Colloid Polym Sci 279:301–304 (2001)

SHORT COMMUNICATION

H.-F. Eicke
W. Meier

Nonmonotonic pattern of the critical percolation temperature due to variations of additive chain length in water-in-oil microemulsions

Received: 20 October 2000
Accepted: 7 November 2000

H.-F. Eicke (✉) · W. Meier
Institut für Physikalische Chemie
Departement Chemie, Universität Basel
4056 Basel, Switzerland

Abstract The nonmonotonic variation of the critical percolation temperature (T_c) of ternary nonionic ($C_{14}E_5$) water-in-oil microemulsions was studied as a function of the alkyl chain length of an ionic additive (*n*-alkyl sulfonate sodium salt). A thermodynamic approach shows the relationship between T_c and additive chain length, which is supplemented by a consideration of a possible molecular mechanism of the observed phenomenon.

Key words Nonionic water-in-oil microemulsions · Nonmonotonic variation of critical percolation temperature · Alkyl chain length dependence of ionic additive on T_c · Thermodynamic approach

Introduction

A ternary system of water, surfactant and oil forms in the simplest case in a certain range of composition and temperature thermodynamically stable microemulsions. The macroscopically homogeneous, isotropic, generally transparent and low viscous emulsions are heterogeneous on a molecular scale. They are dispersions of nanometer-sized droplets of a remarkably small polydispersity [1, 2]. These systems possess a huge oil/water interface consisting of a monolayer of surfactant(s). The properties of microemulsions were elucidated by numerous experimental techniques [3–6], for example, neutron scattering, light scattering, dielectric, and electrical conductivity measurements. The experiments yield a concurring picture of such thermodynamically stable emulsions. The interactions between the nanodroplets consist of a hard-core repulsion and a weak and short-ranged attraction at distances where the surfactant tails overlap. The systems are typically temperature sensitive. Both with decreasing or increasing temperatures (depending on the type of surfactants used) and at a particular composition the droplets show cluster formation. If an "infinite" cluster has been formed (i.e., spanning the whole emulsion) the system is said to be percolated. This process is strictly reversible with respect to changes of temperature and composition if microemulsions are considered. The percolated cluster can be sensitively affected not only by temperature variations but also by small amounts of additives. The critical percolation transition (characterized by T_c or the critical volume fraction, x_c) shows features of a second-order phase transition [7]. The heat capacity and the specific volume show changes at the T_c [8, 9], thus supporting the treatment of the observed phenomena as a phase transition. Water-in-oil microemulsions, in particular, offer the advantage to be investigated by electrical conductivity (σ) measurements, which are especially sensitive with respect to structural transformations. T_c is experimentally sufficiently accurate accessible [10] by σ measurements since the conductivity varies by orders of magnitude at this transition.

Experiments were carried out with water-in-oil microemulsions stabilized by the nonionic surfactant pentaethylene glycol tetradecyl ether ($C_{14}E_5 = \text{nio}$) containing a small amount of an ionic surfactant additive, i.e., sodium *n*-alkyl sulfonates $[\mathrm{H}(-\mathrm{CH}_2-)_n\mathrm{SO}_3^-\mathrm{Na}^+]$. Phase diagrams of similar systems have already been studied phenomenologically [11]. The present system shows a nonmonotonic shift of the percolation temperature as a function of the *n*-alkyl *chain length* of the additive.

Materials and methods

The chemicals, i.e., pentaethylene glycol tetradecyl ether ($C_{24}H_{50}O_6$, >99% DC) and *n*-alkyl sulfonic acid sodium salts, [$H(-CH_2-)_nSO_3^-Na^+$], >98%] as well as isooctane, (p.a.) were purchased from Fluka. The concentration of the ionic additives was small and kept constant, i.e., 3×10^{-3} M with respect to the total volume of the microemulsion (this corresponds to 5io and 340 nio per nanodroplet). The weight fraction of the nanodroplets, i.e., $(w + s)/(w + s + o) = 0.256$, where w, s and o are weight fractions of water, surfactant and oil, and $w/s = 1$, were constant throughout this work. Hence, the concentration of the nanodroplets and their sizes were fixed. Electrical conductivity measurements were thus appropriate to follow the change of the percolation temperature. Details of the measuring technique and equipment are given elsewhere [12]. It was verified that the observed effect is solely due to a variation of the alkyl chain length. The data are satisfactorily reproducible.

