

THERMODYNAMICS OF TRANSFER OF SOME NITROALKANES FROM AQUEOUS TO DODECYLTRIMETHYLAMMONIUM BROMIDE MICELLAR PHASES

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ABSTRACT

The enthalpies of mixing of some aqueous *n*-nitroalkane solutions with dodecyltrimethylammonium bromide micellar solutions were determined. The experimental data were treated by using a previously reported approach giving the enthalpies of transfer of solute from the aqueous to the micellar phases and the distribution constant of solute between the two phases at the same time. From these, the standard thermodynamic quantities of transfer ($\Delta_{\text{trf}}G^\circ$, $\Delta_{\text{trf}}H^\circ$ and $\Delta_{\text{trf}}S^\circ$) are derived. In order to study the effect of the nature of both the solvent and the head group of solute, these properties are compared with those from water to octane and with those of alcohols and nitriles from aqueous to dodecyltrimethylammonium bromide micellar phase.

INTRODUCTION

Knowledge of the thermodynamic properties of a solute in micellar phase provides information about the remarkable solubilizing power of the micellar solutions towards polar and apolar solutes. Their derivation from the bulk properties of solutes needs theoretical models. In recent years, several models [1-4] have been proposed and much progress has been achieved in the understanding of the thermodynamics of water-surfactant-cosurfactant ternary systems. Our approach [3,4] takes into account the association of monomers into micelles through the pseudo-phase transition model and the solute distribution through a mass action model. Provided that the additive concentration approaches the infinite dilution state, the following contributions to the

thermodynamic properties of the solute in micellar solutions are derived on the basis of these models: the shift of the micellization equilibrium due to the presence of the solute, the distribution of the solute between the aqueous phase and the micelles, and the solute-surfactant interaction contribution in the aqueous phase. In order to verify the reliability of our approach and give information about the interactions driving the formation of the mixed micelles, we have for some time been carrying out a systematic study of the thermodynamics of solutes in water-surfactant-solute ternary systems.

Dodecyltrimethylammonium bromide (DTAB) [4-7], sodium dodecylsulfate [8-10] and dodecyldimethylamine oxide [3,11] were used as surfactants, whereas several alcohols were used as solutes. This choice was made so as to investigate the influence of both the head group of the surfactant and the solute, and the alkyl chain length of the solute.

We have shown that, according to the additivity rule, the free energy of transfer ($\Delta_{\text{trf}}G^\circ$) of alcohols from the aqueous to the micellar phases decreases linearly with the number of carbon atoms in the alcohol alkyl chain (n_c). Also, $\Delta_{\text{trf}}G^\circ$ values have shown the comparable affinity towards alcohols of nonionic and cationic dodecylsurfactants micelles, whereas they, in turn, display a smaller affinity than the anionic one. As far as the standard enthalpies and entropies of transfer are concerned, maxima were observed in their plots as a function of n_c . Also, thermodynamics of solvation in micellar phase clearly shows that the solubilization of alcohols in micelles is enthalpy driven [9].

To further clarify the role of the nature of the head group of additives on mixed micelle formation, in this report we discuss the enthalpies of mixing of some shorter alkyl chain aqueous *n*-nitroalkane solutions with DTAB micellar solutions.

EXPERIMENTAL

Method

The calorimetric measurements were made at 298 K with a flow LKB 2107 microcalorimeter. The enthalpies of mixing of the aqueous solutions of nitroalkanes (RNO_2) with DTAB micellar solutions were carried out by taking as baseline the enthalpic effect related to the process of dilution of the surfactant solutions with water. The enthalpy experimentally obtained, $\Delta_{\text{exp}}H$, then corresponds to the difference between the enthalpy of mixing and that of the dilution of surfactant solution.

Solutions were introduced into the microcalorimeter by means of a Gilson

peristaltic pump (Minipuls 2) and the flow rate of each solution ($\sim 0.004 \text{ g s}^{-1}$) was determined by weight.

Materials

DTAB, Sigma product, was crystallized twice from ethanol-acetone and then dried under vacuum at 360 K at least 48 h before use.

