

Catanionic Micelles As a Model to Mimic Biological Membranes in the Presence of Anesthetic Alcohols

Sekh Mahiuddin,^{*,†} Oliver Zech,[‡] Sabine Raith,[‡] Didier Touraud,[‡] and Werner Kunz^{*,‡}[†]Materials Science Division, North-East Institute of Science and Technology, CSIR, Jorhat-785006, Assam, India, and [‡]Institute of Physical and Theoretical Chemistry, University of Regensburg, D-93040 Regensburg, Germany

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We show here the influence of *n*-alcohols (C₂OH–C₈OH) on the solubility behavior of cationic-anionic surfactant mixtures, so-called “catanionics”. We studied catanionics of different compositions composed of sodium dodecyl sulfate (SDS)/cetyltrimethylammonium bromide (CTAB) and sodium dodecanoate (SDod)/CTAB mixtures. Interestingly, with a molar excess of SDS, long chain *n*-alcohols (C₄OH–C₈OH) significantly depress the solubility temperature of the SDS+CTAB catanionic and increase the kinetic stability of the solution. The visual observations of solubility temperatures of catanionics were further confirmed by differential scanning calorimetry (DSC) measurements. For the catanionics a multistep solubilization was observed by DSC, for which the sulfate headgroup is responsible. This was probed by replacing SDS by SDod. A remarkable analogy was found between the influence of the alcohols on the solubility patterns of the catanionic mixtures and on the anesthesia of tadpoles. Possible reasons for this analogy are discussed also in this paper.

Introduction

Aqueous mixtures^{1–10} prepared of anionic and cationic surfactants are called catanionics. They exhibit properties, which are different from the corresponding properties of the individual surfactants.^{11–14} One interesting feature of catanionics is the reduction of the oil/water interfacial tension.¹⁵ For example, the surface tension of sodium dodecyl sulfate (SDS) and of cetyltrimethylammonium bromide (CTAB) solutions above their critical micelle concentration (cmc) were found to be about 36 mN m⁻¹,^{16,17} whereas micellar systems consisting of 70 mol % SDS + 30 mol % CTAB can decrease the surface tension of water down to ~24 mN m⁻¹.¹⁷ The outstanding physicochemical properties of catanionics are governed by various competing

molecular interactions and the resulting variety of microstructures.^{1,18,19} The phase diagrams in terms of solubility temperature of catanionic micelles consisting of SDS and different cationic surfactants have recently been reported.^{7,20}

The solubility temperatures of 1 wt % SDS and 1 wt % CTAB were reported to be 19.7 and 30 °C, respectively. The DSC patterns, in this study, confirm these solubility temperatures. In contrast, the solubility curves of SDS and CTAB mixtures at different compositions below and above the equimolar composition are visibly different from those of the individual surfactants. In the CTAB rich region (SDS mole fraction ≤ 0.3), the solubility temperature increases, whereas it decreases in the SDS rich region (SDS mole fraction ≥ 0.65).^{7,20} For intermediate compositions, the electrostatic interaction is strong between anionic and cationic surfactants. Consequently, the solubility temperature increases sharply and is not detectable up to the boiling temperature of water at equimolar ratio.

The catanionic micelles of SDS and CTAB are not thermodynamically stable and precipitation appears after some time. But one can tune the solubility temperature and increase the stability of catanionic micelles and make a promising candidate for practical applications.^{21–30} For example, undesirable precipitation in washing cycles, where both, cationic and anionic surfactants are

*To whom correspondence should be addressed. E-mail: Werner.Kunz@chemie.uni-regensburg.de (W.K.), mahirrljt@yahoo.com (S.M.).

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required, can be avoided.²¹ Furthermore, cationic and anionic surfactants are applied in secondary oil recovery, and precipitation phenomena can be useful to improve sweep efficiency in the process.²¹ Moreover, these systems may be of practical importance in the field of cosmetics, pharmaceutical products, and optimization of formulations.

