

Retrograde transition in the phase behaviour of surfactant–oil–water systems produced by an oil equivalent alkane carbon number scan

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Abstract

The phase behaviour of surfactant–oil–water systems is affected by the so-called formulation variables, i.e. by the nature of the components or their physicochemical characteristics. One of the formulation variables is the nature of the oil, often rendered through the alkane carbon number (ACN), or the equivalent alkane carbon number (EACN) when the oil phase is not an alkane. In most cases the decrease in the oil ACN contributes to the increase in the interfacial interaction between the surfactant and the oil, which results in a WI→WIII→WII transition, similar to that observed when the water salinity is increased. However, in some cases the Winsor II phase behaviour is never reached with the EACN decrease, and a WI→WIII→WI so-called retrograde transition is exhibited instead. Such an anomalous case is analysed here for a system containing a commercial non-ionic polyethoxylated surfactant, a mixture of *n*-heptane (ACN 7) and benzene (EACN 0), and water. The high performance liquid chromatography analysis of the different phases indicates that the surfactant oligomer partitioning between phases is affected by the alkane–benzene mixture. The retrograde transition due to the increase in benzene is shown to arise from the strong increase in the partitioning of lipophilic and balanced oligomers into the more aromatic oil phase, with the remaining surfactant, in particular the interfacial mixture, becoming more hydrophilic. A phase diagram bidimensional (EACN–water-to-oil ratio) mapping indicates that this phenomenon occurs in very limited situations.

Keywords: Aromatic oil; Microemulsion; Phase behaviour; Surfactant

1. Introduction

The phase behaviour of surfactant–oil–water systems is known to be affected by the so-called formulation variables that describe the nature of the component and/or its contribution to the balance of interactions at interface. The most comprehensive approach was proposed by Winsor [1] more than 40 years ago, and has been used extensively [2] to explain qualitatively the effect of the formulation variable on the phase behaviour. The

Winsor ratio R of molecular interaction (both polar and London) energies per unit interfacial area can be defined as:

$$R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}}$$

where the subscripts C, O, W, H, and L respectively represent the surfactant, oil and water molecules, and the hydrophobic and lipophilic parts of the surfactant molecule. Thus A_{CO} is the interaction

of the surfactant with the oil, A_{OO} the interaction between two oil molecules, A_{LL} the interaction between the hydrophobic groups of two surfactant molecules, and so forth.

When the nature of the oil is changed both A_{CO} and A_{OO} terms are affected. If the oil is an alkane, its nature is rendered by its alkane carbon number (ACN) [2]. When ACN is increased the effects can be approximated as [3] a linear variation in A_{CO} and a quadratic variation in A_{OO} . As a consequence A_{OO} increases in most cases more rapidly than A_{CO} and the R ratio decreases, with the associated WI→WIII→WII transition in the phase behaviour. This is corroborated by experimental results and semiempirical correlations for the attainment of three-phase behaviour at the so-called optimum formulation [2,4,5] at which $R=1$.

2. Equivalent alkane carbon number (oil nature) formulation scan

When the oil phase is not an alkane, the ACN of the equivalent alkane, that is the alkane that exhibits the optimum formulation in the same physicochemical environment, so-called equivalent ACN (EACN), is used instead [2,6]. EACN is a measurement of both the oil bulk and its eventual polarity. For instance, for cyclohexane the EACN is 3, for benzene the EACN is 0, for alkylbenzenes the EACN is equal to the number of carbon atoms in the alkyl groups, for ethyl oleate the EACN is 6, and for soya oil the EACN is 18, a clear indication of the polarity of these last oils [7]. When two oils are mixed the EACN of the mixture is calculated from a linear mixing on a molar fraction basis [7]. Thus by mixing oils of different EACNs a formulation scan is produced. According to the Winsor approach and to most experimental data, the decrease in EACN is associated with the WI→WIII→WII transition in the phase behaviour, as with any change of formulation that results in a greater interaction between the surfactant and the oil phase.

