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Effect of alcohols on the micellar properties in aqueous solution of alkyltrimethylammonium bromides

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Abstract: The effect of *n*-butanol, *n*-propanol, and *n*-hexanol on the critical micelle concentration (CMC) and degree of ionisation of the micelles of dodecyl-, tetradecyl- and hexadecyltrimethylammonium bromides in aqueous solution has been determined by conductimetric techniques. Increase of the molality of added alcohol over the concentration ranges examined (up to 0.3 mol kg^{-1} butanol, 0.07 mol kg^{-1} pentanol and 0.025 mol kg^{-1} hexanol) caused a progressive decrease of CMC and increase of the degree of ionisation for each surfactant-alcohol system. At a constant molality of added alcohol the degree of ionisation increased with a) an increase of the chain length of the surfactant for each alcohol and b) an increase of the chain length of the alcohol for each surfactant. The distribution of each alcohol between the aqueous and micellar phases and the free energy of solubilization were determined from the change of CMC with molality of added alcohol.

Key words: Critical micelle concentration (CMC) – degree of micellar ionisation – alcohols, effect on CMC – micelles of alkyltrimethylammonium bromides – solubilization – distribution coefficients

Introduction

The effect of medium chain-length alcohols on the properties of the micelles of alkyltrimethylammonium bromides has been studied by several workers, often with the objective of studying the role of these alcohols as cosurfactants in microemulsion systems. Zana and coworkers [1–5] have reported extensive studies on the effect of the linear alcohols ethanol to hexanol on the critical micelle concentration (CMC), micelle molecular weight and degree of ionisation p/n (where p is the charge number and n the aggregation number) of the micelles in solutions of alkyltrimethylammonium bromides (octyl to hexadecyl), with particular emphasis on the pentanol-tetradecyltrimethylammonium bromide (TTAB) system. The results have shown a decrease of the CMC and micelle molecular weight at the CMC and an increase of the degree of ionisation with alcohol addition, even with alcohols such as pentanol and hexanol which are partitioned between the micelles and the aqueous phase. The situation was shown to be more complex in the presence of added KBr with a maximum hydrodynamic radius being noted in the presence of 0.1 M pentanol for micelles of TTAB in 0.1 M KBr and a subsequent decrease at higher pentanol concentrations. In contrast, for the tetradecyl- and hexadecyltrimethylammonium bromides in the presence of 0.1 and 0.025 M KBr respectively, the addition of butanol resulted in a decrease of micelle molecular weight. Guveli et al. [6] have demonstrated an increasing hydration of the micelles of dodecyltrimethylammonium bromide (DTAB) in water following the addition of small amounts of ethanol, propanol or butanol, but a decrease in both size and hydration at high alcohol concentration. The addition of hexanol to aqueous solutions of hexadecyltrimethylammonium bromide (CTAB) was shown by Vikholm et al. [7] to cause a shape transition from spherical to longer rod or disk-like micelles followed by a breakdown from large aggregates to spherical swollen micelles at higher hexanol contents.

There are relatively few papers in the literature concerning the distribution of the medium chain length alcohols between the aqueous and micellar phases in alkyltrimethylammonium bromide solutions. Gettins et al. [8] have reported distribution coefficients (K) for butanol, pentanol and hexanol in salt-free solutions of CTAB. Høiland et al. [9] have also reported values for hexanol in aqueous CTAB solutions. The method of determining K used by these workers involved the measurement of the apparent saturation solubility of the alcohol in the surfactant solution. This method has, however, been criticised by Stilbs [10] who has stressed that the monitored 'solubility limit' does not indicate a solubilizate saturation point for the micelles. Stilbs and coworkers [11–13] have carried out extensive studies using Fourier transform NMR pulsed-gradient spin-echo techniques on the solubilization of homologous series of solutes by several surfactants which have included the pentanol-DTAB-H_2O system. Rao and Ruckenstein [14] have reported partition coefficients for medium chain-length alcohols in TTAB micelles, derived by the application of thermodynamic models to the solubilized systems. In a recent paper by Gamboa et al. [15], distribution coefficients for several medium chain-length alcohols between water and the cylindrical micelles of CTAB present in 0.16 M NaBr have been determined using ultrafiltration and dialysis methods.

