ENTHALPIES OF TRANSFER OF PENTANOL FROM WATER TO SODIUM DODECYLSULFATE-DODECYL-DIMETHYLAMINE OXIDE-WATER MIXTURES

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Abstract

At a given surfactant-surfactant ratio, the enthalpies of transfer $\Delta H (W \to W + S)$ of pentanol 0.03 m from water to sodium dodecylsulfate (NaDS)-dodecyldimethylamine oxide-water mixtures as functions of the surfactants mixture concentration (m_t) were determined. For $X_{NaDS} = 0.9$, $\Delta H (W \to W + S)$ increases monotonically with m_t such as observed for pure surfactants. For $X_{NaDS} = 0.12$ and 0.3, $\Delta H (W \to W + S)$ increases with m_t up to 0.12 m beyond which it decreases with m_t. At $X_{NaDS} = 0.6$, two monotonic curves can be distinguished in the $\Delta H (W \to W + S)$ vs. m_t trend. Experimental data were fitted through an equation previously reported for additives in pure surfactants derived by assuming the pseudo-phase transition model for the micellization and a mass action model for the distribution of the additive between the aqueous and the micellar phases. This method did permit to simultaneously obtain the distribution constant of the alcohol between the aqueous and the micellar phase (and, then, the standard free energy of transfer) and its enthalpy of transfer from the aqueous to the micellar phases. By combining these properties the standard entropies of transfer were calculated. From these results, the excess properties of pentanol in the mixed micelles were calculated as a function of the mixture composition. The excess enthalpies and entropies are positive and compensate with each other leading to null values for the excess free energies in the whole range of the mixed micelles composition.

Introduction

There is a growing interest on the surfactant-surfactant mixed micelles formation in water from both the theoretical and the practical point of view. Thermodynamic studies essentially deal with the determination of the critical micelle concentration as a function of the surfactant-surfactant ratio [1]. In fact, through these properties and appropriate models the nonideal free energies of the mixed micelles can be calculatetd. As far as other thermodynamic properties are concerned, sparse volume and enthalpy data are reported [2-4]. A com-

plete thermodynamic investigation concerns the sodium dodecylsulfate-dodecyldimethylamine oxide mixtures [5, 6].

Less attention has been paid to the study of the effect of the mixed micelles composition on the solubilization of additives. A few data dealing with the distribution constant of the additive between the aqueous and the micellar phases are available [7–10] while other thermodynamic properties are practically inexistent. In fact, as far we know, the enthalpy of solution is the only property studied [10].

In order to contribute to this topic we have undertaken thermodynamic studies dealing with the solubilization of pentanol in sodium dodecylsulfate-dodecyldimethylamine oxide mixed micelles whose thermodynamic behavior is well characterized [5, 6]. In this report the enthalpy of transfer of pentanol from water to the surfactants mixtures will be discussed.

Experimental

Materials

Pentanol (PeOH) was purified by refluxing reagent grade product (Merck) over calcium hydride for 12 h followed by fractional distillation. Sodium dodecylsulfate (NaDS), Fluka puriss., was crystallized twice from ethanol, washed with ethyl ether and dried under vacuum at 60°C for at least 48 h before use. Dodecyldimethylamine oxide (DDAO) was a 30% aqueous solution (Fluka). The original solution was diluted ($\approx 0.8\ m$) and the true molality of the stock solution was determined by density measurements as described previously [11].

All solutions were prepared by weight using degassed conductivity water and the concentrations were expressed as moles per kg of water.

Solutions at different total molality ($m_t = m_{NaDS} + m_{DDAO}$) at rigorously constant surfactant-surfactant ratio were obtained by diluting standard solutions. The mixture composition is given by

$$X_{NaDS} = m_{NaDS}/m_t \qquad X_{DDAO} = m_{DDAO}/m_t \qquad (1)$$

Equipments

The enthalpies of mixing between the alcohol and the surfactant mixture solutions were carried out with a LKB 2107 microcalorimeter at 25.00±0.01°C. Measurements were performed by taking as baseline for the mixing process the enthalpy of dilution of the same surfactant mixture solution with water. More details on this procedure are reported elsewhere [12].

The injection of the solutions into the microcalorimeter was made by means of a Gilson peristaltic pump (Minipuls 2) and the flow of each solution was determined by weight.

