

# Transport Properties of Concentrated Aqueous Sodium Dodecyl Sulfate Solutions in Polymer Membranes Derived from Cellulose Esters

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Polymer membranes with differing degrees of hydrophilicity were prepared from mixtures of cellulose acetate butyrate and cellulose acetate hydrogen phthalate. The degree of hydrophilicity was determined from measurements of water uptake and the apparent water diffusion coefficient. The transport properties of sodium dodecyl sulfate through these membranes were studied by measuring permeability using the time-lag technique. The mutual differential diffusion coefficients of the surfactant are 1–2 orders of magnitude lower than in aqueous solution. The permeability and partition coefficients between the aqueous subphase and membranes were found to depend on the hydrophilicity of the polymer blend, but to be virtually independent of temperature. Possible applications of these systems in surfactant purification are suggested.

## Introduction

Interactions between polymers and surfactants are of considerable practical importance, and studies on polymer–surfactant systems have been extensively reviewed.<sup>1–5</sup> Various models have been presented for these interactions,<sup>3,6–9</sup> which differ in their degree of sophistication. However, they can be considered in terms of two limiting cases, one where the interactions are strongly cooperative, and surfactant monomer binds to the polymer, and a second limit where surfactant micelles retain their integrity to form discrete clusters (pearl-necklace model) along the polymer chain. The relevant model to be applied depends strongly on the degree of hydrophilic character of the polymer.

Particular interest has been focused on the interactions between ionic surfactants, such as sodium dodecyl sulfate (SDS) and cellulose derivatives.<sup>10–20</sup> With the water-soluble ethyl(hydroxyethyl)cellulose (EHEC) these inter-

actions lead to the formation of gel phases under certain conditions.<sup>13,15–18</sup> These have a number of important practical applications. The surfactant–polymer interactions have been studied by various physical techniques, including cloud point measurements,<sup>10</sup> gel filtration,<sup>14</sup> electrical conductivity,<sup>12</sup> time-resolved fluorescence quenching,<sup>12</sup> rheology measurements,<sup>13,16,17</sup> dynamic light scattering,<sup>13</sup> nuclear magnetic resonance (NMR) self-diffusion,<sup>15</sup> vibrational spectroscopy,<sup>18</sup> and use of surfactant-selective electrodes.<sup>19</sup> The results indicate that there is a strong temperature-dependent interaction between SDS and EHEC, both below and above the conditions for gel formation. The surfactant critical micelle concentration (cmc) decreases in the presence of the polymer, and at low temperatures above the cmc small surfactant micellar aggregates form within the polymer domain.<sup>12</sup> These appear to involve mainly binding of the sulfate headgroups to the side chains of the polymer.<sup>18</sup> As the temperature increases more specific surfactant binding to the polymer occurs.<sup>12,15</sup> This may be associated with interactions between the surfactant headgroup and glucose rings on the cellulose ether chain, in addition to interactions with polymer-bound water molecules.<sup>18</sup> Although some details of these interactions remain to be clarified, a fairly detailed picture is now available for surfactant interactions with this water-soluble cellulose derivative. In contrast, rather less is known about interactions with SDS and water-insoluble cellulose derivatives, although these are likely to be important in many areas, including textile<sup>21</sup> and

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**Table 1. Composition of Membranes Prepared in 10 % (w/v) THF<sup>a</sup>**

| polymer blend | CAB fraction/wt % | CAHP fraction/wt % | pH <sup>b</sup> |
|---------------|-------------------|--------------------|-----------------|
| I             | 100               | 0                  | 6.239           |
| II            | 33.3              | 66.7               | 3.781           |
| III           | 14.3              | 85.7               | 3.594           |

<sup>a</sup> THF = tetrahydrofuran; CAB = cellulose acetate butyrate; CAHP = cellulose acetate hydrogen phthalate. <sup>b</sup> pH values of water (80 mL, initial pH 6.315) after 1 week of contact with membranes (approximately 20–40 mg).

paper<sup>22</sup> processing, and separation science.<sup>23</sup> Although quantitative studies have been reported on the interactions of SDS with latex particles,<sup>24</sup> we are not aware of any detailed results on the interactions of SDS with films of cellulose derivatives.

