

Conductivity of Sodium Bis(2-ethylhexyl)sulfosuccinate/Isooctane/Water Microemulsions Containing Phase-Transfer Catalysts

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The effects of temperature and cryptand complex concentration upon the conductivity of the system sodium bis(2-ethylhexyl) sulfosuccinate + 2,2,4-trimethylpentane + water have been studied. The cryptand complexes (potential phase-transfer catalysts) used in the ternary systems were 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, and 4,7,13,-18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane.

Introduction

Microemulsions are transparent isotropic dispersions of an apolar compound in water in the presence of a surfactant. They have been described as spherical droplets of a disperse phase separated from a continuous phase by a film of surfactant. Microemulsions present great interest from the point of view of the chemical industry (Mittal, 1977; Elworthy et al., 1969; García-Río et al., 1995, 1996), permitting an important number of applications (Kuhn, 1963; Turkyilmaz et al., 1998; Herzog et al., 1998; Castagnola and Dutta, 1998). In the present work, microemulsions formed by ternary mixtures of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water will be studied. Under normal conditions and at room temperature, microemulsions have very low conductivities (10^{-9} – 10^{-7} S·cm⁻¹) compared with the conductivity of pure 2,2,4-trimethylpentane (conductivity of alkanes $\sim 10^{-14}$ – 10^{-9} S·cm⁻¹). This is due to the fact that these ternary systems carry charge. On increasing temperature, the conductivity of these systems increases gradually until percolation occurs (see Figure 1).

It is well-known that the values of the threshold to percolation can be modified by small quantities of additives (Álvarez, 1998a–c). In particular, the addition of macrocycles (cryptand complexes and crown ethers) to water-in-oil microemulsions leads to drastic rheological changes (Schuebel, 1998). A mixture of a 20 wt % solution of crown ethers in water with an oil stock solution of sodium bis(2-ethylhexyl)sulfosuccinate is biphasic but can be transformed into a homogeneous, transparent, viscoelastic solution by simple shaking. This gelly phase demixes again after hours up to several days. In addition, anomalous percolation properties (García-Río et al., 1997; Schuebel, 1998) were found for mixtures containing small amounts of macrocycles. On the other hand, the high solubility of certain cryptand complexes, such as 4,7,13,16,21,24-hexaoxa-

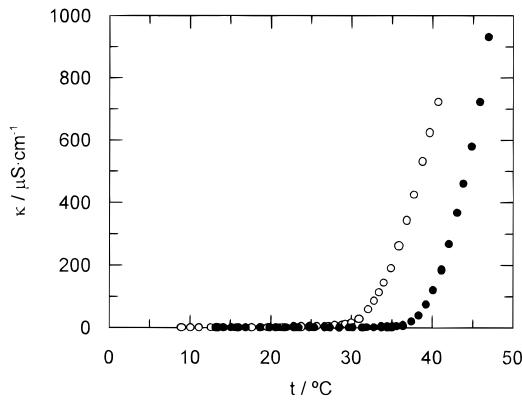
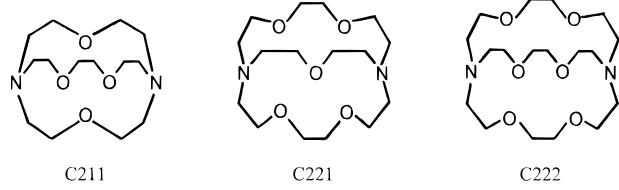


Figure 1. Influence of temperature upon the conductivity of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) + 2,2,4-trimethylpentane + water microemulsions in the presence of different concentrations of C222 ([AOT] = 0.5 mol dm⁻³, $w = [\text{H}_2\text{O}]/[\text{AOT}] = 22.2$): (○) [C222] = 4.48×10^{-2} mol dm⁻³; (●) [C222] = 4.88×10^{-4} mol dm⁻³.

Chart 1



1,10-diazabicyclo[8.8.8]hexacosane (C222), 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane (C221), and 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (C211), in apolar solvents and their capacity to include cations within their cavity confer on them a potential use as phase-transfer catalysts (Lehn, 1995).

