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Water Uptake and Dioctyldimethylammonium Chloride Distribution in Water + Hydrocarbon Microemulsions Containing an Alcohol and Sodium Chloride at 296.1 K

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Experimental liquid−liquid equilibrium data were obtained for systems containing water, NaCl, a linear hydrocarbon solvent, a straight chain alcohol, and the two-tailed cationic surfactant dioctyldimethylammonium chloride (DODMAC). The experiments were carried out at 296.1 K and at atmospheric pressure. The solvents used were octane, decane, dodecane, tetradecane, and hexadecane. The alcohols utilized were 1-decanol and 1-dodecanol. High concentrations of water in the organic media and three phase transitions were observed for all solvent−alcohol combinations. The experimental results indicate the formation of water + hydrocarbon microemulsions for all systems.

Introduction

Biomolecules are often obtained as solutes dissolved in an aqueous medium. These target compounds can be extracted from the aqueous solution by contacting it with an organic phase which contains a surfactant (Khoshkbarchi and Vera, 1995). The ability of a nonpolar medium to solubilize hydrophilic molecules such as amino acids is due to the formation of reverse micelles within the organic phase. Reverse micelles are aggregates of amphiphilic molecules around a water core. Hydrocarbon phases containing reverse micelles are called water-in-oil microemulsions (Bourrel and Schechter, 1988). When a water-in-oil microemulsion co-exists with an excess aqueous phase, it is necessary to have an electrolyte dissolved in the aqueous phase to avoid the migration of the surfactant out of the organic solvent. The extraction of amino acids from aqueous solutions using the two-tailed cationic surfactant dioctyldimethylammonium chloride (DODMAC) has been studied by Wang et al. (1995a,b). These studies were based on previous work (Wang et al., 1994) in which reverse micelles of DODMAC were formed in the absence of biomolecules. Rabie et al. (1995) have studied the effect of the nature of the surfactant counterions on the behavior of reverse micelles of DODMAC. All these studies were performed using 2,2,4-trimethylpentane (isooctane) as the organic solvent. Alcohols used as co-surfactants ranged from pentanol to decanol (Wang et al., 1994, 1995a,b; Rabie et al., 1995). The solubilities of the organic solvent, and of the co-surfactant, in water are of concern for practical applications, since these chemicals would contaminate the residual aqueous phase. On the other hand, for anionic surfactants like sodium bis(2-hexylethyl) sulfosuccinate, Aerosol-OT, it is known that reverse micelles are not formed in *n*-alkane solvents with a hydrocarbon chain length larger than 12 carbon atoms (Miletti, 1989; Ladanowski, 1991). Thus, it is interesting to investigate whether a similar effect is present with the cationic surfactant DODMAC. In this work we study the effect of the chain length of the organic solvent and also of the alcohol, used as co-surfactant, on the formation of water-in-oil microemulsions.

From a solubility point of view, the use of 2,2,4-trimethylpentane (isooctane), as organic solvent, is a poor choice since branching increases the solubility of hydrocarbons in water. In fact, the solubility of isooctane at 298 K is about 5 times higher than that of octane (Yaws et al., 1990a). On the other hand, the solubility of octane in water at 298 K is greater than the solubilities of decane, dodecane, tetradecane, and hexadecane by factors of about 8, 100, 200, and 450, respectively (Yaws et al., 1990a). A similar consideration holds for the alcohols used as co-surfactants. The solubility of 1-pentanol at 298 K is hundreds of times higher than that of 1-decanol, and 1-decanol is 9 times more soluble than 1-dodecanol (Yaws et al., 1990b). Within the homologous series of linear primary alcohols, 1-dodecanol is the longest chain alcohol which is liquid at 298 K. All comparisons of solubility are made on a mass fraction basis following the work of Yaws et al. (1990a,b). Due to the lower solubility in water of the longer chain hydrocarbons, it would be desirable to use them as solvents for the extraction of biomolecules from aqueous solutions. Hence, the possibility of forming reverse micelles using long linear hydrocarbon solvents and long linear alcohols as co-surfactants was the main motivation of this study.

The present work provides a more complete characterization of the behavior of the cationic surfactant DODMAC for the formation of reverse micelles. The possibility of forming reverse micelles with DODMAC, using linear alkane solvents from octane to hexadecane and the linear primary alcohols decanol and dodecanol as co-surfactants, is explored.