At a given mixture composition, experiments were carried out at constant alcohol concentration (0.03 mol·kg^{-1}) at different total molalities. The alcohol and surfactants mixture concentrations after the mixing were obtained as product between the initial molality and the corresponding dilution factor f_i

$$f_i = \frac{\Phi_i^w}{\Phi_i^w + \Phi_j^w} \qquad f_j = 1 - f_i \qquad (2)$$

where Φ_i^w and Φ_j^w are the flow of water in the alcohol and surfactants mixture solutions, respectively.

Results and discussion

The measured enthalpy (ΔH^{exp}) corrected for the enthalpy of dilution of PeOH with water (ΔH_{id}^R) corresponds to the enthalpy of transfer of the additive from water to the surfactants mixture solution, $\Delta H (W \rightarrow W + S)$

$$\Delta H (W \rightarrow W + S) = \Delta H^{exp} - \Delta H_{id}^R \qquad (3)$$

The ΔH_{id}^R value was obtained through the Eq. (4)

$$\Delta H_{id}^R = h_{RR}[(m_{R,f}) - (m_{R,i})] + h_{RRR}[(m_{R,f})^2 - (m_{R,i})^2] \qquad (4)$$

where $m_{R,i}$ and $m_{R,f}$ are the initial and final molality, respectively, while h_{RR} and h_{RRR} are the alcohol-alcohol pair and triplet interactions parameters, respectively, whose values are reported in the literature [2].

Experimental enthalpies as functions of the initial ($m_{t,i}$) and final ($m_{t,f}$) total molality at the different mixture compositions are reported in Table 1 while the enthalpies of transfer vs. $m_{t,f}$ are plotted in Fig. 1. As can be seen, only for $X_{NaDS} = 0.9$, the $\Delta H (W \rightarrow W + S)$ vs. $m_{t,f}$ trend is a monotonic curve as those in pure surfactants [13, 14]. For $X_{NaDS} = 0.12$ and 0.3, $\Delta H (W \rightarrow W + S)$ increases with $m_{t,f}$ up to 0.12 m beyond which it decreases. In case of $X_{NaDS} = 0.3$, the high viscosity of the solution did not permit to perform measurements above 0.15 m. Peculiar is the $\Delta H (W \rightarrow W + S)$ vs. $m_{t,f}$ trend at $X_{NaDS} = 0.6$ since with increasing the surfactant mixture concentration the enthalpy of transfer slowly increases up to 0.07 m beyond which it increases sharphly tending to a constant value at high concentration.

Table 1 Enthalpies of mixing of pentanol aqueous solution with sodium dodecylsulfate-dodecyldimethylamine oxide micellar solutions at different mole fractions

$m_{t,i}$ / mol·kg^{-1}	$m_{t,f}$ / mol·kg^{-1}	ΔH^{exp} / J·mol^{-1}	$m_{t,i}$ / mol·kg^{-1}	$m_{t,f}$ / mol·kg^{-1}	ΔH^{exp} / J·mol^{-1}
$X_{NaDS} = 0.1241$			$X_{NaDS} = 0.3007$		
0.01499	0.008001	254	0.02006	0.01009	201
0.02497	0.01314	407	0.03892	0.02058	504
0.04996	0.02537	672	0.07988	0.04107	1251
0.07492	0.03826	973	0.09913	0.05169	1601
0.1015	0.05486	1312	0.1197	0.06105	1890
0.1249	0.06740	1725	0.1497	0.07736	2294
0.1494	0.08046	1843	0.2003	0.1025	2591
0.1747	0.09455	2060	0.2499	0.1274	2614
0.2001	0.1079	2056	0.2961	0.1420	2449
0.2250	0.1213	2297	0.3464	0.1571	2385
0.2499	0.1277	2329	0.3985	0.1497	2360
0.2748	0.1395	2296			
0.2995	0.1516	2222			
0.3498	0.1771	2189			
0.3999	0.1992	2193			
0.4996	0.2403	2163			
0.6078	0.2783	2226			
$X_{NaDS} = 0.5989$			$X_{NaDS} = 0.9001$		
0.01491	0.007367	181	0.03996	0.02089	908
0.01988	0.009669	264	0.05997	0.03108	1248
0.03991	0.01921	568	0.07999	0.04047	1559
0.05996	0.02964	704	0.09996	0.05169	1788
0.08012	0.03866	909	0.1196	0.06152	1965
0.09587	0.06164	1298	0.1500	0.07527	2249
0.09999	0.04789	1153	0.1747	0.08904	2272
0.1089	0.06919	1557	0.1999	0.1028	2438
0.1500	0.07220	2191	0.2500	0.1274	2714
0.1903	0.1219	3409	0.2993	0.1503	2722
0.1988	0.08711	2903	0.3501	0.1720	2905
0.2988	0.1453	3886	0.4002	0.1960	3060
0.3360	0.2108	4058	0.5203	0.2530	3137
0.3510	0.1678	3835	0.5496	0.2654	3169
0.4015	0.2481	4200	0.6990	0.3307	3275