The aim of this work is to measure the specific conductivity (κ) of these ternary systems with three different cryptand complexes at varying concentrations and temperatures.

Experimental Section

The aqueous solutions of the cryptand complexes were prepared with distilled-deionized water ($\kappa = 0.10$ – 0.50

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

| <i>t</i> /°C | <i>κ</i> /μS·cm ⁻¹ | <i>t</i> /°C | <i>κ</i> /μS·cm ⁻¹ | <i>t</i> /°C | <i>κ</i> /μS·cm ⁻¹ | <i>t</i> /°C | <i>κ</i> /μS·cm ⁻¹ |
|---|-------------------------------|--------------|-------------------------------|--------------|-------------------------------|--------------|-------------------------------|
| $[C_{222}] = 4.48 \times 10^{-2}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 9.0 | 0.39 | 19.7 | 0.90 | 27.2 | 4.60 | 34.1 | 144.00 |
| 10.1 | 0.42 | 20.7 | 1.04 | 28.0 | 6.17 | 34.9 | 190.00 |
| 11.2 | 0.43 | 21.5 | 1.18 | 28.9 | 8.90 | 35.9 | 260.00 |
| 12.6 | 0.45 | 22.0 | 1.27 | 29.3 | 11.23 | 36.9 | 341.00 |
| 13.5 | 0.48 | 22.9 | 1.50 | 30.0 | 15.30 | 37.8 | 423.00 |
| 14.2 | 0.50 | 23.8 | 1.81 | 31.0 | 27.00 | 38.8 | 530.00 |
| 16.9 | 0.62 | 24.9 | 2.31 | 32.1 | 59.00 | 39.7 | 623.00 |
| 17.7 | 0.69 | 25.7 | 2.97 | 32.9 | 86.00 | 40.7 | 722.00 |
| 18.8 | 0.79 | 26.7 | 3.85 | 33.4 | 110.17 | | |
| $[C_{222}] = 2.99 \times 10^{-2}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 9.0 | 0.29 | 18.7 | 0.58 | 27.3 | 2.30 | 35.0 | 81.00 |
| 10.1 | 0.31 | 19.8 | 0.65 | 28.3 | 2.97 | 35.9 | 121.00 |
| 11.2 | 0.33 | 20.8 | 0.74 | 29.2 | 4.05 | 36.9 | 177.00 |
| 12.6 | 0.35 | 21.9 | 0.84 | 30.0 | 5.50 | 37.6 | 222.00 |
| 13.5 | 0.38 | 22.8 | 0.95 | 30.8 | 7.93 | 38.5 | 300.00 |
| 14.2 | 0.40 | 23.9 | 1.12 | 31.7 | 12.40 | 39.5 | 381.00 |
| 15.8 | 0.45 | 24.6 | 1.27 | 32.3 | 17.90 | 40.3 | 480.00 |
| 16.9 | 0.49 | 25.4 | 1.47 | 33.1 | 28.50 | 41.3 | 595.00 |
| 17.5 | 0.52 | 26.4 | 1.82 | 34.1 | 49.70 | | |
| $[C_{222}] = 9.77 \times 10^{-4}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 14.6 | 0.23 | 21.8 | 0.29 | 29.6 | 0.51 | 36.6 | 21.50 |
| 15.6 | 0.24 | 22.7 | 0.30 | 30.6 | 0.59 | 37.3 | 39.00 |
| 16.5 | 0.25 | 23.3 | 0.31 | 31.4 | 0.69 | 38.2 | 72.00 |
| 17.3 | 0.26 | 24.3 | 0.32 | 32.6 | 0.92 | 39.0 | 110.00 |
| 18.0 | 0.26 | 25.6 | 0.34 | 33.4 | 1.19 | 39.7 | 180.00 |
| 18.9 | 0.28 | 26.5 | 0.35 | 34.5 | 1.93 | 40.9 | 275.00 |
| 19.3 | 0.28 | 27.7 | 0.41 | 35.4 | 3.25 | 42.1 | 400.00 |
| 20.4 | 0.29 | 28.7 | 0.46 | 36.4 | 10.80 | | |