Nitromethane (MeNO_2), Hoechst sample for gas-chromatography, nitroethane (EtNO_2), C. Erba product, nitropropane (PrNO_2), Janssen product, and nitrobutane (BuNO_2), Fluka purum, were used as received. All solutions were prepared by weight, using degassed conductance water.

TABLE 1

Experimental enthalpies of mixing of the nitroalkanes in DTAB micellar solutions.

m_s	$10^6 \phi_s$	$10^6 \phi_r$	$\Delta_{\text{exp}}H$	m_s	$10^6 \phi_s$	$10^6 \phi_r$	$\Delta_{\text{exp}}H$
NITROMETHANE ($m_r = 0.04011$)				NITROETHANE ($m_r = 0.04010$)			
0.04002	4.249	4.263	117	0.04002	4.230	4.270	148
0.07970	3.891	4.058	147	0.07970	3.879	4.051	227
0.1002	4.205	4.886	165	0.1002	4.163	4.286	247
0.1003	3.389	3.648	171	0.1255	4.473	4.106	315
0.1498	4.014	4.331	175	0.1599	3.586	3.867	362
0.1599	3.591	3.871	174	0.2003	3.934	4.464	399
0.1992	3.590	4.072	175	0.2559	4.804	4.255	478
0.2003	3.876	3.801	238	0.2993	3.990	3.985	508
0.2051	4.767	4.871	216	0.3179	4.104	4.196	551
0.2559	4.999	4.430	238	0.4072	4.049	3.848	611
0.2606	2.429	4.466	205	0.4415	4.009	4.188	575
0.3179	4.071	4.235	264	0.5927	4.115	4.011	655
0.4415	3.893	4.303	304				
0.5927	4.337	4.303	316				
NITROPROPANE ($m_r = 0.03571$)				NITROBUTANE ($m_r = 0.02786$)			
0.04002	4.223	4.223	175	0.04002	4.247	4.126	93
0.07970	3.742	4.028	261	0.04976	5.330	4.999	160
0.1003	3.462	3.719	337	0.05915	4.225	4.290	118
0.1255	4.473	3.992	341	0.06883	4.321	3.973	170
0.1599	3.592	3.860	422	0.07970	3.871	3.970	162
0.2003	4.348	4.601	495	0.1599	3.654	3.990	260
0.2559	5.010	4.413	539	0.2051	4.756	5.051	330
0.3179	4.095	4.177	578	0.2606	2.418	4.314	314
0.4415	4.087	4.086	626	0.2993	4.025	4.025	335
0.5927	3.575	3.590	717	0.4415	4.051	4.083	390

Units are: mol Kg^{-1} for m_r and m_s , Kg sec^{-1} for ϕ_r and ϕ_w , J mol^{-1} for $\Delta_{\text{exp}}H$.

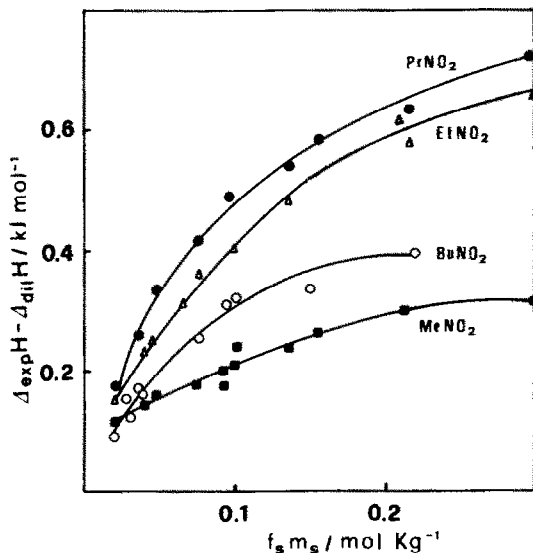


Fig. 1. Plot of the enthalpies of mixing of nitroalkanes aqueous solutions with DTAB micellar solutions against surfactant concentration.