The dependence of ΔH ($W \rightarrow W + S$) on concentration reflects not only all contributions present in case of pure micelles (distribution of the additive between the aqueous and the micellar phases, micellization equilibrium shift, in-
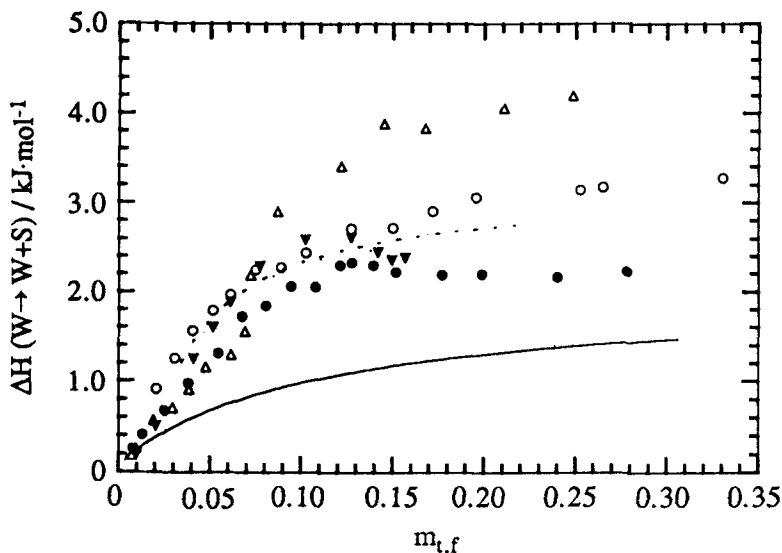
Fig. 1 Enthalpy of transfer of pentanol from water to sodium dodecylsulfate-dodecyldimethyl-amine oxide-water mixtures as a function of the final total molality.
● X_{NaDS} = 0.1241; ▼ X_{NaDS} = 0.3007; Δ, X_{NaDS} = 0.5989; o, X_{NaDS} = 0.9001; solid line, X_{NaDS} = 0; broken line, X_{NaDS} = 1

teractions in both phases) but also the effect of the additive and the total molality on the change of the mixed micelle composition. The latter contribution can be neglected since the alcohol concentration and the lowest surfactant concentration analyzed are sufficiently low and high, respectively [6]. Therefore, the enthalpies of transfer can be rationalized through the equation reported in the literature [13] for additives in pure surfactants

$$\Delta H\ (W \rightarrow W + S)\ =\ \Delta H^o_{t,w} - (\Delta H^o_t - A_{cdc}\ \Delta H_m)\ N_f \tag{5}$$

where $\Delta H^o_{t,w}$ and ΔH^o_t are the standard enthalpy of transfer of the additive from water and the aqueous phase to the micellar phase, respectively. $A_{cdc}\Delta H_m$ is the contribution of the shift of the micellization equilibrium due to the presence of the additive while N_f is the fraction of the additive solubilized in the aqueous phase. The last two quantities are given by

$$N_f = \frac{1}{1 + K\ (m_t - cmc)} \tag{6}$$

$$A_{cdc}\Delta H_m = \frac{cmc\Delta H_m}{2} \left\{ 2.3Ks + (1 + \beta)K \right\} \tag{7}$$

where K is the distribution constant, *cmc* is the critical micelle concentration while Ks and β are the Setchenov constant and the degree of ionization of the micelles, respectively.

