

## Molecular Association in Alcoholic Media as Studied by Dielectric Measurements. Applications to Microemulsions

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Relative dielectric constants ( $\epsilon_{12}$  and  $\epsilon_{123}$ ) of alcohol–water and alcohol–water–surfactant solutions are reported. The binary systems show a decrease in  $\epsilon_{12}$ , when water is added to the solution of a long-chain alcohol. This behaviour is explained by an extensive hydrogen bonding, which may end up with a maximum of four alcohol molecules bound to each water molecule. The importance of the hydroxylic concentration in the pure alcohol for the association is pointed out. When discussing w/o microemulsions at the highest contents of the alcohol, *i.e.* at weight fractions of n-nonanol and n-decanol exceeding 0.90, special attention is directed towards the hydration conditions of the surfactant molecule.

When comparing the amphiphilic aggregation in aqueous and non-aqueous media, a question of, at least, phenomenological interest is the existence of a critical micelle concentration, c.m.c., in the water-free environment.<sup>1–8</sup> In order to view this problem, the role of the solvent must be briefly discussed. The unique structure of water and its specific interactions with the amphiphilic molecules resulting from aggregation, have been put forward as factors favouring the formation of micelles in an aqueous medium.<sup>9–10</sup> When describing the micellization phenomenon in nonpolar solutions a generalization is dangerous, since the details of the process certainly depend on the type of the amphiphile as well as on the degree of intermolecular hydrogen bonding in the solvent. When proceeding from the polar, aqueous medium to the semi-polar or alternatively to the completely nonpolar environment, the aggregational pattern is certainly different, thus making it difficult to fix a critical micelle concentration as easily as in the polar medium. The concept of a “step-wise” or a

continuous association has been widely used to describe the formation of reversed micelles in organic solvents.<sup>6–8,11</sup>

The purpose of this paper is twofold. First we want to manifest the importance of dielectric studies in investigations of the complex equilibria in binary aqueous systems of alcohols with low contents of water. Secondly it is our intention to elucidate the aggregational behaviour of an ionic surfactant in hydroxylic media. Therefore we have undertaken an investigation of the relative dielectric constant of solutions consisting of sodium octanoate–water–n-alcohols. In this report the alcohols are restricted to n-nonanol and n-decanol. When discussing the reversed micelles we must notify the efforts of identifying these aggregates with w/o microemulsions.<sup>11–14</sup> Classically this is justified in fourcomponent systems, with an apolar hydrocarbon as the fourth compound, as documented by Schulman *et al.*<sup>15–18</sup> We are, however, aware of the fact that the concept of microemulsions has been also introduced for so-called “surfactant phases”, the structure of which is so far not understood.<sup>19–22</sup> In this paper we use the word w/o microemulsion as a parallel denomination to that of reversed micelles. One condition to be kept in mind is that water-in-oil solution phases, *i.e.*  $L_2$  phases, are just one part of the complicated equilibria occurring in ternary surfactant systems. In order to view the whole transition from micelles in an aqueous environment to reversed micelles in an organic solvent, we have inserted the detailed phase diagram of sodium octanoate and water with n-decanol as the co-surfactant in Fig. 1.<sup>23–26</sup>

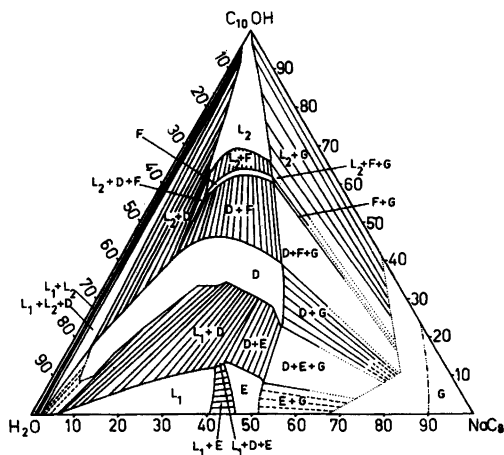


Fig. 1. Phase equilibria in the system water-n-decanol-sodium octanoate at 293 K. Concentrations are expressed as per cent by weight.<sup>23-26</sup>