In this paper we report the results of a study of the effect of butanol, pentanol and hexanol on the CMC and degree of ionisation of micelles in aqueous salt-free solutions of DTAB, TTAB and CTAB. We have evaluated the distribution coefficient of the alcohols from the variation of CMC with the ratio of components in the system using a modification of the theory of mixed micellar systems proposed by Motomura et al. [16].

Experimental

Dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB) and hexadecyltrimethylammonium bromide (CTAB) were obtained from Sigma Chemical Co. (stated purity > 99%). *n*-Butanol, *n*-propanol and *n*-hexanol were of AnalaR grade (BDH). Water was de-ionized distilled water.

CMCs were determined by measuring conductivity at 298.15 ± 0.01 K with a Wayne Kerr (Type B642) Autobalance Universal Bridge as mixtures of high concentration were continuously diluted with alcohol/water solution of known molality using a peristaltic pump under the control of an IBM PC-AT; the cell constant was determined using KCl solutions in conjunction with the data published by Shedlovsky [17] and Chambers et al. [18].

Results and discussion

CMC values were determined from inflections in plots of conductivity, κ, against surfactant molality, m_S, for aqueous solutions of the alkyltrimethylammonium bromides in the presence of added butanol, pentanol and hexanol of molality, m_A. The difference in the magnitude of the gradients above and below the inflection points in each system became progressively smaller with increase of m_A leading to a concomitant increase in the uncertainty of the CMC value. Figure 1 illustrates this effect for the CTAB-alcohol solutions; similar plots (not shown) were obtained for DTAB- and TTAB-alcohol systems. Figure 2 shows decreases of log CMC with increasing alcohol molality for all systems, over the alcohol concentrations examined. Similar effects have been reported by other workers for these systems [2, 6, 7] and there is general agreement with the reported CMC values (see Fig. 2).

The variation of the CMC with m_A can be described by the second-order polynomial

$$\mathrm{CMC} = a_0 + a_1 m_A + a_2 m_A^2 \tag{1}$$

with values of the coefficients a_0, a_1 and a_2 as given in Table 1. Values of a_0, the CMC in the absence of added alcohol, compare with literature values (mol dm^{-3}) at 25 °C of 0.015 [19], 0.0154 [20], 0.0168 [6] for DTAB; 0.0034 [19], 0.0038 [20], 0.0037 [6] for TTAB; 0.00085 [19], 0.00096 [20], 0.0008 [6] for CTAB.

The degree of ionisation of the micelles, p/n, was calculated from the gradient, S_m, of plots of