| $[C_{222}] = 4.88 \times 10^{-4}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 13.2 | 0.23 | 23.5 | 0.30 | 31.9 | 0.80 | 39.3 | 74.00 |
| 14.1 | 0.24 | 24.9 | 0.34 | 32.8 | 0.91 | 40.2 | 120.00 |
| 15.2 | 0.24 | 25.4 | 0.35 | 33.8 | 1.33 | 41.2 | 183.00 |
| 16.1 | 0.25 | 26.8 | 0.36 | 34.5 | 1.75 | 42.1 | 265.00 |
| 17.0 | 0.25 | 27.4 | 0.38 | 35.1 | 2.25 | 43.1 | 367.00 |
| 18.7 | 0.26 | 28.6 | 0.43 | 35.7 | 3.50 | 43.9 | 460.00 |
| 19.9 | 0.27 | 29.7 | 0.53 | 36.4 | 5.80 | 44.9 | 580.00 |
| 20.9 | 0.28 | 30.2 | 0.55 | 37.5 | 20.50 | 45.9 | 720.00 |
| 21.9 | 0.28 | 31.4 | 0.70 | 38.4 | 39.00 | 47.0 | 930.00 |
| 22.9 | 0.29 | | | | | | |
| $[C_{222}] = 1.22 \times 10^{-4}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 12.9 | 0.24 | 21.8 | 0.29 | 31.5 | 0.64 | 38.4 | 23.50 |
| 13.6 | 0.24 | 23.2 | 0.30 | 32.5 | 0.79 | 39.3 | 48.70 |
| 14.3 | 0.24 | 24.7 | 0.32 | 33.6 | 1.11 | 40.2 | 86.00 |
| 15.4 | 0.25 | 26.2 | 0.35 | 34.5 | 1.60 | 41.2 | 139.00 |
| 16.0 | 0.25 | 27.5 | 0.38 | 35.5 | 2.67 | 42.2 | 221.00 |
| 17.3 | 0.26 | 29.2 | 0.45 | 36.4 | 4.82 | 42.9 | 286.00 |
| 18.6 | 0.27 | 30.6 | 0.54 | 37.4 | 10.50 | 43.6 | 350.00 |
| 20.0 | 0.28 | | | | | | |
| $[C_{222}] = 3.66 \times 10^{-5}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 12.1 | 0.23 | 21.2 | 0.29 | 29.5 | 0.53 | 36.9 | 8.60 |
| 13.1 | 0.24 | 22.0 | 0.30 | 30.2 | 0.65 | 37.9 | 18.90 |
| 14.2 | 0.24 | 22.7 | 0.30 | 31.4 | 0.73 | 38.8 | 36.50 |
| 15.3 | 0.24 | 23.2 | 0.31 | 32.4 | 1.06 | 39.7 | 71.00 |
| 16.4 | 0.25 | 24.3 | 0.32 | 33.2 | 1.63 | 40.6 | 113.00 |
| 17.3 | 0.25 | 25.2 | 0.34 | 34.3 | 2.70 | 41.6 | 176.00 |
| 18.2 | 0.26 | 26.2 | 0.35 | 35.2 | 3.42 | 42.5 | 257.00 |
| 19.2 | 0.27 | 27.4 | 0.38 | 35.9 | 4.17 | 43.5 | 368.00 |
| 20.1 | 0.28 | 28.5 | 0.48 | | | | |
| $[C_{211}] = 1.40 \times 10^{-2}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 12.1 | 0.27 | 19.2 | 0.33 | 26.3 | 0.48 | 33.1 | 5.40 |
| 13.1 | 0.28 | 20.2 | 0.34 | 27.2 | 0.54 | 34.0 | 18.50 |
| 14.1 | 0.29 | 21.1 | 0.35 | 28.3 | 0.62 | 35.0 | 48.25 |
| 15.1 | 0.30 | 22.4 | 0.36 | 29.2 | 0.74 | 36.0 | 100.00 |
| 16.1 | 0.30 | 23.9 | 0.39 | 30.1 | 0.92 | 36.9 | 170.00 |
| 17.2 | 0.31 | 24.2 | 0.42 | 31.0 | 1.47 | 39.3 | 400.00 |
| 18.1 | 0.32 | 25.6 | 0.45 | 32.0 | 2.50 | | |
| $[C_{211}] = 6.98 \times 10^{-3}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 11.0 | 0.25 | 18.1 | 0.29 | 26.0 | 0.40 | 33.0 | 2.10 |
| 12.1 | 0.25 | 19.2 | 0.30 | 27.3 | 0.46 | 34.0 | 3.50 |
| 13.2 | 0.25 | 20.0 | 0.31 | 28.2 | 0.50 | 35.0 | 8.40 |

