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Influence of the Third Component on the Temperature of the Crystal Surfactant–Micellar Solution Equilibrium

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The effect of additives on the temperature of precipitation of a nonionic surfactant from micellar solutions is studied experimentally and on the basis of thermodynamic relationships for the pseudophase separation model. The derived formulas connect the decrease in the precipitation temperature (ΔT effect) produced by amphiphilic additives with the composition of mixed micelles "basic surfactant–additive" and also with the temperature and the heat of the dissolution of the individual surfactant. Experimental data on the dissolution temperatures of crystalline *N*-dodecanoyl-*N*-methylglucamine (MEGA-12) in aqueous micellar solutions containing additives of various chemical nature are presented; the data for systems with alkanol C₂–C₄ additives relate to a wide range of the surfactant and alkanol concentrations. The enthalpies of dissolution of the crystalline MEGA-12 in water and water–alkanol mixtures determined by the Calvet calorimetry are given. The dependencies of the ΔT effect on the concentrations of MEGA-12 and alkanol (ethanol, propanol, or butanol) calculated from the model are in good agreement with the experimental data. The composition of mixed micelles formed by MEGA-12 and an alkanol C₂–C₄ is found from the ΔT data with the help of the model; the distribution of the alkanols between the micellar and aqueous pseudophases is evaluated. Nonideality of the aqueous alkanol solutions is taken into account in the model calculations. The results of measurements for aqueous and aqueous–alkanol mixtures of MEGA-12 containing salt additives evidence that the addition of salts (potassium, sodium, and ammonium chlorides, nitrates, carbonates, and sulfates) to aqueous solutions of MEGA-12 does not change significantly the temperature of the solid surfactant–micellar solution equilibrium, but a pronounced decrease of the temperature is observed when the salts are added to aqueous MEGA-12 mixtures containing alkanols, which is in correspondence with the model predictions.

Introduction

The precipitation temperature (the dissolution temperature) is a property of practical importance with respect to the utility of a surfactant. In some cases it is desirable to decrease this temperature by adding other substances to aqueous surfactant solutions. So the study and modeling of the third-component effect on the micellar solution–solid surfactant equilibrium is both of practical importance and also an interesting physicochemical problem that has not been thoroughly investigated.^{1,2}

Experimental data on the third-component effects for micellar systems are not numerous and relate mainly to ionic surfactants.^{3,4} Not much is made in thermodynamic modeling of the effects. Until recently only general thermodynamic expressions for the change of the surfactant dissolution temperature on the third component addition were considered in the literature.^{5,6} More detailed thermodynamic analysis and modeling have been per-

formed by the authors of the present work.^{7,8} It follows from thermodynamic relations that the effect of an additive on the surfactant dissolution temperature (ΔT effect) is determined mainly by changes in the surfactant activity and should depend on the ability of the additive to form mixed micelles with the basic surfactant. The particular case of precipitation for mixtures of anionic surfactants in the presence of added salts was considered with the help of relations for the solubility product.³

One can recognize the following main types of behavior of a component added to the surfactant (1)–water (2) micellar solution:

- The additive does not influence the composition of micelles.
- A nonpolar additive (a hydrocarbon for example) is solubilized inside the micellar hydrocarbon core.
- Amphiphilic molecules with small polar groups and short alkyl chains, like light alcohols, fatty acids, or amines, are partly incorporated into micelles, forming mixed micelles with the basic surfactant.
- The additive itself is apt to micellization, components 1 and 3 have comparable sizes of polar and alkyl groups, and the concentration of nonaggregated molecules 3 is negligible.

If the third-component molecules do not penetrate inside micelles, staying only in their surroundings (case a), then the change of the surfactant chemical potential in micelles is due only to the surface effects (for the micelle–mixed

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solvent interface), i.e. to the change in the interaction of micelles with the surroundings. In the case of large aggregation numbers, such effects should not be significant, at least for nonionic surfactants and in the absence of strong chemical interactions. A substantial influence on the surfactant chemical potential cannot be expected either from nonpolar additives solubilized inside the micellar hydrocarbon core (b). On the other hand, amphiphilic substances forming mixed micelles with the basic surfactant (cases c and d) can produce substantial changes in the value of the chemical potential, as in this case the micelle itself becomes a solution. The surfactant chemical potential in a mixed micelle is lower than that in a one-component aggregate, and the difference is of the same order as in the case of formation of a molecular solution from pure components. The typical structure of a mixed micelle is as follows: polar groups of additive molecules are close to the micellar surface, in contact with the basic surfactant polar heads, whereas alkyl tails penetrate into the micellar hydrocarbon core (certainly intermediate structures are possible). So in the cases c and d a pronounced effect of the third component on the temperature of the micellar solution–solid phase equilibrium may be expected. It is important for modeling that a substantial amount of a low molecular additive forming mixed micelles with the basic surfactant may stay in the aqueous surroundings, the distribution of the additive between micelles and the aqueous medium depending on the chemical nature of the surfactant and the additive (on the concentration and the temperature too). In case d, unlike case c, the concentration of nonaggregated molecules of the third component is very small. Literature on precipitation in mixed surfactant systems is reviewed in ref 9.

In this paper main attention will be paid to effects of light amphiphilic substances on the micellar solution–solid surfactant equilibrium. It will be assumed that the concentration of the third component is not very high (this component is only an additive; the solvent remains to a great extent aqueous). The solid phase in equilibrium with micellar solutions is supposed to be the pure crystalline surfactant 1 (According to the data of Fu et al.,¹⁰ this is just the case for the *N*-dodecanoyl-*N*-methylglucamine–water system), but there will be no specificity in the consideration of the equilibrium with the hydrated crystalline surfactant.⁷ The dependence of the ΔT effect on the surfactant chemical nature and concentration will be analyzed with the help of the pseudophase separation model. A more extended model consideration than in the earlier publication⁷ will be proposed. Experimental data for aqueous mixtures of *N*-dodecanoyl-*N*-methylglucamine (MEGA-12) with various additives will be presented to illustrate the model approach. In particular, the effect of alkanols C_2 – C_4 as additives will be thoroughly studied, the ability of these substances to form mixed micelles with various surfactants being well-known.^{5,11–13} A small change of the temperature along the Krafft plateau and a rather high ag-

gregation number in the binary MEGA-12–water micellar system¹⁴ give credibility to the application of the pseudophase separation model for interpreting the third-component effects.