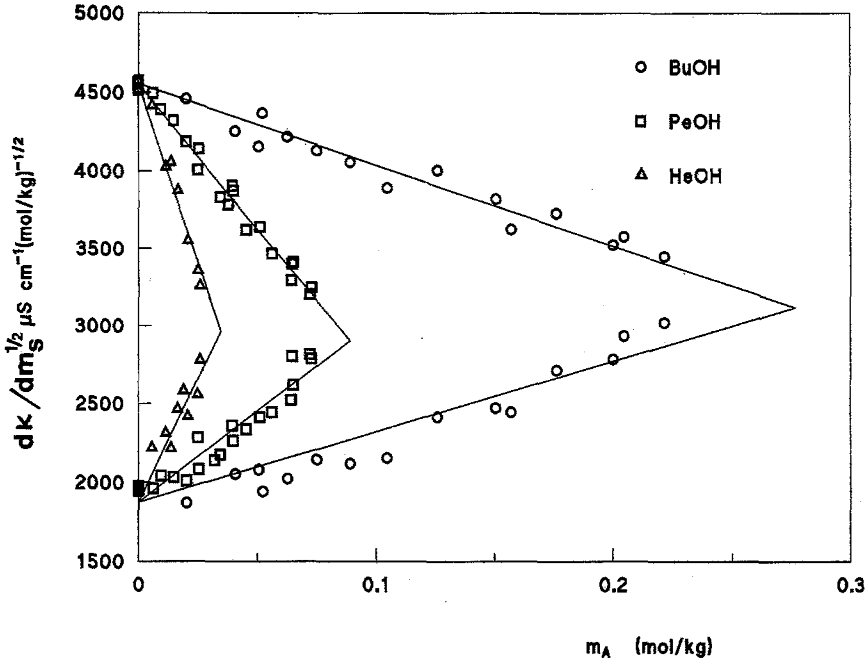

Fig. 1. Gradients of graphs of conductivity, κ, vs. (surfactant molality, $m_S)^{1/2}$ plotted as a function of molality of added alcohol, m_A, for CTAB-alcohol systems. Upper lines: $m_S <$ CMC. Lower lines: $m_S >$ CMC

κ against m_S above the CMC as proposed by Evans [21]. Assuming that the micelles do not contribute significantly to the conductivity, S_m, may be approximated by [22]

$$S_m = \lambda_m/n + p\lambda_{Br^-}/n \,, \tag{2}$$

where λ_m and λ_{Br^-} are the molar ionic conductivities of micelles and counterion respectively. Since the CMC is at very low concentration, the ionic conductivities of Eq. (2) may be approximated by the limiting ionic conductivities $\lambda_{0,m}$ and λ_{0,Br^-}. $\lambda_{0,m}$ may be calculated using Stokes Law giving

$$S_m = (p/n)(F^2/(6\pi N_A \eta_0 r_m) + \lambda_{0,Br^-}) \,, \tag{3}$$

where F is Faraday's constant, N_A is Avogadro's constant and η_0 is the solvent viscosity. The value of the limiting ionic conductivity of the Br$^-$ counterion was 78.14 ohm^{-1} cm^2 mol^{-1} [23] and the viscosity of the solvent was calculated from the relation [24]

$$\log \eta_0 = X_W \log \eta_W + X_A \log \eta_A \,, \tag{4}$$

where X_W and X_A are the mole fractions, and η_W and η_A the viscosities, of water and alcohol, respectively. An approximate r_m value was calculated assuming micellar sphericity for all systems and ignoring the effect of alcohol on the micellar size at the CMC (although it is clear from the work of Candau and Zana [3] that such effects are not insignificant). r_m was equated with the length of the extended alkyl chain, l_c, as calculated from [25]

$$l_c = 1.5 + 1.265 n_c \,, \tag{5}$$

where n_c is the number of carbon atoms in the hydrocarbon chain. As a consequence of these assumptions, the calculated values of the degree of ionisation should be regarded as approximate values only, although since $\lambda_{0,m}$ is considerably smaller than λ_{0,Br^-} ($\lambda_{0,m} \simeq 0.1\ \lambda_{0,Br^-}$), the error is not thought to be excessive. Other workers [22] have made similar approximations in the calculation of p/n using Eq. (3). Similar trends in the variation of the degree of ionisation with m_A to those shown in Fig. 3 were obtained when p/n was calculated from the ratio of the slopes of plots of κ against m_S above and below the CMC [19, 26], although values calculated by this more approximate method were consistently lower than those from Eq. (3). The increase of degree of ionisation with increase of m_A which is observed for each alkyltrimethylammonium bromide-alcohol system is in agreement with the results of other workers. For example, Zana et al. [1] noted similar trends following the addition of increasing amounts of butanol, pentanol or hexanol to

