Colloid Polym Sci 279:655–663 (2001)

ORIGINAL CONTRIBUTION

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Interfacial composition, structural parameters and thermodynamic properties of water-in-oil microemulsions

Received: 12 September 2000
Accepted: 27 October 2000

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Abstract The formation and structural characteristics of water-in-oil microemulsions comprising hexadecylpyridinium chloride (CPC), alkanols (C_4–C_6) and alkanes (C_5, C_8–C_{10}) have been investigated by the method of dilution. The compositions of the surfactant and the cosurfactant in the interfacial region (interphase) of the microemulsion droplets have been determined. The thermodynamics of transfer of the cosurfactants (alkanols) from the continuous oil (alkane) phase to the interface have been evaluated from dilution measurements at different temperatures. The structural parameters, radii of the droplet and the waterpool, aggregation numbers of CPC and the alkanols in the interphase of a droplet, and the nanoparticle density of solution have been estimated assuming monodispersity of the droplets. The thermodynamics and structural parameters have been examined in terms of the chain lengths of the alkanols and alkanes.

Key words Microemulsions · Interfacial composition · Distribution constant · Structural parameters and thermodynamic properties

Introduction

Microemulsions are optically isotropic, transparent and thermodynamically stable systems consisting of water (or brine), a surfactant, oil and a cosurfactant [1]. The cosurfactants used with ionic-surfactant-based microemulsions are mostly lower alkanols and amines.

In recent years, microemulsions have found extensive use and application in various fields of science and technology, for example, enhanced oil recovery, photoredox reactions and organic syntheses, lubrication, ultrafine cleaning, synthesis of nanoparticles, cosmetic formulation, drug delivery systems and organ preservation fluids [2–11]. For the optimization of a process, fundamental understanding of the phase behaviors, interfacial characteristics and the dynamic nature of microemulsions is required [12–15].

In the elucidation of the nature of the oil/water interface, detailed knowledge of the interfacial composition, the distribution of alkanol between the oil and water and the solubilization limit of the latter in the waterpool in water-in-oil (w/o) microemulsion systems are essential. These properties are strongly influenced by the nature of the oil and the length of the alkyl chains of the oil and the amphiphiles (surfactants and cosurfactant) [11–15].

The distribution of the cosurfactants between the interfacial plane and bulk oil phase can be determined by various techniques, such as conductivity, dynamic light scattering, small-angle neutron scattering and interfacial tension methods [15–20]. A simple method of dilution has been used by several workers for the determination of the interfacial and bulk concentrations of the cosurfactant [21–28] and thereby the related process energetics.

In this article, we communicate results of the dilution method at different temperatures on the w/o microemulsion systems using hexadecylpyridinium chloride (CPC) as surfactant, water as the disperse phase, C_4–C_6 alkanols as cosurfactants and C_5, C_8–C_{10}

alkanes as oils. From the values of the composition of the cosurfactant and surfactant in the interphase, the distribution of cosurfactant between the bulk phase and the interphase has been calculated along with various other structural parameters of the microemulsion droplets [29–31]. To gain insight into the thermodynamic stability of microemulsions as a function of oil chain length, the standard Gibbs energy ($\Delta_{trans}G^0$) for the transfer of cosurfactant from the continuous oil phase to the interfacial region has been computed. Previously obtained results for hexane and heptane systems [24] have been combined with the present results and this enabled us to understand the effects of the alkyl chain length of the oil and the alkanol on the distribution and energetic parameters of the systems. Since the alkylpyridinium chloride surfactant along with a cosurfactant is known to yield microemulsions with better water solubilizing capacities than the corresponding quaternary ammonium salts of equal chain length [32], it was chosen as the surfactant in the present study.

Experimental

Materials

CPC, obtained from Sigma, was purified as described earlier [24]. The *n*-alkanols and *n*-alkanes were purchased from Aldrich with a stated purity of above 99% and were used as received. Water was deionized and the specific conductivity was less than 2 μS/cm.

Dilution experiments

Dilution experiments were performed following the procedure described earlier [24]. At a given temperature, a microemulsion was first formed by the appropriate addition of surfactant, water and oil. This viscous and turbid mixture was titrated with a cosurfactant, while stirring constantly using a magnetic stirrer, until the solution became just clear. Sufficient time was allowed for equilibrium to be reached. The volume of cosurfactant was noted at that point. A known but small volume of oil was added to the clear mixture to destabilize the microemulsion. The resulting cloudy mixture was titrated with a cosurfactant while stirring to obtain a clear and stable w/o microemulsion and the volume was noted again. This process was repeated to obtain several points. In order to calculate various thermodynamic parameters, the entire procedure was repeated at different temperatures. Each set of experiments was repeated three to four times and the average values of the slopes and intercepts thus obtained were employed for data processing and analysis.

