Self-Organization of Amphiphilic Molecules: Micelles and Micro-Phases *

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Abstract

The self-organizational formation of reverse micelles in binary surfactant/solvent mixtures and of aqueous microphases in ternary water/surfactant/oil systems is reported. In particular, recent results regarding the surface thermodynamics (interfacial free energy) of individual microphases, electro-optical pulsed Kerr-effect measurements to study various dipolar relaxation processes, and conductive percolation phenomena in these thermodynamically stable emulsions are discussed. Finally, applicative aspects of microphases in various scientific and technological domains are mentioned.

Introduction

The interplay of many sub-systems, like atoms, molecules, generally unanimated systems, may form (eventually spontaneously) spatial, spatio-temporal, or temporal structures. This kind of self-organizing from complete disorder [1] reminds one of typical phase transitions. If the sub-systems increase in size and/or complexity these self-organizing processes may occur inter- and intramolecularly (cf. e. g. «polysoaps» [2]). This paper will discuss phenomena created by the interaction of relatively simple molecular species (low molecular weight surface active molecules) in binary and ternary fluid mixtures. Nevertheless the wealth of information which is obtained might be surprising. Also, many phenomena should be of more general interest beyond the particular context considered in the following report.

Micelles

Our particular interest is concerned with the self-assembly of amphiphilic molecules, i. e. surfactants or soaps, as they are frequently called. Due to their peculiar structure being composed of a hydrophilic and hydrophobic moiety, (hence being «amphiphilic»), these molecules tend to accumulate in interfaces or, in cases where the interfaces are negligible compared with the volume of the system, to assemble above a particular concentration, the critical micelle concentration, a thermodynamically well-defined constant of the surfactant-solvent system. The resulting molecular aggregates of frequently rather mono-disperse sizes are the so-called micelles. Since this paper is concerned with continuous hydrocarbon phases these aggregates are termed «inverted» (reversed) micelles. Hence, the hydrophilic groups of the constituting amphiphilic molecules form the polar cores of the aggregates which are thus shielded by the hydrophobic tails of the surfactants from the apolar environment.

It is essential to realize that structure, shape, and size of such micellar aggregates as well as their transition from, for example, spherical to «globular», or cylindrical shapes to so-called bi-layer structures (as met in membranes and vesicles) is predicted not only by thermodynamic principles but also by geometric properties and hence packing constraints of the surfactants (or the naturally occurring lipids). This view has been stressed in particular by *Israelachvili* [3] Fig. 1 displays different aggregational structures of amphiphilic molecules, the corresponding critical packing parameters, and selected examples of molecules. The figure exhibits also the quite natural relationship between «normal» micelles (which are formed in aqueous solutions) and «inverted» ones. The critical packing parameters are not free from a certain arbitrariness, especially l_c, the length of the hydrocarbon chain; however, such geometric considerations have proven valuable in predicting qualitatively the above mentioned properties of these aggregates.

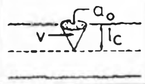
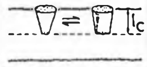
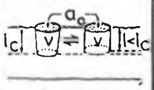
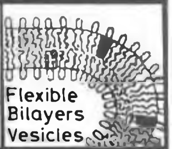
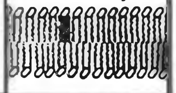
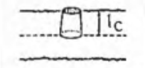
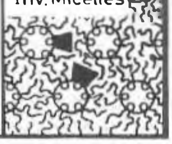
Lipid	Critical Packing Param. $v/a_o l_c$	Critical Packing Shape	Structures Formed
Single-Chained Lipids (Detergents) With Large Head-Group Areas: *NaDS in Low Salt*	<1/3	Cone 	Spherical Micelles 
Single-Chained Lipids With Small Head-Group Areas: *NaDS in High Salt* *Non-Ionic Lipids*	1/3 -1/2	Truncated Cone or Wedge 	Glob. or Cylindr. Micelles 
Double-Chained Lipids With Large Head-Group Areas Fluid Chains: *Lecithin*	1/2-1	Truncated Cone 	 Flexible Bilayers Vesicles
Double-Chained Lipids With Small Head-Group Areas Anionic Lipids in High Salt	~1	Cylinder 	Planar Bilayers 
Non-Ionic Lipids, Poly(cis) Unsaturated Chains, High Temp: *Cholesterol*	>1	Inverted Truncated Cone 	Inv. Micelles 