## EXPERIMENTAL

The sodium octanoate ( $\text{NaC}_8$ ) was prepared by neutralization of octanoic acid (Aldric Chemical Company, Inc. >99.5%) with an equivalent amount of  $\text{NaOH}$  (Merck AG, titrisol). The salt was then purified and dried in vacuum at  $110^\circ\text{C}$ . The molar mass, checked by titration with perchloric acid in glacial acetic acid, using crystal violet as an indicator, differed less than 0.5% from the theoretical value. The alcohols, methanol ( $\text{C}_1\text{OH}$ ) (Merck AG, zur Analyse, 99.5%), ethanol ( $\text{C}_2\text{OH}$ ) (Oy Alko Ab, 99.5%), propanol ( $\text{C}_3\text{OH}$ ) (Merck AG, zur Analyse, 99%), butanol ( $\text{C}_4\text{OH}$ ) (Merck AG, zur Analyse, 99.5%), pentanol ( $\text{C}_5\text{OH}$ ) (Merck AG, zur Analyse, 99%), hexanol ( $\text{C}_6\text{OH}$ ) (Merck AG, zur Analyse, 98%), heptanol ( $\text{C}_7\text{OH}$ ) (Merck AG, zur Synthese, 98%), octanol ( $\text{C}_8\text{OH}$ ) (Merck AG, reinst, 97%), nonanol ( $\text{C}_9\text{OH}$ ) (Fluka AG, purum, 98%) and decanol ( $\text{C}_{10}\text{OH}$ ) (Ega-Chemie, 99.5%) were used without further purification. The water was double-distilled and ion-exchanged immediately before use. The dielectric constant of anhydrous solvents and aqueous solutions as well as of the alcohol-water-surfactant mixtures was measured at a constant frequency of 2 MHz with a Dipolmeter DM 01 (Wissenschaft-Technische Werkstätten GmbH, Weilheim, BRD). The measuring cell MFL 2 had a volume of  $50\text{ cm}^3$ .

The dipolmeter was calibrated with hexanol, pentanol, butanol, propanol, acetone, ethanol and methanol. The calibration curve was a straight line when the dielectric constants of the solvents were presented as a function of the capacitance reading

(C). The average slope  $d\varepsilon_1^0/dC$  of the line was 0.0062. This value was obtained from several recalibrations of the dipolmeter. The measuring cell was held at a constant temperature ( $298.2 \pm 0.1\text{ K}$ ) with water circulating from a Haake thermostat.

With the available experimental equipment it was possible to study the association procedure in media consisting of n-nonanol and n-decanol. We made efforts to extend the results to cover the whole solution phase  $L_2$  in both systems. We noticed, however, a distinct adsorption of surfactant molecules on the walls of the measuring cell at high contents of the amphiphile. This phenomenon highly affected the sensitivity of the reading, wherefore these data have been excluded from Figs. 4-5. This kind of adsorption has been observed earlier.<sup>27</sup>

Preliminary investigations on surfactant systems with short-chain alcohols pointed out the insufficient capacity of the described measuring cell. Experiments with other kinds of cells for these systems have been initiated.