Recently, the effect of alkali salts on the solubility behavior of SDS + CTAB cationics has been studied.⁷ Except for potassium, alkali salts decrease the solubility temperature of the cationics in the SDS rich region. Nevertheless, the stability of the cationics is not improved. On the other hand, *n*-alcohols with chain lengths $\geq C_5$ significantly decrease the solubility temperature and increase the stability of the cationic solutions containing objects of different size and shape (micelles, vesicles, rod like micelles, disks). Yu et al.,³¹ Zhang et al.,³² and Wang et al.³³ demonstrated that *n*-alcohols ($\leq C_4OH$) at different concentrations significantly influence the solubility temperature of cationics and formation of vesicles. Nevertheless, the transformation to vesicles could be observed, and the vesicles showed a remarkable increase in stability compared to the pure cationic systems.³⁴ In these reports, neither a systematic variation of concentration nor a systematic variation of the alcohols' chain lengths and their influence on the solubilization of cationics has been studied. It should be mentioned that the dielectric constant of the medium was found to govern the size of large objects,³⁵ an observation that will be important for the interpretation of the results presented below.

The solubility of SDS + CTAB cationics with and without salts and *n*-alcohols is not straightforward because different types of interactions prevail compared to pure surfactants in solution. The cationics in the presence of *n*-alcohols spontaneously form micelles and vesicles.^{7,31,32,36} Visually, we observed that the solubility of SDS + CTAB cationics took place over a small time scale, during which different polymorphs and mesophases are formed. This indicates that the solubility process of the SDS + CTAB cationics follows multiple steps. These visual observations could further be confirmed by DSC measurements.

n-Alcohols act as anesthetic agents and their potency on model biological membranes are reported.^{37,38} Surfactant mixtures well above the cmc are good examples of biological cell membranes.^{39–42} Further, we could recently demonstrate that the cationic microemulsion is a superior medium compared to a cationic microemulsion for enzymatic activity.⁴¹ We note that there is an interesting theory about the influence of inserting hydrophobic molecules in membranes on the propagation of nerve impulses.⁴³

It seems that the insertion of such molecules can induce a change in curvature, which inhibits a necessary reversible phase transition. In the present study we do not consider such phase transitions, and they will be discussed in the next phase of our investigations. Nevertheless, we indicate this type of mechanism because it might also be part of the final explanation of the anesthetic action of alcohols.

As already mentioned, in the present paper we are interested in the effect of *n*-alcohols on the solubility of SDS + CTAB and sodium dodecanoate (SDod) + CTAB cationics. Particularly, we investigate the effect of added *n*-alcohols (*n*-C₂OH to *n*-C₈OH) as well as benzyl alcohol in the SDS rich region. The reason for the incorporation of SDod is to examine the influence of the surfactant headgroup. The visual observations have further been confirmed by DSC measurements. Finally, the trend in which the different alcohols decrease the solubility temperature of the cationics has been compared to their capacity to produce a general anesthesia of tadpoles.⁴⁴

Experimental Section

SDS ($\geq 99\%$, Merck, Germany), CTAB ($> 99\%$, Acros, U.S.A.), sodium dodecanoate (99–100%, Sigma, U.S.A.), ethanol (99.9%, JT Baker, The Netherlands), *n*-propanol ($\geq 99.5\%$, Merck, Germany), *n*-butanol (99.5%, Merck, Germany), *n*-pentanol ($> 99\%$, Aldrich, Germany), *n*-hexanol (98%, Merck, Germany), *n*-heptanol (99%, Alpha Aesar, Germany), *n*-octanol (98%, Acros, U.S.A.) and benzyl alcohol (99%, Sigma, Germany) were used as received. Millipore water was used for preparing solutions.