RESULTS

The calorimetric experiments were performed as a function of the surfactant concentration at a given nitroalkane concentration, since, as observed for alcohols [5], the experimental enthalpies were assumed to be independent of the solute concentration when this is sufficiently low.

The nitroalkanes and surfactant concentrations at the equilibrium were given by the product between the initial concentrations and the dilution factors, f_s and f_r

$$f_s = \phi_s / (\phi_s + \phi_r) \quad f_r = \phi_r / (\phi_s + \phi_r) \quad (1)$$

where ϕ_s and ϕ_r represent the flows of water in the surfactant and nitroalkane solutions respectively. They are summarized in Table 1, together with the initial nitroalkane (m_r) and surfactant (m_s) concentrations and the experimental enthalpies ($\Delta_{\text{exp}}H$). The plots of $\Delta_{\text{exp}}H$ as a function of the final surfactant concentration ($f_s m_s$) are shown in Fig. 1. As it can be seen, their curvatures and the values of $\Delta_{\text{exp}}H$ at the plateau depend on the nitroalkane alkyl chain length since they are related to the distribution constant and to the enthalpies of transfer of each nitroalkane from the aqueous to the micellar phase, respectively.

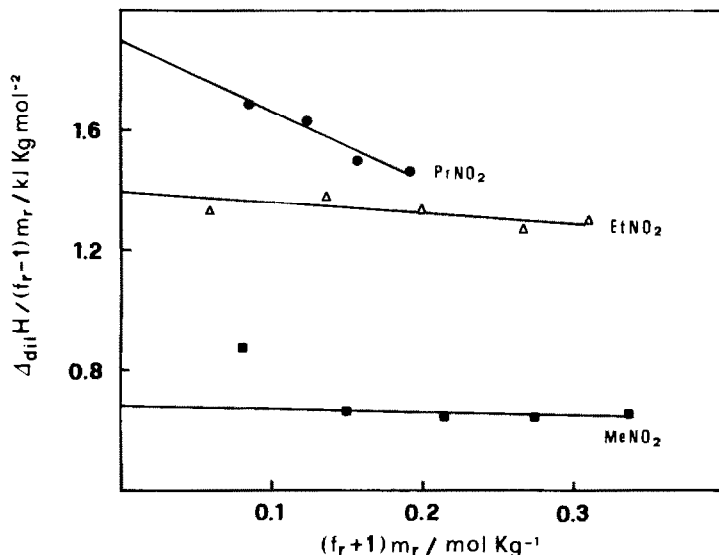


Fig. 2. Plot of the enthalpies of dilution of nitroalkanes in water according to eqn. (3).

As will be seen later, the enthalpies of dilution of nitroalkanes in water are needed to rationalize $\Delta_{\text{exp}}H$. These were determined as a function of the solute concentration. As far as nitrobutane is concerned, the solubility was too low for any effect to be observed. The final solute concentrations ($f_r m_r$) were calculated as above, by taking the following dilution factor for the nitroalkane solutions

$$f_r = \phi_r / (\phi_w + \phi_r) \quad (2)$$

where ϕ_w indicates the flow of water.

According to the McMillan-Mayer approach [12], the enthalpies of dilution per mole of nitroalkane ($\Delta_{\text{dil}}H$) were rationalized in terms of the pair (h_{rr}) and triplet (h_{rrr}) solute-solute interaction parameters. The higher order parameters were neglected and the following equation was used

$$\Delta_{\text{dil}}H / (f_r - 1) m_r = h_{rr} + h_{rrr} (f_r + 1) m_r \quad (3)$$

Eqn. (3) predicts a linear correlation between the quantity on the left hand side and $(f_r + 1) m_r$. Fig. 2 shows the plot of the enthalpies of dilution according to eqn.(2), whereas Table 2 summarizes the experimental results. The h_{rr} and h_{rrr} values are reported in Table 3.