Materials and Experimental Methods

The commercial product BARDAC LF-80 was provided by Lonza Inc. (Fair Lawn, NJ). BARDAC LF-80 is a well-defined mixture containing 80 mass % DODMAC, 10 mass % water, and 10 mass % ethanol. The value of the concentration of DODMAC in BARDAC LF-80 was verified by potentiometric titration using a solution of sodium lauryl sulfate as titrant and a surfactant electrode Orion model 93-42 coupled to a double junction reference electrode Orion model 90-02 (Orion Research Inc., Boston, MA). BARDAC LF-80 was used directly in the preparation of samples. The concentrations of DODMAC which are reported throughout the present work correspond to active DODMAC in BAR-

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Table 1. Effect of NaCl Content on the Equilibrium Values of *w*, *C*(DODMAC, aq), and *C*(Na$^+$, aq) at 296.1 K[a]

C(NaCl, aq) initial/ mol·dm^{-3}	100*w*	*C*(DODMAC, aq)/ mmol·dm^{-3}	*C*(Na$^+$, aq)/ mol·dm^{-3}
Solvent: Octane			
0.050	3.23	10.43	0.039
0.101	3.21	6.73	0.093
0.251	2.94	2.82	0.230
0.400	2.80	2.10	0.373
0.550	2.59	1.68	0.510
0.700	2.49		0.664
0.850	2.38		0.802
Solvent: Decane			
0.050	3.46	11.26	0.042
0.101	3.37	7.06	0.082
0.251	3.00	2.96	0.221
0.400	2.76	2.45	0.371
0.550	2.59	1.81	0.517
0.700	2.46		0.618
0.850	2.39		0.800
Solvent: Dodecane			
0.050	3.77	11.30	0.040
0.101	3.51	7.83	0.077
0.251	3.06	3.32	0.218
0.400	2.79	2.50	0.364
0.550	2.64	1.80	0.498
0.700	2.50		0.645
0.850	2.41		0.751
Solvent: Tetradecane			
0.050	4.22	12.93	0.039
0.101	3.78	7.83	0.085
0.251	3.15	3.87	0.210
0.400	2.85	2.50	0.366
0.550	2.70	1.94	0.503
0.700	2.51		0.639
0.850	2.42		0.794
Solvent: Hexadecane			
0.050	4.68	12.38	0.040
0.101	3.88	8.43	0.081
0.251	3.22	3.55	0.216
0.400	2.94	2.37	0.362
0.550	2.70	2.04	0.490
0.700	2.60		0.620
0.850	2.44		0.777

[a] w = water uptake =mass fraction of water in the equilibrium organic phase. *C*(DODMAC, aq) = concentration of DODMAC in the equilibrium aqueous phase. *C*(Na$^+$, aq) = concentration of Na$^+$ in the equilibrium aqueous phase. Initial organic phase:solvent, *C*(DODMAC) = 0.10 mol·dm^{-3}, *C*(1-decanol) = 0.25 mol·dm^{-3}. Initial organic phase volume: 20 mL. Initial aqueous phase:water and variable NaCl concentration. Initial aqueous phase volume: 20 mL. Stirring time:1 h. Phase disengagement time: 11 days. Concentrations of DODMAC are expressed on the basis of being free from the water and the ethanol present in BARDAC-LF 80.

Table 2. Effect of NaCl Content on the Equilibrium Values of *w*, *C*(DODMAC, aq), and *C*(Na$^+$, aq) at 296.1 K (Double Concentration of Surfactant and Co-Surfactant)[a]

C(NaCl, aq) initial/ mol·dm^{-3}	100*w*	*C*(DODMAC, aq)/ mmol·dm^{-3}	*C*(Na$^+$, aq)/ mol·dm^{-3}
Solvent: Octane			
0.050	5.59	9.55	0.037
0.101	5.54	5.55	0.085
0.251	5.07	2.78	0.237
0.400	4.82	1.82	0.388
0.550	4.61	1.25	0.542
0.700	4.43		0.669
0.850	4.30		0.838
Solvent: Decane			
0.050	5.80	11.03	0.039
0.101	5.64	5.60	0.088
0.251	5.10	2.75	0.242
0.400	4.81	2.13	0.385
0.550	4.59	1.27	0.531
0.700	4.42		0.681
0.850	4.31		0.824
Solvent: Dodecane			
0.050	6.08	11.98	0.039
0.101	5.93	6.64	0.086
0.251	5.21	2.79	0.235
0.400	4.98	2.09	0.383
0.550	4.71	1.38	0.532
0.700	4.51		0.679
0.850	4.30		0.829
Solvent: Tetradecane			
0.050	6.39	11.30	0.038
0.101	6.22	6.86	0.084
0.251	5.43	3.34	0.231
0.400	5.07	2.18	0.374
0.550	4.76	1.50	0.541
0.700	4.54		0.680
0.850	4.37		0.791
Solvent: Hexadecane			
0.050	6.79	11.43	0.040
0.101	6.34	7.00	0.082
0.251	5.59	3.10	0.236
0.400	5.08	2.04	0.380
0.550	4.81	1.56	0.538
0.700	4.60		0.689
0.850	4.25		0.827