Table 1 (Continued)

| <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 | $\kappa/\mu\text{S}\cdot\text{cm}^{-1}$ |
|---|---|--------------|---|--------------|---|--------------|---|
| $[\text{C}211] = 6.98 \times 10^{-3}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 14.3 | 0.26 | 22.5 | 0.32 | 29.7 | 0.60 | 35.9 | 18.00 |
| 15.2 | 0.27 | 23.3 | 0.34 | 31.0 | 0.80 | 36.8 | 35.50 |
| 16.2 | 0.27 | 24.3 | 0.36 | 32.0 | 1.26 | 37.4 | 56.00 |
| 17.2 | 0.28 | 25.1 | 0.38 | | | | |
| $[\text{C}211] = 1.40 \times 10^{-3}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 10.2 | 0.26 | 19.2 | 0.31 | 27.7 | 0.41 | 35.1 | 3.31 |
| 12.1 | 0.26 | 20.1 | 0.31 | 28.9 | 0.46 | 35.9 | 18.00 |
| 13.2 | 0.27 | 21.2 | 0.32 | 30.0 | 0.52 | 36.5 | 34.00 |
| 14.1 | 0.27 | 22.5 | 0.32 | 31.0 | 0.63 | 36.9 | 44.00 |
| 15.1 | 0.28 | 23.7 | 0.33 | 31.9 | 0.79 | 37.4 | 59.00 |
| 16.1 | 0.28 | 24.5 | 0.34 | 32.7 | 0.97 | 37.8 | 75.00 |
| 17.2 | 0.29 | 25.7 | 0.36 | 33.4 | 1.39 | 38.3 | 100.00 |
| 18.1 | 0.30 | 26.4 | 0.38 | 34.1 | 2.00 | | |
| $[\text{C}211] = 6.98 \times 10^{-4}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 13.1 | 0.27 | 20.3 | 0.30 | 27.3 | 0.40 | 34.1 | 2.55 |
| 14.2 | 0.27 | 21.3 | 0.30 | 28.1 | 0.44 | 35.4 | 4.30 |
| 15.4 | 0.27 | 22.1 | 0.31 | 29.1 | 0.48 | 35.8 | 8.80 |
| 16.1 | 0.27 | 23.3 | 0.32 | 30.1 | 0.54 | 36.1 | 18.00 |
| 17.1 | 0.28 | 24.2 | 0.34 | 31.4 | 0.76 | 36.4 | 33.00 |
| 18.2 | 0.29 | 25.2 | 0.35 | 32.5 | 1.08 | 37.0 | 60.00 |
| 19.2 | 0.29 | 26.4 | 0.38 | 33.3 | 1.65 | | |
| $[\text{C}211] = 1.40 \times 10^{-4}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 15.4 | 0.28 | 23.2 | 0.33 | 31.0 | 0.62 | 37.0 | 35.00 |
| 16.3 | 0.28 | 24.1 | 0.35 | 31.7 | 0.67 | 37.3 | 46.00 |
| 17.1 | 0.28 | 25.1 | 0.36 | 33.0 | 1.05 | 37.6 | 51.00 |
| 18.2 | 0.29 | 26.4 | 0.37 | 33.8 | 1.26 | 38.1 | 60.00 |
| 19.2 | 0.30 | 27.3 | 0.39 | 34.0 | 1.65 | 39.0 | 74.00 |
| 20.1 | 0.30 | 28.1 | 0.41 | 34.9 | 3.90 | 39.6 | 89.00 |
| 21.1 | 0.31 | 29.2 | 0.47 | 35.8 | 8.20 | 40.0 | 100.00 |
| 22.5 | 0.32 | 30.0 | 0.52 | 36.5 | 16.25 | | |
| $[\text{C}211] = 6.98 \times 10^{-5}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 18.2 | 0.27 | 25.1 | 0.32 | 31.5 | 0.85 | 36.5 | 8.90 |
| 19.2 | 0.27 | 26.3 | 0.35 | 32.6 | 1.21 | 37.2 | 16.25 |