Results and discussion

Basics of the dilution method

In the dilution method, the concentration of the cosurfactant (alkanol) in the continuous oil phase of a stable w/o microemulsion remains constant at a given temperature. The total number of moles of the alkanol, n_a, present in the stable microemulsion is given by

$$n_a = n_a^i + n_a^w + n_a^o \ , \tag{1}$$

where n_a^i, n_a^w and n_a^o are the number of moles of alkanol in the interfacial, water and oil phases respectively. Since the solubility of alkanol in oil is constant at a given temperature, the constant k can be written as

$$k = n_a^o/n_o \ , \tag{2}$$

where n_o is the total number of moles of oil in the system. Combining Eqs. (1) and (2) we get

$$n_a = n_a^i + n_a^w + kn_o \ . \tag{3}$$

Since the moles of alkanol in the interface and in the dispersed phase (water) depend on the surfactant concentration, Eq. (3) may be converted into a more convenient form by dividing throughout by n_s to give

$$\frac{n_a}{n_s} = \frac{n_a^i + n_a^w}{n_s} + k\frac{n_o}{n_s} \ . \tag{4}$$

The slope (S) and intercept (I) of a plot of n_a/n_s versus n_o/n_s should yield the values of k and n_a^i, respectively, if the value of n_a^w is known at the temperature of measurement. The distribution of alcohol between the continuous phase (oil) and the interphase of the droplet on the mole fraction scale can be expressed in terms of the distribution constant, K_x, by the relation [24]

$$K_x = X_a^i/X_a^o = \frac{n_a^i/n_a^i + n_s}{n_a^o/n_a^o + n_o} = \frac{n_a^i(n_a^o + n_o)}{n_a^o(n_a^i + n_s)} = \frac{n_a^i(1+S)}{S[(1+I)n_s - n_a^w]} \ . \tag{5}$$

In the present case it is assumed that the surfactant molecules are present at the interface only. For negligible n_a^w, the equation becomes

$$K_x = \frac{I(1+S)}{S(1+I)} \ . \tag{6}$$

The values required for the calculation of K_x can be readily obtained from the intercept and slope of the plot of n_a/n_s versus n_o/n_s as described earlier [24].

Thermodynamics of transfer

The standard Gibbs energy of transfer ($\Delta_{trans}G^o$) of alkanol from the oil phase to the interfacial phase can be obtained from the following relation:

$$\Delta_{trans}G^o = -RT\ln K_x \ . \tag{7}$$

Representative plots of n_a/n_s versus n_o/n_s for the dilution experiments are illustrated in Figs. 1 and 2. The plots are linear and in the calculation of n_a^i/n_s

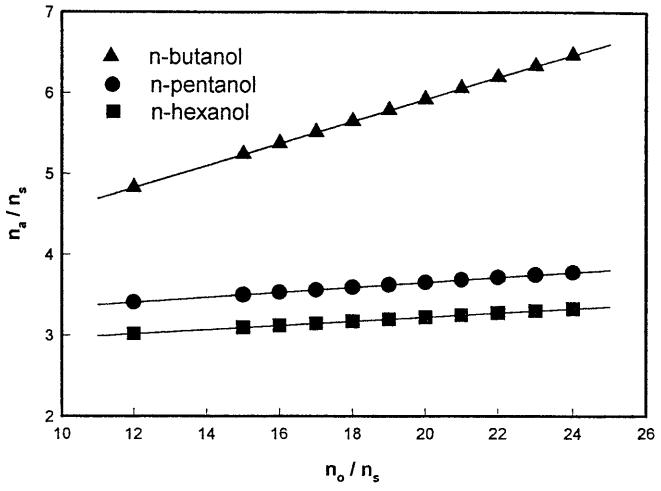

Fig. 1 Plots of n_a/n_s versus n_o/n_s according to Eq. (4) for the water/hexadecylpyridinium chloride (*CPC*)/alkanol/*n*-pentane microemulsion sytem at 298 K

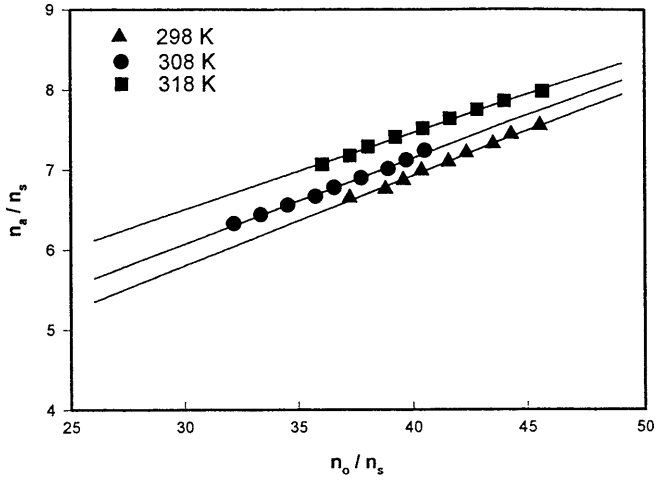

Fig. 2 Plots of n_a/n_s versus n_o/n_s for the water/CPC/hexanol/*n*-nonane microemulsion system at different temperatures

from the intercept the solubility of *n*-butanol and *n*-pentanol in water at the pertinent temperature has been taken into account [24].