Fig. 1: Dynamic packing properties of surfactants and the corresponding structures (according to [3]).

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* Based on a lecture given February 23, 1982, to the Chemical Society of Fribourg.

Micro-Phases

The systems mentioned so far refer to binary solutions, i. e. surfactant and solvent. If a third component is added, in the present case water, the nucleation of «microphases» can be studied and with increasing aliquots of water the properties of such microphases. An ensemble of these microphases is conventionally called water-in-oil «microemulsions» [4]. The latter expression is used to denote a thermodynamically stable emulsion.

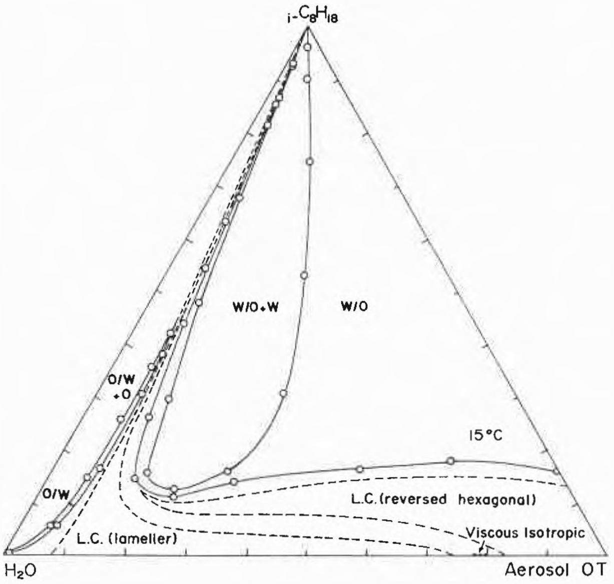

Fig. 2: Phase diagram of the ternary system: H_2O/Aerosol OT/i-octane, T = 288 K.

In order to present the above information and additional details in a concise and unambiguous manner, ternary phase diagrams are preferable (Fig. 2). From this figure essential properties of the Aerosol OT (AOT, sodium di-2-ethylhexyl sulfosuccinate) can be obtained, in particular its tendency to form micelles in hydrocarbons. The extension of the microemulsion domain also comprises phenomenologically the micellar state, according to Fig. 2. Some authors [5] prefer to make a strict distinction between the micellar and the microphase state. Actually, there is a transition from the micellar (in the limit $[H_2O]/[AOT] = w_o = 0$) to the microemulsion state at least in apolar media (nucleation regime of microphases) which does not advocate drawing a sharp boundary line between these two phenomena. Especially, small amounts of water appear to be necessary for many surfactants to form micelles in liquid hydrocarbon solutions [6, 7]. Such transitions are nicely exhibited in Figs. 3 and 5 where in the former the activity of water in an isooctane solution of AOT is plotted as a function of the added amount of water [8]. This graph corresponds to the well-known Raoult's law which becomes apparent if the activity is displayed as a function of mole fraction of water at constant amount of AOT. Deviations from Raoult's law coincide with the sharp downward bending of the activity plot as shown in Fig. 3. The plot is, moreover, theoretically [8] predictable. This description is based on the postulate that the total free energy of the oil/water interface covered by surfactant molecules (the interfacial tension), γ_{final} is approximately zero. Earlier, *Schulman* [9] stated this assumption as a necessary prerequisite for the spontaneous formation of microphases.