3. Retrograde transition and surfactant fractionation

However, an exception to this rule was recently [8] reported when a lipophilic alcohol (*n*-pentanol) was added in order to increase the interaction between the surfactant (commercial ethoxylated alkylphenol) and the oil phase (alkane); instead of the normally expected WI→WIII→WII transition, an abnormal so-called retrograde transition of the WI→WIII→WI type was exhibited in some special cases. This occurrence was linked with the existence of two opposite effects: on the one hand the normal increase in interactions between the amphiphilic mixture (surfactant+pentanol) and the oil phase, which drives the WI→WIII→WII transition, and on the other hand the increase in the oil phase in alcohol content, which makes the oil become more and more polar. Since the polarity is associated with a lower EACN, the second effect could be thought to be equivalent to an EACN decrease and as such it would also favour a WIII→WII transition after the optimum formulation is passed. However, the experimental phase behaviour data reveal the opposite to occur, that is the WIII→WI transition trend. The analysis of the physicochemical situation indicates that the effect is probably due to the fractionation of more and more of the surfactant species into the oil phase, a phenomenon that strips the interface of the more lipophilic and balanced species to leave only the most hydrophilic species.

The fractionation of surfactant mixtures has been found to produce very significant effects whenever the mixture contains surfactant species with widely different HLB characteristics, as in commercial non-ionic surfactants that contain oligomers with extremely variable degree of ethoxylation (EON). The fractionation of ethoxylated octylphenols between water and iso-octane was successfully modelled [9] a few years ago. Very recently a large amount of data have been available to extend the model to many other systems [10,11], thanks to the development of enhanced analysis techniques [12].

The present paper is aimed at showing that the retrograde transition is not a very extraordinary effect linked to the alcohol presence, but that it

can be attained whenever the change in the nature of the oil nature results in a large variation in the surfactant partitioning.

4. Materials and experimental procedures

This report deals with systems containing commercial ethoxylated nonylphenol mixtures, distilled water and an oil phase which is a variable mixture of *n*-heptane and benzene, respectively HPLC and pro analysis grade from Baker. The ethoxylated nonylphenol surfactant, sold as MAKON 6 by Stepan Chemicals, referred to as NP6, has an average number of ethylene oxide groups per molecule, so-called EON. All studied systems contain 1.5 wt.% surfactant and, for the analysed scan, a water-to-oil ratio (WOR) equal to 40:60. The heptane–benzene oil mixture composition is scanned and its EACN is calculated on a molar fraction basis.

The systems are left to equilibrate in graduated vials for two weeks at constant temperature (25°C), with a gentle stirring from time to time during the first 48 h. The phase behaviour transition is visually observed, and the excess oil and water phases of all three-phase systems are analysed by high performance liquid chromatography according to a technique reported elsewhere [11,12]. These data allow the computation of the distribution of the EON of oligomers in both excess phases; this lead to the estimation of the partition coefficient between the water and oil phases, as a function of the oil mixture composition.

5. Phase behaviour and retrograde transition

Since the WOR is known to affect the oligomer fractionation to some extent [9], a bidimensional formulation–WOR phase behaviour diagram is constructed. The formulation variable is here the oil mixture composition referred to as EACN or as percentage by volume of benzene.

Fig. 1 indicates the phase diagram on a bidimensional EACN–WOR map. The lower right part of this diagram is perfectly normal; as the benzene

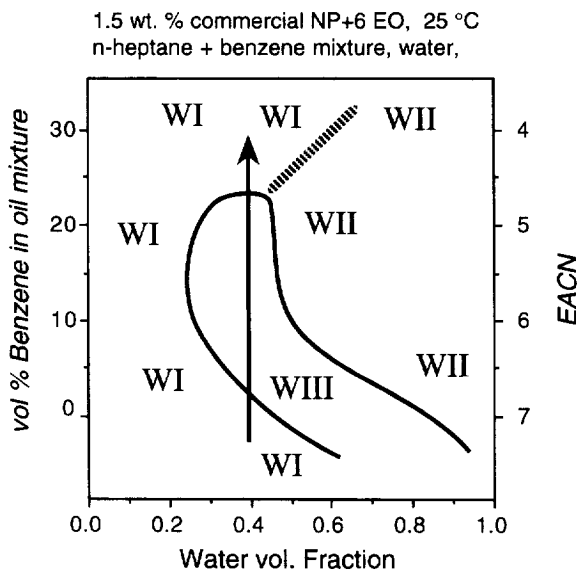


Fig. 1. Phase behaviour on a bidimensional scan.

content increases (from bottom to top), the EACN decreases and a WI→WIII→WII transition occurs. The abnormal feature is that the three-phase behaviour band does not cross over the whole diagram but vanishes at 25% benzene and 40% water. Above this vanishing frontier, the phase behaviour is WI in contrast to the WII type which is expected when the EACN is lower than the value at optimum formulation. Actually the limit between the WI and WII phase behaviour is the slanted broken line in Fig. 1. Such an abnormality was mentioned some time ago [13] but with no explanation.

