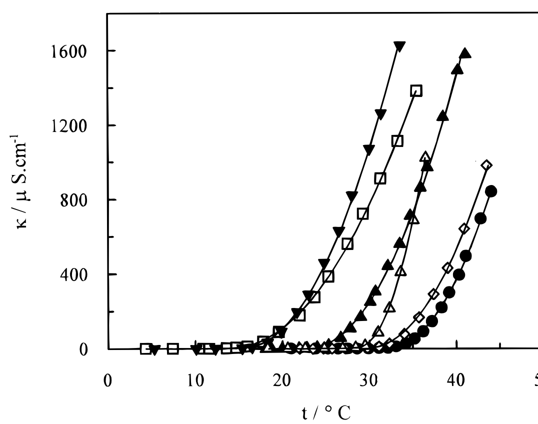

Figure 4. Fit of temperature−conductivity of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions to eq 1 in the presence of different additive concentrations ([AOT] = 0.5 mol·dm^{-3}, [H_2O]/[AOT]= 22.2): (—) from calculation with eq 1, (●) without additive, (□) with [FOR] = 0.160 mol·dm^{-3}, (▲) with [MFOR] = 0.080 mol·dm^{-3}, (▼) with [DMFOR] = 0.160 mol·dm^{-3}, (♦) with [ETGL] = 0.080 mol·dm^{-3}, and (▲) with [MNTS] = 0.003 mol·dm^{-3}.

deionized water. All the reactives were supplied by Merck and Sigma and are of the highest purity available (>99%). All solutions were prepared by mass with deviations of less than ±0.2% from the desired concentrations. The concentrations of additives considered in this work were less than 1 mol/dm^3. In all of the cases the additive concentration has been referred to the total volume of microemulsion because all of the additives are soluble in the three components of the microemulsion. Microemulsions were prepared by direct mixing of the three components and additives under stirring.

The electrical conductivity was measured employing a conductivimeter Radiometer CDM 3 with a conductivity cell with a constant of 1 cm^{-1}. The conductivimeter was calibrated using a solution of KCl. The accuracy of these measurements was of ±0.5%. During the measurements 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 through the study of the influence of the temperature on the electrical conductivity of the microemulsions.

Results and Discussion

The effects of the nature and the concentration of the additive on the process of electrical percolation have been studied. A series of conductivity/temperature data for a group of amides, formamide, *N*-methylformamide, *N*,*N*-dimethylformamide, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, and ethylene glycol, varying the concentration of the additive (0.003 mol/dm^3 and 0.16 mol/dm^3), have been measured.

Figure 1 shows the important effect observed on the electrical conductivity of the sodium bis(2-ethylhexyl)sulfosuccinate + 2,2,4-trimethylpentane + water (AOT + isooctane + water) microemulsions in the presence of amides and ethylene glycol. At a moderate additive concentration, a meaningful variation in percolation threshold is observed. Figure 2 shows the effect of increasing the concentrations of additive on the behavior of the system.

The experimental data of electrical conductivity/temperature, κ/t, obtained for different additive concentrations are shown in Table 1. From these data it is possible to obtain the temperature of percolation, t_p, using the method described elsewhere (Alvarez et al., 1998a) and illustrated in Figure 3. In Table 2 are given the values for the temperature of percolation in the presence of different

Table 2. Fitting Parameters (Equation 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})

additive	$[H_2O]/[AOT]$	[additive]/(mol·dm^{-3})	A	B	C	t_p
none	22.20		32.60	0.39	−3.30	33.0
none	49.26		29.45	0.17	−0.92	30.0
formamide	22.20	0.0400	22.62	0.55	−2.74	23.5
formamide	22.20	0.1600	14.09	0.57	−1.81	14.0
N-methylformamide	22.20	0.0400	27.96	0.42	−2.11	29.0
N-methylformamide	22.20	0.0800	23.63	0.43	−1.78	24.7
N,*N*-dimethylformamide	22.20	0.0400	26.64	0.43	−2.68	27.5
N,*N*-dimethylformamide	22.20	0.0800	22.24	0.44	−2.48	23.0
N,*N*-dimethylformamide	33.30	0.1600	15.35	0.46	−1.92	16.0
N-methyl-*N*-nitroso-*p*-toluenesulfonamide	22.20	0.0090	33.05	0.41	−3.47	34.0
N-methyl-*N*-nitroso-*p*-toluenesulfonamide	33.30	0.0030	28.81	0.24	−2.31	29.0
ethylene glycol	22.20	0.0402	30.58	0.43	−3.09	31.0
ethylene glycol	22.20	0.0804	29.94	0.44	−3.16	30.0
ethylene glycol	22.20	0.1610	28.44	0.45	−3.26	29.0

additives and different concentrations for various compositions of the microemulsion.

