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SHORT COMMUNICATION

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The effect of *n*-butyl glycol ethers on the phase diagrams of microemulsions formulated with nonionic surfactants

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Abstract The effect of *n*-butyl glycol ethers used as cosurfactants on the microemulsions formulated with two nonionic surfactants, hexaoxyethylene glycol monolauryl ether and sorbitan monolaurate, is presented on ternary phase diagrams. The solubilization parameters as well as isothermal invariant points (IIP) of microemulsions were correlated with the solubility parameters of cosurfactants. An optimum solubility parameter of cosurfactants was established around 9 $(\mathrm{cal/cm^3})^{1/2}$ where both IIP and solubilization parameters are optimal for water and oil solubilization with the lowest concentration of amphiphilic compounds. The mixture of cosurfactants can be used to obtain a certain transition on the phase diagram and so to achieve certain characteristics for microemulsions, especially to tailor the solvency of the system.

Key words Microemulsions – cosurfactants – solvency – solubility parameter – solubilization

Microemulsions are amorphous, isotropic solutions containing considerable quantities of water and oil and amphiphilic compounds as surfactants and cosurfactants. They are thermodynamically stable systems in contrast with emulsions that are thermodynamically unstable. Microemulsions are often called "solubilized micellar solutions" or "swollen micellar solutions" [1]. The term "microemulsions" was introduced first in 1959 by Schulman [2] to describe the transparent or translucent systems obtained by titration of an ordinary emulsion with medium chain alcohols until clarification is reached. Alcohols and similar materials were later named cosurfactants or "cosolvents", and they are used in combination with the primary surfactants in microemulsion formulation [3].

The most fundamental role of the alcohols is their ability to destroy liquid–crystalline and/or gel structure of surfactants which disturbs the formation of microemulsions.

The phase behavior of microemulsions is characterized by the existence of many phases in equilibrium, each having a particular structure. Usually, the microemulsions are defined according to Winsor's [4] classification as complex systems where micellar phases are in equilibrium with excess oil, water or both. A Winsor I type system consists in a lower-phase microemulsion and excess oil; a Winsor II type system consists in an upper-phase microemulsion and excess water. If the microemulsion is in equilibrium with both water and oil in excess, this is called Winsor III type, the microemulsion's phase has an intermediate density, and it is located in the middle in a test tube. For that reason it is called "middle phase". It is rich both in water and oil. When the middle phase is extended and encompasses the whole system, one speaks of a Winsor IV microemulsion.

The microstructure of type I may be visualized as direct swollen micelles containing solubilized oil surrounded by Water (S1) while the type II is inverse micelles containing solubilized water surrounded by Oil (S2). A type III system can be considered as a mixture of S1 and S2 structures, or as Scriven [5] has proposed – a bicontinuous structure when both the aqueous region and oil region are continuous.

Many factors including temperature, salinity, nature of oil, surfactants, and cosurfactants determine the type of the system as well as the transitions that can take place from one system to another [6–8].

One simple way to control the nature of microemulsion systems formed and to promote a certain transition is by using cosurfactants, typically medium-chain alcohols [9]. They are included in the interfacial layer C as well as in the bulk phases depending on their solubility. The phase changes promoted by adding alcohols are dependent on their amphipilic character (chain length). Alcohols containing more than four carbon atoms will increase the interaction of the C layer with oil-promoting type II systems, while adding lower-chain alcohols promotes type I systems.

The simplest way to present the phase equilibria in microemulsions systems containing three or more components is by using ternary diagrams. When both a surfactant (*S*) and cosurfactant (*A*) are present in the system, the diagram will be a pseudoternary one. Keeping the surfactant/cosurfactant ratio constant, they can be thought of as a pseudocomponent.

Any system whose overall composition falls within the two-phase regions will coexist as two conjugate phases whose compositions are represented by the ends of the tie lines, one rich in amphiphilic compounds and the other very poor. The minimum concentration of the amphiphilic compounds ($S + A$) that form a three-phase system is very important for describing the effectiveness of microemulsion formation and is called isothermal, invariant point (IIP).