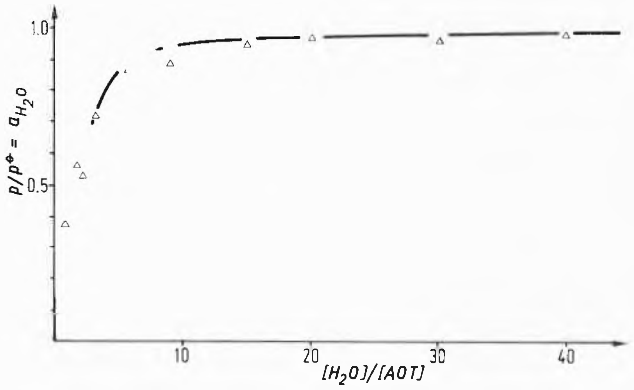

Fig. 3: Activity of water against the added water in the ternary system: H_2O/Aerosol OT/i-octane, $T = 298$ K [8].

It can be shown [10, 11] that γ_{final} is composed of two contributions, namely short range effects (γ_o) which are to a first approximation independent of the curvature of the interface and electrostatic interactions which are, due to their long ranges, dependent on the microphase sizes. According to the above postulate, the electrostatic contribution to the free interfacial energy compensates the

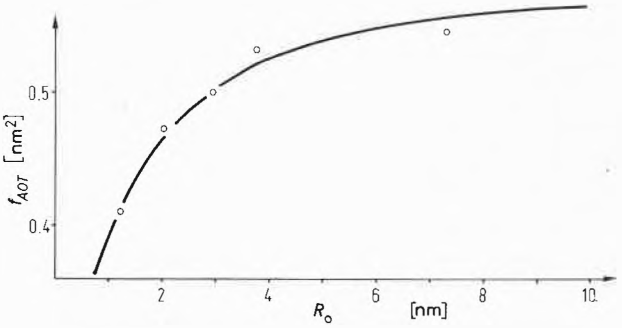

Fig. 4: Aerea of the oil/water interface covered by one AOT-molecule, f_{AOT}, as a function of the aqueous core radius (R_o) of the spherically assumed microphase [8].

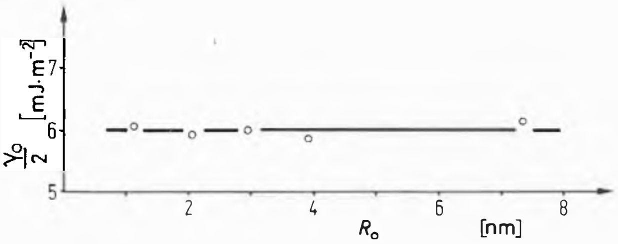

Fig. 5: Interfacial free energy γ_o of a single microphase for different aqueous core radii [8].

short range effects. In spite of the considerable charge density in the interfacial region (see Fig. 4) γ_o stays constant as could be verified experimentally (Fig. 5).

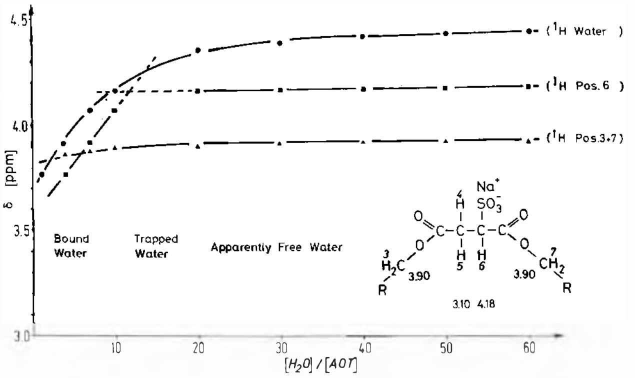

Fig. 6: Chemical shift (δof water and Aerosol OT protons against the added water in the ternary system: H_2O/Aerosol OT/i-octane, at T = 298 K [4].