[a] w = water uptake = mass fraction of water in the equilibrium organic phase. *C*(DODMAC, aq) = concentration of DODMAC in the equilibrium aqueous phase. *C*(Na$^+$, aq) = concentration of Na$^+$ in the equilibrium aqueous phase. Initial organic phase:solvent, *C*(DODMAC) = 0.20 mol·dm^{-3}, *C*(1-decanol) = 0.50 mol·dm^{-3}. Initial organic phase volume: 20 mL. Initial aqueous phase:water and variable NaCl concentration. Initial aqueous phase volume: 20 mL. Stirring time:1 h. Phase disengagement time: 9 days. Concentrations of DODMAC are expressed on the basis of being free from the water and the ethanol present in BARDAC-LF 80.

DAC LF-80; i.e., they are expressed on a water and ethanol free basis. Sodium chloride 99+% was from Anachemia (Montreal, PQ). It was completely dried before use. The alcohols 1-decanol 99+% and 1-dodecanol reagent grade were from A&C (American Chemicals Ltd. Montreal, PQ). The solvents octane 99+%, decane 99+%, dodecane 99%, tetradecane 99%, and hexadecane 99% were from Sigma Chemical Co. (St. Louis, MO). Deionized water, with a resistivity of 18 MΩ cm was used for all experiments. The alcohols and solvents were used without further purification.

The experimental procedure was as follows. The components of the system to be studied were loaded into a 125 mL capped transparent glass flask. To facilitate the attainment of equilibrium, the glass flask was vigorously shaken for 1 h in a constant temperature room at 296.1 K and settled for no less than 9 days at 296.1 K. After this period, the phases were separated and stored for analysis. The phases were separated by withdrawing, very slowly, less than 50% of the volume of each phase by means of 10 mL Becton Dickinson syringes. In addition, to avoid contamination of the sample, the tips of the syringe needles had been cut to form blunt edges, and the syringes were held fixed with clamps to a stand during the sampling process.

The concentration of water in organic media (water uptake) was measured by Karl Fischer titration using a model 701 Metrohm automatic titrator (Metrohm Ltd. Herisau, Switzerland). The value of the titer, i.e., the mass of water titrated by a unit volume of titrant, was verified daily. The concentration of DODMAC in the aqueous phase was measured with a 5890A Hewlett-Packard gas chromatograph, with a flame ionization detector using 2-butoxyethanol as the internal standard (Wang et al., 1994). The column was an 8 ft long, 10% Carbowax 20 M

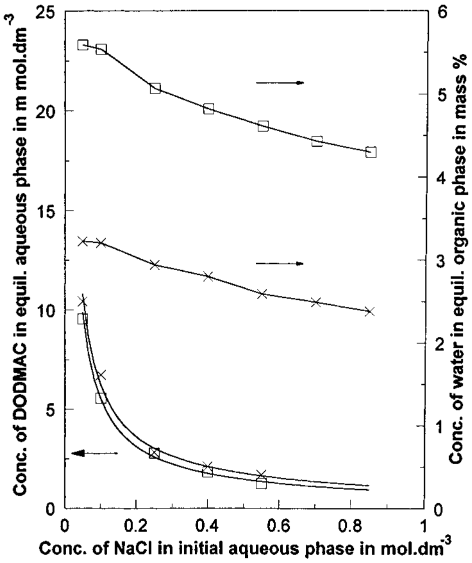

Figure 1. Effect of the initial aqueous phase concentration of NaCl on the equilibrium concentrations of water in the organic phase and of DODMAC in the aqueous phase at 296.1 K. Solvent: octane. Initial organic phase: (×) DODMAC 0.10 mol·dm^{-3}, 1-decanol 0.25 mol·dm^{-3} or (□) DODMAC 0.20 mol·dm^{-3}, 1-decanol 0.50 mol·dm^{-3}. Initial aqueous phase: 20 mL of NaCl solution. Initial organic phase volume: 20 mL.