| 20.1 | 0.27 | 27.2 | 0.37 | 33.7 | 1.48 | 37.5 | 32.00 |
| 21.3 | 0.27 | 28.1 | 0.39 | 34.5 | 2.19 | 38.0 | 51.00 |
| 22.1 | 0.28 | 29.1 | 0.46 | 35.2 | 3.41 | 39.2 | 79.00 |
| 23.0 | 0.29 | 30.2 | 0.59 | 35.9 | 5.38 | 41.0 | 115.00 |
| 24.0 | 0.30 | | | | | | |
| $[\text{C}211] = 1.40 \times 10^{-5}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 16.8 | 0.28 | 24.5 | 0.31 | 32.2 | 1.60 | 36.5 | 23.00 |
| 17.7 | 0.28 | 25.6 | 0.33 | 32.7 | 1.95 | 37.0 | 44.00 |
| 18.1 | 0.28 | 26.5 | 0.35 | 33.0 | 2.10 | 38.0 | 76.00 |
| 19.2 | 0.28 | 27.4 | 0.38 | 33.5 | 2.70 | 39.0 | 100.00 |
| 20.0 | 0.28 | 27.9 | 0.40 | 34.4 | 3.30 | 40.0 | 145.00 |
| 21.2 | 0.29 | 29.0 | 0.46 | 34.7 | 4.00 | 41.0 | 165.00 |
| 22.3 | 0.29 | 29.8 | 0.54 | 35.2 | 6.10 | 42.0 | 185.00 |
| 23.4 | 0.30 | 30.9 | 0.86 | 35.9 | 12.00 | | |
| $[\text{C}221] = 8.42 \times 10^{-3}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 14.1 | 0.29 | 20.0 | 0.36 | 26.6 | 0.80 | 32.1 | 7.20 |
| 15.1 | 0.29 | 21.0 | 0.39 | 27.8 | 1.10 | 33.3 | 18.50 |
| 16.3 | 0.30 | 22.3 | 0.43 | 28.6 | 1.40 | 34.0 | 27.00 |
| 17.1 | 0.31 | 23.4 | 0.49 | 29.4 | 1.95 | 35.0 | 44.00 |
| 18.2 | 0.33 | 24.7 | 0.56 | 30.4 | 2.80 | 36.0 | 68.00 |
| 19.0 | 0.34 | 25.7 | 0.68 | 31.5 | 4.95 | 37.0 | 98.00 |
| $[\text{C}221] = 4.21 \times 10^{-3}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 28.3 | 0.44 | 31.5 | 0.94 | 35.2 | 5.40 | 38.1 | 31.00 |
| 29.1 | 0.52 | 32.5 | 1.33 | 35.6 | 9.20 | 39.0 | 48.00 |
| 29.9 | 0.60 | 33.5 | 2.13 | 36.5 | 14.20 | 39.9 | 70.00 |
| 30.5 | 0.69 | 34.3 | 3.25 | 37.4 | 22.00 | | |
| $[\text{C}221] = 8.42 \times 10^{-4}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 16.1 | 0.29 | 24.1 | 0.33 | 31.8 | 0.96 | 37.8 | 52.00 |
| 17.1 | 0.30 | 25.3 | 0.34 | 32.9 | 1.50 | 38.0 | 62.00 |
| 18.1 | 0.30 | 26.5 | 0.38 | 33.9 | 2.75 | 38.6 | 98.00 |
| 19.1 | 0.30 | 27.7 | 0.43 | 34.5 | 4.00 | 39.0 | 136.00 |
| 20.1 | 0.31 | 28.6 | 0.49 | 35.3 | 8.10 | 40.1 | 205.00 |
| 22.1 | 0.31 | 29.7 | 0.59 | 36.0 | 13.00 | 40.9 | 240.00 |
| 23.2 | 0.32 | 30.9 | 0.76 | 36.9 | 28.00 | | |
| $[\text{C}221] = 4.21 \times 10^{-4}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 20.3 | 0.35 | 26.6 | 0.44 | 32.0 | 0.49 | 36.7 | 9.00 |
| 21.2 | 0.36 | 27.6 | 0.46 | 33.3 | 0.62 | 37.5 | 21.00 |
| 22.8 | 0.38 | 28.5 | 0.47 | 34.2 | 0.92 | 38.3 | 46.00 |