Results and discussion

Figure 1 shows T_c against the chain length of the sodium *n*-alkyl sulfonates (expressed by the number of $-CH_2-$ groups in the *n*-alkyl chain) passing a maximum at $n \approx 8$–10. It represents a phase diagram displaying the percolated (i.e., containing an infinite cluster of nanodroplets) and nonpercolated regions of the microemulsions. A thermodynamical approach tries to clarify the physical background of the phase diagram if one considers the nanodroplets as an independent component, i.e., a pseudobinary system (i.e., nanodroplets in oil) is assumed. The weight fraction of water and surfactant corresponds to that of the nanodroplets. The experimental data tend to substantiate such a proceeding. We now assume an equilibrium between nonpercolated [$x = (s' + w')/(s + w + o)$] and percolated [“infinitely“ clustered, i.e., $\alpha - x = (s'' + w'')/(s + w + o)$] aqueous nanodroplets in oil of arbitrary composition, where α is the total weight fraction of nanodroplets. The equilibrium is considered in the presence of small amounts of the ionic additive with equal ionic headgroups but varying alkyl chain lengths. This corresponds to the $-CH_2-$ group concentration, i.e., $\xi = N/(s + w + o)$, where N (n times the weighed-in amount of surfactant additive) is the number of the $-CH_2-$ groups added to the system via the *n*-alkyl sulfonic sodium salts. To the oil no physical property has been attached except to act as a dispersing agent. Hence no information can be obtained from results regarding the effect of varying the oil.

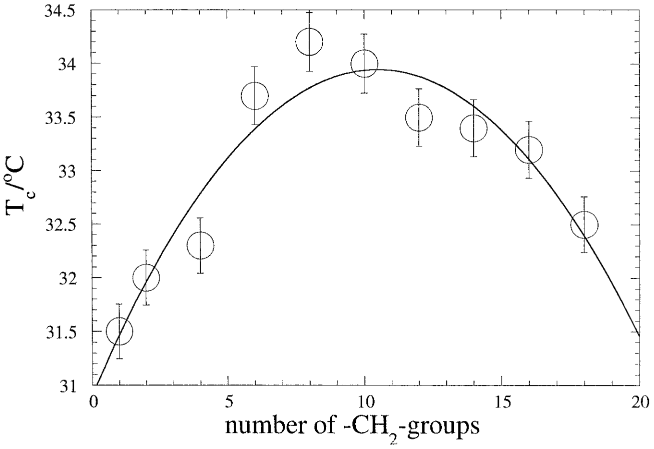

Fig. 1 Percolation temperature (T_c) against chain length (number of $-CH_2-$ groups) of $[H(-CH_2-)_nSO_3^-Na^+$ ($n = 1$–18) water/ pentaethylene glycol tetradecyl ether, $[H(-CH_2-)_nSO_3^-Na^+$/iso-octane water-in-oil microemulsion, $(w + s)/(w + s + o) = 0.256$, $w/s = 1$, $[H(-CH_2-)_nSO_3^-Na^+ = 3 \times 10^{-3}$ mol dm^{-3} (with respect to volume of microemulsion)

A quantitative description of the observed dependence of T_c on n requires the dependence of the chemical potential of the nanodroplets in the binary system on the additive, which is characterized by the number of its $-CH_2-$ groups (n) [15]. Its chemical potential can be described under idealized conditions by considering Henry's law, i.e.,

$$\mu = \mu^0 + RT_c \ln\left(\frac{\xi}{s}\right) \quad , \tag{1}$$

where $s(\xi_n)$ is the solubility of the additive in the binary system at fixed chain length of the additive, while $\mu^{o,}$ and RT_c have their usual meaning.

We now proceed to calculate the dependence of the chemical potential of the nanodroplets on the additive by applying the Gibbs–Duhem relation for isothermal conditions, $\sum_i x_i d\mu_i = 0$ [14] (with respect to x and ξ), i.e.,

$$x\frac{\partial\mu}{\partial\xi} + RT_c\left(1 + \xi\frac{\partial \ln\left(\frac{1}{s}\right)}{\partial\xi}\right) = 0 \tag{2}$$

and

$$x\frac{\partial\mu}{\partial x} + \xi RT_c\frac{\partial \ln\left(\frac{1}{s}\right)}{\partial x} = 0 \quad . \tag{3}$$