General Thermodynamic Treatment and Equations from the Pseudophase Separation Model

Ternary surfactant (1)–water (2)–additive (3) solutions in equilibrium with the pure solid component 1 are under consideration. The following strict thermodynamic relations are valid for such systems:

$$\left(\frac{dT}{dx_3}\right)_{P,x_1/x_2} = \frac{T}{\Delta H_1} \left(\frac{\partial \mu_1}{\partial x_3}\right)_{P,T,x_1/x_2} = \frac{RT^2}{\Delta H_1} \left(\frac{\partial \ln a_1}{\partial x_3}\right)_{P,T,x_1/x_2} \quad (1)$$

where T is the temperature, P is the pressure, x_i denotes the mole fraction of the component i in the saturated solution ($i = 1, 2, 3$), μ_1 stands for the chemical potential, a_1 stands for the activity of the surfactant, and ΔH_1 is the partial molar enthalpy of its dissolution. The ΔH_1 value at low additive concentrations does not differ considerably from the heat of dissolution for the binary surfactant–water system, and consequently the difference in the $(dT/dx_3)_{P,x_1/x_2}$ magnitude for various additives should result mainly from the different influence of the additives on the surfactant chemical potential. The μ_1 value may be treated as the surfactant chemical potential in micelles (per 1 mol of the surfactant) or as the chemical potential of the monomers in the solution (μ_{11}). Substituting $\mu_1 = \mu_{11}$ ¹⁵ and using the ideal micellar solution approximation, we obtain from eq 1

$$\left(\frac{dT}{dx_3}\right)_{P,x_1/x_2} \approx \frac{RT^2}{\Delta H_1} \left(\frac{\partial \ln x_{11}}{\partial x_3}\right)_{P,T,x_1/x_2} \quad (2)$$

For micellar solutions (at least for highly diluted ones) it holds that

$$\left(\frac{\partial \ln x_{11}}{\partial x_3}\right)_{P,T,x_1/x_2} \approx \left(\frac{\partial \ln \text{cmc}}{\partial x_3}\right)_{P,T} \quad (3)$$

which states that a correlation exists between the third-component effects on the cmc and those on the solid surfactant precipitation temperature:

$$\Delta T \approx \frac{RTT_0}{\Delta H_1} \ln \frac{\text{cmc}}{\text{cmc}_0} \quad (4)$$

where T_0 and cmc_0 relate to the binary system and T and cmc relate to the system with an additive; $\Delta T = T - T_0$. Correlation of such a kind was observed for zwitterionic surfactants with salt additives.⁶ More general consideration of the correlations would be of interest. But here we shall analyze the relationship (eq 1) from a different point of view, that is in connection with the third-component effect on the surfactant chemical potential in micelles.

As was mentioned earlier, systems where the third component is an amphiphilic substance forming mixed micelles with the basic surfactant will be under study. It will be assumed that the additive is only partly aggregated; its content in the aqueous surroundings of micelles may

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be significant (so the specificity of low molecular amphiphilic additives will be taken into account).

Further derivations will be based on the pseudophase separation model.^{5,16} According to the model, the temperature of the micellar solution–solid surfactant equilibrium in the surfactant–water binary system should be constant (that is the Krafft plateau should be horizontal). So if the temperature change along the Krafft plateau in the binary system under investigation is small (as in the case of the MEGA-12–water system), the pseudophase separation model seems to be a reasonable approximation for the description of the third-component effects.

The micellar solution of an overall composition x_1 , x_2 , x_3 is considered as consisting of micellar (M) and aqueous (W) pseudophases. The mole fractions x_i^M ($i = 1, 3$) and x_i^W ($i = 2, 3$) characterize the composition of these phases; $x_1^M + x_3^M \approx 1$; $x_2^W + x_3^W \approx 1$. Assuming the surfactant activity to be unity in the micelles composed only of component 1 and neglecting the ΔH_1 concentration dependence, we obtain from eq 1

$$\Delta T \approx \frac{RTT_0}{\Delta H_1} \ln a_1(x_3^M) \quad (5)$$

where T_0 is the Krafft plateau temperature for the surfactant–water binary system and T is the surfactant dissolution temperature for the ternary mixture under study, $\Delta T = T - T_0$. If the micellar phase behaves like an ideal solution, then

$$\Delta T \approx \frac{RTT_0}{\Delta H_1} \ln(1 - x_3^M) \quad (6)$$

The following applications of formulas 5 and 6 may be of interest: (1) determination of the surfactant activity a_1 in multicomponent micellar solutions from ΔT data, (2) estimation of the mixed micelle composition (x_1^M), (3) prediction of the $\Delta T(x_1, x_3)$ dependencies, and (4) explanation of regularities in the influence of the molecular structure of additives. Applications 1 and 2 are straightforward; points 3 and 4 need special consideration.

Let us introduce the distribution coefficient for component 3 as

$$K_x = \frac{x_3^M}{x_3^W} \quad (7)$$

Using the material balance equations, one can easily express x_3^M and x_3^W through the overall mole fractions of the components and through the K_x value for the mixture. The expression for x_3^M is as follows:

$$x_3^M = \frac{(1 - y)x_3}{(1 - y)x_3 + x_1} \quad (8)$$

where y is the ratio of the number of moles of component 3 in the aqueous phase (m_3^W) and in the whole system (m_3): $y = m_3^W/m_3$; y may be found from the following quadratic equation

$$K_x = \frac{1 - y}{y} \frac{yx_3 + x_2}{(1 - y)x_3 + x_1} \quad (9)$$

Equations 8 and 9 are valid even in the case that $K_x \neq$ constant. One should only know the K_x value for the mixture composition under consideration.

