

24. Blockcopolymers in Microemulsions Differential Heats of Solution and Shift of the Percolation Temperature in W/O Microemulsions

by Hans-Friedrich Eicke*, Rolf Hilfiker, and Gu Xu

Institut für Physikalische Chemie, Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

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Solutions of blockcopolymers (POE-b-PI-b-POE) in fluids of interacting aqueous nanodroplets (W/O microemulsions) are studied. The interaction strength between the (pseudo) two components is measured by the shift of the percolation temperature relative to that of the pure microemulsion. A quantitative measure of the interaction, the differential heat of solution, is thermodynamically related to the slopes of the equilibrium temperature of the system with varying monomeric nanodroplet concentration and the experimental percolation line in the presence of copolymer.

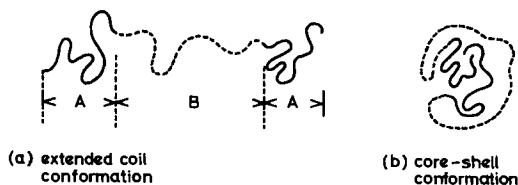
Introduction. – Steric stabilization of particles by polymers is a common procedure in emulsion technology. To get an idea of the magnitude of this stabilization, W/O microemulsions proved to be suitable, since they form so-called flocs (clusters) of aqueous nanodroplets under appropriate conditions of temperature and composition. The redispersion of such flocs by the polymer would, thus, indicate its stabilizing action.

We selected blockcopolymers, particularly ABA triblockcopolymers, with hydrophilic A- and hydrophobic B-blocks because of their sufficient anchoring in the droplets' interface. These copolymers are poorly soluble in apolar dispersion media. They may overcome their insolubility in these solvents by adopting a core-shell conformation. This, however, is not possible, if the weight ratio A/B is large. Under such conditions, W/O microemulsions greatly improve the solubility of these copolymers.

In the present experiments, POE(polyoxyethylene)/PI(polyisoprene)/POE triblock copolymers were dissolved in water-in-oil microemulsions (*i.e.* water/AOT/isooctane). In case the A/B ratio is sufficiently large, chemical reasoning lets one suppose that the hydrophilic POE blocks tend to be hydrated in the aqueous nanodroplets, while the PI blocks dissolve easily in the apolar dispersion medium (isooctane), thus giving rise to interconnected nanodroplets. The copolymer-aqueous nanodroplet complexes thus formed are pseudo core-shell structures and fulfil the same function as the above mentioned core-shell conformations of the pure copolymers regarding the solute-solvent interactions. The sol state comprises, therefore, both types of core-shell structures. *Fig. 1* sketches an intuitive model of our triblock copolymer-W/O microemulsion system. Since calorimetric measurements are difficult to conduct in these systems due to excessive equilibration times, we had recourse to an interesting phenomenon occurring in these microemulsions, *i.e.* a (temperature-controlled) percolation threshold due to diffusion-controlled cluster-cluster aggregation of nanodroplets. Contrary to pure geometric percolation which does

not represent a phase transition in a thermodynamic meaning (no *Hamiltonian*), we consider a system of interacting droplets whose interaction can be controlled by temperature and other parameters.

Copolymer conformations in solution



Nanodroplet-copolymer complexes in microemulsions

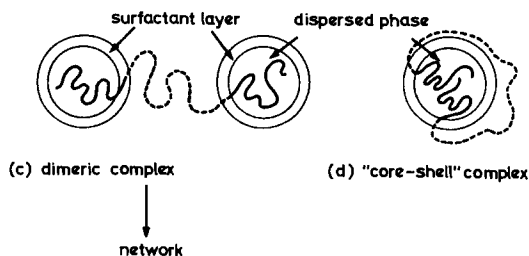


Fig.1. Possible conformations of triblockcopolymers ABA (A is the hydrophilic and B the hydrophobic block) and the proposed aqueous nanodroplet-copolymer complexes (from [4])

According to these considerations, one expects that the percolation threshold and, thus, the percolation cluster in such a particular copolymer solution is affected by the copolymers depending on their composition and conformation. It has been confirmed experimentally that the droplet structure is preserved during the manipulations discussed here. Since the percolation threshold can be precisely determined by temperature-dependent electric conductivity measurements, a shift of the percolation-threshold temperature can be most easily followed up and, thus, indicate the stabilizing (or destabilizing) effect of the blockcopolymers.