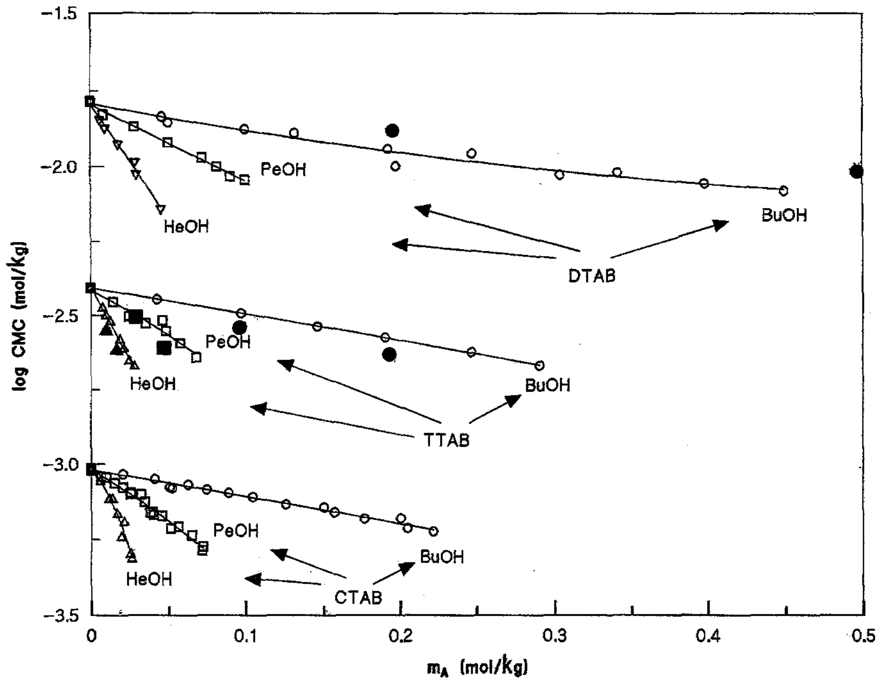

Fig. 2. Log CMC against molality of added alcohol, m_A. Filled symbols are values from Guveli et al. [6] (DTAB) and Zana et al. [1] (TTAB)

Table 1. Values of the coefficients a_0, a_1 and a_2 of Eq. (1)

System	*) a_0 mmol kg^{-1}	a_1 kg mol^{-1}	a_2 (kg mol^{-1})^2	$10^4 \times$ std dev
DTAB + BuOH	16.08	− 0.0306	0.0306	5.49
DTAB + PeOH	16.08	− 0.0928	0.2233	2.85
DTAB + HeOH	16.12	− 0.2645	1.5623	3.95
TTAB + BuOH	3.92	− 0.0076	0.0054	0.15
TTAB + PeOH	3.86	− 0.0252	0.0476	1.27
TTAB + HeOH	3.93	− 0.0852	0.7083	0.31
CTAB + BuOH	0.958	− 0.0019	0.0016	0.14
CTAB + PeOH	0.962	− 0.0070	0.0128	0.17
CTAB + HeOH	0.960	− 0.0140	− 0.1652	0.26

*) a_0 = CMC in alcohol-free systems

TTAB in 0.1 M KCl. Similarly, increases of p/n for the micelles of sodium dodecylsulphate have been noted following the addition of alkanols (C_4 to C_7) [26–28]. Such increases of ionisation are thought to be a consequence of a reduction in the surface charge density due to the presence of solubilized alcohol, causing a release of counterions from the micelles to compensate for this decrease [27].

Figure 3 shows an increase of the degree of ionisation as the chain length of the alkyltrimethylammonium bromide is increased at constant m_A for each surfactant-alcohol system. Similar results were reported by Zana et al. [1], although these workers observed a decrease of ionisation with alkyl chain length in alcohol-free systems, which is contrary to the results reported here. In this respect it should be noted that conflicting results appear in the literature, with some workers [29, 30] reporting a decrease of ionisation and others [20] an increase with increase of alkyl chain length.