On differentiating Eq. (2) with respect to x and Eq. (3) with respect to ξ, one finds

$$\frac{\partial\mu}{\partial\xi} + x\frac{\partial^2\mu}{\partial\xi\partial x} + RT_c\xi\frac{\partial^2 \ln\left(\frac{1}{s}\right)}{\partial\xi\partial x} = 0 \tag{4}$$

and

$$x\frac{\partial^2\mu}{\partial x\partial\xi} + RT_c\frac{\partial \ln\left(\frac{1}{s}\right)}{\partial x} + RT_c\xi\frac{\partial^2 \ln\left(\frac{1}{s}\right)}{\partial x\partial\xi} = 0 \quad . \tag{5}$$

Subtracting Eq. (5) from Eq. (4) yields

$$\frac{\partial\mu}{\partial\xi} + RT_c\frac{\partial \ln\left(\frac{1}{s}\right)}{\partial x} \quad , \tag{6}$$

which describes the dependence of the chemical potential of the nanodroplets on the solubility of the additive.

In order to ensure that the equilibrium condition of the percolated and nonpercolated states for any variation of the variables x, ξ, and T_{c} are maintained, the coexistence relation must hold, i.e.,

$$(\mathrm{d}\mu)_x = (\mathrm{d}\mu)_{\alpha-x} \ , \tag{7}$$

where

$$\mathrm{d}\mu = RT_{\mathrm{c}}\left(\frac{\partial \ln\left(\frac{1}{s}\right)}{\partial x}\right)_{T_{\mathrm{c}}}\mathrm{d}\xi + \left(\frac{\partial \mu}{\partial x}\right)_{T_{\mathrm{c}},\xi}\mathrm{d}x + \left(\frac{\partial \mu}{\partial T_{\mathrm{c}}}\right)_{\xi}\mathrm{d}T_{\mathrm{c}} \ . \tag{8}$$

From Eqs. (7) and (8) one finds

$$\begin{aligned} &RT_{\mathrm{c}}\left(\frac{\partial \ln\left(\frac{1}{s}\right)}{\partial x}\right)_{x,T_{\mathrm{c}}}\mathrm{d}\xi + \left(\frac{\partial \mu}{\partial x}\right)_{T_{\mathrm{c}},\xi}\mathrm{d}x + \left(\frac{\partial \mu}{\partial T_{\mathrm{c}}}\right)_{x,\xi}\mathrm{d}T_{\mathrm{c}} \\ &\quad = RT_{\mathrm{c}}\left(\frac{\partial \ln\left(\frac{1}{s}\right)}{\partial x}\right)_{\alpha-x,T_{\mathrm{c}}}\frac{s_{\alpha-x}}{s_x}\mathrm{d}\xi + \left(\frac{\partial \mu}{\partial x}\right)_{T_{\mathrm{c}},\xi}\mathrm{d}(\alpha-x) \\ &\qquad + \left(\frac{\partial \mu}{\partial T_{\mathrm{c}}}\right)_{\alpha-x_{\mathrm{c}},\xi}\mathrm{d}T_{\mathrm{c}} \end{aligned} \tag{9}$$

A partition coefficient has been introduced in Eq. (9) to consider a different solubility of the ionic surfactant additive in the percolated state, i.e., $(s_{\alpha-x}/s_x)\xi$, if the concentration in the nonpercolated state is ξ.

In order to calculate the variation of the equilibrium temperature where both phases coexist in the presence of the additive, one starts out from a fixed composition of one phase, i.e., x. Hence, by introducing the condition $\mathrm{d}x = 0 = \mathrm{d}(\alpha - x)$ into Eq. (9), we obtain

$$\begin{aligned} &\mathrm{d}T_{\mathrm{c}}\left[\left(\frac{\partial \mu}{\partial T_{\mathrm{c}}}\right)_{\alpha-x,\xi} - \left(\frac{\partial \mu}{\partial T_{\mathrm{c}}}\right)_{x,\xi}\right] \\ &\quad = RT_{\mathrm{c}}\left[\left(\frac{\partial \ln\left(\frac{1}{s}\right)}{\partial x}\right)_{x,T_{\mathrm{c}}} - \left(\frac{\partial \ln\left(\frac{1}{s}\right)}{\partial x}\right)_{\alpha-x,T_{\mathrm{c}}}\frac{s_{\alpha-x}}{s_x}\right]\mathrm{d}\xi \end{aligned} \tag{10}$$