Equation (5) is a three parameters equation (ΔH_t^o, $\Delta H_{t,w}^o$ and K) which can be solved by a nonlinear regression. From the K values converted into the partition constants (Kc, molarity scale) as $Kc = K/V_s$, where V_s is the partial molar volume of the micellized surfactant, the standard free energy of transfer of the additive from the aqueous to the micellar phases (ΔG_t^o) can be calculated. By combining the latter property with ΔH_t^o, the standard entropies of transfer ($T\Delta S_t^o$) are also obtained. So, a complete set of the standard transfer properties as a function of the surfactant-surfactant micelles composition is available. In addition, the standard enthalpy of solution of the additive in the micelles ($\Delta H_{S,b}^o$) can be calculated by adding the enthalpy of solution in water, whose value is reported in the literature [15], to $\Delta H_{t,w}^o$.
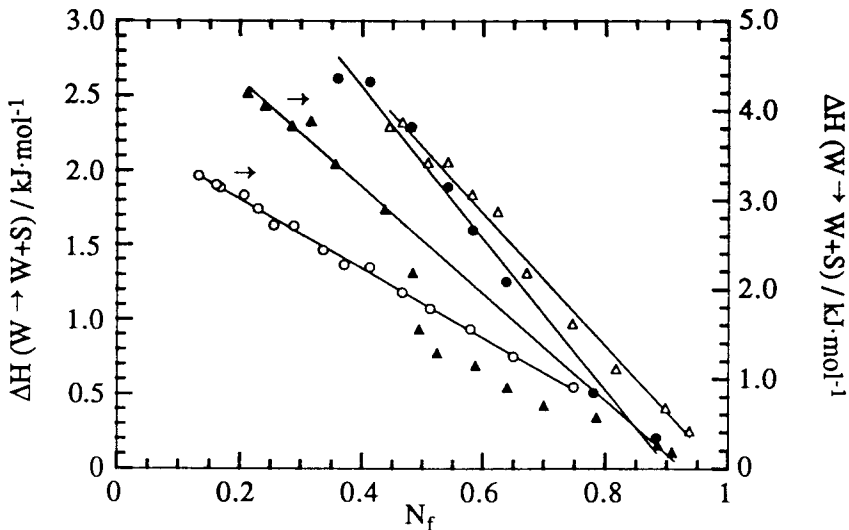

Fig. 2 Best fits of Eq. (5). $\triangle$ $X_{NaDS} = 0.1241$; $\bullet$ $X_{NaDS} = 0.3007$; $\blacktriangle$ $X_{NaDS} = 0.5989$; o $X_{NaDS} = 0.9001$

Since the quantity in the brackets at the right hand side of Eq. (5) is constant, then, Eq. (5) predicts that ΔH ($W \rightarrow W + S$) increases or decreases monotonically with m_t depending on the ($\Delta H_t^o - A_{cdc}\Delta H_m$) sign. Therefore, for $X_{NaDS} = 0.12$ and 0.3 it is difficult to discriminate which surfactant concentration region can be analyzed through Eq. (5). Indeed maxima were also detected in the trends of ΔH ($W \rightarrow W + S$) vs. the surfactant concentration of hydrophobic alcohols in pure surfactants [13, 14]. In those cases, the maxima were present near the *cmc* and were ascribed to the predominance of the shift of the

micellization equilibrium contribution on that of distribution. This is not the case here since the maxima are present at surfactant concentration very far from the *cmc*. On the other hand, volume data [16] show peculiarities at about the same concentration where the maxima are detected suggesting that a micellar transition likely occurs. On this basis, in the minimizing procedure the decreasing regions were not considered.

More complex is the case of $X_{NaDS} = 0.6$ since two monotonic trends can be distinguished (Fig. 2). Therefore, it is impossible to assess a priori which region reflects the distribution process. So, Eq. (5) was applied to both curves and in both cases unrealable results were obtained. Results consistent with those of other mixtures were obtained when points comprised between 0.015 and 0.07 $m_{t,f}$ are excluded. This implies the presence of a minimum localized at the intersection of the two curves.