## RESULTS AND DISCUSSION

*1. Binary alcohol-water systems.* In order to elucidate the aggregational pattern for sodium octanoate in alcoholic media, there is an obvious necessity of considering the circumstances governing the binary alcohol-water systems. In Fig. 2 this is done from a dielectric point of view. The figure presents the relative dielectric constant,  $\varepsilon_{12}$ , as a function of the mol fraction of the alcohol from n-butanol up to n-decanol. It is shown that an initial addition of water to a more apolar alcohol lowers the dielectric constant of the mixture in comparison with the pure alcohol. The pentanol-water system is perhaps phenomenologically the most interesting, since here the curve passes through a minimum at  $x_{\text{C}_5\text{OH}} \approx 0.83$ . Obviously the trends of the curves of the long-chain alcohols would be analogous to that of pentanol, if the alcohols hexanol to decanol could dissolve higher amounts of water. Fig. 2 agrees with earlier dielectric measurements on binary systems presented by Brown *et al.*<sup>28</sup> and Franks *et al.*<sup>29</sup> on n-butanol, by Lawrence *et al.*<sup>30</sup> and Tjia *et al.*<sup>31</sup> on heptanol, by Lippold *et al.*<sup>32</sup> on octanol, by D'Aprano *et al.*<sup>33-35</sup> on pentanol and hexanol, and by Sjöblom<sup>36</sup> on nonanol and decanol+water mixtures.

When discussing the aliphatic alcohols in terms of relative dielectric constants we have to distinguish between the short-chain alcohols, *i.e.* methanol

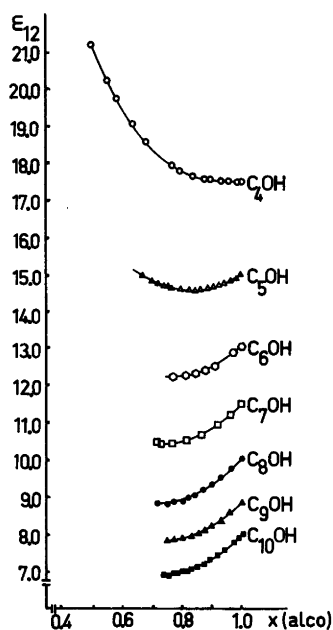


Fig. 2. The relative dielectric constant  $\epsilon_{12}$  of binary alcohol-water solutions plotted versus the mol fraction of alcohol at 298.2 K.

—propanol, and those with a longer hydrocarbon chain, pentanol–decanol. In some respect *n*-butanol can be considered an exception, since diluting *n*-C<sub>4</sub>OH with water does not immediately end up with any direct dielectrical effects. Consequently the curve in Fig. 2 is almost horizontal for the lowest amounts of water. According to Ref. 28 these mixtures should be characterized by a tetrahedral structure, *i.e.* H<sub>2</sub>O·(C<sub>4</sub>OH)<sub>4</sub>, with two butanol molecules hydrogen bonded to the oxygen of the water molecule and one attached to each of the water protons. This configuration is considered to end up with a net dipole moment of zero according to Ref. 28.

In the discussions of the alcohols one should notice the marked difference in the content of hydroxylic groups. Tjia *et al.*<sup>31</sup> diluted *n*-ethanol with methylcyclopentane thus obtaining a mixture with a concentration of OH groups comparable to that of *n*-heptanol. Addition of water to this mixture resulted in a decrease in the dielectric constant, as for mixtures of *n*-heptanol + water. The conclusion of this experiment was that the content of alcoholic

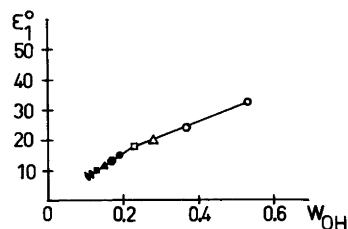


Fig. 3. The relative dielectric constant  $\epsilon_1^\circ$  for pure alcohols plotted versus the weight fraction of the hydroxylic group in the alcohol,  $w_{OH}$ .  $\circ$ , methanol;  $\bigcirc$ , ethanol;  $\triangle$ , propanol;  $\square$ , butanol;  $\bullet$ , pentanol;  $\blacklozenge$ , hexanol;  $\blacktriangle$ , heptanol;  $\blacksquare$ , octanol;  $\blacklozenge$ , nonanol;  $\diamond$ , decanol.

hydroxylic groups was decisive for the mode and degree of association.