Fig. 6 demonstrates again an obvious transition region between the so-called micellar solution ($[H_2O]/[AOT] \rightarrow 0$) and the microemulsion. The plot of the chemical shift of the water proton above $w_o = 20$ indicates that the environment of the proton in water within the dispersed state (in the microphase) is almost the same as that in bulk water. This result does not contradict various experimental observations of apparent deviations from bulk water properties; due to the considerably increased oil/water interface it is to be expected that all processes which are influenced by the interfacial region should display anomalies.

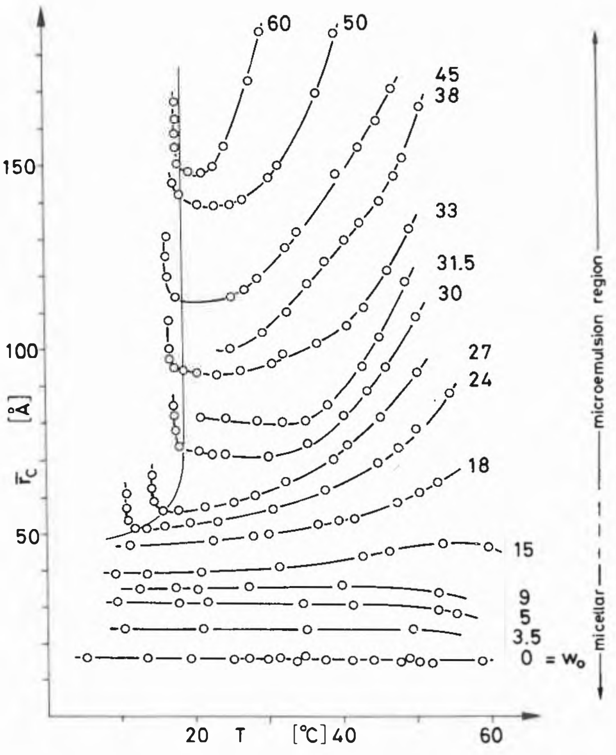

Fig. 7: Mean correlation radii ($\bar{r}_c$) of the aqueous microphases against temperature. Parameter: amount of water. The vertical line denotes a lower phase boundary of the water-in-oil microemulsion.

Another experiment applying quasi-elastic light scattering yields mean correlation radii ($\bar{r}_c$) (measuring rather the extension of the aqueous microphase than the actual hydrodynamic radius) which show a particular temperature and water core-size dependence (Fig. 7); at about $w_o = 10$ the volume ratio of surfactant to water per aggregate is 3.7 [12]. (This corresponds to a suggestion made by *Prince* [13] to differentiate micellar from microemulsion aggregates). The $\bar{r}_c$ against temperature-plots exhibit a markedly increased temperature and pressure sensitivity. These features are characteristic for the formation of «macroscopic» interfaces, i.e. in the present case, aqueous microphases. We would like to stress this criterium, since it appears very suitably to distinguish microphases from micellar aggregates.

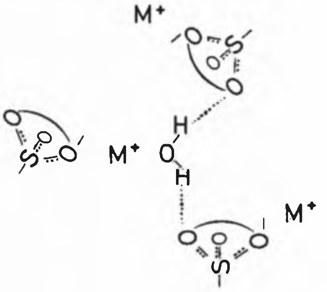

Fig. 8: Model of structure formation of Aerosol OT at very low water content in apolar media [6].

The remarkable thermal stability of the latter in the special case of AOT may be inferred from Fig. 8. The figure suggests the formation of hydrogen bonds and effects of dipole-dipole interactions which could be verified experimentally [14]. It provides reasonable arguments in favour of the observation that AOT micelles in iso-octane were found in the temperature range from −85 to 99 °C with constant size [12]. Thus, these micellar aggregates can be considered to adopt the behaviour of macromolecules.