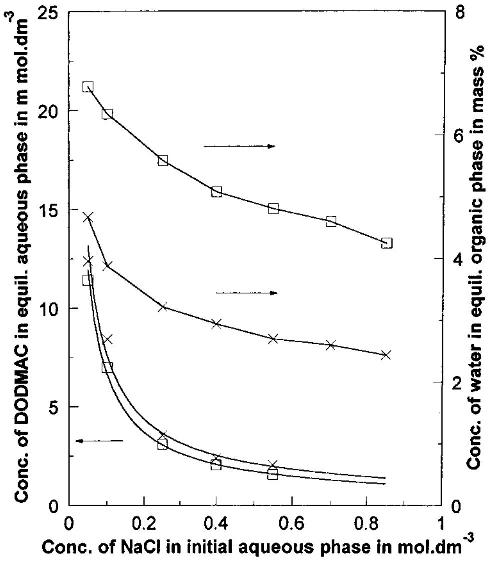

Figure 2. Effect of the initial aqueous phase concentration of NaCl on the equilibrium concentrations of water in the organic phase and of DODMAC in the aqueous phase at 296.1 K. Solvent: hexadecane. Initial organic phase: (×) DODMAC 0.10 mol·dm^{-3}, 1-decanol 0.25 mol·dm^{-3} or (□) DODMAC 0.20 mol·dm^{-3}, 1-decanol 0.50 mol·dm^{-3}. Initial aqueous phase: 20 mL of NaCl solution. Initial organic phase volume: 20 mL.

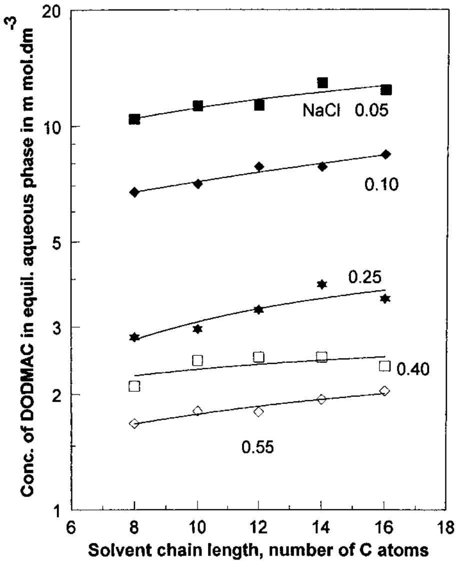

Figure 3. Effect of solvent chain length on the equilibrium concentration of DODMAC in the aqueous phase, for different values of the initial aqueous phase concentration of NaCl, in mol·dm^{-3}, at 296.1 K. Initial organic phase: DODMAC 0.10 mol·dm^{-3}, 1-decanol 0.25 mol·dm^{-3}. Initial aqueous phase: 20 mL of NaCl solution. Initial organic phase volume: 20 mL.

+ 2% KOH, Chromosorb P, AW, 80/100, 0.125 in. o.d., Ni. The conditions of the analysis were the following: oven temperature 463 K, injection temperature 548 K, detector temperature 548 K, He flow rate 30 cm^3/min, H_2 flow rate 30 cm^3/min, air flow rate 300 cm^3/min. The samples were properly diluted at constant concentrations of 2-butoxyethanol and NaOH before analysis (Wang et al., 1994). The chromatograph was calibrated by injecting solutions of known concentration of DODMAC. The concentration of sodium in the aqueous phase was measured with a Thermo Jarrel Ash Corp. atomic absorption spectrophotometer, model Smith-Hieftje 11, at 330.2 nm wavelength, using an air acetylene flame. The accuracy of the water uptake, surfactant concentration, and sodium concentration measurements are of the order of 2, 10, and 5%, respectively.

Results

The only electrolyte used in the experiments was NaCl. Thus, any exchange between the surfactant counterion (Cl^-) with another anion was avoided (Rabie et al., 1995). When such exchange does happen, different forms of the surfactant coexist in the reverse micellar phase (Rabie et al., 1995), each with a different behavior. Two different sets of experiments were carried out. In the first set, 20 mL of an aqueous solution of NaCl was contacted with 20 mL of an organic solution containing DODMAC and 1-decanol. The organic solvents were octane, decane, dodecane, tetradecane, and hexadecane. Tables 1 and 2 and Figures 1−4 show the results corresponding to the first set of experiments. The initial solutions and the equilibrium phases were always clear. In all cases corresponding to Tables 1 and 2, only two phases were present at equilibrium.