In order to test the above idea, we have in Fig. 3 plotted the static dielectric constant,  $\epsilon_1^\circ$ , for the pure alcohols as a function of the weight fraction of their hydroxylic groups,  $w_{OH} = M_{OH}/M_{C_nOH}$ . The functional dependence can schematically be described by two linear sections, with an intersecting point at  $w_{OH} \approx 0.22$ , *i.e.* the value for pure butanol. The decrease in  $\epsilon_1^\circ$  with increasing hydrophobicity is not linear over the entire range and thus indicating structural differences between the lower alcohols up to butanol and the more apolar homologues. Recent spectroscopic works<sup>37</sup> also support the conclusions from Figs. 2 and 3. If we want to analyze the dielectric constant of pure water only by means of the content of hydroxylic groups, this can be done from Fig. 3 by an extrapolation of the curve to  $w_{OH} = 0.9444$ . Hereby we notice that extrapolating the state of the long-chain alcohols gives a value of  $\epsilon_1^\circ = 77.3$  for pure water. The agreement with the experimental value of 78.5 is quite obvious. Although a determination of the dielectric constant of water in this way is an oversimplification, the comparison between the states of the hydroxylic groups in long-chain alcohols and water might indicate a high degree of selfassociation for the more hydrophobic alcohols. Our conclusions are in agreement with those of Dannhauser *et al.*<sup>38-41</sup> who underlined the possibility of finding complexes with an open chain for *n*-octanol. From studies on *n*-heptanol and branched isomers Lawrence *et al.*<sup>30</sup> concluded from the decrease in  $\epsilon_1^\circ$  for the anhydrous C<sub>7</sub>OH with increasing temperature, that the linear multimers are broken up to smaller units.

Our opinion is that for normal, long-chain

alcohols the linear complex formation might predominate. Rupturing this molecular degree of self-association, *i.e.* adding water or raising the temperature, probably results in more symmetrical configurations, where in the case of an aqueous dilution we obtain a long-lived water-centered complex with up to a maximum of four alcohol molecules oriented to each water molecule. Since this molecular organization is supposed to have a low net dipole moment due to the cancelling effects of opposite OH moments, the properties of the whole solution are characterized by a decreasing dielectric constant. The outlined structure should represent a saturation of the alcoholic solution with water. Experimentally the limiting solubility of water in long-chain alcohols is approximately  $x_{\text{H}_2\text{O}} = 0.25-0.30$  expressed as mol fractions. Before obtaining the "final" state with four alcohol "ligands", the complexation has surely passed through states with less than four alcohol molecules bound to the water.

2. Ternary alcohol-water-surfactant systems. When proceeding from binary aqueous solutions of alcohols to ternary solutions with an ionic surfactant as the third component, it is obvious that the complex behaviour of the system is enhanced. Therefore it is of importance to distinguish the predominating interactions in each part of the alcohol-rich solution phase  $L_2$ . In order to do so, it might be of some value to summarize recent results on this phase in the model system  $\text{C}_{10}\text{OH}-\text{H}_2\text{O}-\text{NaC}_8$ . Calorimetric investigations<sup>42-44</sup> indicate that the partial molar enthalpies of all the components undergo their largest changes at the highest contents of decanol, whereafter the properties remain unchanged. An important conclusion pointed out in the calorimetric study is the complete hydration of the ionic species. NMR spectroscopy<sup>45-46</sup> gives further support to this result indicating a conspicuous increase in the interionic effects in the regions with the lowest contents of water in the  $L_2$  phase. Theoretical calculations of the micellar radii and aggregation numbers<sup>26,47</sup> have pointed out the need of a detailed knowledge of the distribution of water between the micellar core and the surrounding decanolic medium. Neglecting this equilibrium and supposing a spherical micelle model we obtain constant aggregation numbers and an invariable extension of the micellar core, when one proceeds along a line with a fixed ratio  $n_w/n_s$  towards higher amounts of decanol. Thus the concentration of the

