

ISSN 0011-1643

UDC 541.1

CCA-2063

Original Scientific Paper

A Dynamic Approach to the Formation of Lamellar Liquid Crystal Aggregates

Durdica Težak

*Laboratory of Physical Chemistry, Faculty of Science, University of Zagreb,
Marulićev trg 19, 41001 Zagreb, P.O. Box 163, Croatia*

Received March 18, 1992

The unusual kinetics of aggregation of amphiphilic micelles in aqueous solutions was demonstrated using light scattering, microscopic and X-ray diffraction data.

Dynamics of the formation of the lamellar mesophases is explained as a consecutive process caused by short-range interactions of growth and curvation of the bilayers, and by long-range aggregation interactions. These driving forces cause the maximum aggregation rate to occur during the periods of non-equilibrium states, as well as the zero aggregation rate in the periods of steady states.

INTRODUCTION

The first dynamic stages of the non-equilibrium processes in the formation of heterogeneous phases from homogeneous aqueous ionic solutions do not present a phenomenon of simple attractions. Normally, the precipitation kinetics is shown by smooth curves, describing either the continuous growth or very fast changes in the characteristics of particles. This type of dynamics is usually found in stable inorganic colloid systems.¹ Investigations of the unusual kinetics of aggregation in the mixed electrolyte and surfactant aqueous solutions described in this paper have to be considered as preliminary research. These systems are so complicated that a truly quantitative analysis is difficult to make. The interactions are due to the coulombic interactions in the electrolytic aqueous solutions, to the association properties of amphiphilic molecules, as well as to chemical interactions of ions. Nevertheless, the phenomena of mutual interactions in so complicated systems containing water-soluble reagents are important from chemical ecological, structural and biological points of view.²⁻⁴

EXPERIMENTAL

Materials

The chemicals used in the experiments were of *p.a.* grade, all of them dissolved in doubly distilled water. Water solutions of AgNO_3 , KI , $\text{Mg}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$, prepared from the chemicals from »Merck«, Darmstadt, were standardized potentiometrically and complexometrically, resp. The thionine water solution was prepared by exact weighing of a pure chemical and by its dissolving in water. The dodecylbenzenesulfonic acid (HBDS) from »Ventron« Alfa, Germany, was used without further purification and standardized potentiometrically with NaOH standard solution.

Methods

The samples were prepared by mixing the interacting components. The relative intensity of scattered light (I_{45}) of 545 nm was measured using the Brice Phoenix static light scattering photometer, model DU 2000. Liquid crystal phases were characterized using a Leitz Wetzlar light microscope with polarizing equipment. Samples for the transmission electron microscope (TEM) (by courtesy of the University of Braunschweig, Germany) were prepared by the freeze-etching technique. X-Ray diffraction spectra were obtained using a standard Siemens X-ray diffractometer with a counter and Si-crystal monochromatized $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSION

Interpretation of Light Scattering Data

The kinetic experiments were performed by recording the relative intensity of scattered light at an angle of 45° (I_{45}) as a function of time. These curves are presented in Figure 1 for the flocculation of positively charged AgI colloid in the presence of thionine. It is obvious that the unusual dynamics is characterized by steady state or non-equilibrium time periods.

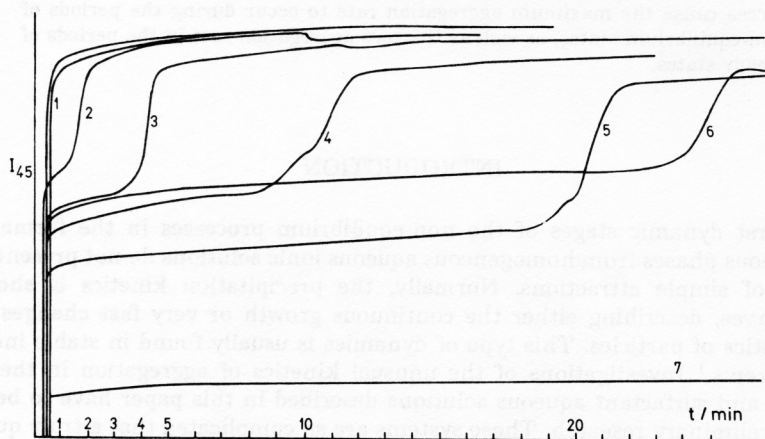


Figure 1. Relative light scattering intensity arbitrary units recorded *versus* time. Experimental systems prepared by simultaneous mixing of the reacting components. All concentrations in mol dm^{-3} : $\text{AgNO}_3 = 4 \times 10^{-4}$, $\text{KI} = 5 \times 10^{-4}$, Thionine: (1) 1.15×10^{-5} , (2) 1.10×10^{-5} , (3) 1.00×10^{-5} , (4) 9.75×10^{-6} , (5) 9.50×10^{-6} , (6) 9.00×10^{-6} , (7) 0.