Properties of Micro-Phases

The aqueous microphases formed by AOT and water in liquid hydrocarbons display several physico-chemical properties (which make their study relevant also from a more general point of view) such as the shape of the plots shown in Fig. 7 with increased temperatures and the steepening of the curves at larger w_o-values within the same temperature range. These experimental results contain information on the physical properties of the single microphases. Their sensitivity towards temperature variations can be followed up with a variety of different techniques, as for example, light-scattering-, ultracentrifuge, viscosity-, and Kerr-effect measurements. The apparent increase in particle size has been identified with a partial coalescence process which is completely reversible if the temperature of the system is lowered again. It originates from the fact that the increased solubility of the AOT in the aqueous microphases and/or the oil-continuous phase reduces the interfacial AOT concentration, hence causing the system to reduce its total interfacial area. The correlation radius determined with the help of the Stokes-Einstein relationship from quasi-elastic light-scattering experiments [12, 14] is composed of the hydrodynamic radius of the spherically assumed microphase-volume which grows due to the coalescence process and due to a contribution which is ascribed to fluctuations of the temperature- and water core-size dependent correlation range of the microphases [15].

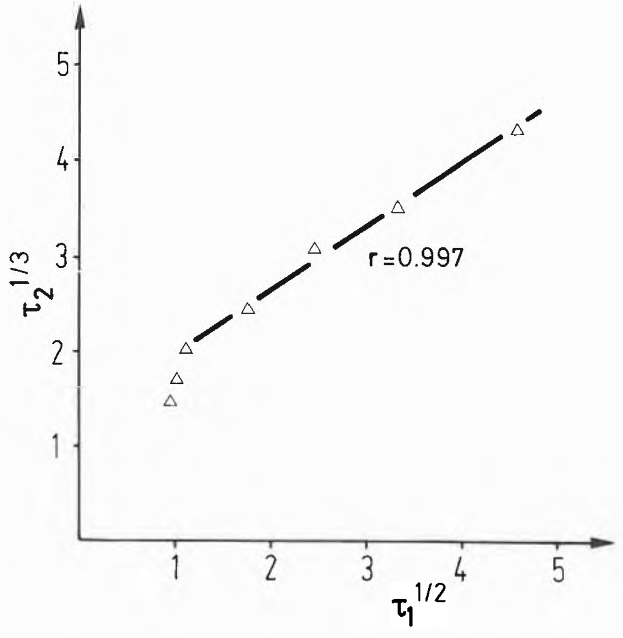

Fig. 9: Correlation of two relaxation times: (τ_1) = relaxation of polarization of double layer and (τ_2) = orientation relaxation of pairs of charged micro-phases; r = correlation coefficient [16].

The special composition of the water-in-oil microemulsion which has been selected for the present discussion, i. e. the choice of an ionic surfactant allowed one to apply electro-optical Kerr-effect measurements. This method is more sensitive than light-scattering techniques since the transmittance is the relevant physical parameter. These experiments were carried out with pulsed electric fields. The evaluation of the results indicate two relaxation processes [16] which are attributed to the decay of an anisotropy of the whole sample, i. e. to the decay of the field-dependent distribution function of the microphases. This anisotropy is due to two molecular phenomena: the orientation of induced dipoles (produced by polarization of the electric double layer of each microphase) and an orientation of ionie pairs of charged microphases with large dipole-moments (> 100 D). The charges are generated by partial dissociation of the micro-phases with following ion exchange due to collisional processes. These collisions cause a very small natural polydispersity of the micro-phases. A proof for the consistency of such assumption is rendered by a correlation diagram relating the aggregate radii as determined by both relaxation models (Fig. 9). Hence Kerr-effect investigations permit one to follow correlation radii-plots almost up to the so-called phase-inversion temperature where the W/O- inverts into a O/W-microemulsion. Close to this temperature the system becomes quite suddenly turbid and the transmittance drops to nearly zero. These graphs are displayed in Fig. 10 and