A stock suspension of 70 mol % SDS + 30 mol % CTAB cationics in Millipore water was prepared keeping the total surfactant concentration at 1 wt %, and it was stirred to ensure homogeneous suspension. Five milliliters of the suspension was transferred to a series of preweighed screw-capped sample tubes, and the final weights were taken. To these suspensions different amounts of a particular alcohol were added, the final weights were taken, and the concentration of alcohol was calculated. The resultant mixtures were stirred for 5 min and then kept at about -40°C for complete freezing. After ~ 12 h the sample tubes were placed in a water bath, and the temperature was increased at $\sim 1^\circ/10$ min. The solubility temperatures of all suspensions, detected by visual observation, were noted with an accuracy of $\pm 0.1^\circ\text{C}$.

The DSC thermograms of 70 mol % SDS + 30 mol % CTAB cationics in the presence of 0.05 mol kg^{-1} *n*-alcohols and benzyl alcohol were recorded with a Micro DSC-III (Setaram, France). The solubility patterns of cationics at different compositions and in the presence of 0.5 mol kg^{-1} *n*-butanol were also recorded via DSC. About $500\ \mu\text{L}$ of the suspension was transferred in a preweighed cylindrical stainless steel cell, and the final weight was taken. The cell containing the suspension and the reference cell with water were cooled down to -10°C (at this temperature the suspension freezes) and were held for 2 h. The DSC thermograms were recorded through the instrument software at a heating rate of $1^\circ/\text{min}$ up to 70°C . The total concentration of surfactants was kept at 1 wt % (which is 0.022 mol kg^{-1} SDS and $0.0096\text{ mol kg}^{-1}$ CTAB corresponding to a 70:30 molar ratio) for our studies.

Results and Discussion

Solubility Behaviors. The solubility patterns of 70 mol % SDS + 30 mol % CTAB cationics in the presence of different concentrations of *n*-alcohols (C₂OH to C₈OH) and benzyl alcohol as a function of temperature are shown in Figure 1. For better observation, the inset in Figure 1 exhibits the variation of the

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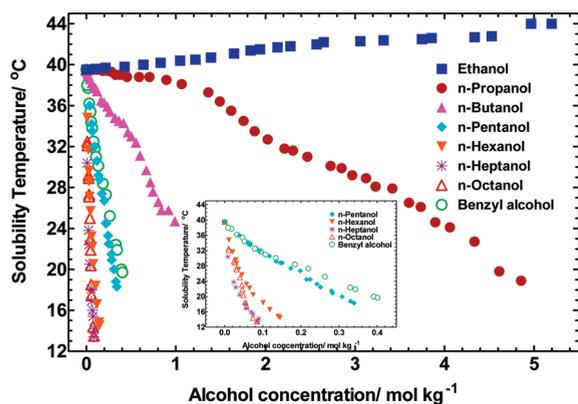


Figure 1. Solubility of 70 mol % SDS + 30 mol % CTAB as function of temperature at different concentrations of *n*-alcohols and benzyl alcohol. Inset: solubility of the same cationic surfactant pair in the presence of alcohols having chain length C_5 to C_8 . The total concentration of the surfactant pair was kept at 1 wt %. The experimental points correspond to the concentration and temperature, where a homogeneous and single phase was obtained. Below these limits, all systems separated into two phases.

solubility temperatures in the presence of higher alcohols ($\geq C_5OH$) on an extended scale. We can distinguish between two kinds of solubility patterns, and *n*-butanol roughly demarcates these patterns. For ethanol and *n*-propanol the solubility temperature of cationics remains quite constant up to $\sim 0.05 \text{ mol kg}^{-1}$; thereafter it increases for ethanol, whereas it decreases for *n*-propanol. On the contrary, for longer chain alcohols ($\geq C_4OH$) the solubility temperatures of cationics decrease significantly as a function of their concentrations.