Figure 2 shows the best fits of Eq. (5) for the mixtures analyzed. In order to extract ΔH_t^o from the slope of the plots in Fig. 2, the $A_{cdc}\Delta H_m$ term should be calculated (Table 2). To this purpose, the *cmc* value reported elsewhere [5] were used while the ΔH_m values were calculated from literature data [6]. As far ad Ks and β are concerned, because of the lack of literature data it was assumed that: i) the Setchenov constant is equal to that in pure NaDS (−0.42) [17]; ii) the degree of ionization of the mixed micelle (β) changes linearly with X_{NaDS} as $\beta = \beta_o X_{NaDS}$ where β_o (0.38) [18] refers to pure NaDS micelle. The latter hypothesis disagrees with literature results [19] for ionic-nonionic mixed micelles whose degree of dissociation is a nonlinear function of the mole fraction. However, calculations show that the very low *cmc* values lead to micellization shift contributions which are always smaller than the uncertainties on the slopes of $\Delta H^f (W \rightarrow W + S)$ vs. N_f plots. Therefore, the above approximations do not affect the ΔH_t^o evaluation.
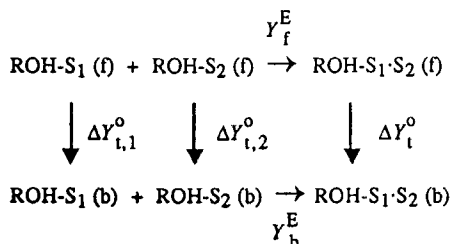
Table 2 Enthalpy of micellization, critical micelle concentration, partial molar volume of micellized surfactant and shift of micellization equilibrium contribution for sodium dodecylsulfate-dodecyldimethylamine mixtures

X_{NaDS}	[a]ΔH_m / kJ·mol^{-1}	[b]cmc / mol·kg^{-1}	$A_{cdc} \Delta H_m$ / kJ·mol^{-1}	[b]V_s / cm^3·mol^{-1}
0.1241	2.8	0.520	0.01	253.6
0.3007	−1.3	0.611	−0.01	252.0
0.5989	−2.9	1.07	−0.03	251.2
0.9001	−1.5	4.09	−0.07	250.6

[a]Calculated from data in Ref. [6]. [b]From Ref. [5].

The values of the properties of transfer are collected in Table 3 where the enthalpies of solution in the micelles are also reported.

According to the following scheme, it is possible to calculate the excess property of alcohol in the mixed micelles with respect to the pure micelles (Y_b^E)

$$Y_f^E$$
$$ROH\text{-}S_1\ (f)\ +\ ROH\text{-}S_2\ (f)\ \rightarrow\ ROH\text{-}S_1\cdot S_2\ (f)$$

$$\downarrow \Delta Y_{t,1}^o \qquad \downarrow \Delta Y_{t,2}^o \qquad \downarrow \Delta Y_t^o$$

$$ROH\text{-}S_1\ (b)\ +\ ROH\text{-}S_2\ (b)\ \rightarrow\ ROH\text{-}S_1\cdot S_2\ (b)$$
$$Y_b^E$$

where S_1 and S_2 indicate the two surfactants while f and b indicate the aqueous and the micellar phases, respectively.

From the above scheme it follows

$$Y_b^E = Y_f^E + (\Delta Y_t^o - X_1\,\Delta Y_{t,1}^o - X_2\,\Delta Y_{t,2}^o) \tag{9}$$

For the present system, H_f^E is negligible as data in Table 3 show. G_f^E was calculated through the following equation

$$G_f^E = 2.3RTKs\ (cmc - X_1\,cmc_1 - X_2\,cmc_2) \tag{10}$$

which derives from scheme (8) and the standard free energy of transfer of alcohol from water to the aqueous phase [20] by assuming, as mentioned above, a constant value for Ks. Because of the very low cmc values, G_f^E is negligible.

Table 3 Standard free energy, enthalpy and entropy of transfer of pentanol from the aqueous phase to mixed micelles, enthalpy of transfer from water to mixed micelles and standard enthalpy of solution in mixed micelles

X_{NaDS}	K	ΔG_t^o	ΔH_t^o	$T\Delta S_t^o$	$\Delta H_{t,w}^o$	$\Delta H_{s,b}^o$
0^a		−8.82	2.08	10.9	2.03	−5.97
0.1241	9±2	−8.8±0.5	4.5±0.5	13±1	4.4±0.5	−3.6
0.3007	14±5	−10.0±0.7	5.1±0.5	15.1±1.2	4.6±0.7	−3.3
0.5989	16±3	−10.3±0.4	5.8±0.2	16.1±0.6	5.4±0.3	−2.4
0.9001	18±2	−10.6±0.2	3.76±0.06	14.4±0.3	3.83±0.06	−4.23
1^b		−11.0	3.28	14.28	3.45	−4.55

Units are: $kJ\cdot mol^{-1}$ for the properties of transfer; $kg\cdot mol^{-1}$ for K. [a]From Ref. [13]. [b]From Ref. [14].