TABLE 2

Integral enthalpies of dilution of aqueous nitroalkanes solutions.

m_r	$10^6 \phi_r$	$10^6 \phi_w$	$-\Delta_{dil}H$	m_r	$10^6 \phi_r$	$10^6 \phi_w$	$-\Delta_{dil}H$
NITROMETHANE				NITROETHANE			
0.05139	5.127	4.931	22	0.04198	5.069	4.902	27
0.1000	5.111	4.898	43	0.08848	5.044	4.745	59
0.1417	5.091	4.907	45	0.1309	4.990	4.858	86
0.1809	5.075	3.918	57	0.1756	4.962	4.885	115
0.2225	5.053	4.891	72	0.2076	4.950	4.886	134
NITROPROPANE							
0.05511	4.729	4.882	47				
0.08186	4.897	4.833	66				
0.1017	4.854	4.900	76				
0.1272	4.699	4.882	95				

For units, see Table 1.

DISCUSSION

On the basis of our approach [5,11], the experimental enthalpies were rationalized by means of the following equation

$$\Delta_{exp}H - \Delta_{dil}H = \Delta_{trf}H^\circ(w \rightarrow mcl) - (\Delta_{trf}H^\circ - A_{cdc}\Delta_{mcl}H)N_f \quad (4)$$

This is valid for a solute concentration tending to zero or so low that the physicochemical properties (size, shape, counterion binding, etc.) of the micelles are unchanged. The physical meanings of its symbols are:

$\Delta_{trf}H^\circ(w \rightarrow mcl)$: standard enthalpy of transfer of the solute from water to the micellar phase

$\Delta_{trf}H^\circ$: standard enthalpy of transfer of the solute from the aqueous to the micellar phases

$\Delta_{mcl}H$: enthalpy of micellization

A_{cdc} : shift of the micellization equilibrium due to the solute added at the cmc

N_f : the fraction of the solute in the aqueous phase

The A_{cdc} term was rationalized [3] through salting effect between surfactant monomers and the added solute, and through the formation of the mixed micelles. For 1:1 ionic surfactant, which is the case here, and for solute concentrations tending to zero, the shift of the micellization equilibrium is

TABLE 3
Pair and triplet solute-solute interaction parameters.

	MeNO ₂	EtNO ₂	PrNO ₂	BuNO ₂
$h_{rr} / \text{kJ Kg mol}^{-2}$	0.68	1.40	1.80	0
$h_{rrr} / \text{kJ Kg}^2 \text{ mol}^{-3}$	-0.13	-0.33	-2.40	0

given by

$$A_{cdc} = [2.3Ks + (1+\beta)K] \text{ cmc}/2 \quad (5)$$

where Ks represents the Setchenov constant and β the degree of dissociation of micelles.

The fraction of the solute in the aqueous phase was correlated [3] to the distribution constant (K) and the surfactant concentration by

$$N_f = 1/[1 + K(m_s - \text{cmc})] \quad (6)$$

A linear relationship is predicted between the quantity on the left hand side of eqn. (4) and N_f if K is known. If not, eqn. (4) can be solved by linear regression by adjusting the K value to minimize the standard deviation of the plot of $(\Delta_{\text{exp}}H - \Delta_{\text{dil}}H)$ vs N_f . The best fits to the experimental points for the systems analyzed here are shown in Fig. 3, whereas the intercepts and slopes of the straight lines with the K values are summarized in Table 4.

The $A_{cdc}\Delta_{\text{mcl}}H$ terms are needed to recover $\Delta_{\text{trf}}H^\circ$ from the slopes. They were calculated by means of eqn. (5) by taking the following values: 0.0152 for cmc [13], 0.22 for β [14], -1.0 kJ mol^{-1} for $\Delta_{\text{mcl}}H$ [5]; as for the Ks values, they were calculated in the mole fraction scale by means of the following equation reported by Treiner [15]

$$Ks = 0.484 - 0.1464 \sigma \quad (7)$$

where σ is the hard-sphere diameter of the solutes; these latter were calculated by using the relation of De Ligny [16]