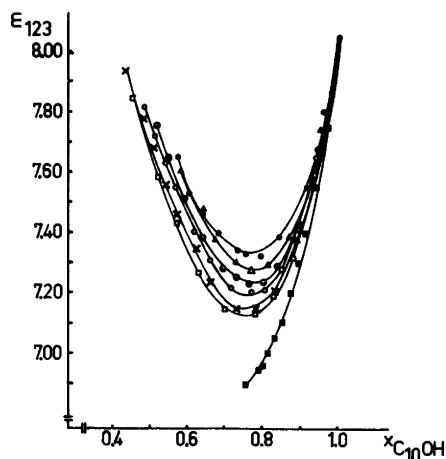


Fig. 4. The relative dielectric constant  $\epsilon_{123}$  of ternary mixtures in the decanol-rich phase  $L_2$  as a function of the mol fraction of decanol at 298.2 K. ■ represents the binary decanol+water solutions ( $\epsilon_{12}$ ); □,  $n_{\text{H}_2\text{O}}/n_{\text{NaC}_8} = 26.18$ ; ×, 22.18; ○, 18.43; ⊙, 14.41; △, 10.70; ●, 6.73.

micelles should be quite decisive when describing the micellization in the alcohol-rich phase.

In order to give a detailed picture of the competitive forces acting in the  $L_2$  phase as illustrated by dielectric constants, we have measured in Figs. 4 and 5  $\epsilon_{123}$  values for six different

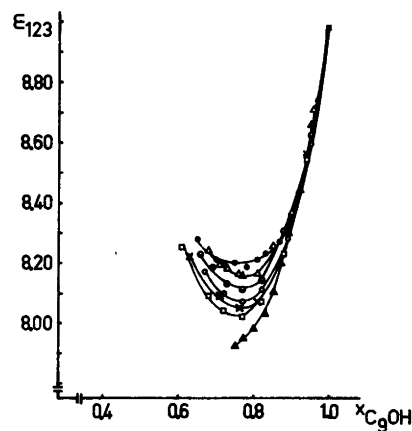


Fig. 5. The relative dielectric constant  $\epsilon_{123}$  of ternary mixtures in the nonanol-rich phase  $L_2$  as a function of the mol fraction of nonanol at 298.2 K. ▲ represents the binary nonanol+water solutions ( $\epsilon_{12}$ ); □,  $n_{\text{H}_2\text{O}}/n_{\text{NaC}_8} = 25.77$ ; ×, 22.46; ○, 17.82; ⊙, 14.10; △, 10.16; ●, 6.30.

ratios between the amounts of water and sodium octanoate. Since the binary system decanol and nonanol + water just shows a lowering of the dielectric constant,  $\epsilon_{12}$ , the existence of a distinct minimum in the ternary system must be attributed to the structural modifications which take place when sodium octanoate is present. Although the shape of the curve with  $n_w/n_s = 26.18$  deviates from that of mixtures containing only decanol and water, it is obvious from Fig. 4 that the bulk conditions in these solutions of all the presented curves in the figure are closest related. This must of course be the situation, since when  $n_w/n_s$  obtains its highest values, the possibility of composing an extensive hydrogen bond network between water and decanol is highest. When  $n_w/n_s$  diminishes, the interactions between ionic species and water will more or less dictate the localization of the water molecules, wherefore the state of water in this region and in a concentrated electrolyte solution is quite comparable.<sup>26</sup> In Fig. 4 this is registered as the largest deviation for  $n_w/n_s = 6.73$  from that of the binary state. The conclusion drawn from Fig. 4 seems to be valid for the nonanol system (Fig. 5) as well. The only detectable discrepancy from the decanol system is that in Fig. 5 the differences in  $\epsilon_{123}$  for various ratios of water to sodium octanoate are even smaller than in the decanol system.