In accord with the phase separation model it holds that

$$K_x = \frac{\gamma_3^W}{\gamma_3^M} = \frac{f_3^W}{f_3^M} K_x^* \quad (10)$$

where

$$K_x^* = \lim_{x_3 \rightarrow 0} K_x = \frac{\gamma_3^{W\infty}}{\gamma_3^{M\infty}} = \exp\left(-\frac{\Delta\mu_3^\circ}{RT}\right)$$

the activity coefficients γ_3^M and γ_3^W are defined taking the pure liquid as the standard state for component 3 ($\gamma_3 = 1$ at $x_3 = 1$); $f_3^W = 1$ when $x_3 \rightarrow 0$ and $f_3^M = 1$ when $x_3^M \rightarrow 0$ (the standard state relates to the infinitely diluted solution W or M); $\Delta\mu_3^\circ$ is the reference chemical potential for the transfer of the third component from the aqueous phase to the micellar phase; and $\gamma_3^{M\infty}$ and $\gamma_3^{W\infty}$ are the activity coefficients in infinitely diluted solutions of component 3 in the micelles and water ($f_3^M = \gamma_3^M/\gamma_3^{M\infty}$; $f_3^W = \gamma_3^W/\gamma_3^{W\infty}$). The K_x value remains equal to K_x^* in the concentration range where the laws of highly diluted (or ideal) solutions are valid for both micellar and aqueous phases and where the temperature dependence of K_x may be neglected. For the limiting slope of the T versus x_3 curves at $x_1/x_2 =$ constant one can write

$$\left(\frac{dT}{dx_3}\right)_{P, x_1/x_2}^* = \lim_{x_3 \rightarrow 0} \left(\frac{dT}{dx_3}\right)_{P, x_1/x_2} = -\frac{RT^2}{\Delta H_1} \frac{K_x^*}{K_x^* x_1 + x_2} \quad (11)$$

that is the slope depends on the surfactant and water concentrations. For $K_x^* x_1 \ll x_2$

$$\left(\frac{dT}{dx_3}\right)_{P, x_1/x_2}^* \approx -\frac{RT^2}{\Delta H_1} K_x^* \quad (12)$$

Evidently, the higher the K_x^* value, the greater the temperature decrease effect produced by the third component, the comparison being made for different additives to the same binary. In the case of $K_x^* = 0$, that is when the third component does not penetrate inside micelles, the phase separation model gives $(dT/dx_3) = 0$.

From eq 11 after some rearrangements one can obtain

$$\left[\frac{d\tilde{w}_3}{dT}\right]_{P, w_1/w_2}^* = a(1 + b\tilde{w}_1) \quad (13)$$

where a and b are constants:

$$a = -\frac{\Delta H_1}{RT^2 K_x^*} \frac{M_3}{M_2}$$

$$b = K_x^* \frac{M_2}{M_1} - 1$$

\tilde{w}_i is the weight fraction, and M_i is the molar mass of component i ($i = 1, 2, 3$). Equation 13 says that the dependence of the $(d\tilde{w}_3/dT)_{P, w_1/w_2}^*$ magnitude on the surfactant weight fraction in the system should be linear.

The temperature dependence of the K_x^* value may be described by the formula

$$\frac{\partial \ln K_x^*}{\partial T} = \frac{\Delta H_3^{W-M}}{RT^2} \quad (14)$$

where ΔH_3^{W-M} is the partial molar enthalpy for the transfer of the third component from the infinitely diluted

aqueous solution (1–3) to the micellar phase, also at infinite dilution.

One can use the model for the discussion of some regularities in the change of the ΔT effect for a homologous series of amphiphilic additives (for example, alkanols). It follows from eqs 10–12 that the ΔT effect depends on the $RT \ln K_x^* = -\Delta\mu_3^\circ$ value. For amphiphilic homologues forming mixed micelles with the basic surfactant (polar groups of the additive molecules are near the micellar polar surface; alkyl tails are inside the micellar hydrocarbon core) the $\Delta\mu_3^\circ$ value should correlate with the transfer free energy of alkyl tails from the aqueous to the hydrocarbon medium. It is known that the latter, being negative, is less in its absolute value for the branched hydrocarbon chain than for the normal chain of the same length.¹⁷ Hence the distribution coefficient K_x^* for amphiphiles with the normal alkyl group appears to be higher than that for the isomers with a branched chain. So, the most strong effect on the temperature decrease should be awaited from additives of a normal structure. The fact that the absolute $\Delta\mu_3^\circ$ value increases with the increase of the alkyl tail length permits us to expect the growing ΔT effect in the series of C_2 , C_3 , etc. homologues. However, the lowering of the effect for higher homologues is probable, which may be caused by several reasons. One of them may be the change in the structure of mixed micelles. When alkyl tails of amphiphilic homologues having a small polar group (alkanols, for example) become longer, the substances behave more and more like nonpolar ones and there are more chances for their molecules to be incorporated totally inside the hydrocarbon core of micelles. In this case their effect on the activity of the basic surfactant becomes weaker. It is possible also that on addition of higher homologues not a precipitation of the crystal basic surfactant but another phase transition, in particular, gel formation, may occur on the temperature decrease.

From the equations given above some conclusions may be drawn concerning the combined effect of two additives, one of which (component 3) is partly incorporated in mixed micelles. Let us suppose that some component 4 does not penetrate inside micelles and being added to the surfactant (1)–water (2) system does not produce any significant change in the surfactant precipitation temperature. But if this component salts out component 3 from its aqueous solution (the $\gamma_3^{W\infty}$ magnitude is getting higher), then the lowering of the precipitation temperature may be observed on addition of component 4 to the surfactant (1)–water (2)–additive (3) system.

Experimental Data for Aqueous *N*-Dodecanoyl-*N*-methylglucamine Mixtures with Additives

The data on the micellar solution–crystal surfactant equilibrium for the binary *N*-dodecanoyl-*N*-methylglucamine–water system are presented in the preceding publication by the authors.¹⁴ We refer to this work for the characteristics of the surfactant (MEGA-12) and for the description of the method of its purification. Substances used as additives had a grade “pure”.