Thermodynamic Considerations. – In order to describe thermodynamically the shift of the percolation temperature due to the addition of the blockcopolymer, we adopt the recently advocated model of a ‘one-component macrofluid’ [1] to characterize the W/O microemulsion and, thus, to reduce the number of thermodynamically relevant components. The microemulsion is supposed to behave like a fluid of nanodroplets whose ‘molecules’ are the only macroscopic objects present in the suspension. At the percolation threshold, a sol-gel equilibrium of nanodroplets can be envisaged which will be shifted at constant composition of nanodroplets in the presence of blockcopolymer.

Hence, we consider three chemical potentials, *i.e.* μ_{nd}^{sol} , μ_{nd}^{cl} , and μ_p (*cl* = nanodroplet (*nd*) cluster and *P* = copolymer), and their dependences on the composition of the system expressed by $x = n_{nd}^{sol}/(n_{nd}^{sol} + n_{nd}^{cl})$, $1 - x = n_{nd}^{cl}/(n_{nd}^{sol} + n_{nd}^{cl})$, and $x = n_p/(n_{nd}^{sol} + n_{nd}^{cl})$. Thus, we assume a dilute polymer solution. The requested relation is provided by a *Gibbs-Duhem* equation, *i.e.*

$$x(\partial\mu_{nd}^{sol}/\partial\xi) + (1-x)(\partial\mu_{nd}^{cl}/\partial\xi) + \xi(\partial\mu_p/\partial\xi) = 0 \quad (1)$$

$\mu_p = \mu_p^o + RT \ln(\xi/s)$ expresses the concentration dependence of the chemical potential of the block copolymer [2]. μ_p^o refers to the saturation mole fraction of ξ assuming ideal behaviour; s is the solubility of the block copolymer in the nanodroplet phases. The third term in *Eqn. 1* yields RT leading to *Eqn. 1a*

$$x(\partial\mu_{nd}^{sol}/\partial\xi) + (1-x)(\partial\mu_{nd}^{cl}/\partial\xi) + RT = 0 \quad (1a)$$

The corresponding variation of the chemical potentials with respect to the two nanodroplet phases is

$$x(\partial\mu_{nd}^{sol}/\partial x) + (1-x)(\partial\mu_{nd}^{cl}/\partial x) + \xi RT[\partial \ln(1/s)/\partial x] = 0 \quad (2)$$

Differentiating *Eqn. 1a* with respect to x and *Eqn. 2* with respect to ξ yields

$$\partial\mu_{nd}^{sol}/\partial\xi - \partial\mu_{nd}^{cl}/\partial\xi = RT[\partial \ln(1/s)/\partial x] \quad (3)$$

Combining *Eqn. 3* with *Eqn. 1a*, one obtains

$$\partial\mu_{nd}^{sol}/\partial\xi = -RT\{1 - (1-x)\partial \ln(1/s)/\partial x\} \quad (4)$$

and

$$\partial\mu_{nd}^{cl}/\partial\xi = -RT\{1 + x\partial \ln(1/s)/\partial x\}$$

The dependence of the chemical potentials of both components (nanodroplets in the sol and cluster phases) on the added blockcopolymer is derived from integrating *Eqns. 4* with respect to ξ at constant x and T , *i.e.*

$$\mu_{nd}^{sol} = \mu_{nd}^{o,sol} - RT\xi\{1 + (1-x)\partial \ln s/\partial x\} \quad (5)$$

and

$$\mu_{nd}^{cl} = \mu_{nd}^{o,cl} - RT\xi\{1 - x\partial \ln s/\partial x\}$$

The co-existence of both nanodroplet phases for varying composition, varying amounts of blockcopolymer and different temperatures demands

$$d\mu_{nd}^{sol} = d\mu_{nd}^{cl} \quad (6)$$

i.e.

$$\begin{aligned}
 & -RT\{1 + (1-x) \partial \ln s / \partial x\}_T d\xi + (\partial \mu_{nd}^{sol} / \partial x)_{\xi, T} dx + (\partial \mu_{nd}^{sol} / \partial T)_{\xi, x} dT = \\
 & -RT\{1 - x \partial \ln s / \partial x\}_T d\xi + (\partial \mu_{nd}^{cl} / \partial x)_{\xi, T} dx + (\partial \mu_{nd}^{cl} / \partial T)_{\xi, x} dT
 \end{aligned} \quad (7)$$