or, finally,

$$\mathrm{d}T_{\mathrm{c}} = -\frac{RT_{\mathrm{c}}^2}{\Delta H}\cdot\frac{(\partial s/\partial x)_x - (\partial s/\partial x)_{\alpha-x}}{s_x}\mathrm{d}\xi \ , \tag{11}$$

which shows that the shift of the percolation temperature is directly proportional to the concentration of the additive (as long as small amounts of additives are considered) at fixed number of $-\mathrm{CH}_2-$ groups. According to Eq. (11) the observed nonmonotonic pattern of $\Delta T_{\mathrm{c}}(n)$ is controlled by the difference of the "solubility coefficients" in the two states. ΔH is the difference of the excess heats of mixing of the additive in the percolated and nonpercolated states.

The interpretation of the whole plot (Fig. 1) with the help by Eq. (11) would be difficult for two reasons: firstly, the equation is an approximation and, secondly, the solubility coefficients $(\partial s/\partial x)$ are according to experience not easy to interpret and hence moderately fruitful. Instead we propose a model, which might qualitatively interpret the underlying mechanism to generate the ΔT_{c} shift with chain length of the additive.

The model assumes two chain-length-dependent counteracting phenomena of the ionic surfactant, which allow the interaction of the aqueous nanodroplets in an oil continuum to be simulated. First, there exists a distribution equilibrium between adsorbed and dissolved ionic surfactants: at shorter chain lengths the ionic surfactant is predominantly adsorbed at the water–oil interface, while with increasing number of $-\mathrm{CH}_2-$ groups the oil solubility of this surfactant prevails (experimentally confirmed). The second phenomenon refers to a molecular-weight- (proportional to the chain length) dependent electrolytic dissociation (ideal lattice gas model) of the ionic surfactant. For low molecular weights (i.e., in the adsorbed state) dissociation increases with chain length with a concomitant charging of the aqueous nanodroplets (counter charges form a "space charge" in the oil). This process leads to a repulsion of the nanodroplets and hence to an increase in the percolation temperature. The increasing number of $-\mathrm{CH}_2-$ groups causes desorption (larger solubility of ionic surfactant in oil) and a corresponding decrease of dissociation (proportional to the decay of the charge of the nanodroplets). This results in a decrease of the percolation temperature. A superposition of both phenomena is expected to yield a nonmonotonic pattern of the plot.

A quantitative elaboration of this idea shows the typical nonmonotonic plot in the case of electrical conductivity measurements.

Acknowledgements The authors are grateful to H. Hammerich for carrying out the experiments and to D. Stauffer for comments and suggestions.

References

1. Borkovec M (1992) Adv Colloid Interface Sci 37:195
2. Borkovec M, Eicke H-F, Ricka J (1989) J Colloid Interface Sci 131:366
3. (a) Eicke H-F, Hilfiker R, Thomas H (1985) Chem Phys Lett 120:272; (b) Eicke H-F, Hilfiker R, Thomas H (1986) Chem Phys Lett 125:295
4. van Dijk MA, Casteleijn G, Joosten JGH, Levine YK (1986) J Chem Phys 85:626

5. Eicke H-F, Geiger S, Sauer FA, Thomas H (1987) Ber Bunsenges Phys Chem 90:872
6. Richter D, Farago B, Huang JS (1987) Phys Rev Lett 59:2600
7. (a) Stauffer D, Aharony A (1994) Introduction to percolation theory. Taylor and Francis, London; (b) Hilfer R (1986) Renormierungsansätze in der Theorie ungeordneter Systeme, Fraktale Modelle und ihre Anwendung. Harry Deutsch, Frankfurt am Main
8. Vollmer D, Vollmer J, Eicke H-F (1994) Europhys Lett 26:389
9. Meier W, Eicke H-F, Odenwald M (1996) Colloids Surf 110:287
10. Eicke H-F, Thomas H (1999) Langmuir 15:400
11. Kahlweit M, Faulhaber B, Busse G (1994) Langmuir 10:2528
12. Eicke H-F, Meier W (1996) Biophys Chem 58:29
13. Eicke H-F (1977) J Colloid Interface Sci 59:308
14. Prigogine I, Defay R (1954) Chemical thermodynamics (translated by Everett DH). Longmans Green, London
15. (a) Lin IJ (1976) Colloid Interface Sci II:433; (b) Lin IJ, Metzer A (1971) J Phys Chem 75:3000