The behavior observed for all cases corresponds to a decrease in the temperature of percolation. This behavior is analogous to that which is observed for the ureas and thioureas (Alvarez et al., 1998a; García-Rio et al., 1994) and would be justified by their capacity of association to the surfactant film. The association to the surfactant film favors the formation of structures with positive curvature, facilitating the mass exchange between droplets (García-Rio et al., 1994). The effect of formamides can be explained in terms of the degree of substitution of the amide; in fact FOR < MFOR. This result is acceptable because the effect of the additive upon the AOT film is related with the volume of the additive molecule. The reason that DMFOR < MFOR is due to the higher solubility of DMFOR in 2,2,4-trimethylpentane. The anomalous behavior of MNTS (the lower effect upon t_p than the other amides) is due to the insolubility of MNTS in water. The difference between the temperature of percolation in the presence of MNTS and without additive is not statistically significant ($t_p = 34 \pm 1$ °C and $t_p = 33 \pm 1$ °C, respectively).

The variation of conductivity of these systems can be rationalized through an empirical equation (Alvarez et al., 1998a) that permits us to predict the values of conductivity at temperatures after and before the threshold of percolation.

$$t = A + B\kappa^{1/2} + \frac{C}{\kappa} \qquad (1)$$

The fitting of eq 1 to the κ/t values was satisfactory in all the studied cases (see Figure 4), and the parameters $A-C$ are collected in Table 2. The value of parameter A is compatible with the threshold of percolation obtained from the literature (Kim and Huang, 1986). Equation 1 reproduces the experimental data with a deviation in the temperature less than $\pm$ 1 °C.

Literature Cited

Alvarez, E.; García-Rio, L.; Leis, J. R.; Mejuto, J. C.; Navaza, J. M. Effect of the Temperature on the Conductivity of Sodium Bis(2-ethylhexyl)sulfosuccinate + 2,2,4-Trimethylpentane + water Microemulsions in the Presence of Ureas and Thioureas. *J. Chem. Eng. Data* **1998a**, *43*, 123−127.

Alvarez, E.; García-Rio, L.; Mejuto, J. C.; Navaza, J. M. Effect of Temperature on the Conductivity of Sodium Bis(2-ethylhexyl)-sulfosuccinate + 2,2,4-Trimethylpentane + Water Microemulsions. Influence of Amines. *J. Chem. Eng. Data* **1998b**, *43*, 433−435.

Alvarez, E.; García-Rio, L.; Mejuto, J. C.; Navaza, J. M. Effect of Temperature on the Conductivity of Sodium Bis(2-ethylhexyl)sulfosuccinate + 2,2,4-Trimethylpentane + Water Microemulsions. Influence of Sodium Salts. *J. Chem. Eng. Data* **1998c**, *43*, 519−522.

Datyner, A. *Surfactant in textile processing*; Marcel Dekker: New York, 1983.

Elworthy, P. H.; Florence, A. T.; McFarlane, C. B. *Solubilization by surface activate agents*; Chapman and Hall: London, 1968.

García-Río, L.; Leis, J. R.; Mejuto, J. C.; Peña, M. E.; Iglesias, E. Effects of Additives on the Internal Dynamics and Properties of Water/AOT/Isooctane Microemulsions. *Langmuir* **1994**, *10*, 1676−1683.

García-Río, L.; Leis, J. R.; Iglesias, E. Influence of Water Structure on Solvolysis in Water-in-Oil Microemulsions. *J. Phys. Chem.* **1995**, *99*, 12318−12326.

García-Río, L.; Leis, J. R.; Mejuto, J. C. Pseudophase Approach to Reactivity in Microemulsions: Quantitative Explanation of the Kinetics of the Nitrosation of Amines by Alkyl Nitrites in AOT/Isooctane/Water Microemulsions. *J. Phys. Chem.* **1996**, *100*, 10981−10988.

Jada, A.; Lang, J.; Zana, R. Relation between Electrical Percolation and Rate Constant for Exchange of Material between Droplets in Water in Oil Microemulsions. *J. Phys. Chem.* **1989**, *93*, 10−12.

Jada, A.; Lang, J.; Zana, R.; Makhloufi, R.; Hirsch, E.; Candau, S. J. Ternary Water in Oil Microemulsions Made of Cationic Surfactants, Water, and Aromatic Solvents. 2. Droplet Sizes and Interactions and Exchange of Material between Droplets. *J. Phys. Chem.* **1990**, *94*, 387−395.

Kim, M. W.; Huang, J. S. Percolation like phenomena in oil-continuous microemulsions. *Phys. Rev. A* **1986**, *34*, 719−722.

Mathew, C.; Patanjali, P. K.; Nabi, A.; Maitra, A. On the Concept of Percolative Conduction in Water-in-Oil Microemulsions. *Colloids Surf.* **1988**, *30*, 253−263.

Mittal, K. L. *Micellization, Solubilization and Microemulsions*; Plenum Press: New York, 1991.

Pileni, M. P. *Structure and Reactivity in Reverse Micelles*; Elsevier: Amsterdam, 1989.

Rieger, M. M. *Surfactants in Cosmetic*; Marcel Dekker: New York, 1977.

Received for review June 2, 1998. Accepted January 4, 1999.

JE980129C