From Eqn. 7, we derive an equilibrium temperature (e.g. the percolation temperature which is particularly easy to determine experimentally) as a function of added block-copolymer at constant composition ($dx = 0$), i.e.

$$(dT/d\xi)_x = -RT(\partial \ln s / \partial x)_T / \{(\partial \mu_{nd}^{cl} / \partial T)_{\xi, x} - (\partial \mu_{nd}^{sol} / \partial T)_{\xi, x}\} \quad (8)$$

The denominator on the right-hand side of Eqn. 8 can be transformed into an experimentally more easily accessible quantity. Thus, we write (with H_i the partial molar (or specific) enthalpy of the i th component)

$$H_i = \mu_i - T (d\mu_i / dT) \quad (9)$$

This equation is introduced into the molar excess heat of mixing,

$$H^E = x (H_{nd}^{sol} - H_{nd}^{o, sol}) + (1-x) (H_{nd}^{cl} - H_{nd}^{o, cl}), \quad (10)$$

i.e.,

$$H^E = x(\mu_{nd}^{sol} - T(\partial \mu_{nd}^{sol} / \partial T) - H_{nd}^{o, sol}) + (1-x)(\mu_{nd}^{cl} - T(\partial \mu_{nd}^{cl} / \partial T) - H_{nd}^{o, cl}), \quad (10a)$$

where $H_{nd}^{o, sol, cl}$ are the enthalpies of the pure sol or cluster states of the nanodroplets. Eqn. 10a is differentiated (considering the *Gibbs-Duhem* relation) and then combined again with Eqn. 10a to yield

$$\partial \mu_{nd}^{sol} / \partial T = 1/T \{ \mu_{nd}^{sol} - H_{nd}^{o, sol} - H^E - (1-x) \partial H^E / \partial x \}, \quad (11)$$

and

$$\partial \mu_{nd}^{cl} / \partial T = 1/T \{ \mu_{nd}^{cl} - H_{nd}^{o, cl} - H^E + x \partial H^E / \partial x \}$$

Insertion of Eqns. 11 into Eqn. 8 yields

$$(dT/d\xi)_x = -RT^2(\partial \ln s / \partial x)_T / \{(\partial H^E / \partial x)_{\xi, T} - \Delta_{sol}^{cl} H_{nd}^o\}, \quad (12)$$

where $\Delta_{sol}^{cl} H_{nd}^o$ is the heat of formation of pure nanodroplet clusters.

Rearranging Eqn. 12 and inserting $-RT^2 / \{(\partial T / \partial x)_{\xi=0} x\}$ for $\Delta_{sol}^{cl} H_{nd}^o$, one obtains

$$(\partial H^E / \partial x)_{\xi, T} = -\{RT^2 / [x(\partial T / \partial x)_{\xi=0}]\} \{1 + (\partial \ln s / \partial \ln x)_T (\partial T / \partial x)_{\xi=0} / (dT/d\xi)_x\} \quad (13)$$

i.e. the differential heat of a (dilute) solution of blockcopolymers in a nanodroplet fluid. $(\partial H^E / \partial x)_{\xi, T}$ is composed of two factors, the first one corresponds to the pure W/O microemulsion, while the second is a correction term arising from the addition of the copolymer to the microemulsion.

Results and Discussion. – The physically relevant quantity $(\partial H^E/\partial x)_{\xi,T}$, i.e. the partial molar (or specific) excess enthalpy of formation of nanodroplet clusters in the presence of copolymers is obtained *via Eqn. 13*. While $(dT/d\xi)_x$ can be directly read out from the shift of the percolation line with varying copolymer concentration (see *Fig. 2*), $(\partial T/\partial x)_{\xi=0}$ cannot be determined directly from the percolation line of the pure microemulsion, since the total weighed-in amount of nanodroplets is plotted on the abscissa. Instead, we require the saturation concentration of the monomeric nanodroplets in equilibrium with clusters.