In the case of ethanol, the solubility temperature of the cationics remains constant ($39.5 \pm 0.1 \text{ }^\circ\text{C}$) up to $\sim 0.1 \text{ mol kg}^{-1}$ and a blueish solution was observed. At very low concentration only fewer ethanol molecules enter the assemblies⁴⁵ because of higher solubility in water, and reside in the layer close to the surfactant's head groups.³¹ As a result, at low concentration of ethanol the packing parameter, P_c , remains in the range of 0.5–1.⁴⁶ As the concentration of ethanol increases, a linear increase in solubility temperature of the cationics and a disappearance of the blueish color was observed. The dielectric constant of water/ethanol mixtures decreases with increasing ethanol concentration⁴⁷ resulting in increase in solubility temperature of the cationics. It is noteworthy that the dielectric constant of the medium critically governs the size of vesicles/micelles.³⁵ A preliminary investigation showed that the size of the objects formed in cationics in the presence of ethanol increases up to a certain concentration (e.g., $\sim 0.15 \text{ mol kg}^{-1}$ ethanol), and then decreases. Parallel to the increase in ethanol concentration more ethanol molecules reside in the polar head group and the packing parameter becomes less than 0.5,⁴⁶ and consequently, the blueish color disappears and precipitation occurred after 24 h.

In contrast, *n*-propanol induces three solubility temperature regions: (i) up to $\sim 0.1 \text{ mol kg}^{-1}$ the solubility temperature of the cationics remains constant ($39.5 \pm 0.1 \text{ }^\circ\text{C}$) as in the case of ethanol, (ii) in between 0.1 and 1.4 mol kg^{-1} the solubility temperature decreases linearly, and (iii) beyond $\sim 1.4 \text{ mol kg}^{-1}$

the decrease of the solubility temperature is significant. However, the stability of the vesicles/micelles on increasing the chain length by one unit did not exceed 24 h at $25 \text{ }^\circ\text{C}$.

At low concentration of *n*-propanol (region-i), as discussed for ethanol, only a small fraction of *n*-propanol resides at the surfactant interface and the cationics form large objects because of optimum hydrophobic and electrostatic interactions resulting in a packing parameter higher than 0.5.⁴⁶ In regions-ii and iii, the trend of the solubility pattern indicates that the dielectric constant of the medium has little effect on the solubility temperature. With the increase in carbon chain length, alcohol molecules prefer to stay in the cationic micelle assemblies or bilayers rather than in the bulk water because of their solubility limits. In addition, there is a proper hydration of the headgroup of the surfactants, which also contribute to cationic micelles formation.⁴⁸

For *n*-alcohols of chain length ≥ 4 , the solubility temperature of the cationics decreases roughly linearly as a function of their concentration. *n*-Butanol decreased the solubility temperature of the cationics by $13.7 \text{ }^\circ\text{C}$ within its solubility limit ($\sim 1.1 \text{ mol kg}^{-1}$),⁴⁹ and the solutions remained blueish. The decrease of the dielectric constant has less effect on the packing parameter compared to shorter alkyl chain length because of the solubility limits. The stability of the large objects and micelles further increased up to 5 days.

n-Alcohols with chain lengths of C_5 to C_8 remarkably decrease the solubility temperature of the cationics. C_5OH - C_8OH , on entering the assemblies, increase the area of the headgroup and keep the packing parameter in the range of 0.5–1. Therefore, all solutions form large objects and are stable up to 30 days at ambient temperature.

These results clearly demonstrate that the solubilization of cationics depends on the chain length of *n*-alcohols. To examine such effects, we further studied the solubility temperature of cationics as a function of benzyl alcohol concentration and is similar to that of *n*-pentanol up to $\sim 1.3 \text{ mol kg}^{-1}$ and then diverges (Figure 1, inset). It can be concluded that alcohols with comparable chain lengths produce roughly similar effects on the solubilization of cationics.