Methods. The dissolution temperature of the surfactant was measured by the *visual method*. Samples (suspensions of MEGA-12 powder, water, and additive) were prepared by weighing in a glass cell which then was placed into a transparent thermostated vessel. The temperature of the vessel was raised with a speed not higher than 0.3 K/min from room temperature up to the clearing temperature. During the course of heating the

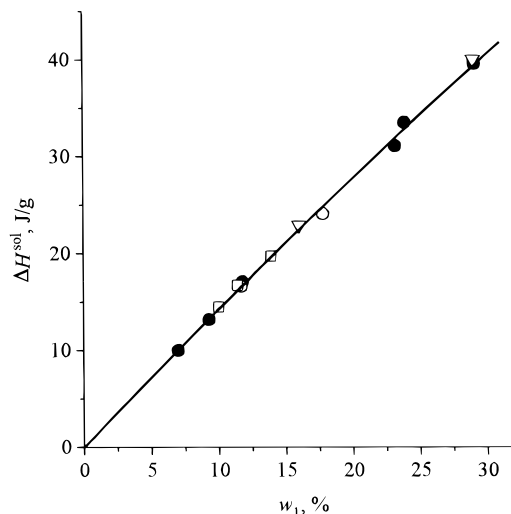


Figure 1. Enthalpy of dissolution of crystalline MEGA-12 in water (●) and aqueous solutions containing ethanol (○), *n*-propanol (▽), and *n*-butanol (□) (the effect per gram of mixture) versus the weight percent of the surfactant (w_1). The concentration of alkanol in the mixtures is 5.0–8.4 wt % (see Table 1).

mixture in the cell was agitated with a magnetic stirrer. Various speeds of heating were tried to confirm that with the speed 0.3 K/min the attaining of the phase equilibrium was ensured. Except when mixtures were very viscous, the clearing temperature could be fixed accurately enough, to within 0.2 K. Only the dissolution temperature of the surfactant was measured. The temperature of precipitation from micellar solutions on cooling of heated homogeneous liquid mixtures could not be observed because long living transparent gels were formed, several hours or sometimes several days being necessary for the surfactant crystals to appear.

Calvet calorimetry^{18,19} was employed to measure the heats of dissolution of crystalline MEGA-12 in water and water–alkanol mixtures. Samples for the study were prepared by weight, the overall mass of the mixture being 3–5 g. The solvent was poured into the calorimetric cell. The probe of the surfactant in a glass sealed capsule was placed in the solvent medium inside the cell. After thermal equilibrium had been attained, the capsule was crashed with the aid of a special device. Stirring of the contents of the cell during the dissolution process was performed. The heat flux was registered and integrated. The reproducibility of the results of measurements was not worse than 4%.

Results. The enthalpies of dissolution of crystalline MEGA-12 in water and water–alkanol (ethanol, *n*-propanol, *n*-butanol) solutions were measured by the Calvet method at 325.2 K. The data are presented in Table 1 and Figure 1, where ΔH^{sol} denotes the effect per gram of the MEGA-12 (1)–water (2) or MEGA-12 (1)–water (2)–alkanol (3) mixture and ΔH_s^{sol} is the effect per gram of the surfactant. It is seen that the ΔH^{sol} value for aqueous solutions varies linearly with the surfactant percentage (w_1) and that the ΔH_s^{sol} value is constant within the limits of the experimental error. The average ΔH_s^{sol} value per mole (52 kJ/mol) may be taken as the differential molar enthalpy of dissolution (ΔH_1) of crystalline MEGA-12 in water for the micellar range. As is seen in Figure 1, the ΔH^{sol} values for the dissolution of MEGA-12 in

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Table 1. The Enthalpies of Dissolution ΔH^{sol} (per Gram of Mixture) and ΔH_s^{sol} (per Gram of Surfactant) for MEGA-12 (1) in Water and Aqueous Solutions Containing Alkanols (3) at 325.2 K

| w_1 , % | w_3 , % | ΔH^{sol} , J/g | ΔH_s^{sol} , J/g |
|-----------|--------------------|-------------------------------|---------------------------------|
| 7.0 | | 10.0 | 142.8 |
| 9.3 | | 13.2 | 141.8 |
| 11.8 | | 17.1 | 144.9 |
| 3.2 | | 31.1 | 134.1 |
| 3.9 | | 33.5 | 140.6 |
| 29.1 | | 39.6 | 135.9 |
| | ethanol | | |
| 11.7 | 8.2 | 16.6 | 141.9 |
| 17.8 | 8.3 | 24.1 | 135.6 |
| | <i>n</i> -propanol | | |
| 16.0 | 8.4 | 22.9 | 142.9 |
| 29.0 | 8.3 | 40.0 | 137.7 |
| | <i>n</i> -butanol | | |
| 10.0 | 5.4 | 14.5 | 146.1 |
| 11.4 | 5.2 | 16.7 | 146.3 |
| 13.9 | 5.0 | 19.7 | 141.8 |

water–alkanol mixtures lie close to the ΔH^{sol} versus w_1 line for the MEGA-12–water binary system. The results give evidence that the effect of alkanols C_2 – C_4 on the heat of dissolution of MEGA-12 is not very pronounced in the studied concentration range (5–8 wt % alkanol). So it will not be a rude approximation to neglect the concentration dependence of the ΔH_1 value in model calculations for the mixtures under consideration.

The ΔH_1 value determined by the Calvet method differs considerably from the quantity resulting from DSC measurements for MEGA-12–water mixtures (37 kJ/mol).¹⁴ The discrepancy exceeds significantly the experimental errors for the two methods. The magnitude of the heat of the phase transition per gram of MEGA-12 was reproduced with an accuracy of about 8% in the DSC experiments performed at various speeds of heating (0.1 and 0.2 K/min) and for samples of various masses (the integral effects were 1–4 J). Such a reproducibility confirms that the equilibrium was attained in the heating process. It can be inferred that the difference in the ΔH_1 values from the Calvet and DSC measurements stems from different starting states in the two experimental procedures. In the measurements made with the Calvet calorimeter the heat of mixing of pure crystalline surfactant and water is registered. So the effect relates directly to the dissolution of the crystalline surfactant. As for the DSC measurements the initial state is a heterogeneous system formed after a long contact of the solid surfactant with water inside the sealed cell. Though the solubility of MEGA-12 in water at ambient temperatures is very small, the contact of the surfactant with water may result in structural changes for the system; the difference between the Calvet and DSC data on the heat of dissolution is likely due to such changes. In particular, the possibility of crystal hydrate formation must be kept in mind. However, the data by Fu et al.¹⁰ do not provide support for this assumption in the case of the MEGA-12–water system. Further comparison of the results given by the two calorimetric methods may be of interest, but evidently for the direct data on the heats of dissolution of the crystalline surfactant one should use the Calvet method. In the further calculations the value $\Delta H_1 = 52$ kJ/mol will be used.