In the present contribution, the effect of cosurfactants of the type *n*-butyl glycol ethers on the phase diagrams of microemulsion formulated with two nonionic surfactants is investigated. Generally, the role of medium-chain alcohols on microemulsions is very well documented [10, 11].

The influence of changing the hydrophilic part of cosurfactants, keeping constant the hydrophobic part, has attracted less theoretical attention. The use of *n*-butyl glycol ethers as cosurfactants in microemulsion formulation is encouraged by their environmental soundness and low VOC.

Materials and methods

The compounds used in the microemulsion formulation are given in Table 1.

One of the two surfactants used in relatively hydrophilic, L_{12-6}, and the other, SML, is more hydrophobic. Only a single surfactant from the two does not insure the formation of a microemulsion domain. It is known that a single balanced nonionic surfactant can be effective in microemulsion formation, but two surfactants are generally more efficient in lowering interfacial tension.

The glycol ethers used as cosurfactants are listed in Table 2.

The phase diagrams were obtained by dissolving amphiphilic compounds ($S + A$) in oil followed by a slow titration with water at 25 °C until the system became turbid as a result of reaching the two- or three-phase regions (in such titration $C_{S+A}/C_O = ct$). For some systems, the equilibrium values of phase volumes were obtained.

Table 1 The components of microemulsions investigated

Quality	Component	Symbol	HLB	Density g/ml
Surfactant 1	Sorbitan monolaurate	SML	8.0	1.056
Surfactant 2	Hexaoxyethylene monolauryl ether	L_{12-6}	12.4	0.987
Cosurfactants	Oxyethylene- and oxypropylene-monobutyl ethers	C_4EO_m C_4PO_m		
Oil	Medium mineral oil $C_{12}H_{26}$ 95%	OMS	7.4	0.755

Table 2 The cosurfactants used in microemulsions' formulation

Cosurfactant	Formula	Symbol	Solubility parameter $(cal/cm^3)^{1/2}$	Water solubi. g/100 g
n-Butyl alcohol	C_4H_9–OH	C_4OH	11.3	7.37
Diethylene glycol *n*-butyl ether	$C_4H_9(OCH_2CH_2)_2OH$	C_4EO_2	9.5	
Propylene glycol mono *n*-butyl ether	$C_4H_9(OCH_2CHCH_3)OH$	C_4PO_1	8.9	6.40
Dipropylene glycol mono *n*-butyl ether	$C_4H_9(OCH_2CHCH_3)_2OH$	C_4PO_2	8.2	5.0
Tripropylene glycol mono *n*-butyl ether	$C_4H_9(OCH_2CHCH_3)_3OH$	C_4PO_3	8.6	3.0

Results

Part of the phase diagrams of the systems formulated with two surfactants are presented in Fig. 1. One can point out the presence of two domains where the systems are homogeneous-monophasic, separated by a nonhomogeneous, turbid region that could consist of a macroemulsion, various liquid–crystalline phases or gel structures. It is very likely that the first homogeneous domain located at higher amphiphilic concentrations consists of an inverse micellar solution with solubilized water.

In the second monophasic domain, located at much lower surfactant concentrations, the microemulsions contain high quantities of both water and oil and are very extended, from oil corner to water corner. It is very likely that these microemulsions are structurally not identical throughout. Also, it should be pointed out that there is not a well-defined IIP.

The addition of *n*-butyl alcohol to the previous system caused obvious changes in the pseudoternary phase diagram (Fig. 2). First of all, the macroemulsions and liquid–crystalline phases at higher amphiphilic concentrations disappear and a well-defined IIP appears on the coexistence curves. The addition of a more hydrophilic C_4EO_2 (Fig. 3) causes a II-III-I transition comparative to C_4OH for all *A*/*S* ratios. In the same manner, a less hydrophilic C_4PO_2 (Fig. 4) changes the phase diagram, but much less pronouncedly.

A mixture (1:1) of C_4EO_2 and C_4PO_1 has a behavior closer to C_4EO_2 than the previous mixture. From the above data, one can see that by adding glycol ethers it is possible to alter the phase diagrams over a very broad range and to induce phase change.