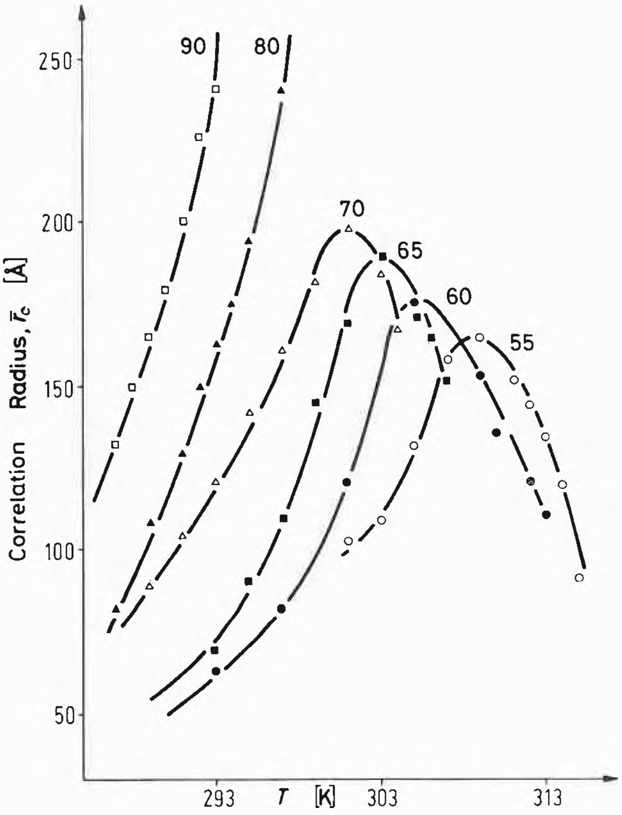

Fig. 10: Mean correlation radii against temperature: parameter w_o = [H_2O]/[AOT].

exhibit characteristic features: they pass through maxima, i. e. reflecting two processes, the coalescence and the increasing solubility of water in the continuous oil phase in the presence of growing amounts of surfactant in the aqueous microphases and the continuous oil phase. This interpretation implies that the critical mixing temperature of water and oil in the presence of AOT is decreasing. It is in line with plots of the temperature-dependent electrical conductivity (Fig. 11). At or close to the $\bar{r}_c$-maxima this conductivity varies jump-like by three to four orders of magnitude reflecting a phase transition. Below the « breaks » of the curves (Fig. 12) the conductiv-

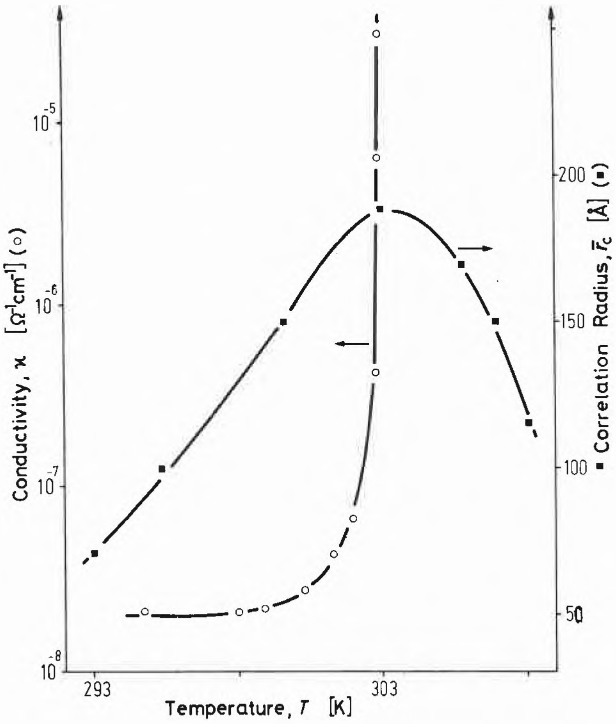

Fig. 11: Temperature-dependence of electrical conductivity and correlation radius of the ternary system: H_2O/Aerosol OT/i-octane.