Dissolution temperatures were measured for mixtures containing additives of various chemical natures. It has been found that nonpolar substances like alkanes and benzene, and polar additives such as dimethylformamide, dimethyl sulfoxide, citric acid, glycerol, Na^+ and K^+ salts, etc., do not produce any significant change in MEGA-12 dissolution temperature. As one could expect, many

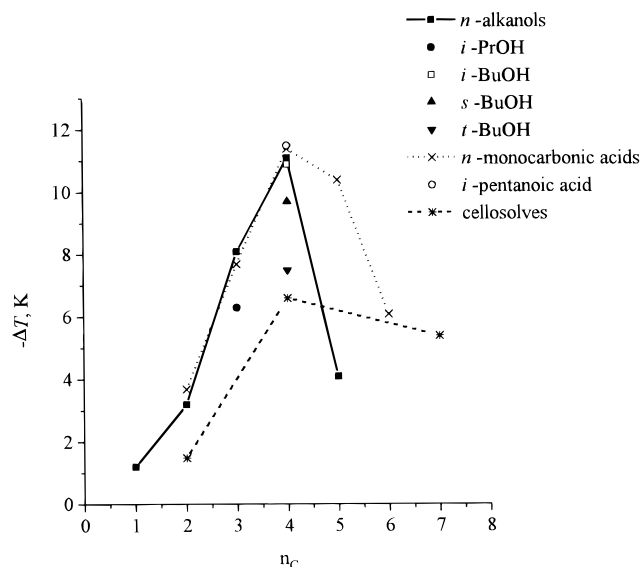


Figure 2. Decrease of the dissolution temperature of MEGA-12 on addition of the third component (8 wt %) to the MEGA-12(1)–water (2) binary system ($w_1/w_2 = 2/3$) versus the number (n) of carbon atoms in a molecule of an added alkanol $C_nH_{2n+1}OH$, *n*-monocarboxylic acid $C_{n-1}H_{2n-1}COOH$, or cellosolve $C_nH_{2n+1}(OCH_2CH_2OH)$.

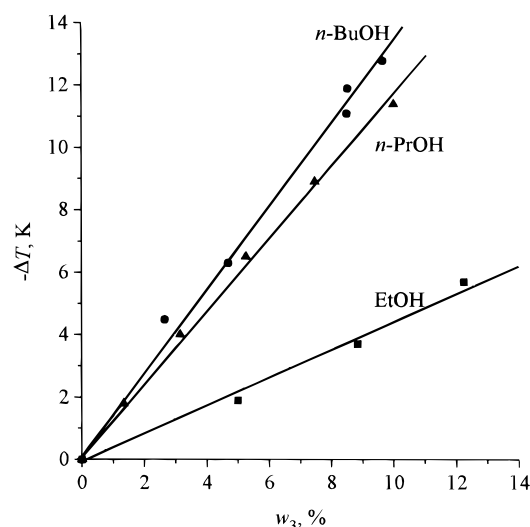


Figure 3. Decrease of the dissolution temperature of MEGA-12 in dependence on the alkanol weight concentration (w_3) for MEGA-12 (1)–water (2) mixtures ($w_1/w_2 = 2/3$) containing ethanol, *n*-propanol, and *n*-butanol.

effective additives are light amphiphilic substances. The results for three homologous series (monocarboxylic acids, alkanols, and cellosolves) are compared in Figure 2, where ΔT values refer to the same additive weight percent (8%); $\Delta T = T(w_1/w_2, w_3) - T(w_1/w_2, w_3=0)$. All the additives under consideration decrease the dissolution temperature. The sequence of the additive efficiency is the following: monocarboxylic acids > alkanols > cellosolves. The effects greatly depend on the length of the alkyl chain and go through maxima which are more pronounced for monocarboxylic acids and alkanols. In Figure 3 the ΔT effects for different concentrations of ethanol, *n*-propanol, and *n*-butanol at $w_1/w_2 = 2/3$ are compared. One can follow the regularities discussed above: *n*-alkanols are more effective additives than their isomers, and the ΔT effect increases with the increase of the alkyl chain length ($C_2 < C_3 < C_4$). As is seen in Figure 2, the maximal effect is produced by *n*-butanol. The lowering of the ΔT value in

Table 2. Experimental and Calculated Results for MEGA-12 (1)–Water (2)–Ethanol (3) Micellar Solutions in Equilibrium with the Solid Surfactant ($K_x^* = 7.8$); $\Delta T = T(w_1/w_2, w_3) - T(w_1/w_2, w_3=0)$

| w_1/w_3 | w_3 | $-\Delta T_{\text{exp}}$ | $-\Delta T_{\text{calc}}$ | K_x | x_3^W | x_1^M | a_1 |
|-----------|-------|--------------------------|---------------------------|-------|---------|---------|-------|
| 1/26 | 7.9 | 3.2 | 3.6 | 4.4 | 0.03 | 0.85 | 0.87 |
| 1/26 | 17.5 | 6.5 | 6.6 | 3.1 | 0.08 | 0.75 | 0.75 |
| 1/26 | 19.6 | 7.2 | 7.1 | 2.9 | 0.09 | 0.73 | 0.73 |
| 1/11 | 30.3 | 10.3 | 9.0 | 2.1 | 0.15 | 0.67 | 0.63 |
| 1/2 | 10.1 | 5.3 | 5.3 | 3.7 | 0.06 | 0.79 | 0.79 |
| 1/2 | 19.9 | 9.4 | 8.2 | 2.4 | 0.12 | 0.69 | 0.66 |
| 1/1 | 9.9 | 5.1 | 5.7 | 3.5 | 0.06 | 0.78 | 0.80 |
| 1/1 | 20.3 | 8.7 | 8.8 | 2.2 | 0.15 | 0.67 | 0.68 |
| 1/1 | 31.2 | 10.3 | 10.6 | 1.5 | 0.24 | 0.62 | 0.63 |
| 5/4 | 10.4 | 4.7 | 6.4 | 3.2 | 0.08 | 0.75 | 0.81 |