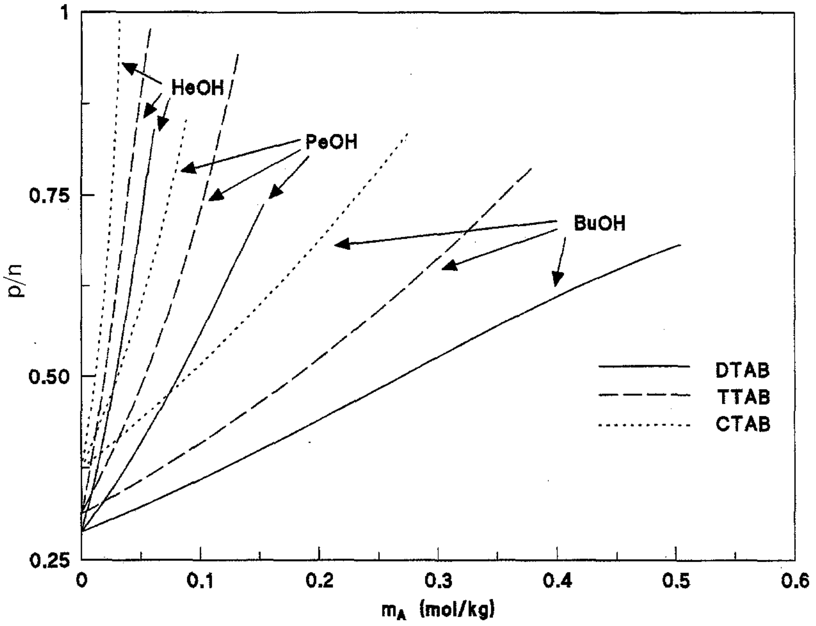

Fig. 3. Variation of degree of micellar ionization, p/n, with molality of added alcohol, m_A

A very pronounced increase of ionisation is observed (Fig. 3), for each surfactant with increase of the chain length of the added alcohol at constant m_A. Such an increase is not observed in the results of Zana et al. [1], although it should be noted that these workers examined only a very limited number of alcohol concentrations.

Motomura et al. [31] have proposed a thermodynamic treatment of mixed micellar systems which permits the calculation of the distribution of components between aqueous and micellar phases from a consideration of the change of CMC with overall composition of the system. According to this approach, the mole fraction, X_2^M, of a component 2 in a mixed micelle formed in a binary mixed system of components 1 and 2 is

$$X_2^M = X_2 \nu_1 [1 - (X_1/\mathrm{CMC})(\partial \mathrm{CMC}/\partial X_2)_{T,p}] / [\nu_2 X_1 + \nu_1 X_2 - (\nu_1 - \nu_2) \times (X_1 X_2/\mathrm{CMC})(\partial \mathrm{CMC}/\partial X_2)_{T,p}] , \quad (6)$$

where ν_1 and ν_2 are the sum of the valencies of the ionic species produced on dissociation of components 1 and 2 respectively, X_1 and X_2 are the mole fractions of components 1 and 2 in the system.

The theoretical approach used by Motomura et al. [31] can be applied to a surfactant-alcohol system to gain information on the partitioning of the alcohol between micelles and water. The total molality, m_T, at the CMC is given by

$$m_T = m_S/X_S = m_A/X_A , \quad (7)$$

where X_S and X_A are the mole fractions of surfactant and alcohol in the system, respectively.