Figure 1 shows the effect of the NaCl concentration of the initial aqueous phase, on the equilibrium concentrations of water in the organic phase (water uptake) and of DODMAC in the aqueous phase. The measurements were performed for two different concentrations of DODMAC, in the initial *n*-octane organic phase, at a constant molar ratio of 1-decanol to DODMAC of 2.5. The values for the aqueous phase concentration of DODMAC indicate that most of the surfactant is located in the organic phase. This fact and the relatively high values of the water uptake indicate the formation of reverse micelles. From Figure 1 it is clear that the water uptake is roughly doubled when the initial concentration of DODMAC is increased from 0.10 to 0.20 mol·dm^{-3} at a fixed 1-decanol/DODMAC molar ratio. However, the concentration of DODMAC in the aqueous phase is insensitive to the variation in the initial concentration of DODMAC in the organic phase. Thus, the larger overall amount of DODMAC in the system, which could be expected to increase the concentration of DODMAC in the aqueous phase, is counterbalanced by the larger overall amount of 1-decanol. On the other hand, as can be seen in Figure 1, the water uptake decreases with an increase in the initial NaCl concentration. This effect

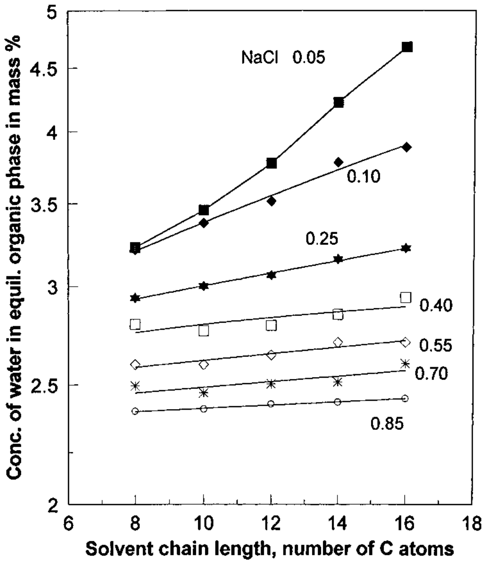

Figure 4. Effect of solvent chain length on the equilibrium concentration of water in the organic phase, for different values of the initial aqueous phase concentration of NaCl, in mol·dm^{-3}, at 296.1 K. Initial organic phase: DODMAC 0.10 mol·dm^{-3}, 1-decanol 0.25 mol·dm^{-3}. Initial aqueous phase: 20 mL of NaCl solution. Initial organic phase volume: 20 mL.

is due to the increase in the charge density inside the reverse micelles which is known to reduce the size of the reverse micelles (Wang et al., 1994). Finally, Figure 1 shows that the concentration of DODMAC in the aqueous phase decreases with an increase in the initial concentration of NaCl. This trend can be ascribed to a salting out effect.

Figure 2 shows the results for the case when the organic solvent used was hexadecane. All conclusions obtained from the consideration of Figure 1 apply to the results shown in Figure 2 and also to the results presented in Tables 1 and 2 for other solvents. Thus, the qualitative behavior of the system is the same for all the organic solvents from octane to hexadecane.

Figure 3 shows the effect of the molecular weight of the organic solvent on the aqueous phase concentration of DODMAC at equilibrium, for different values of the NaCl concentration. As shown in Table 2, similar results were obtained using initial concentrations of DODMAC and 1-decanol at twice the values of those used in Figure 3. Considering the experimental error associated with the DODMAC analysis, the results shown in Figure 3 indicate that there is no clear trend for the variation of the aqueous concentration of DODMAC as a function of the *n*-alkane chain length. Thus, the concentration of DODMAC in the aqueous phase is insensitive to the molecular weight of the normal alkane used as organic solvent for the formation of reverse micelles.

Figure 4 shows the effect of the solvent chain length on the water uptake at several NaCl concentrations. At low NaCl concentrations, i.e., at low ionic strength, there is a clear increase in the water uptake with the increase in the alkane molecular weight. However, at high NaCl concentrations the water uptake is unaffected by the solvent chain length. As shown in Table 2, similar results were obtained using initial concentrations of DODMAC and 1-decanol at twice the values of those used in Figure 4.