It is evident that the values of the slope (Tables 1, 2) decrease for a given alkane with increasing alkanol chain length. Similarly a decrease was observed for the values of the intercept with alkanol chain length, except for nonane and decane. In these two cases, the intercept increased from C_4 alkanol to C_5 alkanol and then decreased for C_6 alkanol. Thus, for a given alkane, the mole fraction of the alkanol at the interface depends on the alkanol chain length. In all the cases studied, the mole fraction of alkanol in the interphase (X_a^i) is higher for the C_4 alkanol compared to the C_5 and C_6 alkanols.

The values of the Gibbs energy of transfer ($\Delta_{trans}G^o$) of the alkanols from the continuous phase to the interfacial region between water and oil were obtained at various temperatures by employing Eq. (7). The entropy ($\Delta_{trans}S^o$) and enthalpy of transfer ($\Delta_{trans}H^o$) are obtained as follows:

$$\frac{\partial}{\partial T}\left[\Delta_{trans}G^0\right]_p = -\Delta_{trans}S^0 \tag{8}$$

and

$$\Delta_{trans}H^o = \Delta_{trans}G^o + T\Delta_{trans}S^o \ . \tag{9}$$

The thermodynamic parameters are also listed in Tables 1 and 2. The values of the Gibbs energy of transfer depend on the carbon number of the alkane. For a given alkanol, the values of $\Delta_{trans}G^0$ became more negative with an increase in carbon number. In terms of comparison, the process is more spontaneous for odd-numbered alkanes and less spontaneous for even-numbered alkanes (Fig. 3). The values of $\Delta_{trans}G^0$ varied from −3.4 to −7.0 kJ/mol. Such low values indicate a lack of strong interaction between the surfactant and cosurfactant molecules at the interphase. These values are in agreement with the values of −(5.5–10) kJ/mol observed for various alkanol and different surfactant systems in the literature [17, 24–26]. It is observed that the values of $\Delta_{trans}G^0$ varied linearly with the alkyl chain length of alkanols for all alkanes except nonane. The free energy of transfer is least spontaneous for the C_4 alcohol and becomes slightly more spontaneous with an increase in chain length of the alcohol.

In surfactant chemistry, it has been the practice to measure the effect of alkyl chain length on the free energy of the system [33]. According to Traube's law, the free energy of adsorption of amphiphiles at an air/water interface changes by approximately −3000 J per CH_2 group [33]. In the present investigation, the values for the free energy of transfer per CH_2 group in the C_4 to C_6 alkanol series are found to be −1190, −620, −810, −585 and −1230 J/mol for C_5, C_6, C_7, C_8 and C_{10} alkanes, respectively, at 298 K. The free energy of transfer per CH_2 group is found to be around −800 J/mol for a benzene, sodium stearate, water and alkanol system [26]. The results obtained in this study are 2.5- to fivefold lower than Traube's rule. The discrepancy may arise from the difference in the nature of the interfaces: air/water in Traube's experiment and oil/water in the present study. The presence of surfactant at the oil/water interface makes an entropic contribution to reduce the transfer free energy. The majority of the studies in the literature are limited either to a single oil with a series of alkanols or to a single cosurfactant with a series of alkanes. In this study both the cosurfactant and the oil were varied. The $\Delta_{trans}H^0$ in general increase with the temperature except for the butanol/CPC/pentane system and the entropy values of transfer are both positive and

Table 1 Interfacial composition, distribution constant and thermodynamic parameters for water-in-oil (*w/o*) microemulsion systems (comprising hexadecylpyridinium chloride, *CPC*) with odd-numbered alkanes. Errors in $\Delta_{trans}H^0$, $\Delta_{trans}G^0 = \pm 0.5$ kJ/mol and $\Delta_{trans}S^0 = \pm 5$ J/K/mol