The dependence of Y_b^E on the mixed micelles composition is shown in Fig. 3. As can be seen, the excess enthalpy is positive according to the less negative enthalpies of solution of PeOH in mixed micelles with respect to pure micelles. Excess entropies values indicate that PeOH in mixed micelles is less ordered
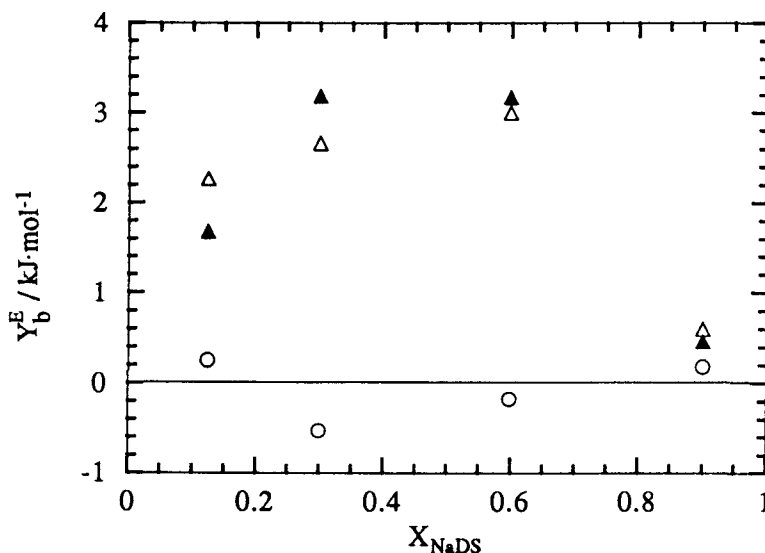
Fig. 3 Dependence of the excess free energy (O), enthalpy (▲) and entropy (△) of pentanol in the sodium dodecylsulfate-dodecyldimethylamine oxide micelles on the mole fraction

with respect to the pure ones. It is to be noted the enthalpy-entropy compensative effect and the consequent $G_b^E = 0$ in the whole range of composition.

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Zusammenfassung — Bei einem bestimmten Verhältnis oberflächenaktive Substanz/oberflächenaktive Substanz wurden die Transportenthalpien ΔH ($W \rightarrow W + S$) von 0.03m Pentanol aus Wasser in Gemische aus Natriumdodecylsulfat (NaDS), Dodecyldimethylaminoxid und Wasser als eine Funktion der Konzentration des Gemisches der oberflächenaktiven Substanzen (m_t) bestimmt. Für $X_{NaDS} = 0.9$ steigt ΔH ($W \rightarrow W + S$) mit zunehmendem m_t - wie für reine oberflächenaktive Substanzen erwartet - monoton an. Für $X_{NaDS} = 0.12$ und 0.3 steigt ΔH ($W \rightarrow W + S$) mit zunehmendem m_t bis 0.12 m an und fällt oberhalb dieses Wertes mit zunehmendem m_t wieder ab. Bei $X_{NaDS} = 0.6$ können bei einem Auftragen von ΔH ($W \rightarrow W + S$) gegen m_t zwei monotone Kurven unterschieden werden. Das Fitting der experimentellen Angaben erfolgte über eine zuvor für Additive in oberflächenaktiven Substanzen entwickelte Gleichung, welche unter Annahme des Pseudophasen-Übergangsmodelles für die Mizellisierung und eines Massenwirkungsmodelles für die Verteilung des Additivs zwischen wäßriger und mizellarer Phase ausgearbeitet wurde. Diese Methode gestattete eine simultane Ermittlung des Verteilungskoeffizienten von Alkohol zwischen der wäßrigen und der mizellaren Phase (und anschließend der freien Transportenergie) und der Transportenthalpie aus der wäßrigen in die mizellare Phase. Durch Kombinierung dieser Eigenschaften wurden die Standardentropien für den Transport berechnet. Anhand dieser Ergebnisse wurden die Überschußgrößen von Pentanol in den gemischten Mizellen als eine Funktion der Gemischzusammensetzung berechnet. Die Überschußenthalpien und -entropien tragen positives Vorzeichen und kompensieren einander, was im gesamten Bereich der Zusammensetzung der gemischten Mizellen zu Nullwerten für die freien Energien führt.