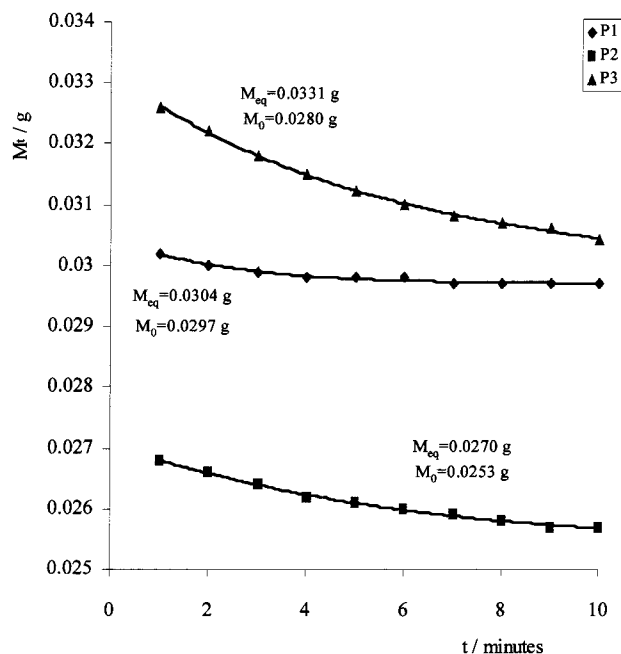
We have previously reported the application of our method, originally developed for calculating mutual differential diffusion coefficients of electrolytes in aqueous solution<sup>25–27</sup> from electrochemical conductivity measurements, to the study of diffusion of electrolytes in polymer membranes.<sup>28–31</sup> These measurements are extended to a study of the diffusion of ionic surfactants in polymer films, and we report the diffusion of the surfactant SDS in cellulose ester membranes of differing hydrophilicity. The materials were prepared from mixtures of the relatively hydrophobic polymer cellulose acetate butyrate and the more hydrophilic cellulose acetate hydrogen phthalate, and their degree of hydrophilicity was quantified.

### Experimental Section

**Reagents.** Experiments on SDS permeability through cellulose-derivative membranes were performed using aqueous solutions (0.11–0.44 mol dm<sup>-3</sup>), obtained by dissolving the corresponding amount of solid SDS (Merck, pro analysis) in distilled water. SDS standard solutions were prepared by dilution of the above concentrated solution and used to study the dependence of conductivity on SDS concentration.

**Preparation and Characterization of Membranes.** Table 1 shows the composition of three different polymer blends derived from cellulose acetate butyrate (CAB) (containing 17% butyrate) and cellulose acetate hydrogen phthalate (CAHP).

The two polymers were initially dissolved in tetrahydrofuran (Merck) (concentration 10% w/v) and stirred for 24 h. Subsequently, the polymer blend of required composition was prepared by mixing appropriate quantities of each solution and stirring for a further 24 h. The solution was then deposited on a flat glass support and spread out with a specially designed apparatus to produce a membrane of uniform thickness (approximately 0.33 mm). After complete evaporation of the solvent at room tem-



**Figure 1.** Water desorption for the three different cellulose ester membranes studied at 25 °C.

perature, the membrane was removed from the glass support with the help of water.

The hydrophilic character of the membranes was characterized by measuring the degree of hydrophilicity ( $H_p$ , taken as the percentage weight gain on water sorption) and the apparent water diffusion coefficient ( $D_w$ , calculated from water desorption curves). Three samples of each membrane were placed in a desiccator containing a saturated solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , which provides a relative humidity of 98%. Each specimen remained inside the desiccator until the sample weight reached an equilibrium value,  $M_{eq}$  (normally 2 days as found by a control experiment). Then, water desorption to constant weight,  $M_o$ , was carried out inside a vacuum oven at 100 °C. After any drops of water were wiped off, the weight of the membrane, ( $M_t$ ) was measured at selected times using an analytical balance (Sartorius Analytical,  $\pm 0.1$  mg).