System	Temperature (K)	$I = (n_a^i + n_a^w)/n_s$	Slope = n_a^o/n_o	$10^3 n_a^i$ (mol)	$10^3 n_a^o$ (mol)	K_x	$\Delta_{trans}G^0$ (kJ/mol)	$\Delta_{trans}S^0$ (J/K/mol)	$\Delta_{trans}H^0$ (kJ/mol)
Pentane	283.0	4.10	0.101	4.52	11.10	7.2	−4.6	−40	−15.8
Butanol/CPC									
	288.0	3.59	0.115	3.98	11.54	6.6	−4.5	−46	−17.9
	298.0	3.19	0.137	3.37	12.59	5.4	−4.1	−60	−22.2
Pentanol/CPC	283.0	2.63	0.067	3.70	6.88	11.4	−5.7	52	9.1
	288.0	2.70	0.070	3.79	7.07	11.1	−5.7	−2	−6.5
	298.0	3.04	0.031	4.23	9.53	7.5	−5.0	−113	−38.5
Hexanol/CPC	283.0	2.59	0.034	3.32	6.12	16.5	−6.6	−200	−63.3
	288.0	2.61	0.034	2.75	5.14	12.2	−6.0	−82	−29.5
	298.0	2.71	0.026	3.37	6.79	14.1	−6.6	157	40.0
Nonane									
Butanol/CPC	298.0	4.21	0.165	10.72	5.29	10.2	−5.8	−129	−44.1
	308.0	3.48	0.220	8.78	6.27	6.8	−4.9	21	1.6
	318.0	3.75	0.193	9.58	7.48	8.2	−5.5	171	48.9
Pentanol/CPC	298.0	5.81	0.157	8.12	3.80	15.0	−6.7	140	35.1
	308.0	6.41	0.052	9.00	2.92	17.8	−7.4	52	8.7
	318.0	6.67	0.066	9.40	3.90	14.9	−7.1	−36	−18.5
Hexanol/CPC	298.0	2.45	0.112	3.45	7.22	7.1	−6.5	48	9.5
	308.0	2.85	0.108	4.01	6.11	7.6	−5.2	78	18.9
	318.0	3.75	0.095	5.28	6.27	9.0	−5.8	108	28.6

Table 2 Interfacial composition, distribution constant and thermodynamic parameters for w/o microemulsion systems with even-numbered alkanes. Errors same as in Table 1

System	Temperature (K)	$I = n_a^i + n_a^w)/n_s$	Slope = n_a^o/n_o	$10^3 n_a^i$ (mol)	$10^3 n_a^o$ (mol)	K_x	$\Delta_{trans}G^0$ (kJ/mol)	$\Delta_{trans}S^0$ (J/K/mol)	$\Delta_{trans}H^0$ (kJ/mol)
Octane	298.0	4.26	0.143	10.85	13.18	6.3	−4.6	−73	−26.3
Butanol/CPC									
	308.0	3.46	0.165	8.72	12.30	5.1	−4.1	−5	−5.7
	318.0	3.74	0.171	9.87	15.44	5.4	−4.5	63	15.6
Pentanol/CPC	298.0	2.92	0.091	8.28	18.48	7.6	−5.0	77	18.0
	308.0	2.68	0.093	7.50	12.37	8.6	−5.5	81	19.5
	318.0	2.88	0.090	8.60	14.08	9.8	−6.0	85	21.1
Hexanol/CPC	298.0	2.72	0.078	7.59	10.85	10.1	−5.7	−77	−28.8
	308.0	2.32	0.088	6.51	10.18	8.7	−5.5	−21	−12.1
	318.0	2.55	0.083	7.12	11.64	9.4	−5.9	34	5.1
Decane	298.0	11.03	0.202	14.39	10.08	4.6	−3.8	−82	−28.3
Butanol/CPC									
	308.0	9.19	0.284	11.97	12.12	3.8	−3.4	−50	−18.9
	318.0	8.73	0.301	11.32	12.71	3.6	−3.4	−18	−9.2
Pentanol/CPC	298.0	3.84	0.158	5.15	7.49	5.6	−4.3	356	101.8
	308.0	6.72	0.079	9.47	4.34	11.8	−6.5	96	23.0
	318.0	5.36	0.088	7.53	4.11	10.4	−6.2	−164	−58.3
Hexanol/CPC	298.0	4.18	0.069	5.87	4.00	12.4	−6.2	37	4.8
	308.0	4.25	0.069	5.98	3.74	12.6	−6.5	13	−2.5
	318.0	4.49	0.075	6.30	3.62	11.7	−6.5	11	−10.0

negative. It can be concluded that the microemulsion systems in the present study can be more ordered and disordered depending on their chemical and thermal condition.