$$\pi\sigma^3N/6 = -10 + 1.13 V_w \quad (8)$$

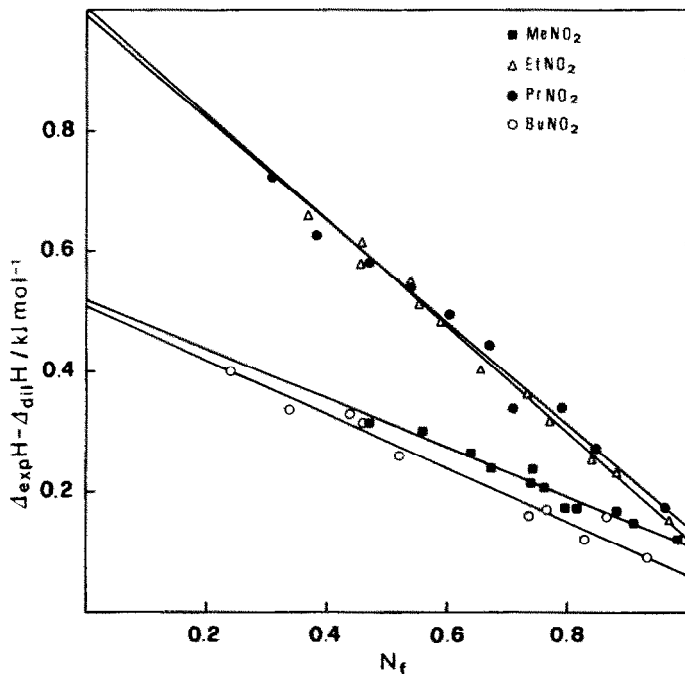


Fig. 3 - Fit of eqn. (4) at the K values which minimize the standard deviation for the transfer of nitroalkanes from aqueous to DTAB micellar phases.

TABLE 4

Intercept (i) and slope (s) at the K value minimizing the standard deviation of the fit to eqn.(4).

	MeNO ₂	EtNO ₂	PrNO ₂	BuNO ₂
K	4	6	8	15
i	529 ± 23	990 ± 18	988 ± 22	495 ± 25
s	-404 ± 29	-871 ± 27	-812 ± 33	-428 ± 37

where N is the Avogadro number and V_w the Van der Waals volumes calculated using data reported in the literature [17]. The constant quantity of -0.016 [18] was added to convert the Setchenov constant from the mole fraction to the molality scale. The values of V_w , σ and K_s are summarized in Table 5.

In order to calculate the standard free energies of transfer of the nitroalkanes from the aqueous to the micellar phase, the binding constants K were converted

TABLE 5

van der Waals volumes (V_w), hard sphere diameters (σ) and Setchenov constant (K_s) values of nitroalkanes.

	MeNO ₂	EtNO ₂	PrNO ₂	BuNO ₂
$V_w / \text{cm}^3 \text{ mol}^{-1}$	30.47	40.70	50.93	61.16
$\sigma / \text{Å}$	4.26	4.85	5.32	5.72
$K_s / \text{Kg mol}^{-1}$	-0.16	-0.24	-0.28	-0.37

into the partition constant (K_c) in the molarity scale [8]

$$K_c = K / V_s \quad (9)$$

where V_s indicates the partial molar volume of the micellized surfactant. The value of $0.2948 \text{ dm}^3 \text{ mol}^{-1}$ for V_s [4] was taken.

Then, the following standard thermodynamic quantities were calculated

$$\Delta_{\text{trf}}G^\circ = -RT \ln K_c \quad (10)$$

$$T\Delta_{\text{trf}}S^\circ = \Delta_{\text{trf}}H^\circ - \Delta_{\text{trf}}G^\circ \quad (11)$$

The values of K_c , $\Delta_{\text{trf}}G^\circ$, $\Delta_{\text{trf}}H^\circ$ and $T\Delta_{\text{trf}}S^\circ$ for the solutes analyzed here are summarized in Table 6. The trends of these standard thermodynamic quantities as a function of n_c are shown in Fig. 4. As it can be seen, by increasing n_c free energies decrease linearly according to the additivity rule, whereas enthalpies and entropies display slow curvatures. Similar behaviour had already been observed for primary and secondary alcohols.