$M_{eq}$  and  $D_w$  were computed using a Fickian approach to fitting the water desorption curves (Figure 1)

$$M_t/M_{eq} = 1 - 4(D_w t/\pi^2 l^2)^{0.5} \quad (1)$$

following which  $H_p$  was calculated as

$$H_p = (M_{eq} - M_o)100/M_o \quad (2)$$

The polymer CAHP contains an ionizable carboxylic acid group. To assess the degree of dissociation of this acid in contact with water, samples of the three membranes (20–40 mg) were kept in contact with 80 mL of water at 25 °C, and the pH of the aqueous phase was measured after a week, using a combined pH electrode and a Radiometer PHM240 pH meter, with a pH resolution of 0.001. These values are also presented in Table 1. While “pH” within a polymer membrane is a dubious concept, the fact that the values for the supernatant phases in contact with membranes P2 and P3 are below typical values for model aromatic carboxylic acids, such as 2-acetoxybenzoic acid ( $pK_a = 4.57$ ),<sup>32</sup> strongly suggests that the carboxylic acid group is predominantly protonated under these conditions.

**Permeability Measurements.** SDS transport properties were analyzed by measuring the permeability of this surfactant through polymer membranes using the time-lag technique.<sup>33</sup>

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**Table 2. Degree of Hydrophilicity  $H_p$ , and Apparent Water Diffusion Coefficients,  $D_w$ , in Cellulose Derivatives at 25 °C**

| polymer blend | $H_p(\pm s)/\%$ | $D_w(\pm s)/(10^{-11} \text{ m}^2 \text{ s}^{-1})$ |
|---------------|-----------------|--|
| P1            | 3.4(0.5)        | 8.3(0.3)   |
| P2            | 8.3(0.4)        | 2.9(0.3)   |
| P3            | 20(1)           | 1.2(0.2)   |

Since this technique has been described in detail elsewhere,<sup>34</sup> we will only specify details relating to our experimental conditions. The device consisted of two 250 mL cells filled with surfactant solution (A) and water (B), respectively. These two cells were connected by two 7 mm radius horizontal tubes. The polymer membrane was sealed, with silicone, between these two tubes. Control experiments were performed to ensure that there is no silicone in the permeation area, and that the mass transport occurs at the polymer–solution interface only. To prevent any contribution from the hydrostatic pressure<sup>34</sup> to the mass flux, cell A was filled with 180 mL of SDS solution, while 170 mL of water was used in the other cell. The membranes were immersed in water for at least 3 days prior to the experiments. The change in the SDS concentration in cell B was determined during the permeability experiment by measuring the electrical conductivity in this cell by a YSI 3200 instrument. The conductivity instrument was calibrated (i.e., the dependence of the conductivity on the SDS concentration measured) prior to each experiment using at least five freshly prepared standard solutions of SDS with different concentrations at least an order of magnitude lower than the cmc. The same conditions were used for calibration and permeability experiments. Constant temperature ( $\pm 0.1$  °C) was maintained throughout the experiments by immersing the system in a thermostat bath (Velp Scientifica Multistirrer 6). Solutions in both cells were stirred at ca. 200 rpm to decrease the Nernst layer in the membrane–solution interface and to increase the reproducibility of the conductivity sensor. Data were recorded during the first 10 h for each experiment, with the time being sufficient to secure a steady-state flux of surfactant, but such that its concentration in cell B was always well below the cmc ( $\leq 10\%$ ).

**Time-Lag Method.** The permeability of SDS through the polymeric membranes can be described in terms of Fickian diffusion<sup>35</sup>

$$\partial C/\partial t = \partial/\partial x (D_F \partial C/\partial x) \quad (3)$$

with the boundary and initial conditions  $C(0, t) = C_{\text{SDS}}$ ,  $C(l, t) = 0$ , (where  $C_{\text{SDS}}$  is the concentration of the surfactant in the membrane) and  $C(x, 0) = 0$ , resulting in the simple formulas for calculation of the permeability ( $P$ ) and apparent diffusion coefficient ( $D_F$ )

$$P_s = J/l c_{\text{SDS}} \quad (4)$$

$$D_F = l^2/6\theta \quad (5)$$

where  $l$  is the thickness of the polymeric membrane, measured after each experiment at 25 °C using a Helias micrometer ( $\pm 0.01$  mm),  $J$  is a steady-state flux through the membrane,  $\theta$  is its time-lag, and  $c_{\text{SDS}}$  is the bulk concentration of the SDS ( $c_{\text{SDS}} = Kc_{\text{SDS}}$ ;  $K$  is the partition coefficient).