The thermodynamic results collected in the present investigation were tested for the so-called enthalpy–entropy compensation effect. This compensation effect was observed to be valid for micellar and microemul-

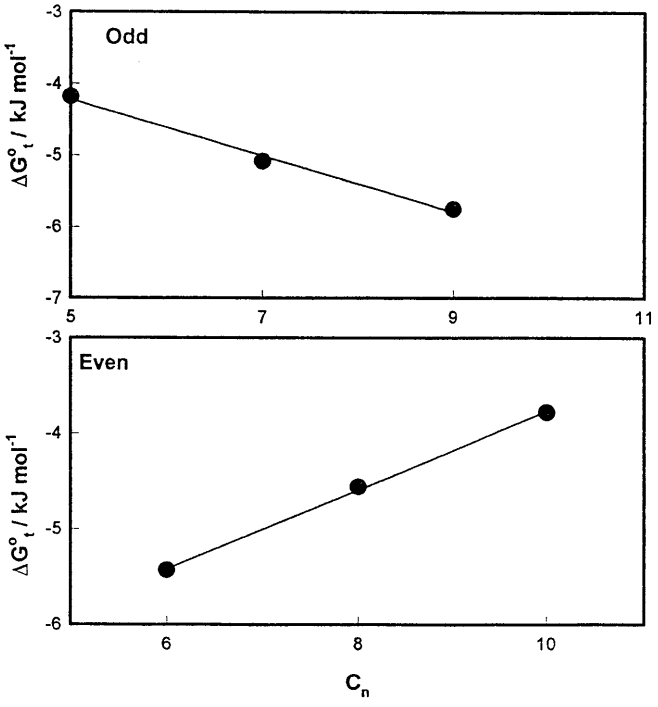

Fig. 3 Plots of $\Delta_{trans}G^0$ as a function of alkane carbon number for the water/CPC/*n*-butanol/alkane microemulsion system at 298 K

sion systems [34–36]. The plots of $\Delta_{trans}H^0$ versus $\Delta_{trans}S^0$ are illustrated in Fig. 4 at three temperatures. Good correlations were observed at these temperatures. The compensation temperatures (T_{comp}) obtained from the slopes of the lines are 298.2, 302.4 and 318.8 K vis-à-vis the experimental temperatures of 298, 308 and 318 K, respectively. The fitting of the transfer enthalpies and entropies obtained with different alkanol/alkane combinations in the formation of microemulsions in one linear course suggests a comparable energetic behavior for different systems at the same temperature.

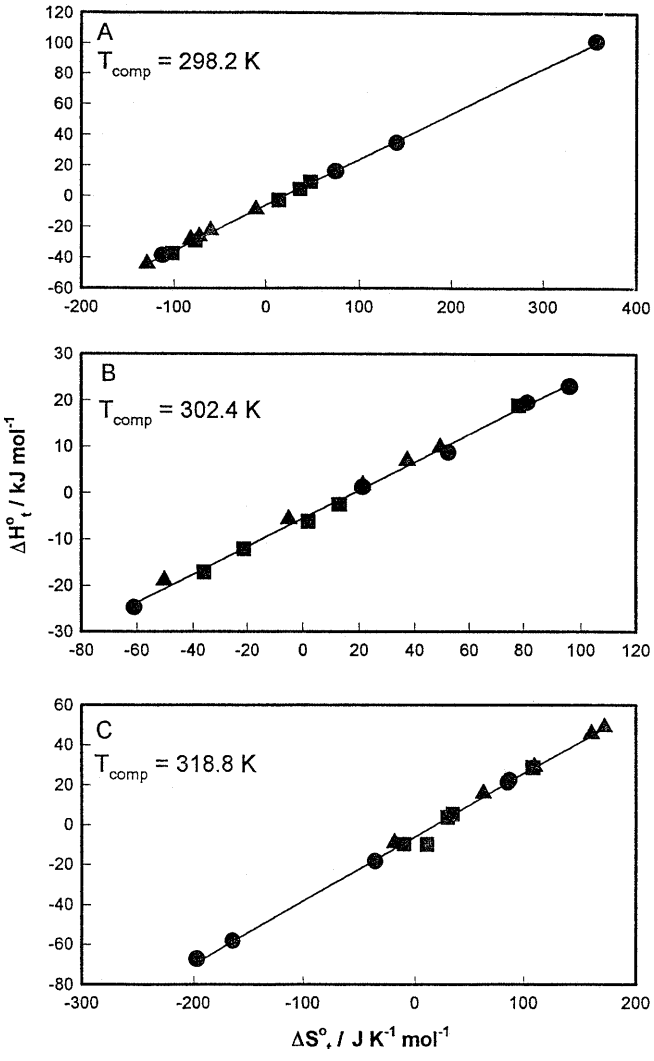

Fig. 4 Enthalpy–entropy compensation plots for the water/CPC/alcohol/alkane microemulsion system: **A** 298 K, **B** 308 K, **C** 318 K. Symbols same as in Fig. 1

Structural parameters

Various structural parameters have been computed using a simplified structural model. In this model, a monodispersed population of spherical droplets of the dispersed phase is considered to be separated from the organic phase by a monolayer of surfactant and cosurfactant that are arranged closely and orderly in the interphase. The total volume (V_d) of the droplets is given by

$$V_d = (4/3)\pi R_e^3 N_d \ , \tag{10}$$

where N_d is the total number of microemulsion droplets and R_e is the effective radius of the droplet.