The effect of various glycol ethers used as cosurfactants on the pseudoternary phase diagrams can be explained qualitatively using the *R*-theory of Winsor [4].

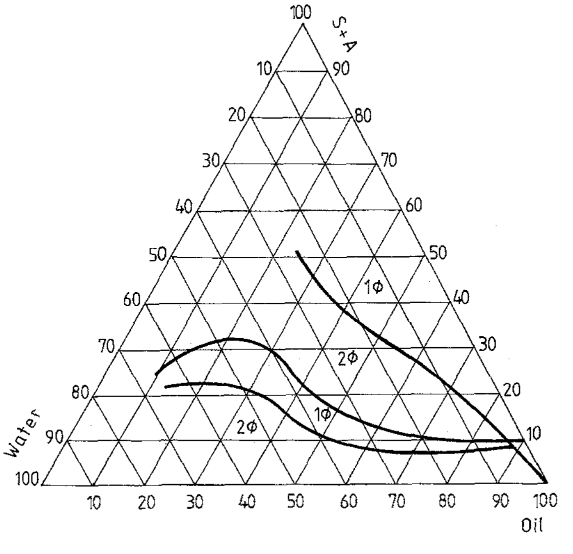

Fig. 1 Ternary phase diagrams of microemulsions formulated with SML + L_{12-6} (1:1 by weight)

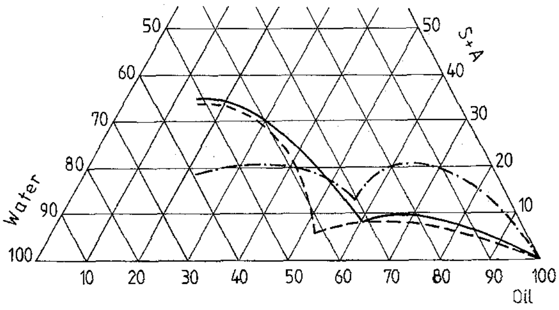

Fig. 2 Pseudo-ternary phase diagrams of microemulsions formulated with SML + L_{12-6} (1:1) and C_4OH as cosurfactant —— *A*/*S* = 0.62 molar ratio (0.114 by weight); — — *A*/*S* = 1.00 (0.18); -●- *A*/*S* = 1.44 (0.265)

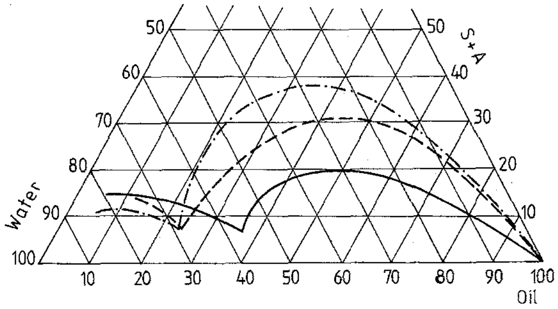

Fig. 3 Pseudo-ternary phase diagrams of microemulsions containing SML + L_{12-6} (1:1) and C_4EO_2 as cosurfactant: —— *A*/*S* = 0.62 (0.248); — — *A*/*S* = 1.00 (0.40); -●- *A*/*S* = 1.44 (0.55)

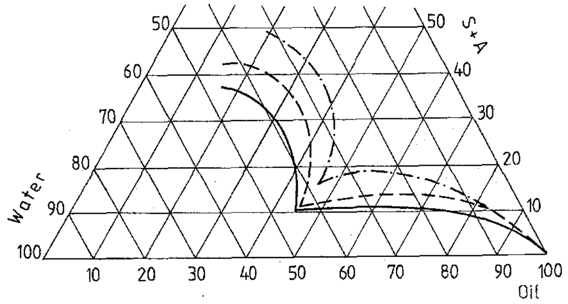

Fig. 4 Pseudo-ternary phase diagram of microemulsions containing SML + L_{12-6} (1:1) and C_4PO_2 as cosurfactant: —— *A*/*S* = 0.62 (0.29); — — *A*/*S* = 1.00 (0.47); -●- *A*/*S* = 1.44

As discussed by Bourrel and Schechter [7], the R-ratio becomes:

$$R = \frac{a^{S}_{co} - (a^{S}_{co} - a^{A}_{co})x_{A}}{a^{S}_{cw} - (a^{S}_{cw} - a^{A}_{cw})x_{A}}, \qquad (1)$$

where: a^{S}_{co} and a^{S}_{cw} are the molecular interaction energies of the surfactant in the C layer with the bulk oil and water respectively, and a^{A}_{co} and a^{A}_{cw} – the molecular interaction energies of cosurfactants (alcohols), x_A-fraction of cosurfactant in the C layer.