Tables 1 and 2 show that the equilibrium concentration of Na ion in the aqueous phase is consistently smaller than its concentration in the initial aqueous phase. In addition, the Na concentration is not affected by the nature of the alkane used as solvent.

Some qualitative experiments were performed using NaOH instead of NaCl. In this case, the surfactant will exchange its counterion to some extent. The initial concentrations of DODMAC and 1-decanol in the organic phase were 0.20 and 0.50 mol·dm^{-3}, respectively. The concentrations of NaOH in the initial aqueous phase were 0.20 and 0.50 mol·dm^{-3}. The solvents were octane, decane, dodecane, tetradecane, and hexadecane. For all points measured, the water uptake was about 9 to 11 mass %. These results show that reverse micelles were also formed, for all solvents, when NaOH was used as electrolyte.

The second set of experiments had the purpose of studying the effect of the concentration of alcohol on the formation of reverse micelles with DODMAC. The alcohols used were 1-decanol and 1-dodecanol. For these experiments, the samples were prepared by introducing into the equilibrium flask 20 mL of pure organic solvent, a variable weight of alcohol, and 20 mL of an aqueous solution containing DODMAC and NaCl. In all cases the aqueous solution was 0.20 mol·dm^{-3} in DODMAC and 0.10 mol·dm^{-3} in NaCl, and had the aspect of a clear yellowish liquid. Except for a few cases, the equilibrium phases were also clear. In all cases, at well-defined alcohol concentrations, three phase regions were observed. The results of this set of experiments are reported in Tables 3 and 4 and shown in Figures 5 and 6.

Table 3 shows the results for the case when 1-decanol was used as a co-surfactant. The initial concentration of 1-decanol is expressed in moles of alcohol per liter of solvent. In all cases, the water uptake reported corresponds to the concentration of water in the top phase, for any number of phases at equilibrium. At low alcohol concentrations the system presents two phases and the organic phase has a very low water content. These are Winsor I type systems (Bourrel and Schechter, 1988). At intermediate alcohol concentrations a third phase appears and the top phase has still a very low water uptake. These are Winsor III type systems (Bourrel and Schechter, 1988). A further increase in 1-decanol concentration produces a two-phase system with very high water uptake value just after the transition from three phases to two phases. The water uptake decreases with further increments in the alcohol concentration. This two-phase system is a Winsor II type system (Bourrel and Schechter, 1988). There are two possible explanations for the decrease in water uptake with the increase in alcohol concentration (Wang et al., 1994): first, that the alcohol, acting as a co-surfactant, has a screening effect for the repulsive forces between the positively charged heads of the surfactant in the interface of the reverse micelles; second, that the alcohol acts as a co-solvent, and more surfactant gets dissolved in the bulk organic phase as the concentration of alcohol increases. Table 4 reports results for 1-dodecanol which are similar to those reported in Table 3 for 1-decanol. The values of water uptake reported for low alcohol concentrations are not quantitatively accurate, and this fact is indicated by the symbol "$\approx$ " in Tables 3 and 4. These results, however, are of qualitative value since they show the regions in which the water uptake is low.

The bottom and the middle phases were not clear for a concentration of 0.160 mol of 1-decanol/L of dodecane (Table 3). The top phase was cloudy for 0.296 mol of 1-decanol/L of tetradecane (Table 3). The top and middle phases were cloudy for 0.278 mol of 1-dodecanol/L of hexadecane (Table 4). Finally, it was observed that the top phase of the sample having 0.274 mol of 1-dodecanol/L of tetradecane (Table 4) was unstable when separated from the system. It split into two phases of similar size some

Table 3. Effect of 1-Decanol Concentration, in mol·dm^{-3} of Solvent, on the Equilibrium Number of Phases *N* and Top-Phase Water Uptake *w*, at 296.1 K[a]