The total surface area (A_d) of the droplets is given by

$$A_d = 4\pi R_e^2 N_d \ . \tag{11}$$

The total volume (V_d) can be related to the volumes of water (V_{H_2O}), surfactant (V_s) and cosurfactant at the interface (V_a^i) as follows

$$V_d = V_{H_2O} + V_s + V_a^i \ . \tag{12}$$

The value of V_a^i can be computed if the value of n_a^i (i.e. the number of moles of the cosurfactant at the interface) is known. The value of n_a^i is obtained from the experimental value of the intercept in the dilution method and is given by

$$n_a^i = In_s - n_a^w \ , \tag{13}$$

where n_s is the number of moles of surfactant and n_a^w is the solubility of cosurfactant in water at a given temperature. The value of n_a^w can be neglected except for *n*-butanol and *n*-pentanol. The V_a^i is given by the following equation

$$V_a^i = \frac{n_a^i M_a}{\rho_a} \quad , \tag{14}$$

where M_a and ρ_a are the molar mass and the density of the cosurfactant, respectively.

The total surface area ($\mathbf{A}_d$) is obtained from the relation

$$\begin{aligned} A_d &= (n_s A_s + n_a^i A_a) N_A = 4\pi R_e^2 N_d \\ &= n_s A_s N_A + (I n_s - n_a^w) A_a N_A \quad . \\ &= \left[n_s (A_s + I A_a) - n_a^w A_a \right] N_A \end{aligned} \tag{15}$$

For negligible solubility of cosurfactant in water, $n_a^w = 0$, so

$$A_d = n_s (A_s + I A_s) N_A \quad .$$

In this equation, N_A is Avogadro's number and A_s and A_a are the areas of the polar head groups of surfactant and cosurfactant, respectively. The values of $A_s = 7.1 \times 10^{-19}$ m^2 for CPC and $A_a = 2.0 \times 10^{-19}$ m^2 for alkanol were used in the calculation.

The values of R_e and N_d are obtained as follows

$$R_e = 3V_d / A_d \tag{16}$$

and

$$N_d = \frac{3V_d}{4\pi R_e^3} \quad . \tag{17}$$

The average aggregation number of surfactant ($\tilde{N}_s$) and cosurfactant ($\tilde{N}_{cs}$) in a reversed micelle is given by

$$\tilde{N}_s = n_s N_A / N_d \tag{18}$$

and

$$\tilde{N}_{cs} = n_a^i N_A / N_d \quad . \tag{19}$$

The equation to calculate the effective radius of the water droplet (R_w) of the disperse phase including the contributions of the anchored amphiphile and cosurfactant head groups is

$$R_w = \left(\frac{(V_{H_2O} + V_s^h + V_{cs}^h)}{V_d} \right)^{1/3} R_e \quad , \tag{20}$$

Table 3 Structural parameters for w/o microemulsion systems with odd-numbered alkanes

System	Temperature (K)	R_e (nm)	R_w (nm)	N_d	$\tilde{N}_s$	$\tilde{N}_{cs}$
Pentane Butanol/CPC	283.0	4.70	4.49	4.12×10^{18}	205	661
	288.0	4.83	4.63	3.71×10^{18}	230	647
	298.0	5.05	4.87	3.12×10^{18}	269	651
Pentanol/CPC	283.0	5.11	4.85	3.20×10^{18}	265	697
	288.0	5.09	4.83	3.25×10^{18}	260	703
	298.0	4.95	4.68	3.62×10^{18}	236	704
Hexanol/CPC	283.0	5.39	5.09	2.74×10^{18}	309	730
	288.0	5.53	5.27	2.44×10^{18}	350	680
	298.0	5.36	5.06	2.80×10^{18}	304	724
Heptane Butanol/CPC	298.0	3.35	2.42	1.68×10^{19}	100	35
	308.0	3.47	2.56	1.42×10^{19}	120	331
	318.0	3.35	2.42	1.69×10^{19}	100	348
Pentanol/CPC	298.0	3.64	2.64	1.30×10^{19}	131	367
	308.0	3.74	2.78	1.12×10^{19}	152	341
	318.0	3.71	2.73	1.17×10^{19}	144	351
Hexanol/CPC	298.0	3.78	2.65	1.28×10^{19}	133	426
	308.0	3.88	2.81	1.07×10^{19}	159	380
	318.0	3.86	2.80	1.09×10^{19}	158	376
Nonane Butanol/CPC	298.0	3.30	2.36	1.82×10^{19}	93	355
	308.0	3.41	2.49	1.54×10^{19}	109	342
	318.0	3.36	2.43	1.66×10^{19}	102	348
Pentanol/CPC	298.0	4.30	3.28	6.78×10^{18}	124	721
	308.0	4.19	3.15	7.62×10^{18}	111	711
	318.0	4.15	3.10	7.98×10^{18}	106	709
Hexanol/CPC	298.0	5.34	4.38	2.84×10^{18}	299	732
	308.0	5.21	4.22	3.18×10^{18}	267	760
	318.0	4.96	3.91	4.01×10^{18}	211	793