For a certain surfactant a^{S}_{co} and a^{S}_{cw} should be constant and also $a^{S}_{co} > a^{A}_{co}$; $a^{S}_{cw} > a^{A}_{cw}$.

For an n-alcohol series a^{A}_{cw} must be constant so that an increase in a^{A}_{co} will lead to an increase in the R ratio if $a^{A}_{co} > a^{A}_{cw}$. This way, a I-III-II transition is promoted. If $a^{A}_{co} < a^{A}_{cw}$ a II-III-I transition is promoted. Both types of transitions were observed [8]. It was proved that butanol is located in the neutral zone [9] and also does not require a change in ethylene oxide content of surfactant to maintain the optimal conditions for a system by adding this alcohol.

In the case of butyl glycol ethers, a^{A}_{co} = constant, and the effect should be determined by a^{A}_{cw}.

Adding C_4EO_2, a more hydrophilic compound than butanol, a II-III-I transition is observed (Fig. 3) which is in accord with R-theory. For C_4PO_2, it is very likely that a^{A}_{cw} will be smaller than for C_4EO_2 and the net result is a behavior closer to butanol (Fig. 2). The behavior of 1 : 1 mixture by weight of C_4EO_2 and C_4PO_2 is closer to C_4EO_2-pseudoternary diagram (Fig. 3).

Optimum compositions and the solubility parameter of cosurfactants

In order to use R-theory to explain the phase changes caused by glycol ethers it is necessary to know the partition of the cosurfactants between the C layer and the two bulk phases, oil and water. The changes in the interactions of the C layer with water and oil by adding alcohols of more complex structures such as glycol ethers are difficult to explain even qualitatively. For this reason, the solubility parameters of glycol ethers used as cosurfactants were chosen to describe the phase behavior of microemulsions. The solubility parameter, δ, [12] is a measure of all types of physical interactions in a monocomponent condensed phase, it should also reflect the way a cosurfactant interacts within the C layer.

One of the most important characteristics of a microemulsion is the optimal composition defined by the concentration of amphiphilic compounds where equal volumes of water and oil are solubilized in a Winsor III or Winsor IV system.

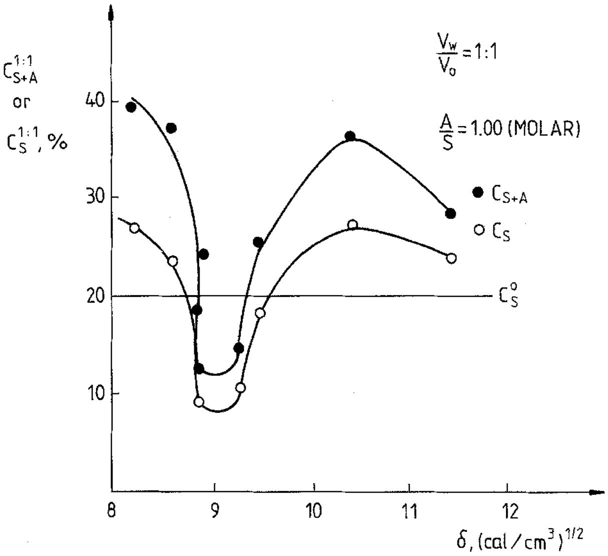

Fig. 5 The dependence of the minimum amphiphile concentration that forms a monophasic Winsor IV system for water/oil = 1 and A/S = 1.00

Figure 5 shows the correlation between concentration of the amphiphilic compounds for equal volumes of water and oil solubilized vs. the solubility parameter of cosurfactants, δ.