To summarize the effect of the chain length, we show in Figure 2 the solubility temperature as a function of the chain lengths of the alcohols at 0.05 mol kg^{-1} . In addition a plot of the slope of solubility temperature versus SDS/(SDS + alcohol) (Supporting Information, Figure 1S) as a function of chain length of alcohols used is also shown in Figure 2, which clearly demonstrates that the short ($C_{2-3}OH$), intermediate ($C_{4-6}OH$), and long ($\geq C_7OH$) chain alcohols exhibit different effects on the solubility curve of the cationics with onset of depression of the solubility temperature at $\sim 0.05 \text{ mol kg}^{-1}$ *n*-butanol. Note that the effect of chain lengths of *n*-alcohols correlates with the transition temperature of the membranes of liposomes.^{50,51}

The solubility behaviors of cationics at three different compositions as a function of *n*-butanol concentration are discussed in the Supporting Information and illustrated in the Supporting Information, Figure 2S.

Differential Scanning Calorimetry. The DSC thermogram patterns of 1 wt % CTAB and of 1 wt % SDS are illustrated in the Supporting Information, Figure 3S. The DSC curves of different

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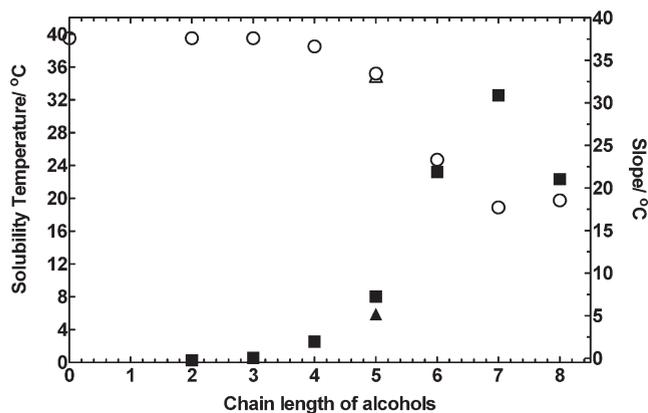


Figure 2. Effect of chain length of *n*-alcohols on the solubility temperature of 70 mol % SDS + 30 mol % CTAB in aqueous solutions with 1 wt % total surfactant concentration at a fixed concentration (0.05 mol kg^{-1}) of alcohols. The plot of the slope of solubility temperature versus SDS/(SDS + alcohol), Supporting Information, Figure 1S, as function of chain length of alcohols is also shown. Open symbols represent the solubility temperature and the closed symbols represent the slope, and the open and closed triangle represents benzyl alcohol. The data points are taken from Figure 1.

molar ratios of SDS + CTAB and SDod + CTAB catanionics are shown in Figure 3. DSC patterns of 70 mol % SDS + 30 mol % CTAB catanionics with different alcohols at a fixed concentration of 0.05 mol kg^{-1} [SDS/(SDS + alcohol) = 0.31] and the SDS + CTAB catanionics at three compositions and with 0.5 mol kg^{-1} *n*-butanol are shown in Supporting Information, Figures 4S and 5S, respectively. The corresponding enthalpy and entropy of solubilization steps are given in Supporting Information, Table 1S.

The DSC thermogram of 1 wt % SDS (Supporting Information, Figure 3S) indicates that the solubility of SDS in water takes place in multiple steps with three distinct endothermic peaks. In contrast, the solubility of 1 wt % of CTAB occurs in a single step. The trends of DSC thermograms are not surprising and are in accordance with surfactants having sulfate and tetraalkylammonium head groups.^{52,53} The multiple endothermic peaks are due to the presence of mesophases in aqueous SDS solutions. The small endothermic peak at around $\sim 14^\circ\text{C}$ (below the complete solubilization) indicates presolubility or pretransition chain rotation.⁵⁴ It could also be due to a certain chain melting of the molecules in the interfacial film. On the contrary, the solubility of 1 wt % CTAB is completed in a single step. Nevertheless, the total enthalpy of solubilization for both systems is very low (390.4 and 512.7 J/mol) in comparison to few kJ/mol for melting of solid single chain surfactant pair.^{55,56}