Hence

$$\begin{aligned} \partial \ln \mathrm{CMC}/\partial X_A &= \partial \ln m_T/\partial X_A \\ &= -\partial \ln m_T/\partial X_S \\ \therefore \ \partial \ln \mathrm{CMC}/\partial X_A &= -\partial \ln(m_S/X_S)/\partial X_S \\ &= 1/X_S - \partial \ln m_S/\partial X_S \\ &= 1/X_S + \partial \ln m_S/\partial X_A . \end{aligned} \quad (8)$$

Substituting Eq. (8) into the Motomura expression (Eq. (6)) and noting that $\nu_A = 1$ gives

$$X_A^M = -\nu_S X_S X_A [(\partial \ln m_S/\partial X_A)_{T,p}]/[1 + X_S X_A \times (1 - \nu_S)(\partial \ln m_S/\partial X_A)_{T,p}] , \quad (9)$$

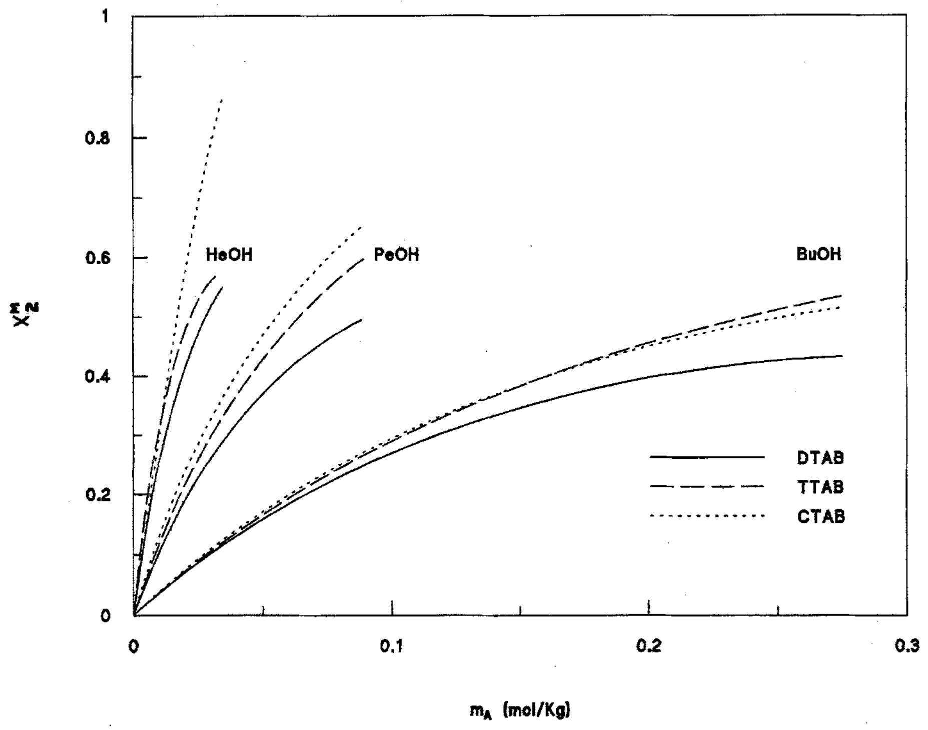

Fig. 4. Mole fraction, X_2^M, of alcohol in mixed micelles as a function of molality of added alcohol m_A

where $\partial \ln m_S/\partial X_A$ represents the change in ln CMC of the system with the mole fraction of added alcohol. For the systems under investigation we have from Eq. (1)

$$\partial \ln m_S/\partial X_A = (a_1 + 2a_2 m_A)(m_S + m_A)^2/ m_S(a_0 - a_2 m_A^2) \,. \qquad (10)$$

The variation of the mole fraction of alcohol in the micelle with the total molality of alcohol in the system, as calculated from Eqs. (8) and (9), is shown in Fig. 4, from which it is clear that the solubilization increases with the chain length of the alcohol as expected. Figure 5 shows the change in the standard free energy of solubilization, ΔG_m^0, with alcohol molality for each system as calculated from

$$\Delta G_m^0 = -RT \ln K = -RT \ln(X_A^M/X_A) \,. \qquad (11)$$

Values of $(\Delta G_m^0)_{m_A=0}$ as determined by extrapolation of the plots of Fig. 5 to zero alcohol molality, are given in Table 2. The variation of $(\Delta G_m^0)_{m_A=0}$ with the chain length, l_A, of the alcohol can be represented by the linear equations