where the new terms V_s^h and V_{cs}^h represent the volumes of the head groups of surfactant and cosurfactant, respectively, and are given by the relations

$$V_s^h = \frac{4}{3\pi^{1/2}} A_s^{3/2} \tilde{N}_s \quad (21)$$

and

$$V_{cs}^h = \frac{4}{3\pi^{1/2}} A_a^{3/2} \tilde{N}_{cs} \ . \quad (22)$$

Various structural parameters were obtained by employing the procedures described previously and are listed in Tables 3 and 4. The microemulsion droplet size (R_e) values for a given alkane increased with the chain length of the alcohol. The values of R_w are lower than those of R_e in all cases. The ratio or R_e/R_w is, on the whole, independent of the alcohol, alkane (chain length) and temperature. The average value of this ratio obtained in the temperature range 298–318 K for all the systems investigated in the present study is 1.37. This average value is slightly higher than the value of 1.16–1.18 observed for butanol/hexane and pentanol/hexane and other microemulsion systems investigated [15, 37, 38]. This difference may be attributed to the use of different values of surfactant/cosurfactant ratios (σ) and water weight fraction (W_w).

The values of R_w (2.55 nm) and R_e (3.46 nm) obtained in the present study for the butanol/hexane microemulsion system at $\sigma = 0.36$ and $W_w = 0.085$ at 298 K compares well with the values of R_w (2.51 nm) and R_e (3.41 nm) at $\sigma = 0.33$ and $W_w = 0.065$ obtained from conductivity measurements [37]. Similarly, the values of $R_w = 2.85$ nm and $R_e = 3.63$ nm obtained from conductivity studies at $\sigma = 0.33$ and $W_w = 0.10$ for pentanol/hexane microemulsions are in line with our present results of R_w (2.71 nm) and R_e (3.69 nm) at $\sigma = 0.36$ and $W_w = 0.085$.

The number density of droplets (N_d) varies against alkanol size in the order $C_4 > C_5 > C_6$ for a given alkane, except for the pentane system. No systematic dependence of N_d on temperature was observed. The N_d values varied between 5 and 15% depending on the system and the temperature.

The aggregation numbers of surfactant ($\tilde{N}_s$) and cosurfactant ($\tilde{N}_{cs}$) with each droplet and their dependence on temperature are important aspects of microemulsion stability. In all the cases studied, the values of $\tilde{N}_s$ and $\tilde{N}_{cs}$ depend on temperature and the alkanol chain length for a given alkane (Tables 3, 4). For the

Table 4 Structural parameters for w/o microemulsion systems with even-numbered alkanes

System	Temperature (K)	R_e (nm)	R_w (nm)	N_d	$\tilde{N}_s$	$\tilde{N}_{cs}$
Hexane Butanol/CPC	298.0	3.46	2.55	1.44×10^{19}	117	335
	308.0	3.50	2.60	1.36×10^{19}	124	327
	318.0	3.46	2.56	1.43×10^{19}	118	334
Pentanol/CPC	298.0	3.69	2.71	1.20×10^{19}	140	360
	308.0	3.70	2.71	1.19×10^{19}	141	358
	318.0	3.71	2.74	1.17×10^{19}	144	353
Hexanol/CPC	298.0	3.88	2.82	1.07×10^{19}	159	384
	308.0	3.88	2.80	1.08×10^{19}	155	393
	318.0	3.90	2.85	1.03×10^{19}	164	376
Octane Butanol/CPC	298.0	3.29	2.35	1.85×10^{19}	92	354
	308.0	3.41	2.50	1.54×10^{19}	110	342
	318.0	3.34	2.41	1.71×10^{19}	100	347
Pentanol/CPC	298.0	3.63	2.62	1.32×10^{19}	127	377
	308.0	3.67	2.68	1.24×10^{19}	136	365
	318.0	3.61	2.60	1.36×10^{19}	124	381
Hexanol/CPC	298.0	3.86	2.77	1.13×10^{19}	149	406
	308.0	3.90	2.84	1.04×10^{19}	163	378
	318.0	3.88	2.80	1.09×10^{19}	155	395
Decane Butanol/CPC	298.0	3.47	2.49	1.54×10^{19}	55	562
	308.0	3.64	2.69	1.23×10^{19}	69	586
	318.0	3.69	2.75	1.14×10^{19}	74	595
Pentanol/CPC	298.0	4.77	3.83	4.26×10^{18}	198	728
	308.0	4.14	3.09	8.08×10^{18}	105	706
	318.0	4.37	3.36	6.28×10^{18}	135	722
Hexanol/CPC	298.0	4.86	3.78	4.41×10^{18}	192	802
	308.0	4.84	3.76	4.49×10^{18}	189	802
	318.0	4.79	3.70	4.70×10^{18}	180	807