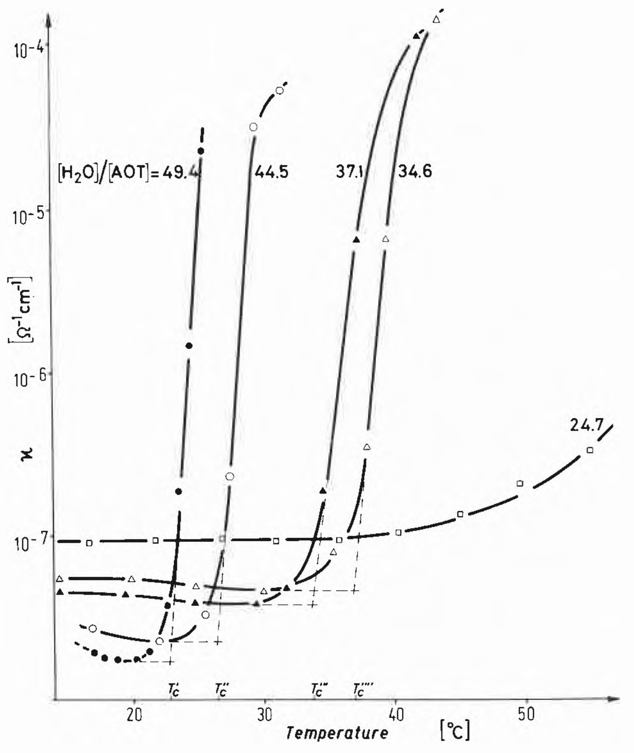

Fig. 12: Temperature-dependence of the electrical conductivity of the ternary system: H_2O/Aerosol OT/i-octane.

ity is seen (at least in some instances) even to decrease with increasing temperature. The different appearrance of the two conductivity-«branches» suggests two conduction mechanisms. The low-temperature branch corresponds to the coalescence process. A ln $\{\varkappa/\varkappa_0\}$ against $(1/T)$-plot (Fig. 13) allows one to determine the activation enthalpy of the coalescence. Its value is small compared to the thermal energy of the system, i.e. the process is diffusion-controlled, or in other words, a Smoluchowski mechanism applies.