Interesting information could be obtained by studying the effect of the nature of the solvent on the distribution of the nitroalkanes compounds. To this purpose, the thermodynamic quantities of transfer determined here are compared with those from water to octane [19] and from octane to DTAB micelles. The latter were calculated by subtracting the corresponding quantity of transfer of nitroalkanes from water to octane from the present results.

$$\Delta_{\text{trf}}Y^\circ (\text{OCT} \rightarrow \text{DTAB}) = \Delta_{\text{trf}}Y^\circ (\text{W} \rightarrow \text{DTAB}) - \Delta_{\text{trf}}Y^\circ (\text{W} \rightarrow \text{OCT}) \quad (12)$$

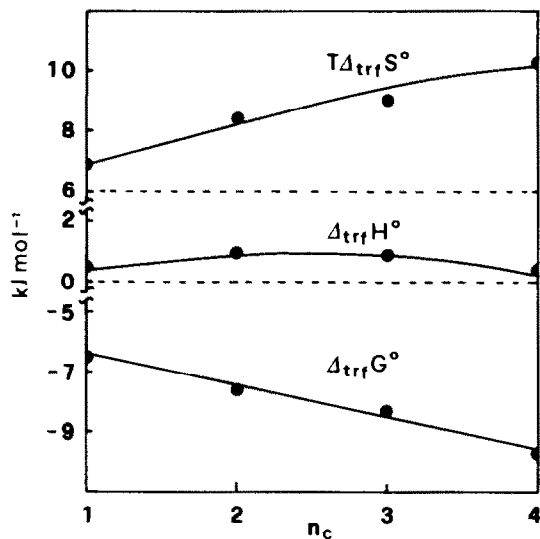


Fig. 4. Standard enthalpies, entropies and free energies of transfer of nitroalkanes from the aqueous to DTAB micellar phases vs the number of carbon atoms in the nitroalkane alkyl chain.

TABLE 6

Standard thermodynamic quantities of transfer (kJ mol⁻¹) of nitroalkanes from the aqueous to the micellar phases.

	MeNO ₂	EtNO ₂	PrNO ₂	BuNO ₂
K _c	13.6	20.4	27.1	50.9
$\Delta_{trf}G^\circ$	-6.46	-7.46	-8.17	-9.73
$\Delta_{trf}H^\circ$	0.44	0.92	0.88	0.56
$T\Delta_{trf}S^\circ$	6.90	8.38	9.05	10.29

where $\Delta_{trf}Y^\circ$ indicates a given thermodynamic property.

As mentioned above, the free energies of transfer we have determined involve the aqueous and the micellar phases as initial and final states respectively. So, in order to calculate the free energies of transfer of the nitroalkanes from octane to DTAB micellar phase, the solute transfer from water to the aqueous phase must be taken into account. This contribution can be expressed in terms of the Setchenov constant as [9,20]