It is evident that an optimal solubility parameter exists around δ = 9.00 for the molar ratio A/S = 1.00. Around this value, both C_{S+A} and C_S are located under the value of C^{O}_{S} = 20% specific for the system without cosurfactants. This effect is in contradiction with the general trend of alcohol behavior which determines a decrease in solvency of surfactants.

The dependence of IIP on the solubility parameter of cosurfactants passes through a minimum almost at the same δ (Fig. 6) practically for all A/S ratios investigated.

The fact that IIP's are independent of A/S ratios is an indication of some specific interactions that are saturated at lower concentration of cosurfactants than those investigated.

While IIP is reached for various water/oil ratios, a more adequate parameter to characterize the specific behavior of cosurfactants is the solubilization parameter defined as the ratio of water or oil solubilized by the unit volume of surfactant:

$$SP_W = V_W/V_S \quad \text{and} \quad SP_O = V_O/V_S\,. \qquad (2)$$

The solubilization parameters for an optimal system, when equal volumes of water and oil are solubilized ($SP^{1:1}_{O} = SP^{1:1}_{W}$) are presented vs. solubility parameters of cosurfactants δ, in Fig. 7. There is evidence of a strong maximum in the curves located in the same range of the

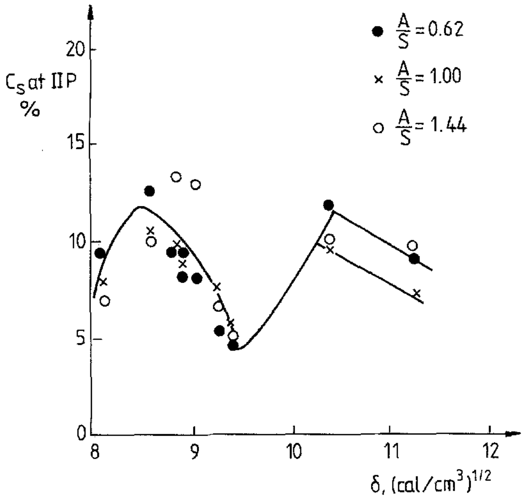

Fig. 6 The isothermal, invariant point (IIP) vs. solubility parameter of cosurfactants

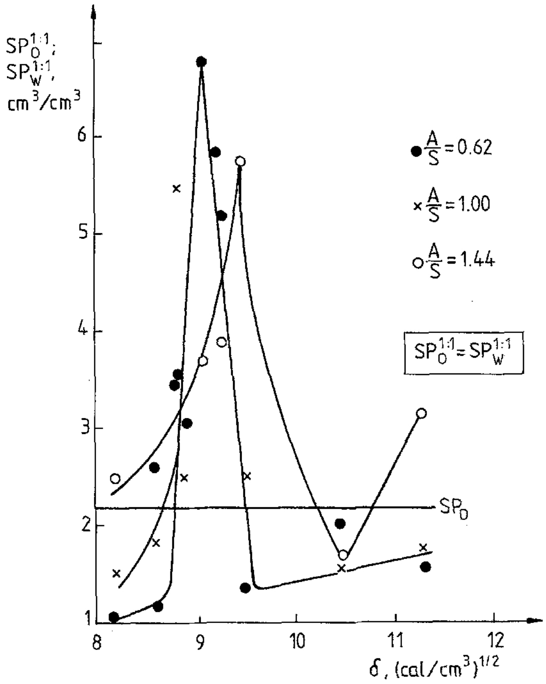

Fig. 7 The correlation of solubilization parameter at equal volumes of water and oil with the solubility parameter of cosurfactants

solubility parameter of cosurfactants as on IIP vs. δ curves or $C_S^{1:1}$ vs. δ curves. The values of $SP_O^{1:1}$ around the maximum are located above SP_O^S (solubilization parameter without cosurfactant) but the solubilization parameters of the systems far from the optimal fall under SP_O^S. From this, one can conclude that there is an optimal solubility parameter of cosurfactant for this system of surfactants. It is very likely that this optimal solubility parameter could be correlated with the HLB of the surfactant used in formulation. More data are necessary in order to extend this concept.

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