Fig. 2 indicates the characteristics of the EACN scan carried out at a WOR of 40:60, along the vertical arrow indicated in Fig. 1. This scan is selected so that the phase behaviour transition along the path is WI→WIII→WI, i.e. a retrograde transition. Fig. 2(a) indicates that the micro-emulsion is the lower phase, then the middle phase, then the lower phase again, as the benzene content in the oil phase increases. Fig. 2(b) shows that the surfactant partitioning is drastically changed when the three-phase behaviour region is crossed from 4 to 24 vol.% benzene in the oil mixture. With 4% benzene in oil, only 20% of the surfactant is partitioning into the oil phase with most of the

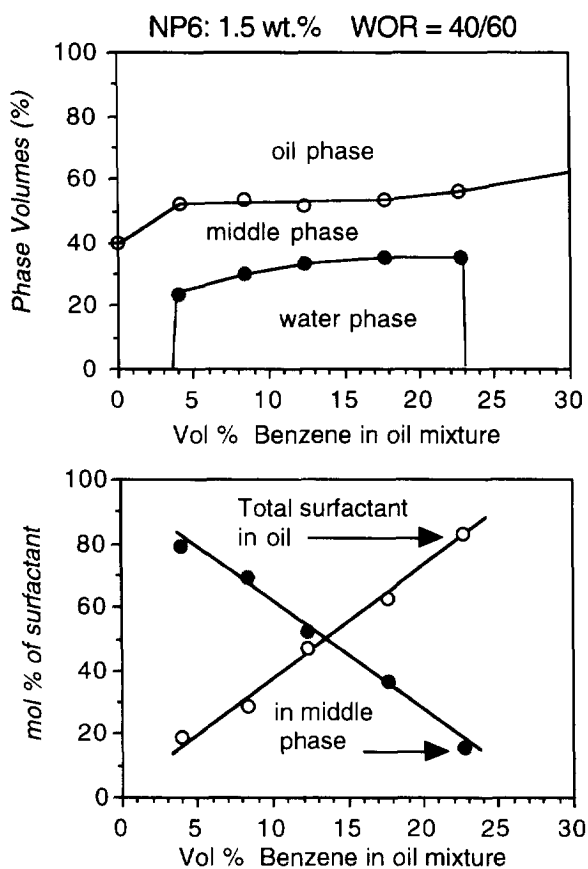


Fig. 2. Phase volumes along a formulation (EACN) scan and associated partitioning of overall surfactant species in the oil and middle phases.

surfactant in the middle phase microemulsion, since the amount in the water phase is essentially the critical micelle concentration, and thus essentially negligible in the overall inventory. With 24% benzene in oil, more than 80% of the surfactant has migrated into the oil phase, leaving less than 20% for the water and interfacial phase (microemulsion). The point is that, because of the selective partitioning of the different oligomers, this 20% is not likely to contain the same distribution as the overall surfactant mixture.

Fig. 3 shows the oligomer mass distribution into the oil phase as a function of the oil phase composition. Note that 0% benzene does not correspond exactly to a WOR of 40:60, as for all other distributions, but to a WOR of 50:50, a probably insignificant change as far as the partitioning is

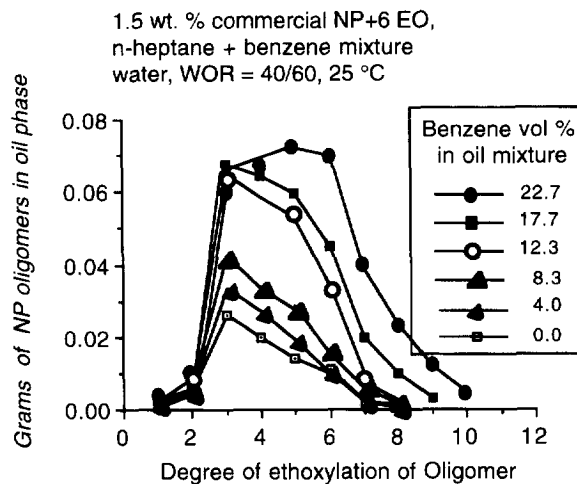


Fig. 3. Mass distribution of oligomers in the oil phase along an EACN scan.

concerned. This figure indicates two main characteristics. First the amount of surfactant in the oil phase, which can be represented by the area below the distribution curve, increases steadily when the benzene content increases, as seen in the previous figure. However, it is obvious that the average of the distribution moves toward higher values when the benzene content in the oil phase increases. This is because the depletion of the microemulsion phase starts with the shortest EON chain surfactants, and then proceeds with longer and longer oligomers as the benzene content increases. As a consequence the average EON increases both in the oil phase and in the microemulsion phase. For instance, it can be calculated that when the oil is pure heptane the average EON is 3.97 in the oil phase (20% of total surfactant) and 5.16 in the microemulsion (80%), while these values rise to 4.73 in the oil phase (62%) and 5.31 in the microemulsion (38%) when the oil phase contains 18% benzene.