Table 1 (Continued)

| $t^{\circ}\text{C}$ | $\kappa/\mu\text{S}\cdot\text{cm}^{-1}$ | $t^{\circ}\text{C}$ | $\kappa/\mu\text{S}\cdot\text{cm}^{-1}$ | $t^{\circ}\text{C}$ | $\kappa/\mu\text{S}\cdot\text{cm}^{-1}$ | $t^{\circ}\text{C}$ | $\kappa/\mu\text{S}\cdot\text{cm}^{-1}$ |
|---|---|---------------------|---|---------------------|---|---------------------|---|
| $[\text{C}221] = 4.21 \times 10^{-4}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 23.3 | 0.39 | 29.6 | 0.48 | 35.5 | 1.60 | 39.8 | 80.00 |
| 24.1 | 0.40 | 30.9 | 0.48 | 36.0 | 2.80 | 41.0 | 125.00 |
| 25.6 | 0.42 | 31.2 | 0.49 | | | | |
| $[\text{C}221] = 8.42 \times 10^{-5}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 15.5 | 0.27 | 23.2 | 0.31 | 30.0 | 0.52 | 36.5 | 6.20 |
| 16.1 | 0.27 | 24.1 | 0.32 | 31.0 | 0.63 | 37.0 | 12.00 |
| 17.2 | 0.28 | 25.4 | 0.33 | 32.0 | 0.77 | 37.5 | 20.00 |
| 18.3 | 0.28 | 26.4 | 0.34 | 33.3 | 1.12 | 38.0 | 31.00 |
| 19.2 | 0.28 | 27.5 | 0.36 | 33.9 | 1.39 | 39.0 | 52.00 |
| 20.1 | 0.29 | 28.6 | 0.42 | 35.0 | 2.05 | 40.0 | 85.00 |
| 21.1 | 0.29 | 29.4 | 0.46 | 36.0 | 3.60 | 41.0 | 130.00 |
| 22.3 | 0.30 | | | | | | |
| $[\text{C}221] = 4.21 \times 10^{-5}/\text{mol}\cdot\text{dm}^{-3}$ | | | | | | | |
| 20.1 | 0.32 | 26.2 | 0.41 | 32.5 | 0.59 | 37.1 | 9.00 |
| 21.1 | 0.33 | 27.1 | 0.42 | 33.4 | 0.66 | 38.6 | 18.00 |
| 22.3 | 0.34 | 28.2 | 0.43 | 34.2 | 0.91 | 39.2 | 25.00 |
| 23.2 | 0.36 | 29.3 | 0.44 | 35.3 | 1.52 | 40.1 | 40.00 |
| 24.1 | 0.37 | 30.5 | 0.48 | 36.2 | 2.60 | 41.5 | 75.00 |
| 25.2 | 0.38 | 31.6 | 0.53 | | | | |