In order to give a qualitatively better picture of the influence of the mixed solute  $H_2O + NaC_8$ , we have fitted a third degree polynomial to the experimental curves and calculated the zero point of the derivative. Due to the high significance level of the mathematical fit,  $d\epsilon_{123}/dx_{C_nOH} = 0$  can be considered to reflect the changes in the physico-chemical properties of the solution. In Fig. 6 we have summarized the result. The zero point of the derivatives  $d\epsilon_{123}/dx_{C_9OH}$  and  $d\epsilon_{123}/dx_{C_{10}OH}$  (expressed in the mol fraction of the alcohol,  $x_{C_nOH}$ ) is presented as a function of the ratio between the amounts of water to sodium octanoate,  $n_w/n_s$ . Figs. 4 and 5 reveal that the position of the minimum is moving towards higher values of  $x_{C_nOH}$  due to the preferential interaction between the surfactant and water. A possible explanation of the anomalous behaviour in Fig. 6, where we notice a distinct breakpoint in the two curves at  $n_w/n_s \approx 14$ , is a change in the hydration conditions of the ionic surfactant and its counter-ion. It is known from studies on short-chain carboxylates in aqueous media<sup>48-49</sup> that a limiting hydration number of  $\sim 8.5$  is reached at infinite dilution for the anion due

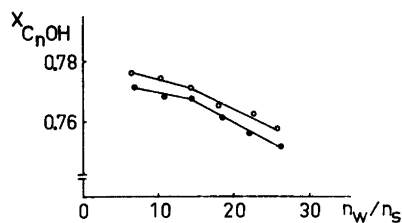


Fig. 6. The position of the minimum in  $\epsilon_{123}$  (expressed as the mol fraction of the alcohol  $x_{C_nOH}$ ) as a function of the ratio between the amounts of water to surfactant. ○, the nonanol system; ●, the decanol system.

to the hydrophilic and semihydrophilic hydration. Proposing a hydration number of 4–5 for the sodium ion,<sup>50-51</sup> a hydration of the surfactant molecule with its counter-ion should thus involve about 14 water molecules. The second section of the curves for the higher  $n_w/n_s$  ratios in Fig. 6 should then illustrate when the attraction between water and the alcohol begins to contribute at a higher degree to the properties of the solution.

Since our study is restricted to the highest contents of the alcohol,  $w_{C_nOH} > 0.9$ , where the minimum occurs at  $w_{C_nOH} \approx 0.95$ , much care must be taken in using these results to predict conditions characteristic for the regions with high concentrations of reversed micelles. We have, however, seen that dielectric constants are sensitive to changes in the interactions between the different moieties. It is our purpose to continue the dielectric characterization of hydroxylic media with small amounts of ionic surfactants as well as to initiate detailed studies of the conditions, where the micellar state dictates the solution properties.

*Acknowledgements.* The authors would like to thank Professor Ingvar Danielsson for his great interest in this project and for valuable comments. Dr. Sune Backlund, Professor Pekka Pyykkö and Dr. Jarl B. Rosenholm are all thanked for reading the manuscript and for constructive criticism. Financially this investigation was supported by Svenska Kulturfonden (J.S.) and by Stiftelsen för Åbo Akademi forskningsinstitut (H.D.). This support is heartily acknowledged.

#### LIST OF SYMBOLS

$\epsilon_1^0$  = the relative dielectric constant of a pure component

- $\epsilon_{12}$  = the relative dielectric constant of a binary mixture (alcohol – water)  
 $\epsilon_{123}$  = the relative dielectric constant of a ternary mixture (alcohol – water – surfactant)  
 $x_i$  = the mol fraction of component  $i$   
 $n_s$  = the amount of surfactant  
 $n_w$  = the amount of water  
 $w_i$  = the weight fraction of component  $i$   
 $M_i$  = the molar mass of component  $i$

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Received October 20, 1980.