However, when the surfactant concentration in solution is above the cmc, the diffusion of the surfactant is complicated by the aggregation equilibrium between single surfactant molecules and micelles. In this case, which is the case for our experimental conditions, the flux of the surfactant through a polymer membrane depends on the concentrations of counterions, monomers, and micelles.<sup>36,37</sup>

The formation and destruction of micelles are much faster processes than surfactant diffusion.<sup>36</sup> Since at concentrations

**Table 3. Diffusion Coefficients,  $D_m$ , of SDS Monomers in Polymer Blends Derived from Cellulose at 25 and 40 °C**

| polymer blend | [SDS]/M | $T = 25$ °C  | $T = 40$ °C  |
|---------------|---------|--|--|
|               |         | $D_m(\pm s)/(10^{-12} \text{ m}^2 \text{ s}^{-1})$ | $D_m(\pm s)/(10^{-12} \text{ m}^2 \text{ s}^{-1})$ |
| P1            | 0.11    | 1.8(0.3)   | 9.4(0.8)   |
|               | 0.22    | 3.0(0.3)   | 14(1)  |
|               | 0.33    | 1.3(0.2)   | 15(2)  |
|               | 0.44    | 2.2(0.2)   | 17(5)  |
| P2            | 0.11    | 1.8(0.6)   | 5.6(0.4)   |
|               | 0.22    | 1.4(0.2)   | 8.8(0.2)   |
|               | 0.33    | 5.5(0.9)   | 19(1)  |
|               | 0.44    | 8.4(1.3)   | 21(5)  |
| P3            | 0.11    | 7.0(0.8)   | 5.3(0.8)   |
|               | 0.22    | 14(1)  | 4.0(0.3)   |
|               | 0.33    | 15(5)  | 4.0(0.5)   |
|               | 0.44    | 12(2)  | 8.4(0.4)   |

above the cmc the concentration of surfactant present as micelles is usually higher than that of free monomer, the diffusion of surfactants is normally micelle controlled.<sup>38</sup> However, this is not the case for the polymer membranes, since the amount of water inside the polymers and the morphological structure and free volume of the membranes do not allow high molecular weight species, such as micelles, to contribute to the diffusion of the surfactant. Although the membranes P2 and P3 are not completely transparent, possibly indicating some microcrystalline zones,<sup>39,40</sup> the solvent evaporation technique used to form these films normally yields membranes with relatively low porosity, which depends on the chemical nature of the polymer.<sup>41</sup> Scanning electron microscopy, thermal analysis, and high-resolution <sup>13</sup>C CP/MAS nuclear magnetic resonance spectral studies on cellulose ester membranes prepared in the same way show that all those films may have zones with different degrees of crystallinity, and that while the surface presents pores and rough zones, the bulk of the film does not show any large pores.<sup>40</sup> Therefore, we assume that the diffusing species permeating the polymer membranes are the surfactant monomers. We may consequently assume that the apparent Fickian diffusion coefficient is that due to the monomer ( $D_F = D_m$ ). These assumptions mean that, as long as the SDS concentration in cell A is above the cmc, the monomer concentration on this side of the polymer membrane remains constant ( $C(0, t) = [\text{SDS}]_{\text{cmc}}$ ) due to the monomer/micelle equilibrium. Therefore eq 6 can be rewritten as

$$P_s = J/l[\text{SDS}]_{\text{cmc}} \quad (6)$$

The critical micelle concentrations for SDS used in eq 6, were  $8.16 \times 10^{-3}$  and  $8.60 \times 10^{-3}$  mol dm<sup>-3</sup> at 25 and 40 °C, respectively.<sup>42</sup> It is also reasonable to assume that the counterion (sodium ion) diffuses with the dodecyl sulfate according to the electroneutrality principle.<sup>43</sup>

The partition coefficient between the membrane and solvent,  $K$ , was finally calculated as  $P/D$ .