Table 3. Examples of the Experimental and Calculated Results for MEGA-12 (1)–Water (2)–*n*-Propanol (3) Micellar Solutions in Equilibrium with the Solid Surfactant ($K_x^* = 34.1$); $\Delta T = T(w_1/w_2, w_3) - T(w_1/w_2, w_3=0)$

| w_3 | $-\Delta T_{\text{exp}}$ | $-\Delta T_{\text{calc}}$ | K_x | x_3^W | x_1^M | a_1 |
|------------------|--------------------------|---------------------------|-------|---------|---------|-------|
| $w_1/w_2 = 1/30$ | | | | | | |
| 1.0 | 1.5 | 1.7 | 32.4 | 0.003 | 0.90 | 0.91 |
| 1.4 | 1.7 | 2.3 | 31.7 | 0.004 | 0.87 | 0.90 |
| 1.8 | 2.8 | 2.9 | 31.1 | 0.005 | 0.84 | 0.85 |
| 2.7 | 4.7 | 4.5 | 29.7 | 0.008 | 0.76 | 0.75 |
| 5.0 | 8.4 | 8.1 | 26.5 | 0.015 | 0.61 | 0.59 |
| 7.0 | 11.4 | 11.5 | 24.0 | 0.021 | 0.49 | 0.49 |
| 8.4 | 13.8 | 13.6 | 22.5 | 0.026 | 0.43 | 0.42 |
| 10.0 | 16.2 | 16.0 | 20.9 | 0.031 | 0.36 | 0.36 |
| $w_1/w_2 = 1/2$ | | | | | | |
| 1.2 | 1.9 | 1.7 | 32.4 | 0.003 | 0.90 | 0.89 |
| 3.0 | 4.2 | 4.0 | 30.1 | 0.007 | 0.78 | 0.77 |
| 4.9 | 6.5 | 6.3 | 28.0 | 0.011 | 0.68 | 0.67 |
| 6.9 | 8.9 | 8.7 | 26.0 | 0.016 | 0.58 | 0.57 |
| 8.5 | 10.6 | 10.4 | 24.7 | 0.019 | 0.52 | 0.52 |
| 10.1 | 12.2 | 12.1 | 23.5 | 0.023 | 0.47 | 0.46 |

Table 4. Examples of the Experimental and Calculated Results for MEGA-12 (1)–Water (2)–*n*-Butanol (3) Micellar Solutions in Equilibrium with the Solid Surfactant ($K_x^* = 102$); $\Delta T = T(w_1/w_2, w_3) - T(w_1/w_2, w_3=0)$

| w_3 | $-\Delta T_{\text{exp}}$ | $-\Delta T_{\text{calc}}$ | K_x | x_3^W | x_1^M | a_1 |
|------------------|--------------------------|---------------------------|-------|---------|---------|-------|
| $w_1/w_2 = 1/30$ | | | | | | |
| 1.1 | 4.4 | 4.3 | 95.3 | 0.002 | 0.77 | 0.76 |
| 1.2 | 4.9 | 4.6 | 94.9 | 0.003 | 0.76 | 0.74 |
| 1.8 | 7.0 | 7.0 | 91.7 | 0.004 | 0.65 | 0.65 |
| 1.9 | 6.9 | 7.2 | 91.4 | 0.004 | 0.64 | 0.65 |
| 3.0 | 11.9 | 11.9 | 86.2 | 0.006 | 0.47 | 0.47 |
| 3.3 | 13.0 | 12.9 | 85.3 | 0.007 | 0.44 | 0.44 |
| 4.8 | 17.0 | 19.0 | 80.4 | 0.009 | 0.30 | 0.34 |
| 8.5 | 30.5 | 31.4 | 74.4 | 0.012 | 0.12 | 0.13 |
| $w_1/w_2 = 1/2$ | | | | | | |
| 0.9 | 1.6 | 1.6 | 99.3 | 0.001 | 0.91 | 0.91 |
| 1.1 | 2.1 | 1.8 | 99.0 | 0.001 | 0.89 | 0.88 |
| 1.5 | 3.1 | 2.6 | 97.8 | 0.001 | 0.86 | 0.83 |
| 1.7 | 3.0 | 3.0 | 97.2 | 0.002 | 0.83 | 0.83 |
| 3.3 | 6.4 | 5.4 | 93.8 | 0.003 | 0.72 | 0.67 |
| 6.5 | 11.8 | 9.8 | 88.4 | 0.005 | 0.54 | 0.48 |
| 8.1 | 14.0 | 11.7 | 86.4 | 0.006 | 0.48 | 0.41 |

the case of *n*-pentanol may be caused by several reasons mentioned above.

The dissolution temperature of crystalline MEGA-12 in aqueous solutions containing ethanol, *n*-propanol, and *n*-butanol was studied over a wide range of surfactant and alkanol concentrations. Several series of $\Delta T(w_3)$ measurements have been performed for the systems, each series relating to $w_1/w_2 = \text{constant}$. The results of measurements (some of them are presented in Tables 2–4 and Figures 4 and 5) indicate that the influence of the w_1/w_2 magnitude on the $\Delta T(w_3)$ value increases significantly from ethanol to butanol.