Since aggregation dynamics in the processes of liquid crystal formation from the solutions can be discontinuous in a very short time period, these different time periods are better characterized by similar slower dynamics, found by the flocculation presented in Figure 1. The two initial aggregation times can be better seen in the log. presentation in Figure 2. The intersections of the steepest lines with the almost parallel lines to x-axis can be considered as critical aggregation times for the equilibrated or non-equilibrated states. The aggregation rate, a derivative of $\Delta I/\Delta t$, plotted *versus* the mean time of each particular period shows (Figure 3) the highest value at the critical time of aggregation, *i.e.* the fast aggregation processes in the non-equilibrium states. The steady state is characterized by the zero aggregation rate. Maximum rates are reached just before the steady states begin. The aggregation rate can be plotted as a function either of the mean time of the non-equilibrium state or as a function of the steady state critical times, as shown in Figure 5 for the liquid crystal formation of Mg-dodecylbenzenesulfonate (MgDBS) from Figure 4. The kinetics of the liquid crystal formation indicates a series of aggregations. During particular time periods, the size of aggregates undoubtedly increases, as shown earlier for AgI coagulation.⁵⁻⁷ For AgI polydispersed colloidal aggregates, the fractal dimensions were found in the range of 1.5 to 2.8.⁸ The fractal dimensions for MgDBS colloidal aggregates were found to be in the same range,⁹ while the values obtained for MgDBS mesophases were in controversy with the classical fractal concept. The scattered intensity, as a function of the magnitude of the scattered wave vector from preliminary investigations of the formation of the lamellar phase, has shown values greater than 3 (between 3 and 4), just as found for solution-grown silica aggregates.¹⁰⁻¹² It can be assumed that the dynamics of liquid crystal formation has to be considered as formation of very well defined particles with surface fractality. The question could be posed whether this is a random, or a self-similar fractal character, or some other model. The calculated slopes over 3 (correlation factor 0.999 was obtained by fitting the linear function) in this case can be due to some sur-

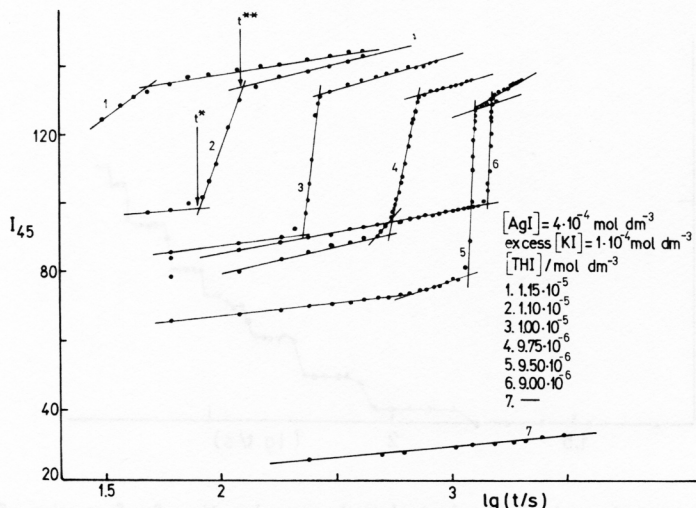


Figure 2. Light scattering intensity plotted *versus* log. time. All concentrations the same as in Figure 1. Critical time of non-equilibrium ($t^*_{\text{non-eq.}}$) and steady states ($t^{**}_{\text{s.t.s.}}$) denoted by arrows.

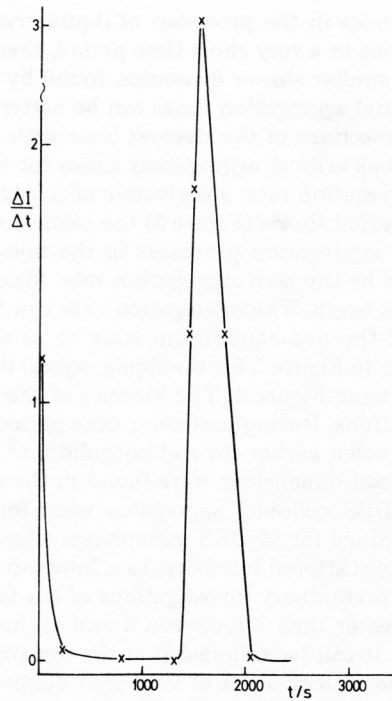


Figure 3. Aggregation rates presented as a function of mean times for system 5 from Figure 2. The first part of the fitted curve shows exponential decay.