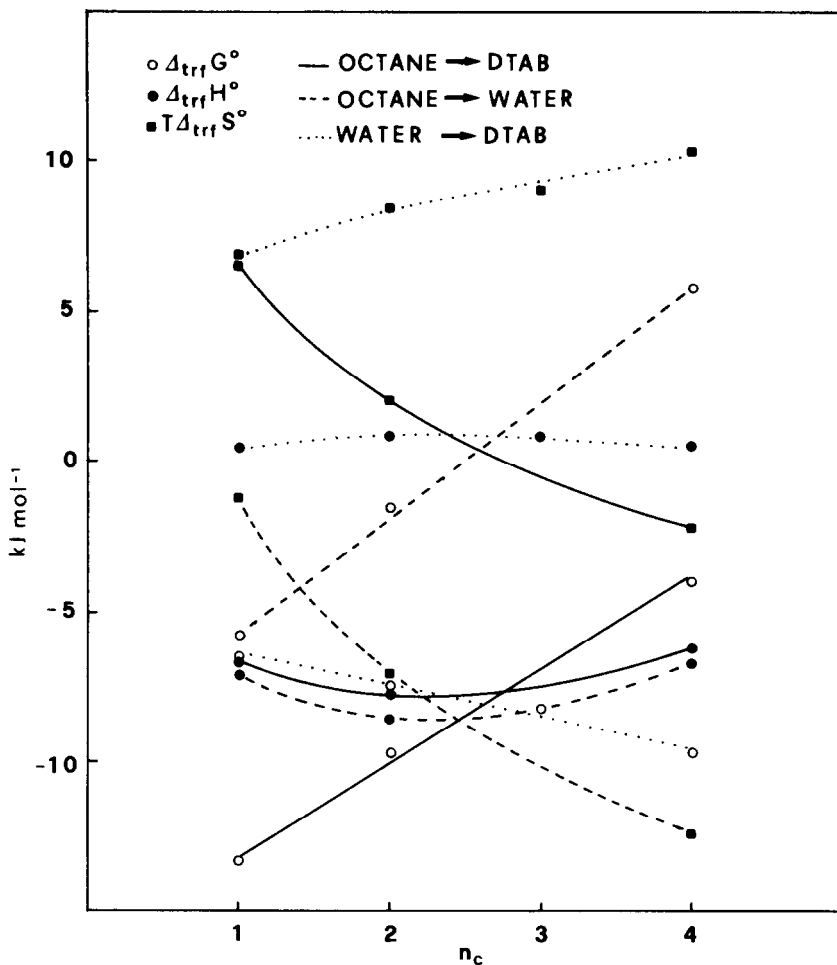


Fig. 5 - Plots of the standard enthalpies, entropies and free energies of transfer of nitroalkanes from octane to DTAB micellar phase (—) and to water (---) and from water (···) to DTAB, vs the number of carbon atoms in the nitroalkane alkyl chain.

$$\Delta_{\text{trf}} G^\circ (\text{W} \rightarrow \text{W} + \text{S}) = 2.3 RT K_s \text{cmc} \quad (13)$$

Then, the free energies of transfer of the nitroalkanes from water to DTAB micelles can be calculated as follows

$$\Delta_{\text{trf}} G^\circ (\text{W} \rightarrow \text{DTAB}) = 2.3 RT K_s \text{cmc} + \Delta_{\text{trf}} G^\circ \quad (14)$$

So, from the values of the free energies calculated by means of eqn. (14) and

from the $\Delta_{\text{trf}}H^\circ(\text{W} \rightarrow \text{mcl})$ values reported in Table 3, the entropies of transfer were easily calculated. The thermodynamic properties of transfer of nitroalkanes from octane to DTAB micelles, from octane to water and from octane to DTAB micelles are shown in Fig. 5.

According to the additivity rule, the intercept and slope of the plots of $\Delta_{\text{trf}}Y^\circ$ vs. n_c represent the hydrophilic and hydrophobic contributions to the transfer process respectively.

Looking at the $\Delta_{\text{trf}}G^\circ$, the intercept values show that the NO_2 group transfer from octane to DTAB micelles is more favoured than that from octane to water, indicating that very strong hydrophilic interactions exist between the nitro-group and the head group of the micelles; the slope values, which represent the contribution of a CH_2 group, are positive for the transfer from octane to DTAB (3 kJ mol^{-1}) and to water (4 kJ mol^{-1}), and negative for the transfer from water to DTAB (-1 kJ mol^{-1}).

As predicted from the present results, $\Delta_{\text{trf}}H^\circ$ values for the transfer from octane to DTAB and to water are essentially parallel and differ by about 10%. As a consequence, the entropy change is responsible for the very large difference between $\Delta_{\text{trf}}G^\circ(\text{OCT} \rightarrow \text{DTAB})$ and $\Delta_{\text{trf}}G^\circ(\text{OCT} \rightarrow \text{W})$.