As a result, the interfacial EON [6], i.e. the active formulation variable as far as the phase behaviour is concerned, increases steadily and the WIII→WI retrograde transition takes place.

The collected distribution data in the oil and water phases of all three-phase systems allow the estimation of the partition coefficient of the different oligomers with *i* ethylene oxide groups

per molecule, since these excess phases do not contain any micelle. The partition coefficient K_i is defined as the ratio between the concentration of the i th oligomer in the water phase to its concentration in the oil phase. In previous studies [9,11,12,14] the partition coefficient has been found to change with the ethoxylation degree i as

$$\log K_i = \log K_0 + 0.45i$$

where the parameter $\log K_0$, i.e. the value for the corresponding non-ethoxylated alkylphenol, is typically in the range from -3.5 to -4.5 , and depends on all formulation variables, that is surfactant hydrophobe, water phase salinity, oil ACN, alcohol type and concentration, as well as temperature.

Fig. 4 shows the variation in $\log K_i$ vs i for systems containing different oil mixtures. The curve-fitting data indicate that the slope changes very significantly with the benzene content in the oil phase. The 0.45 slope is thus typical of n -alkane, and a lower slope is exhibited for oil mixtures containing benzene. As a matter of fact

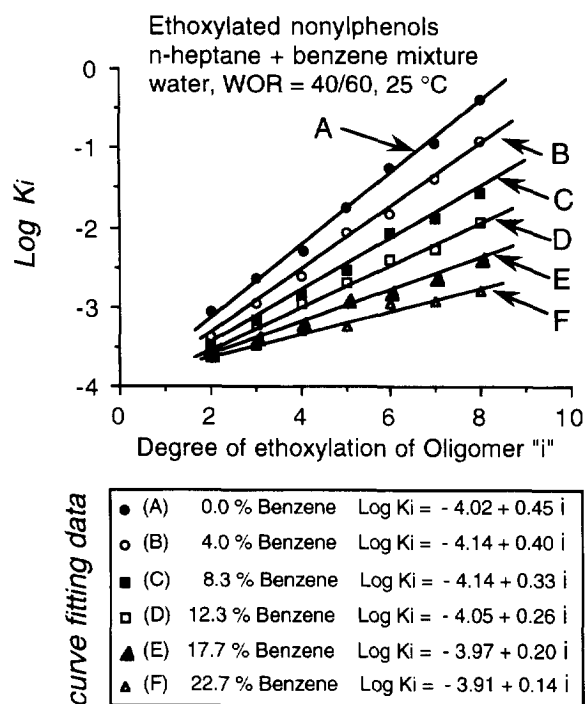


Fig. 4. Variation in the partition coefficients of ethoxylated nonyl phenol oligomers vs oil phase composition.

this means that the more aromatic the oil phase is, the more it solubilizes all oligomers, but the less selective it is in fractionating the different oligomers.

Thus it can be said that the fractionation feature that is responsible for the retrograde transition is primarily due to the increased partitioning of all oligomers into the oil phase, with the selective partitioning as a secondary effect. As a matter of fact, it is worth noting that the increase in partitioning is stronger for higher oligomers than for lower oligomers.

6. Conclusions

When the scan of the nature of the oil phase is carried out to produce a phase behaviour transition, two opposite effects can take place simultaneously when an optimum formulation for three-phase behaviour is reached. On the one hand the reduction in the ACN or EACN of the oil phase tends to produce an increase in interaction between the surfactant and the oil phase with a resulting WIII→WII transition trend. On the other hand, the use of benzene as a low EACN component in the oil mixture produces an increase in aromaticity which results in a drastic increase in the partitioning of all oligomer species into the oil phase. As a consequence the oligomer species left over at the interface are more and more hydrophilic, with the resulting WIII→WI trend that opposes the previous trend. The combination of the two effects can result in the WI→WIII→WI retrograde transition.

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