The DSC thermograms of catanionics at different compositions (Figure 3) exhibit a complex pattern and are not simply superpositions of the individual solubilization patterns. In the CTAB rich region (30 mol % SDS + 70 mol % CTAB), the catanionics produce one major endothermic peak with $\Delta H = 154.1 \text{ J/mol}$ and a minor endothermic peak ($\Delta H = 35.4 \text{ J/mol}$). The major peak at 32.5°C corresponds to the primary solubilization

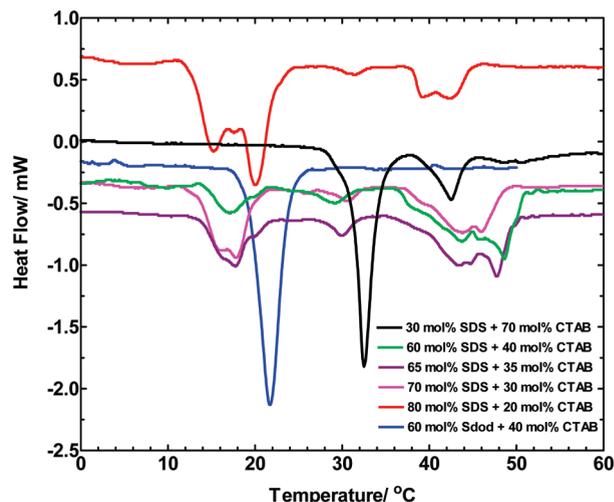


Figure 3. DSC thermograms of SDS + CTAB and SDod + CTAB catanionics at different compositions. Total concentration of the surfactant pair was kept at 1 wt %.

of the catanionic pair and is in good agreement with the reported solubility phase diagram.^{7,20} Therefore, the second endothermic minor peak might correspond to a transition to an isotropic phase.

The thermograms of the catanionics in the SDS rich region (SDS = 60, 65, 70, and 80 mol %) exhibit a multistep solubilization process as well indicating the existence of a number of polymorphs. The patterns of thermograms of catanionics in question follow the similar multiple endothermic peaks for different asymmetric catanionic surfactants pairs.^{56,57} The first and last endotherms at ~ 18 and $\sim 45^\circ\text{C}$, respectively, are a doublet followed by a weak singlet at $\sim 30^\circ\text{C}$. Taking the endotherm of (30 mol % SDS + 70 mol % CTAB) catanionics as the base value, the endotherms become very complex with progressively increasing SDS amounts. The endotherms at $\sim 45^\circ\text{C}$, which correspond to the final solubilization and/or transition to an isotropic phase of catanionics, are broad. We conclude that the sulfate head group is primarily responsible for such complex thermograms. The first minor peaks with small ΔH ($25\text{--}94 \text{ J/mol}$) are due to the beginning of the solubilization process or pre-transition chain rotation.⁵⁴ The DSC thermograms reveal that the solubilization of the catanionics begins at $\sim 12^\circ\text{C}$ and ends at $\sim 50^\circ\text{C}$ with multiple endotherms because of different interactions of different magnitudes resulting in a multistep solubilization.

To justify our views on the effect of the sulfate headgroup on the multiple solubilization pattern, DSC thermogram of 60 mol % SDod + 40 mol % CTAB catanionics is shown in Figure 3 to compare with 60 mol % SDS + 40 mol % CTAB. Note that SDod and SDS have roughly equal chain length but with carboxylate and sulfate headgroups, respectively. It is interesting to note that 60 mol % SDod + 40 mol % CTAB produces a single and sharp endothermic peak with $\Delta H = 0.85 \text{ J/g}$ ($\sim 0.24 \text{ kJ/mol}$), which is less than the total enthalpy ($\Delta H = 0.60 \text{ kJ/mol}$) for 60 mol % SDS + 40 mol % CTAB catanionics. Therefore, the thermogram of 60 mol % SDod + 40 mol % CTAB catanionics indicates that the multisteps solubility patterns are primarily governed by the presence of the sulfate head group. Note that in a recent paper, it was argued that both sulfate and trimethylammonium headgroups are soft and should strongly interact, whereas carboxylate is a hard headgroup, which should interact

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much less with the positively charged headgroup,⁵⁸ and the complex nature of the DSC thermograms of the present catanionics is due to these reasons.