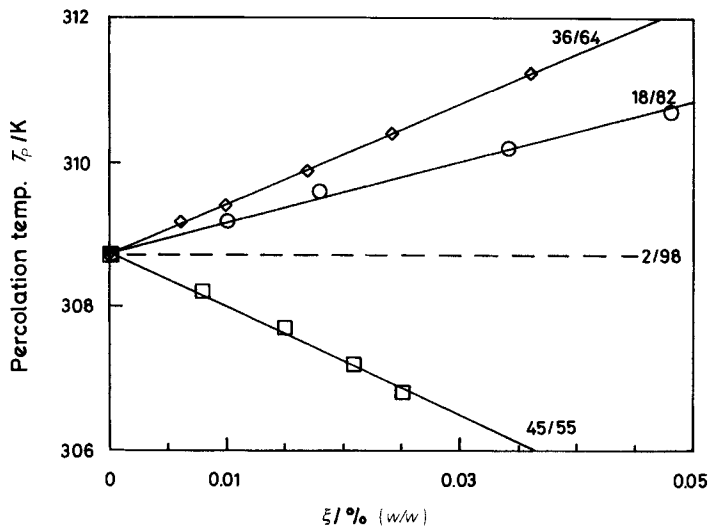


Fig. 2. Shift of the percolation temperature relative to that of pure $H_2O/AOT/isooctane$ microemulsion against weight fraction of triblockcopolymers. POE/PI (w/w): (---): 2/98; (○): 18/82; (◇): 36/64; (□): 45/55. [AOT] = 0.1M ; $[H_2O]/[AOT] = w_0 = 60$ (mol/mol).

We have, however, an (extra-thermodynamic) access to the equilibrium concentration of monomeric nanodroplets (*via* a theoretical model due to *Stauffer*- [5] and *Kerr*-effect measurements [6]) within the mixture and are, thus, able to derive $(\partial T/\partial x)_{\xi=0}$ from experimental data (see *Fig. 3*). Experiments also reveal that $(dT/d\xi)_x$ adopts larger positive values, if the molecular weight of the POE block increases, and the mass ratio of the POE/PI blocks is < 0.6 . Larger positive values of this slope correspond to an increase of the dispersive power (of copolymers) and hence to an enhanced solubility in monomeric nanodroplets. This conclusion gives us a hint how to describe the composition dependent solubility $(\partial \ln s/\partial \ln x)_T$ of the POE blocks. This requires again an extra-thermodynamic consideration analogous to the so-called quasi-chemical models of *Herzfeld-Heitler* and *Wagner* [7]. The model which we adopt is rather crude but presents a simple and, for our purpose, suitable approach. We, thus, assume a certain number n of nanodroplets as immediate neighbors of the POE block. This number depends on the size of the block.

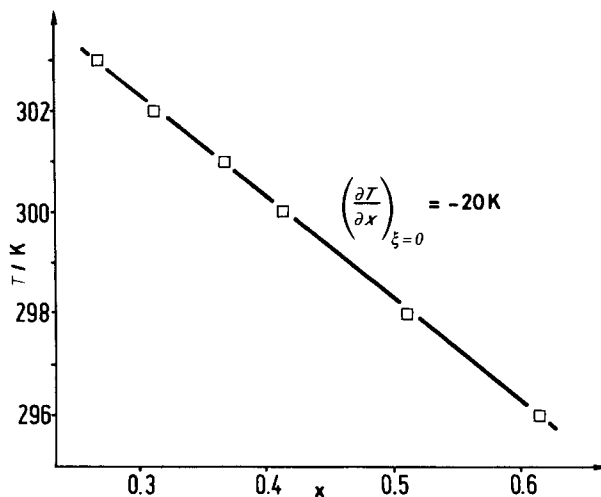


Fig. 3. Equilibrium temperature against mass fraction of monomeric nanodroplets: $w_0 = 60$, $[AOT] = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ derived from Kerr-effect measurements [6].

From these nanodroplets, m are thought to belong to the sol and $n - m$ to the cluster states. The potential energies attributed to these states with respect to the POE blocks are $E_m = (m/n)E_{\text{sol}} + ((n - m)/n)E_{\text{cl}}$. The solubility of the copolymer is then given by

$$s = \text{const} \sum p_m \exp(-E_m/RT) \quad (14)$$

where p_m is the probability that m nanodroplets in the sol state and $n - m$ in the cluster state are immediate neighbors of the POE blocks (without the specific solvent effects expressed by E_{sol} and E_{cl}). Assuming random distribution of the nanodroplets regarding their states, the probability that of n nanodroplets m are in the sol and $n - m$ in the cluster state at given composition x and $1 - x$ is $p_m = \binom{n}{m} x^m (1 - x)^{n - m}$ if the order of choice is irrelevant. One, thus, finds by applying the binomial theorem

$$s = \text{const} \{ x \exp(-(1/n)E_{\text{sol}}/RT) + (1 - x) \exp(-(1/n)E_{\text{cl}}/RT) \}^n \quad (15)$$