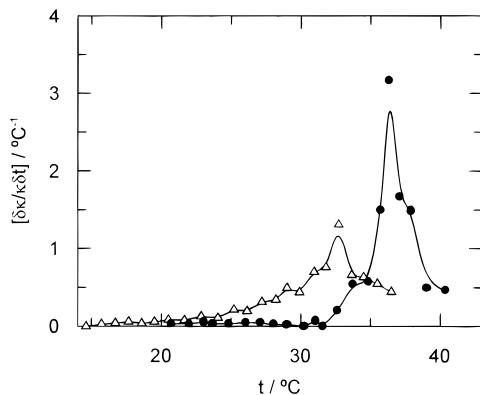


Figure 2. Determination of the percolation temperature by the Kim method (Kim and Huang, 1986), for AOT + 2,2,4-trimethylpentane + water microemulsions in the presence of different cryptand C221 concentrations ($[\text{AOT}] = 0.5 \text{ mol dm}^{-3}$, $w = [\text{H}_2\text{O}]/[\text{AOT}] = 22.2$): (●) $[\text{C}221] = 4.21 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$; (△) $[\text{C}221] = 8.42 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$.

$\mu\text{S}\cdot\text{cm}^{-1}$). All reagents were supplied by Merck and Sigma and were of maximum purity available commercially (>99%). All solutions were prepared by mass with deviations of less than $\pm 0.2\%$ from the desired concentrations. The concentration of the cryptand complexes considered in this work have been referenced to the water volume of the microemulsion. The samples (microemulsion + cryptand complex) were prepared by direct mixing under vigorous stirring.

The specific conductivity was measured by employing a conductivity radiometer CDM 3, with a conductivity cell of constant 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 conductivity, the temperature was regulated using a thermostat–cryostat with a precision of $\pm 0.1 \text{ }^{\circ}\text{C}$. 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 conductivity value reported was an average of five samples, where the maximum deviations from the average value were always less than 2%. The percolation temperature was determined through the study of the influence of temperature on the specific conductivity of the microemulsion.

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

| cryptand | [cryptand]/ $\text{mol}\cdot\text{dm}^{-3}$ | $t_p/{}^{\circ}\text{C}$ | | | |
|----------|---|--------------------------|------|-------|----|
| | | A | B | C | |
| none | 0 ^a | 32.60 | 0.39 | -3.30 | 33 |
| C222 | 4.48×10^{-2} | 27.94 | 0.49 | -7.47 | 28 |
| | 2.99×10^{-2} | 29.71 | 0.51 | -6.36 | 30 |
| | 9.77×10^{-4} | 37.24 | 0.26 | -4.63 | 36 |
| | 4.88×10^{-4} | 37.17 | 0.32 | -4.47 | 37 |
| | 1.22×10^{-4} | 37.11 | 0.29 | -4.79 | 37 |
| | 3.66×10^{-5} | 36.14 | 0.40 | -4.05 | 36 |
| C211 | 1.40×10^{-2} | 33.60 | 0.26 | -3.95 | 33 |
| | 6.98×10^{-3} | 35.29 | 0.25 | -4.08 | 35 |
| | 1.40×10^{-3} | 36.77 | 0.21 | -4.66 | 36 |
| | 6.98×10^{-4} | 36.42 | 0.21 | -4.12 | 36 |
| | 1.40×10^{-4} | 35.37 | 0.39 | -3.22 | 35 |
| | 6.98×10^{-5} | 35.10 | 0.50 | -3.11 | 35 |
| C221 | 1.40×10^{-5} | 34.71 | 0.46 | -3.79 | 35 |
| | 8.42×10^{-3} | 30.88 | 0.63 | -3.98 | 32 |
| | 4.21×10^{-3} | 33.73 | 0.77 | -2.66 | 34 |
| | 8.42×10^{-4} | 34.71 | 0.39 | -3.20 | 35 |
| | 4.21×10^{-4} | 39.20 | 0.28 | -5.56 | 38 |
| | 8.42×10^{-5} | 36.49 | 0.36 | -3.83 | 37 |
| | 4.21×10^{-5} | 35.88 | 0.28 | -5.57 | 36 |

^a Álvarez et al., 1998c.