Among the studied additives were several salts (potas-

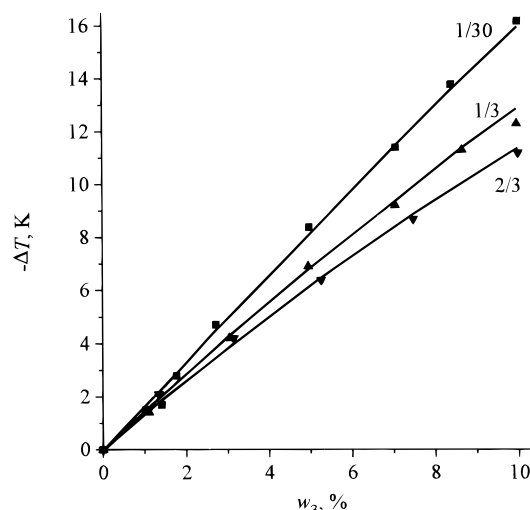


Figure 4. $\Delta T = T(w_1/w_2, w_3) - T(w_1/w_2, w_3=0)$ values versus w_3 for saturated MEGA-12 (1)–water (2)–*n*-propanol (3) solutions at the following values of w_1/w_2 : 1/30, 1/3, 2/3. Points represent experimental data; curves are calculated using eqs 6–10.

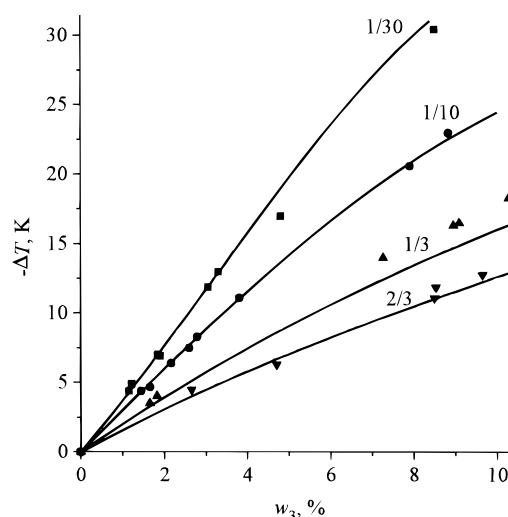


Figure 5. $\Delta T = T(w_1/w_2, w_3) - T(w_1/w_2, w_3=0)$ values versus w_3 for saturated MEGA-12 (1)–water (2)–*n*-butanol (3) solutions at the following values of w_1/w_2 : 1/30, 1/10, 1/3, 2/3. Points represent experimental data; curves are calculated using eqs 6–10.

sium, sodium, and ammonium chlorides, carbonates, nitrates, and sulfates). Their effect on the MEGA-12 dissolution temperature has appeared insignificant. In most cases a slight increase of the temperature (1–2 K at the 8% content of the additive) was observed. But the addition of salts to alkanol-containing mixtures produced a marked decrease of the temperature, as is seen in Figure 6, where the $\Delta T = T(w_1/w_2, w_3, w_4) - T(w_1/w_2, w_3, w_4=0)$ values are displayed in dependence on the salt concentration w_4 ; component 3 is *n*-propanol; $w_3 = 8$ wt %. The nature of the anion appears to be of importance for the ΔT value, and the following sequence may be stated: $\text{CO}_3^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$.

The influence of the cation is rather slight, but the following tendency could be revealed: $\text{Na}^+ > \text{K}^+ > \text{NH}_4^+$. The results may be considered as an illustration of the salting out effect discussed earlier (propanol is salted out of the aqueous medium, and its concentration in micelles grows).

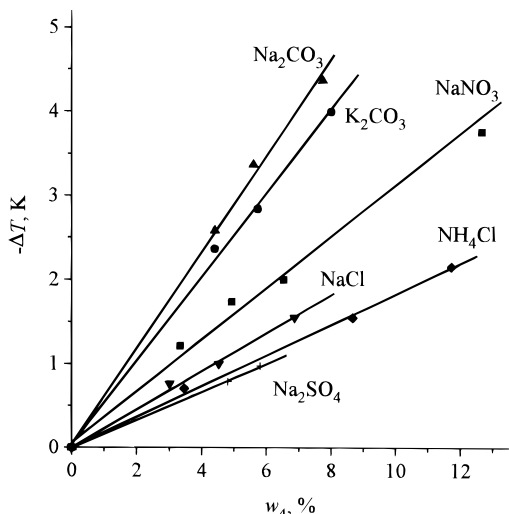


Figure 6. Decrease of the dissolution temperature of MEGA-12 on addition of salts (component 4) to MEGA-12 (1)–water (2)–*n*-propanol (3) mixtures; $\Delta T = T(w_1/w_2, w_3, w_4) - T(w_1/w_2, w_3, w_4=0)$; $w_3 = 8$ wt %, $w_1/w_2 = 2/3$.

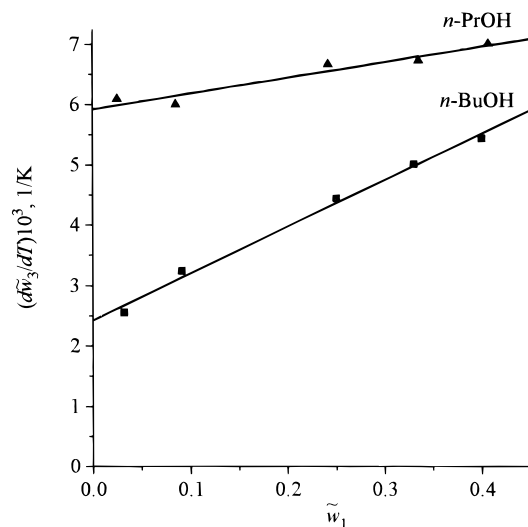


Figure 7. Limiting slopes of the $\tilde{w}_3 - T$ (at $\tilde{w}_1/\tilde{w}_2 = \text{constant}$) curves versus \tilde{w}_1 , where \tilde{w}_1 , \tilde{w}_2 , and \tilde{w}_3 are the weight fractions of MEGA-12, water, and alkanol, respectively; $\tilde{w}_3 \rightarrow 0$. The data relate to mixtures with *n*-propanol and *n*-butanol.