## Results and Discussion

Table 2 shows the water uptake,  $H_p$ , and water diffusion coefficients,  $D_w$  in three different polymeric membranes. These can be related directly to the degree of hydrophilicity of the membranes, and polymer blends P1 and P2 can be characterized as “moderately hydrophilic”, while P3 is classified as “hydrophilic”.<sup>44</sup> This allows an analysis of

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**Table 4. Permeability,  $P_m$ , and Partition Coefficients,  $K$ , of SDS Monomers in Polymer Blends Derived from Cellulose at 25 and 40 °C**

| polymer blend | [SDS]/M | $T = 25\text{ °C}$                    |                      | $T = 40\text{ °C}$                    |                       |
|---------------|---------|---------------------------------------|----------------------|---------------------------------------|-----------------------|
|               |         | $P_m(\pm s)/\text{m}^2\text{ s}^{-1}$ | $K$                  | $P_m(\pm s)/\text{m}^2\text{ s}^{-1}$ | $K$                   |
| P1            | 0.11    | $0.3(0.06) \times 10^{-17}$           | $1.7 \times 10^{-6}$ | $1.7(0.4) \times 10^{-17}$            | $1.8 \times 10^{-6}$  |
|               | 0.22    | $1.3(0.8) \times 10^{-17}$            | $4.3 \times 10^{-6}$ | $1.5(0.3) \times 10^{-17}$            | $1.1 \times 10^{-6}$  |
|               | 0.33    | $1.7(1.0) \times 10^{-17}$            | $13 \times 10^{-6}$  | $3.6(0.9) \times 10^{-17}$            | $2.4 \times 10^{-6}$  |
|               | 0.44    | $2.2(0.3) \times 10^{-17}$            | $10 \times 10^{-6}$  | $2.1(0.3) \times 10^{-17}$            | $1.2 \times 10^{-6}$  |
| P2            | 0.11    | $8.6(0.7) \times 10^{-18}$            | $4.8 \times 10^{-6}$ | $3.1(0.3) \times 10^{-14}$            | $0.55 \times 10^{-2}$ |
|               | 0.22    | $5.9(0.0) \times 10^{-18}$            | $4.2 \times 10^{-6}$ | $9.7(0.1) \times 10^{-14}$            | $1.1 \times 10^{-2}$  |
|               | 0.33    | $10(4) \times 10^{-18}$               | $1.8 \times 10^{-6}$ | $19(8) \times 10^{-14}$               | $1 \times 10^{-2}$    |
|               | 0.44    | $13(0) \times 10^{-18}$               | $1.5 \times 10^{-6}$ | $30(10) \times 10^{-14}$              | $1.4 \times 10^{-2}$  |
| P3            | 0.11    | $0.73(0.11) \times 10^{-13}$          | $1 \times 10^{-2}$   | $0.72(0.09) \times 10^{-13}$          | $1.4 \times 10^{-2}$  |
|               | 0.22    | $1.7(1.3) \times 10^{-13}$            | $1.2 \times 10^{-2}$ | $1.7(1.2) \times 10^{-13}$            | $4.3 \times 10^{-2}$  |
|               | 0.33    | $3.6(0.5) \times 10^{-13}$            | $2.4 \times 10^{-2}$ | $3.4(0.5) \times 10^{-13}$            | $8.5 \times 10^{-2}$  |
|               | 0.44    | $7.5(0.1) \times 10^{-13}$            | $6.3 \times 10^{-2}$ | $4.5(1.7) \times 10^{-13}$            | $5.4 \times 10^{-2}$  |

the potential selectivity of these membranes toward the diffusion of concentrated SDS solutions (0.1–0.44 mol dm<sup>-3</sup>). These values confirm that addition of cellulose acetate hydrogen phthalate increases membrane hydrophilicity. Another contributing factor to the hydrophilic character of the blends may be phase separation of the two polymers, which clearly occurs in P3. However, lower apparent values of water diffusion coefficient in more hydrophilic materials can also be explained by the formation of the water clusters due to a high local water concentration increase combined with these phase separation effects. This feature of the water diffusion coefficient is reported as typical for cellulose derivatives.<sup>44,45</sup> Information on the interaction of water with cellulose ester membranes has also come from NMR spectral<sup>46</sup> and relaxation time<sup>47</sup> measurements, and shows the presence of both polymer-bound and bulk water.

Diffusion coefficients of SDS were measured in the polymer membranes at 25 and 40 °C. The diffusion coefficients of SDS monomers ( $D_m$  as in Table 3) are 1–2 orders of magnitude lower than those reported for an aqueous solution.<sup>48</sup> This shows that the polymeric matrix plays an important role in mass transport by diffusion, and acts essentially as an obstacle to the diffusion process, increasing the effective diffusion path of the SDS.