C(1-decanol) initial	*N*	100*w*
Solvent: Octane		
0.000	2	$\approx$0.00
0.106	2	$\approx$0.00
0.165	3	$\approx$0.00
0.256	2	11.04
0.290	2	
0.338	2	6.98
0.398	2	4.47
Solvent: Decane		
0.000	2	$\approx$0.01
0.112	2	$\approx$0.00
0.181	3	$\approx$0.00
0.258	2	11.86
0.296	2	
0.324	2	8.31
0.410	2	5.95
Solvent: Dodecane		
0.000	2	$\approx$0.00
0.115	2	$\approx$0.01
0.160	3	$\approx$0.01
0.246	3	$\approx$0.17
0.300	2	10.68
0.368	2	7.62
0.430	2	6.01
Solvent: Tetradecane		
0.000	2	$\approx$0.01
0.110	2	$\approx$0.00
0.189	3	$\approx$0.01
0.245	3	$\approx$0.01
0.296	2	
0.357	2	7.73
0.398	2	6.66
0.464	2	5.39
0.559	2	4.39
0.643	2	4.00
0.733	2	3.75
Solvent: Hexadecane		
0.000	2	$\approx$0.01
0.106	2	$\approx$0.01
0.186	3	$\approx$0.01
0.244	3	$\approx$0.01
0.305	3	$\approx$0.21
0.357	2	9.15
0.426	2	6.32
0.444	2	6.24
0.559	2	4.77
0.625	2	4.33
0.714	2	3.86

[a] Formulation: 20 mL of an aqueous solution of *C*(DODMAC) = 0.2 mol·dm^{-3}, *C*(NaCl) = 0.1 mol·dm^{-3}, and 20 mL of solvent + a variable mass of 1-decanol. Stirring time: 1 h. Phase disengagement time: 24 days.

Table 4. Effect of 1-Dodecanol Concentration, in mol·dm^{-3} of Solvent, on the Equilibrium Number of Phases *N* and Top-Phase Water Uptake *w*, at 296.1 K[a]

C(1-dodecanol) initial	*N*	100*w*
Solvent: Octane		
0.000	2	$\approx$0.01
0.104	2	$\approx$0.01
0.166	3	$\approx$0.01
0.247	2	10.70
0.282	2	8.87
0.307	2	
0.365	2	6.59
Solvent: Decane		
0.000	2	$\approx$0.00
0.106	2	$\approx$0.00
0.172	3	$\approx$0.00
0.226	2	13.28
0.276	2	9.02
0.323	2	
0.363	2	
Solvent: Dodecane		
0.000	2	$\approx$0.00
0.113	2	$\approx$0.01
0.176	3	$\approx$0.01
0.217	3	$\approx$0.05
0.280	2	10.03
0.325	2	8.17
0.381	2	6.36
Solvent: Tetradecane		
0.000	2	$\approx$0.01
0.107	2	$\approx$0.01
0.184	3	$\approx$0.02
0.219	3	$\approx$0.02
0.274	2	
0.335	2	8.57
0.385	2	6.40
0.445	2	5.17
0.474	2	
0.595	2	3.81
0.689	2	3.63
Solvent: Hexadecane		
0.000	2	$\approx$0.01
0.125	2	$\approx$0.00
0.165	2	$\approx$0.00
0.218	3	$\approx$0.01
0.278	3	
0.330	2	10.23
0.376	2	7.74
0.438	2	5.85
0.521	2	4.83
0.612	2	4.08
0.715	2	3.54

[a] Formulation: 20 mL of an aqueous solution of *C*(DODMAC) = 0.2 mol·dm^{-3}, *C*(NaCl) = 0.1 mol·dm^{-3}, and 20 mL of solvent + a variable mass of 1-dodecanol. Stirring time: 1 h. Phase disengagement time: 21 days.

time after its separation from the aqueous phase. All these observations correspond to concentrations of alcohol close to or within the three-phase transition region and to settlement times longer than 20 days. This finding can be explained by considering that the three fluid phase transition region is bounded by two critical points, one for the transition from a Winsor I to a Winsor III system and the other for the transition from a Winsor III to a Winsor II system. Since at these transition points the densities of the critical phases are the same, the settlement time tends to infinity at the critical points. In all other cases the phases at equilibrium were clear. The flasks containing the equilibrated phases were always observed with the aid of fluorescent light reflected by plain white paper in line with the equilibrium flask and the observer's eye. As a general rule, the phase where most of the surfactant resided was yellowish at alcohol concentrations close to or within the three-phase region. The yellowish phase was the bottom phase before the transition, the middle phase at the transition, and the top phase after the transition.