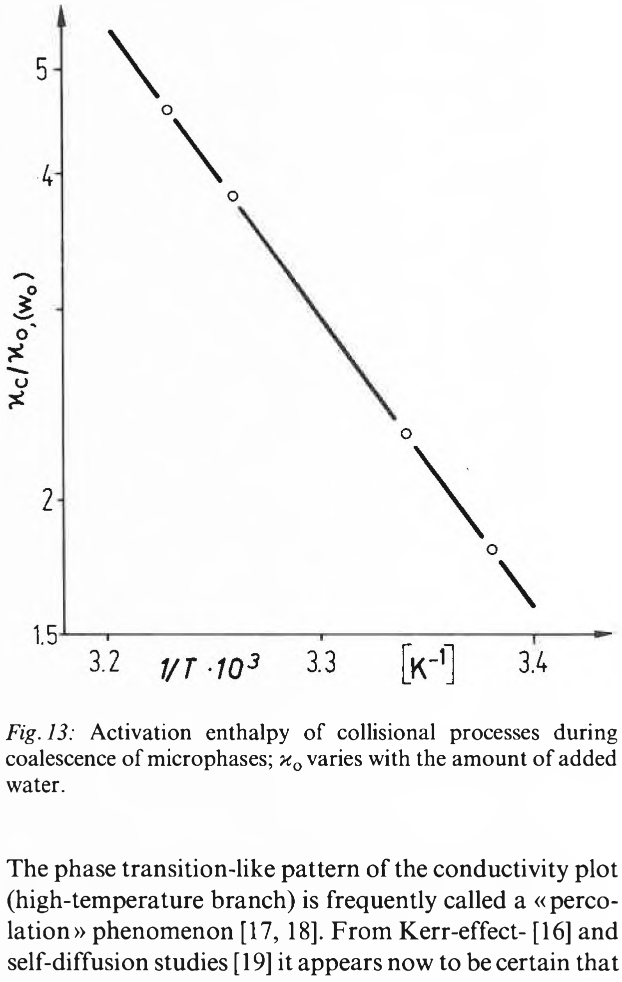

Fig. 13: Activation enthalpy of collisional processes during coalescence of microphases; $\varkappa_0$ varies with the amount of added water.

The phase transition-like pattern of the conductivity plot (high-temperature branch) is frequently called a «percolation» phenomenon [17, 18]. From Kerr-effect- [16] and self-diffusion studies [19] it appears now to be certain that the microphases are not involved in the conduction mechanism. In view of the above discussed diagrams of the correlation radii it is more probable that strongly

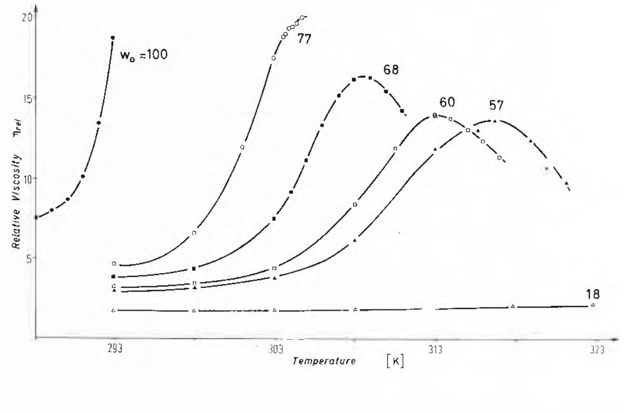

Fig. 14: Temperature-dependence of the relative viscosity of the H_2O/Aerosol OT/i-octane system for varying aliquot of water (w_0 = [H_2O]/[AOT]) [20].

hydrated individual surfactant molecules or small clusters are operative.

Finally, if correlation radii are to be determined, the dependence of the viscosity on temperature has also to be taken into account [20]. From Fig. 14 it is seen that the relative viscosity follows a similar trend with temperature as the correlation radii above a certain aliquot of water.

Applicative Aspects

Microphases have found wide-spread application: the so-called surfactant -polymer flooding in enhanced oil recovery makes use of the low interfacial tension of these systems in liberating crude oil which is immobilized in the deposits by capillary forces [21]. The particular relevance of this process is illustrated by the fact that about half of the total crude oil deposit of the United States is inaccessible to standard conveying systems [22].

Another aspect of microphases is their suitability for the microencapsulation technique [23]. The aqueous core of the microphase contains drugs or vaccines and eventually monomers which are polymerizable. Thus the microphases can be transformed into «nanopellets» or «nanocapsules» depending on whether the effective material is mixed with or separated from the encapsulating molecules.

Also more recently, liquid/liquid stable dispersions were used as blood substitutes, so-called «artificial» blood [24]. Perfluorodecalin with up to 25% perfluoropropylamine and Pluronics (BASF) (nonionic surfactant blend) were mixed to give stable emulsions which were not metabolized in the human body. The perfluorinated hydrocarbons are able to dissolve up to three times as much oxygen as natural human blood. These systems have been successfully tested also with regard to their compatibility. Artificial lungs might be constructed along similar lines [25]. However, this technique leads already to more sophisticated systems, so-called liquid-membranes or multi-phase systems [25] which offer promising separation techniques with many – not yet studied – interesting facets.

Approaches for efficient water fission via photochemical pathways using microphases [26] and very effective enzymatic catalysis via solubilized enzymes have been suggested [27]. There are plans to carry out these in pilot plants.

Acknowledgement

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