Results of Model Calculations

Calculations of the $\Delta T(w_1/w_2, w_3)$ effects were performed for aqueous mixtures of MEGA-12 containing *n*-alkanols C_2 – C_4 .

To check the regularities in the limiting slopes of the $\Delta T(w_3)_{w_1/w_2}$ curves stated by the model, we estimated the values of the $(d\Delta T/d\tilde{w}_3)_{w_1/w_2}^*$ derivatives from the experimental data. As is seen in Figure 7 for mixtures with *n*-PrOH and *n*-BuOH, the $(d\tilde{w}_3/dT)_{w_1/w_2}^*$ versus \tilde{w}_1 dependence is very close to a linear one, which is in agreement with eq 13. In the case of ethanol the difference in the limiting slopes of the curves for various w_1/w_2 values was of the order of experimental errors in the determination of the slopes themselves.

The values of the a parameter in eq 13 were estimated by the data reduction; the limiting values of the distribution coefficient were found as

$$K_x^* = -\frac{\Delta H_1}{RT^2} \frac{M_3}{M_2} \frac{1}{a} \quad (15)$$

Table 5. Limiting Values of the Distribution Coefficient K_x^* and of the Alkanol Activity Coefficients in Aqueous²¹ and Micellar Pseudophases ($T = 323.2$ K)

| alkanol | K_x^* | $\gamma_3^{W\infty}$ | $\gamma_3^{M\infty}$ |
|----------------|---------|----------------------|----------------------|
| EtOH | 7.8 | 4.65 | 0.60 |
| <i>n</i> -PrOH | 34.1 | 17.5 | 0.51 |
| <i>n</i> -BuOH | 102 | 48.9 | 0.48 |

With $\Delta H_1 = 52.0$ kJ/mol and $T_0 = 321.7$ K for the binary MEGA-12–water system the K_x^* values 5.3, 34.3, and 102 were obtained for ethanol, propanol, and butanol, respectively.

The calculations of the ΔT values over a wide range of MEGA-12 and alkanol concentrations were performed with the help of eqs 6–10. With the approximation that the distribution coefficient is constant ($K_x = K_x^*$) the general character of the $\Delta T(w_1/w_2, w_3)$ dependencies is reproduced but the discrepancies between the calculated and experimental results are significant especially at low surfactant concentrations (low w_1/w_2 values) and high alkanol contents. The following more refined approach was then applied. The micellar pseudophase was treated as an ideal solution (in the concentration range under study it was accepted that $\gamma_3^M = \gamma_3^{M\infty} = \text{constant}$), but the change in the alkanol activity coefficients with the change of its content in the aqueous pseudophase was taken into account. In this approximation

$$K_x = K_x^* \gamma_3^W / \gamma_3^{W\infty} \quad (16)$$

The temperature dependence of the K_x^* value was neglected.

The UNIFAC model with the parameters presented in ref 20 was used for rough estimations of the $\gamma_3^W(x_3^W)$ values for aqueous solutions of ethanol, propanol, and butanol. Calculations were performed for K_x^* values found from the limiting slopes of the experimental $\Delta T(w_3)$ curves (these values were given above) and also for the values adjusted with the use of the whole set of experimental data on ΔT effects, K_x^* being the only adjustable parameter for each system (Table 5). The two ways of estimation gave practically the same K_x^* values in the cases of *n*-PrOH and *n*-BuOH; for ethanol some discrepancy was observed, which may be due to experimental errors. The calculated results presented in Tables 2–4 and Figures 4 and 5 were obtained for the K_x^* values from Table 5. The agreement between the calculated and experimental ΔT values is quite satisfactory.

So, we can conclude that the pseudophase model gives a reasonable description of the effects of C_2 – C_4 alkanol additives on the dissolution temperature in the MEGA-12–water system and that it is of importance to take into account the concentration dependence of the alkanol activity coefficient in the aqueous phase.

The treatment of experimental ΔT data on the basis of the pseudophase model permits us to obtain interesting information about mixed MEGA-12–alkanol micelles. With the help of eq 10 one can estimate $\gamma_3^{M\infty}$ values from the K_x^* and $\gamma_3^{W\infty}$ values, that is to find the limiting value of the alkanol activity coefficient in the micellar phase (Table 5). Experimental $\gamma_3^{W\infty}$ values for EtOH, *n*-PrOH, and *n*-BuOH were taken from the literature.²¹ For the alkanols under study we have obtained $\gamma_3^{M\infty} < 1$. Negative values of the excess chemical potential $RT \ln \gamma_3^{M\infty}$ presumably are in great part due to the energy contribu-

(20) Hansen, H. K.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352.

(21) Morachevsky, A. G.; Smirnova, N. A.; Balashova, I. M.; Pukinsky, I. B. *Termodinamika Razbavlenich Rastvorov Neelektrolitov*; Chimia: Leningrad, 1982 (in Russian).

tion. Indeed, at $x_3^M \ll 1$ practically each of alkanol molecule in the micelle has its hydroxyl group in contact with the surfactant polar head whereas the alkanol hydrocarbon tail is plunged into the micellar hydrocarbon core; that is, on average the interaction energy for an alkanol molecule in the micelle is more negative than that in pure alkanol (which is a standard state in the γ_3^W determination).

From the model one can also obtain information about the mixed micelle composition. The calculated x_1^M values (Tables 2–4) are for most of the studied mixtures close to the surfactant activity a_1 estimated from the ΔT data with the help of the eq 5. By this it is meant that the micellar MEGA-12–alkanol pseudophase in a wide range of compositions can be approximately treated as an ideal solution where $a_1^M \cong x_1^M$ (for alkanol $x_3^M \cong a_3^M$ if the alkanol activity coefficient is normalized to infinite dilution; that is, $a_3^M = x_3^M f_3^M$, where $f_3^M = \gamma_3^M / \gamma_3^{M^\infty}$).

Discrepancies between the calculated and experimental results may be due to several factors which the pseudophase model does not take into account. In particular, strengthening of the intermicellar interactions with the increase of the surfactant concentration and changes in water structure and in the micelle size and shape may be of importance, and certainly one of the most serious probable sources of errors may be the disregarding of the micellar phase nonideality.

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