Figure 5 compares the effect of the concentration of 1-decanol on the water uptake in the Winsor II type systems for the five solvents used in the present study. In general, it can be seen that the water uptake increases with the increase in the solvent molecular weight. As shown in Table 4, a similar result was found for the co-surfactant 1-dodecanol. Since the melting point of 1-dodecanol is 297.1 K and the experiments were carried out at 296.1 K, at high enough concentrations of 1-dodecanol, this compound may separate as a solid phase. Precipitates of 1-dodecanol were never observed in our experiments. Figure 6 shows the effect of changing 1-decanol for 1-dodecanol when using tetradecane as solvent (Tables 3 and 4). The water uptake decreases to some extent with the

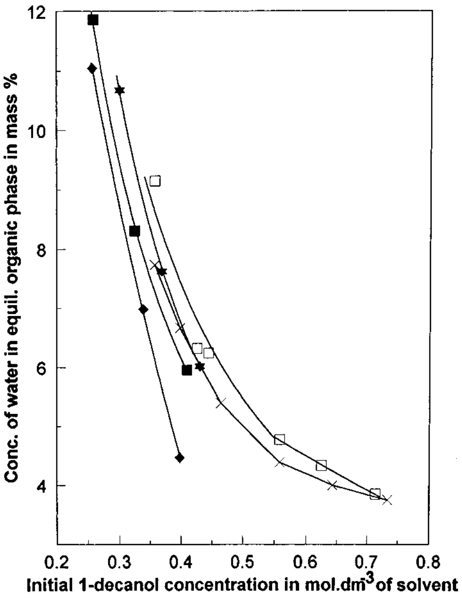

Figure 5. Effect of the initial concentration of 1-decanol on the equilibrium concentration of water in the organic phase at 296.1 K, for different solvents: (◆) octane; (■) decane; (★) dodecane; (×) tetradecane; (□) hexadecane. Formulation: 20 mL of an aqueous solution of 0.2 mol·dm^{-3} DODMAC and 0.1 mol·dm^{-3} NaCl plus 20 mL of solvent and a variable weight of 1-decanol.

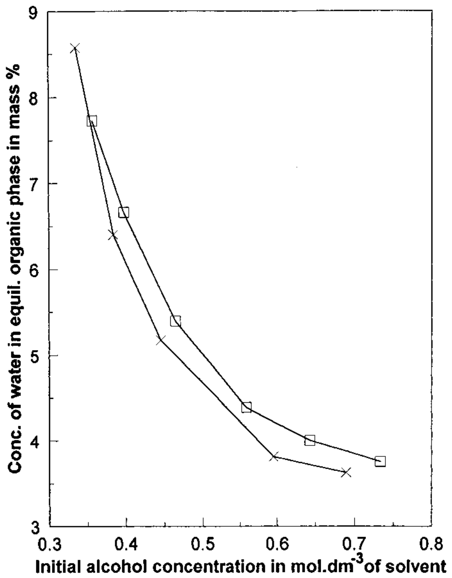

Figure 6. Effect of the initial concentration of alcohol on the equilibrium concentration of water in the organic phase at 296.1 K, for two different alcohols: (×) 1-dodecanol; (□) 1-decanol. Solvent: tetradecane. Formulation: 20 mL of an aqueous solution of 0.2 mol·dm^{-3} DODMAC and 0.1 mol·dm^{-3} NaCl plus 20 mL of tetradecane and a variable weight of alcohol.

increase in the molecular weight of the linear primary alcohol used as co-surfactant. The same result was found when using hexadecane as solvent.

Conclusions

The formation of reverse micelles of dioctyldimethylammonium chloride (DODMAC) in an organic solvent was studied by following two procedures for the preparation of the samples. First, an organic solvent containing DODMAC and an alcohol was contacted with an aqueous solution of NaCl. Second, an aqueous solution containing DODMAC and sodium chloride was contacted with pure organic solvent to which pure alcohol was added. The organic solvents tested were octane, decane, dodecane, tetradecane, and hexadecane, and the alcohols used were 1-decanol and 1-dodecanol. The high values of the concentration of water in the organic phase, the low values of the concentration of DODMAC in the aqueous phase, and the presence of three phase transition regions are all clear indications of the formation of reverse micelles in all the systems studied. The water uptake was found to increase with the increase in the molecular weight of the solvent. The concentration of DODMAC in the aqueous phase was found to be insensitive to the nature of the solvent. Both the water uptake and the concentration of DODMAC in the aqueous phase decreased with the increase in the ionic strength of the aqueous phase. The water uptake also decreased with the increase in the concentration of alcohol and increased with the increase in the concentration of surfactant. These results indicate that isooctane can be replaced by higher molecular weight *n*-alkanes to avoid contamination of the aqueous phase with the organic solvent. These conclusions are important for the potential use of DODMAC microemulsions for extraction of biomolecules from dilute aqueous solutions.

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