Given the fairly large standard deviations inherent in these measurements, it can be seen that, except for blend P2 at 40 °C, the diffusion coefficients are nearly constant for each system, supporting our assumption that the monomer species are the only significant diffusing species inside membranes. This low precision in the determination of integral diffusion coefficients appears to be a common feature of these systems, and may be a consequence of three effects, differences between the polymer membrane samples, an additional flux due to convection, and the formation of Nernst layers, which may all affect the final flux. These will, hence, affect the values determined for the diffusion and permeability coefficients. The surfactant behavior in P2 at 40 °C requires further consideration. Possibly, the increase in  $D_m$  with SDS concentration in this case may be related to structural changes within the blend due to the temperature increase. Such a change in SDS diffusion behavior is accompanied in P2 by alterations in other parameters (solubility and permeability).

The lower diffusion coefficient observed at higher temperature in the blend P3 can be explained by an

increase in the quantity of SDS within the membrane (Table 4), which may result in aggregation due to more intense monomer–monomer or monomer–polymer interactions, as has been reported for SDS and EHEC in aqueous solution<sup>49,50</sup> interactions. The higher concentration of micelles and/or SDS aggregates should reduce measurable apparent diffusion coefficients.<sup>51</sup> In addition, it is possible that changes in the conformation of the polymers occur on increasing temperature. On the basis of a model for the phase behavior of aqueous solutions of poly(ethylene oxide),<sup>52</sup> it has been suggested that conformational changes are important in the temperature dependence of SDS–cellulose ether interactions in solution.<sup>10</sup>

Table 4 shows the permeability,  $P_m$ , and partition  $K$ , coefficients of the monomers of SDS at 25 and 40 °C.

It is not possible to measure SDS permeability at surfactant concentrations below 0.1 mol dm<sup>-3</sup>, and some uncertainty exists in the measurements at the lowest concentrations. However, from these results it can be seen that the solubility and permeability of SDS and, therefore, the selectivity of the membrane to surfactant can be affected in two ways. Homopolymer P1 is characterized by having a lower SDS solubility in the membrane at higher temperature, with the effect being more pronounced at the higher SDS concentrations. When this is combined with an increase of the diffusion coefficient, it results in a surfactant permeability which is nearly independent of temperature. SDS permeability through the blend P3 is also unaffected by temperature. However, the solubility and diffusion dependencies on temperature in this material are exactly the opposite of those in P1. Increasing the temperature increases further the hydrophilicity of P3, leading to an increase in the solubility of the surfactant. An increase in the permeability coefficients is also observed with an increase of the hydrophilicity of the polymer, as measured by the increased water uptake,  $H_p$ . In addition to the hydrophilicity of the polymer, specific interactions increase between SDS and the membranes, such as those observed with EHEC in aqueous solution.<sup>12,15,18,19</sup> Our measurements do not provide any quantitative information on this. However, pH measurements (see the Experimental Section) favor an assumption that the acidic groups in CAHP are all likely to be protonated, such that anion–anion repulsion is not likely to be important, while specific interactions with either the cellulose backbone or the ester side groups will depend strongly on the access of the SDS, and hence on membrane hydrophilicity.

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In general, SDS permeability increases with its concentration, showing that although micelles do not permeate the membrane, they do produce further pressure on the solution–membrane interface. This pressure is an extra factor contributing to the transport process, resulting in an increase in the monomer permeability coefficient. It also shows the difficulties in measurements of SDS permeability at concentrations below  $0.1 \text{ mol dm}^{-3}$ .

### Concluding Remarks

Experimental data on the mass transport of concentrated aqueous solutions of SDS in cellulose ester based membranes show a high selectivity of these materials to SDS, which depends on both the water uptake capacity of the membrane and the temperature. A blend of the two cellulose esters (P2) was prepared, which showed very

interesting behavior in terms of SDS permeability, solubility, and diffusion coefficients, which suggests that the macromolecular structure of this blend is very sensitive to the temperature. This formulation could be a starting material for the development of matrixes with very broad commercial applications in terms of surfactant separation and purification. Work is in progress to extend these studies to surfactants with different chain lengths and charges.

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