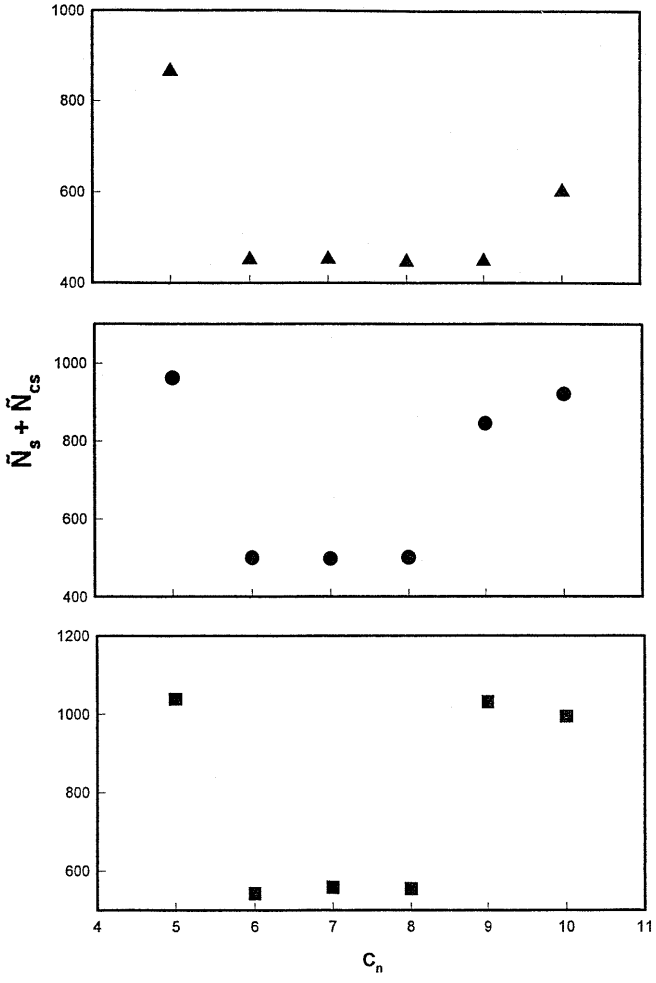

Fig. 5 Plots of total aggregation number versus carbon number of alkane at 298 K. Symbols same as in Fig. 1

butanol systems, the values of $\tilde{N}_s$ and $\tilde{N}_{cs}$ increased up to octane and then decreased for nonane and decane. The total aggregation number, $\tilde{N}_s + \tilde{N}_{cs}$, is relatively constant for all the systems and depends on temperature, alkane and alkanol chain length. The dependency on the alkane chain length is depicted in Fig. 5. The values are fairly constant for C_6–C_9 alkanes in all cases; a sharp increase was observed, thereafter. The lack of reports in the literature on the aggregation aspects of amphiphiles in microemulsions prevents us from making a comparison with the present results. Perhaps a thorough investigation in this direction using different surfactant, cosurfactant and oil combinations would be worthwhile to arrive at a global picture.

Conclusions

The dilution method employed was found to be applicable to investigate the composition of the cosurfactant/surfactant ratio at the interphase. The thermodynamic properties of transfer of the alcohol from the bulk phase to the interphase reveal that the transfer process is spontaneous. The degree of spontaneity depended on the chain length of both alcohol and alkane. The Gibbs energy of alkanol transfer ($\Delta_{trans}G°$) varied in an opposite manner for even-numbered versus odd-numbered alkanes.

Acknowledgements R.P. is thankful to the financial support received from NSERC in the form of an operating grant. L.D. acknowledges the Undergraduate Summer Research Award from NSERC (2000). K.B. thanks the Human Resources department for partial salary supplement.

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