In this context, it is interesting to check if a fundamental difference between SDS and SDod is readily detectable from the area per molecule in the pure anionic solutions, as inferred from the change of surface tension with concentration below the cmc. We calculated the area per molecule for both the anionic surfactants using the reported surface tension at 25 °C^{59,60} and was found to be 49 Å² for both SDS and SDod. Values are in reasonable agreement with closely packed films. No hint of a special melting of SDod chains can be detected. As a consequence, the very different calorimetric patterns for SDS/CTAB and SDS/SDod catanionics must come from the different headgroup interactions and not from the anionic surfactant itself.

The solubility patterns of catanionics and in the presence of different alcohols at 0.05 mol kg⁻¹ are shown in Supporting Information, Figure 4S. Alcohols with chain length ≥ 4 significantly alter the pattern of the endothermic peaks, and the transition temperatures are shifted to lower temperatures, as expected from Figure 2. A small endothermic peak at the beginning for all alcohols indicates the presolubilization process. The major and broad endotherm pattern in the presence of ethanol and *n*-propanol indicates that the final solubilization is comparable to catanionics without alcohol. Moreover, the transition temperature of catanionics at ~ 43 °C is not shifted by 0.05 mol kg⁻¹ of either ethanol or *n*-propanol. The DSC thermograms, therefore, indicate that ethanol and *n*-propanol at 0.05 mol kg⁻¹ do not influence the solubilization process of 70 mol % SDS + 30 mol % CTAB catanionics, in agreement with the results shown in Figure 2. The transition temperature shifting to lower temperature is noticed for C₄OH–C₇OH. In contrast, the transition temperature for *n*-octanol is slightly higher with respect to *n*-heptanol. The DSC thermograms also demonstrate the leveling-off for alcohols in solubilization of catanionics as observed in Figure 2. Another interesting point to note is that the thermograms of 70 mol % SDS + 30 mol % CTAB catanionics in the presence of *n*-pentanol and benzyl alcohol at 0.05 mol kg⁻¹ are roughly equivalent, with transition temperatures at ~ 37 °C. It seems as if the chain lengths and not the detailed structure of the alcohols are the main features determining both the transition temperature and the solubility patterns (Figure 1) of the catanionics.

The solubility patterns of SDS + CTAB catanionics at different compositions as functions of *n*-butanol concentration demonstrated that the systems at ~ 0.5 mol kg⁻¹ *n*-butanol have equivalent solubility temperatures (Supporting Information, Figure 2S), which can be related to similar microstructures. In that case, the enthalpy of SDS + CTAB catanionics at all compositions and 0.5 mol kg⁻¹ *n*-butanol would roughly be equivalent and is discussed in the Supporting Information taking Figure 5S as a reference.

Comparison of the Solubility Results to Studies of the General Anesthesia of Tadpoles. Figure 4 provides information concerning the concentration of alcohols needed to anesthetize whole tadpoles.^{61,62} A comparison of Figures 2 and 4 indicates the similar trend between the two reported phenomena in regard to the activity and concentration of the *n*-alcohols. To our