To show the effect of the hydrophilic head of the solute on the thermodynamics of the mixed micelles formation, we can compare the thermodynamic quantities of the nitroalkanes with those of primary and secondary alcohols [5,6] and nitriles [21]. These quantities are shown versus n_c in Fig.6. Inspection of the free energies functions makes it clear that the transfer of the NO_2 group from the aqueous to the micellar phase is most favoured, indicating that very strong hydrophilic interactions between the NO_2 group and the head group of the surfactant exist. Whereas the polarity of the head of the solubilizate can explain the different hydrophilic contributions to the free energies, it is more difficult to explain the differences in the hydrophobic contributions. Tentatively, they can be attributed to the swelling of the micelles due to the nature of head group of the solute. The $\Delta_{\text{trf}}H^\circ$ values of the nitroalkanes are always less than 1 kJ mol^{-1} , whereas the corresponding values for alcohols lie between 5.9 and 7.4 kJ mol^{-1} .

The slope of the plots in Fig. 6 show that the entropy is always the driving force for the transfer of a methylene group from the aqueous to the micellar phases. More interesting is the fact that the intercepts of the plots of $\Delta_{\text{trf}}H^\circ$ and $T\Delta_{\text{trf}}S^\circ$ as a function of n_c show that the transfer of NO_2 group from the aqueous to the micellar phase is driven by the entropy whereas the transfer of the OH group is driven by the enthalpy. We cannot assess at the present time the importance of this result. In fact, the thermodynamic properties of transfer

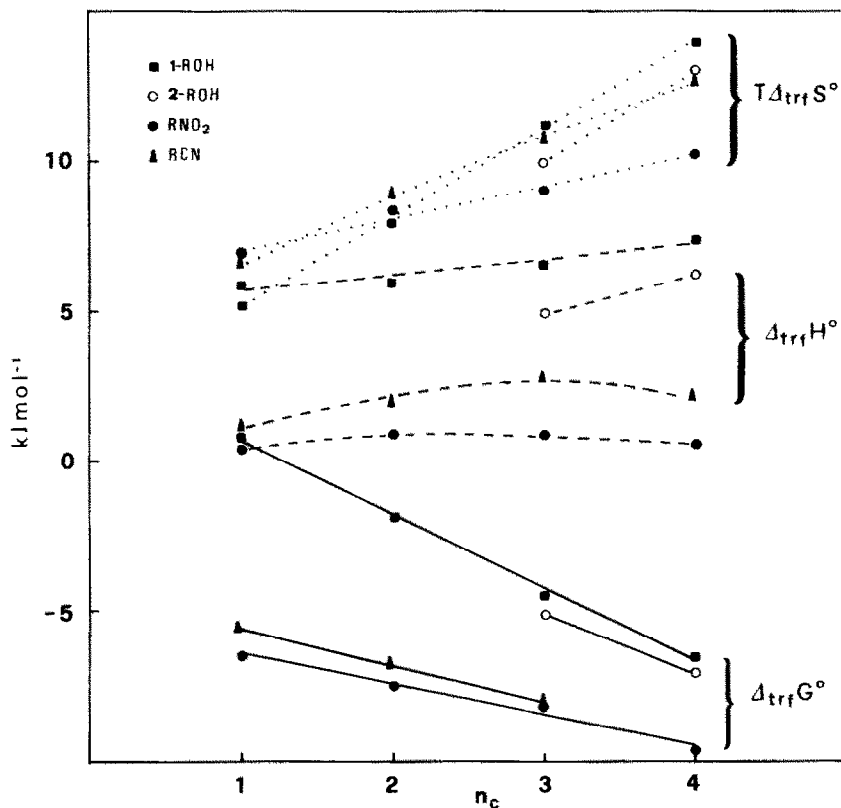


Fig. 6. Plots of the standard enthalpies, entropies and free energies of transfer of primary and secondary alcohols, nitriles and nitroalkanes from the aqueous to the DTAB micellar phases vs. the number of carbon atoms in the solute alkyl chain.

correspond to the difference between those of solvation in the two phases. Therefore, it is difficult to ascertain if the different behaviour of OH and NO₂ groups is to be ascribed to the aqueous phase, to the micellar phase or both. Unfortunately, no free energies and enthalpies of solvation of nitroalkanes in water are reported in the literature.

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