Results and Discussion

The effect of concentration of three cryptand complexes—C222, C221, and C21 (Chart 1)—on the process of electric percolation has been studied. A series of conductivity–temperature data for different cryptand concentrations were measured. In these experiments the macrocycle concentration was varied between 1.4×10^{-5} and $4.48 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ while the microemulsion composition was kept constant and equal to $[\text{AOT}] = 0.5 \text{ mol}\cdot\text{dm}^{-3}$ and $w = [\text{water}]/[\text{AOT}] = 22.2$.

The values of the specific conductivity–temperature, obtained for different cryptand complex concentrations are shown in Table 1. From these data it is possible to obtain the percolation temperature, t_p , using the method described elsewhere (Álvarez et al., 1998a) and illustrated in Figure 2. In Table 2, t_p values induced in the standard microemulsion by cryptand complex concentrations used in this study are listed. Low cryptand concentrations hinder the electric percolation phenomenon, but medium and high concentra-

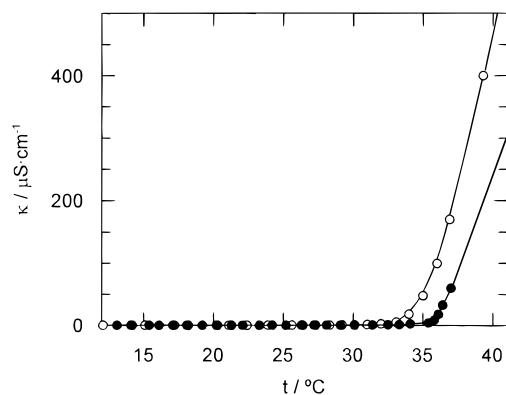


Figure 3. Fit of temperature-conductivity data for AOT + 2,2,4-trimethylpentane + water microemulsions in the absence and presence of different C211 concentrations ($[AOT] = 0.5 \text{ mol dm}^{-3}$, $w = [\text{H}_2\text{O}]/[\text{AOT}] = 22.2$): (○) $[C211] = 1.40 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$; (●) $[C211] = 6.98 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$.

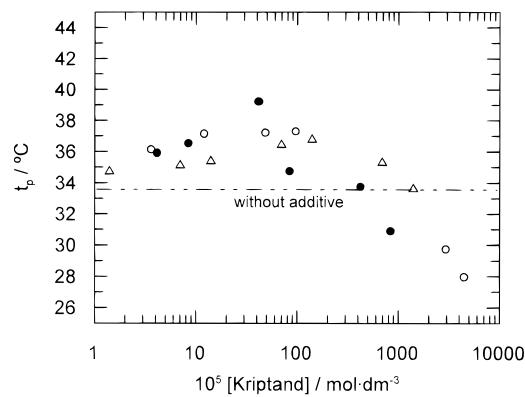


Figure 4. Variation of A from eq 1 (t_p) with cryptand concentration: (△) C211; (●) C221; (○) C222.

tions favor the percolation (see Figure 4). The observed behavior at low cryptand concentration can be justified by taking into account the complexing ability of the cryptand with respect to the Na^+ counterion of AOT ions and their transfer to the AOT film (García-Río et al., 1997; Schuebel, 1998). On the other hand, at high cryptand concentration we cannot forget the organic nature of these substrates, and in this way, its behavior corresponds with that observed for other organic compounds and can be justified by their capacity of association with the surfactant film (Álvarez et al., 1998a; García-Río et al., 1994).

The variation of conductivity in these systems can be rationalized through an empirical equation (Álvarez et al., 1998b):

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

The fit of κ/t values was satisfactory (Figure 3) in all cases studied, and the parameters A , B , and C are shown

in Table 2. The value of parameter A corresponds to the temperature of percolation. Equation 1 reproduces the experimental conductivity data with a deviation of less than 4%.

Acknowledgment

J.P.-J. thanks the Ministerio de Educación y Ciencia for a grant. The authors thank the Xunta de Galicia and Dirección General de Enseñanza Superior for financial support of their work.

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Received for review September 29, 1999. Accepted January 17, 2000.

JE990266P