$$-(\Delta G_m^0)_{m_A=0} = 2.67 l_A + 2.63 \text{ for DTAB} \qquad (12)$$

$$-(\Delta G_m^0)_{m_A=0} = 2.99 l_A + 1.37 \text{ for TTAB} \qquad (13)$$

$$-(\Delta G_m^0)_{m_A=0} = 3.20 l_A + 0.63 \text{ for CTAB} \,. \qquad (14)$$

The gradients of these lines represent the standard free energy per CH_2 group for the transfer of the alcohol from aqueous to micellar phase, ΔG_t^0, in each of the surfactant systems. These values are in reasonable agreement with literature values (kJ mol^{-1} per CH_2 group) of − 3.58 from water to sodium dodecylsulphate [32]; −2.78 from D_2O to sodium dodecylsulphate [11] and −2.78 from water to a series of anionic and cationic surfactants [9]. The free energy of transfer values are also in agreement with literature values for the transfer of alcohols from an aqueous medium to a hydrocarbon solvent. Aveyard and Mitchell [33] have determined a ΔG_t^0 value of −3.18 kJ mol^{-1} for *n*-alcohols transferred from aqueous phase to *n*-octane. Similarly, Lissi [34] quotes a value of −3.56 kJ mol^{-1} for the transfer

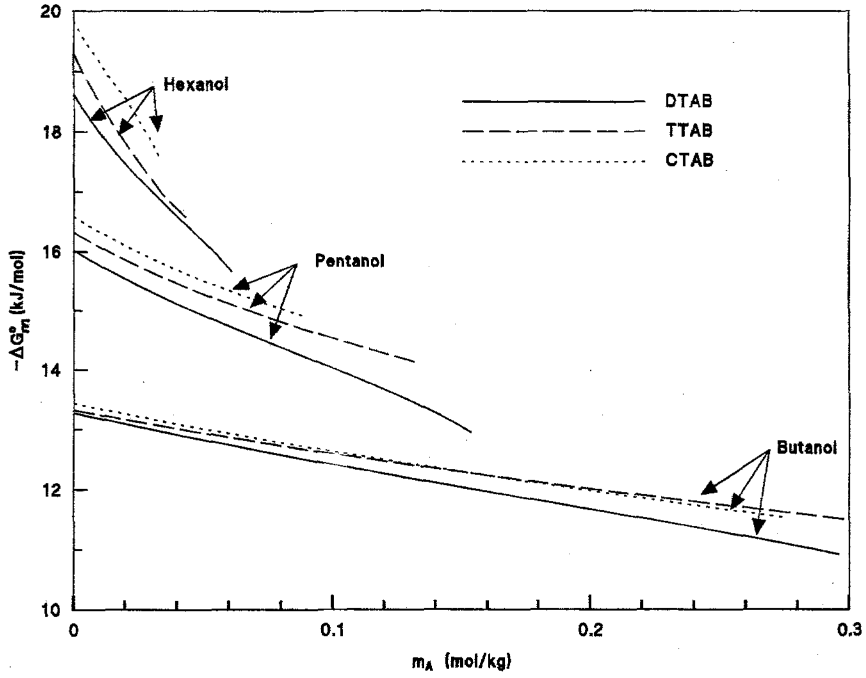

Fig. 5. Free energy of solubilization, ΔG^0_{m}, as a function of molality of added alcohol, m_{A}

Table 2. Values (kJ mol^{-1}) of free energy of solubilization, ΔG^0_{m}, extrapolated to zero molality for each added alcohol

	Butanol	Pentanol	Hexanol
DTAB	− 13.28	− 16.02	− 18.61
TTAB	− 13.32	− 16.32	− 19.30
CTAB	− 13.44	− 16.59	− 19.83

of a series of *n*-alcohols (from methanol to decanol) from water to *n*-heptane.

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