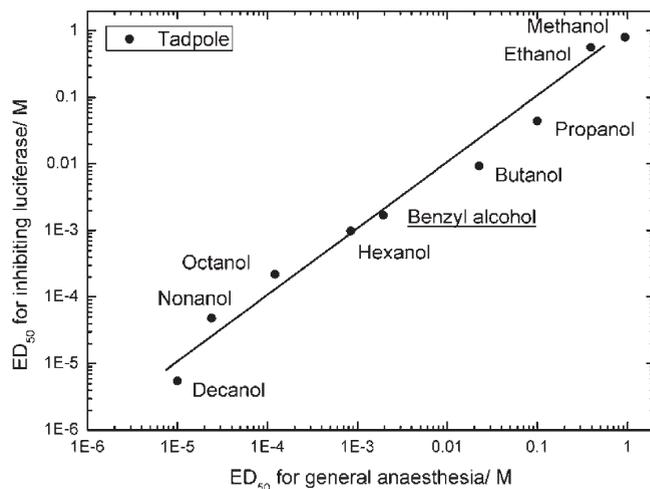


Figure 4. Comparison of general anesthetic concentrations needed to anesthetize whole tadpoles and to inhibit firefly luciferase activity by 50%, for a diverse range of simple anesthetics over a 100,000-fold range of aqueous potencies. The data⁶² are plotted as potencies, defined as reciprocals of aqueous ED₅₀ molar concentrations. ED₅₀ is the aqueous concentration of a given anesthetic agent required to anesthetize 50% of tadpoles. The figure is reproduced with permission from the publisher.

surprise, the position of the benzyl alcohol in Figure 4 coincides with the place where *n*-pentanol is expected (not reported by the authors). Benzyl alcohol and *n*-pentanol also occupy the same position in Figure 2, which further justifies our view that alcohols of comparable chain length exhibit equivalent solubility temperature of the catanionics. To some extent, the present study of the solubility of catanionics by alcohols seems to reflect the so-called anesthetic properties of a series of alcohols.

There is much speculation about possible reasons for the anesthetic action of alcohols.^{44,61,62} Two pathways of action are generally proposed: One is in relation with lipids and the other with membrane proteins. The first pathway of action is described by the so-called Meyer–Overton model. Another explanation for the anesthetic action is that there is a change in curvature of the bilayer that prevents the propagation of the nerve signal.⁴³ Anyway, the correlation between our findings and those described by this model is remarkable. What seems to be clear is that the alcohols are incorporated in lipid membranes and alter their melting points, flexibility, and curvature. For a significant efficiency, the alcohol must be long enough to be incorporated in the hydrophobic parts of the biological membranes. This is the reason why short-chain alcohols are not efficient. Long-chain alcohols can enter into hydrophobic parts of the membranes that contain both cationic and anionic headgroups and can disrupt the strong headgroup pairs, which results in a destabilization (or melting or solubilization or curvature) of the membrane structure. Therefore, we feel that catanionic mixtures could be a good model system to examine some aspects of anesthesia. Of course, the model is very crude, and in our model system a leveling-off is discovered with alcohols having a chain length greater than seven. However, this could be also due to the very small solubility of the long-chain alcohols so that the error bars are high.

Conclusions

The solubility and DSC studies are valuable techniques to investigate the influence of *n*-alcohols of different chain lengths on the catanionics. Ethanol is not inserted into the catanionic film, and the dielectric constant of the medium enhances the solubility

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temperature of the mixtures. *n*-Alcohols with carbon chain lengths in the range $4 \leq C \leq 8$ significantly depress the solubility temperature of the cationics. The general trend of *n*-alcohols and of benzyl alcohol on the depression of solubility temperature of 70 mol % SDS + 30 mol % CTAB cationic is as follows: *n*-octanol \approx *n*-heptanol > *n*-hexanol > *n*-pentanol \approx benzyl alcohol > *n*-butanol > *n*-propanol > ethanol. The DSC thermograms of individual aqueous SDS and CTAB (1 wt %) suggest that the solubility of SDS follows a multistep process. On the contrary, it is single step for CTAB. Therefore, the presence of the sulfate headgroup in SDS is primarily responsible for the multisteps solubility of the SDS + CTAB cationic, which is probed by replacing the sulfate headgroup in SDS + CTAB cationic. The general trend of the solubility temperature depression by alcohols is in line with their anesthesia properties.^{61,62} The reason is that certainly the incorporation into the cationic model systems studied here and the biological membranes studied in the context

of anesthesia follow the Meyer–Overton observation. As the model is very crude, all the possible biological action pathways of long-chain alcohol are not reproduced, and particularly the possibility of a particular activity on defined proteins is not captured.

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Supporting Information Available: Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.