For $x = 1$ and 0 , we obtain the solubilities for the sol or cluster states, s_{sol} and s_{cl} . Hence $s^{1/n} = x(s_{\text{sol}})^{1/n} + (1 - x)(s_{\text{cl}})^{1/n}$ from which we derive two limiting cases, *i.e.* $\partial \ln s / \partial \ln x = n$ and $\partial \ln s / \partial \ln x = -nx / (1 - x)$. Returning now to Eqn. 13, we find that the partial specific excess enthalpy becomes < 0 if $(\partial \ln s / \partial \ln x)_T (\partial T / \partial x)_{\xi=0} / (dT/d\xi)_x$ is < 0 and the absolute value of this term is > 1 . Since $(\partial T / \partial x)_{\xi=0}$ is < 0 , we have to demand that $(\partial \ln s / \partial \ln x)_T |(\partial T / \partial \xi)_{x=0}| > (dT/d\xi)_x$. From the experimental data (see Fig. 2) one derives for Cop-3 (see the Table) $(\partial T / \partial x)_{\xi=0} / (dT/d\xi)_x$ *ca.* -0.3 which requires $(\partial \ln s / \partial \ln x)_T > 3$, a condition which should be readily fulfilled according to the above considerations. Thermodynamic reasoning also requires that the second term in the braces of Eqn. 13 increases with increasing $(dT/d\xi)_x$. This is a consequence of the above argument, *i.e.* larger POE blocks

require larger n values (number of nanodroplets as immediate neighbors); actually, $(\partial \ln s / \partial \ln x)_T$ must be larger than $(dT/d\xi)_x$. Negative slopes of $(dT/d\xi)_x$ are observed for copolymers which induce cluster formation; this implies $(\partial \ln s / \partial \ln x)_T < 0$ according to the above solubility model, since such copolymers dissolve preferentially in the cluster state of the nanodroplets where $s_{cl} \gg s_{sol}$. In this case $(\partial \ln s / \partial \ln x)_T = -nx/(1-x)$ (which is small), thus the second term in braces of *Eqn. 13* is negative but > -1 and, thus, $(\partial H^E / \partial x)_{\xi, T}$ becomes positive. Generally speaking, if the second term is very small compared to 1 the partial specific excess enthalpy equals the specific enthalpy related to the percolation transition in the copolymer-free microemulsion.

Table . *Physical Data of Triblockcopolymers (POE-b-PI-b-POE; from [4])*

Blockcopolymers	Cop-1	Cop-2	Cop-3	Cop-4	Cop-5
\overline{M}_N^{POE}	1740	13500	22000	6500	13050
\overline{M}_N^{PI}	85260	61500	39000	19500	15950
POE/PI (w/w)	2/98	18/82	36/64	25/75	45/55
\overline{M}_N^{COP}	87000	75000	61000	26000	29000
\overline{M}_w^{COP}	119000	108000	71800	31200	33000
$\overline{M}_w / \overline{M}_N$	1.37	1.44	1.18	1.20	1.14

To make a numerical estimate, we may assume n of the order of 5 (number of nanodroplets which are nearest neighbors of a POE block) which would yield together with the above figure of -0.3 (ratio of the slopes of the percolation lines) for the second term in the braces of *Eqn. 13* -1.5 . Thus, in case of Cop-3 $(\partial H^E / \partial x)_{\xi, T}$ would decrease by a factor of -0.5 as compared with the pure W/O microemulsion; hence, the system experiences a considerable stabilization with respect to the nanodroplet state. While for Cop-5 (see the *Table*) taking the same n but $x \approx 0.1$ (nanodroplet cluster state) one finds $+0.86 \Delta_{sol}^{cl} H^o$; *i.e.* if a copolymer is added which promotes nanodroplet cluster formation the transition enthalpy of the pure W/O microemulsion is smaller since less thermal energy is required for desolvation to induce cluster formation. Of course, this estimate is crude, but it shows the order of magnitude of the expected effects.

Summarizing, we have shown by a thermodynamic treatment in which way blockcopolymers can either disperse or flocculate aqueous nanodroplets, thereby stabilizing or destabilizing the nanodroplets. Percolation transitions are experimentally easily observable phenomena in phase diagrams, and their location is particularly sensitive towards the addition of additives. Thus, as shown above, from the ratio of the slopes of the lines as shown in *Figs. 2* and *3*, valuable information regarding the stabilizing actions of additives can be obtained.

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