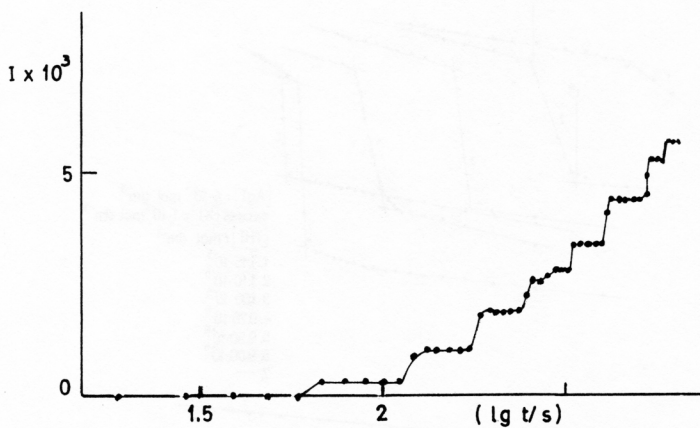


Figure 4. Light scattering (absolute value) plotted *versus* log. time for formation of the liquid crystalline phase obtained by mixing the equimolar $\text{Mg}(\text{NO}_3)_2$ and HBDS of $7.5 \times 10^{-4} \text{ mol dm}^{-3}$ (premicellar regime for HBDS). The discontinuous kinetic phenomena are identical to those obtained by more concentrated HBDS (over c.m.c.).

face structure interactions. The dynamics of formation of the lamellar phase can be explained in terms of the findings in the experimental work described. The first time period after driving together the reacting species in the aqueous solution was characterized by the short-range forces between the interacting ions or molecules. After the basic

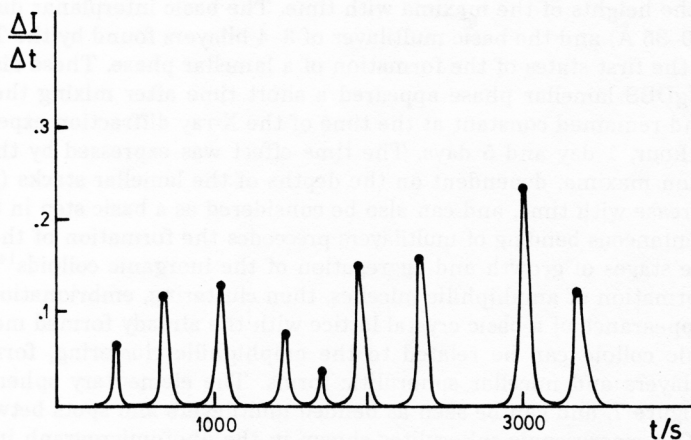


Figure 5. Aggregation rates presented *versus* time for the system in Figure 4.

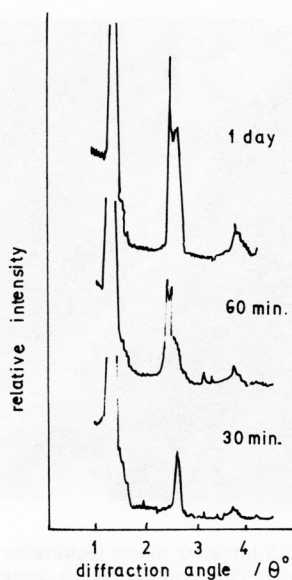


Figure 6. X-Ray diffraction pattern of MgDBS liquid crystal phase taken at 30 minutes, 60 minutes and 1 day after preparing the sample of MgDBS.

structure was formed, further time periods were characterized by the long-range forces between the already formed particles producing consecutive aggregation. Regular self-similarity could be assumed in the dynamic stages of the formation of irreversible clustering in the first time periods, as well as in the formation of the primary particles.

The basic process of the formation of bilayers was confirmed by X-ray diffraction.¹³ The diffusional growth of bilayers into multilayers or stacks is presented in Figure 6 by increasing the heights of the maxima with time. The basic interplanar distances in the bilayers (30–35 Å) and the basic multilayer of 3–4 bilayers found by the TEM (Figure 7) present the first states of the formation of a lamellar phase. These distances of 35 Å of the MgDBS lamellar phase appeared a short time after mixing the reacting components and remained constant at the time of the X-ray diffraction experiment of 30 minutes, 1 hour, 1 day and 5 days. The time effect was expressed by the heights of the diffraction maxima, dependent on the depths of the lamellar stacks (Figure 6). The stacks increase with time, and can also be considered as a basic step in the micellar growth. Spontaneous bending of multilayers precedes the formation of the primary particles. If the stages of growth and aggregation of the inorganic colloids¹⁴ are compared to the formation of amphiphilic micelles, then clustering, emersion, nucleation and the appearance of a basic crystal lattice with the already formed methoric layer of inorganic colloid can be related to the amphiphilic clustering, formation of bilayers, multilayers and micellar spherulitic forms. The elementary spherulites are presented in Figure 7, and can be seen as bended multilayers and spots between sinusoidal traces. The macroscopic spherulites shown in the photomicrograph in Figure 8 are usually polydispersed, but the association into »chains«¹⁵ or macroglobular formations is possible only from the monodispersed spherulites, both on the microscopic (presented in Figure 7 and also by Jahn and Strey¹⁶) or macroscopic level (presented in Figure 8).



Figure 7. TEM micrograph of MgDBS lamellar phase (equimolar $\text{Mg}(\text{NO}_3)_2$ and HDDBS of 6×10^{-2} mol dm^{-3} ; total magnification 53000x. The bending of the lamellar multilayers into a globular form can be clearly seen in the lower right part. The sinusoidal trace in the left part shows the previously existing spherulites. Some round traces have also remained from the individual spherulitic positions (the upper right part).

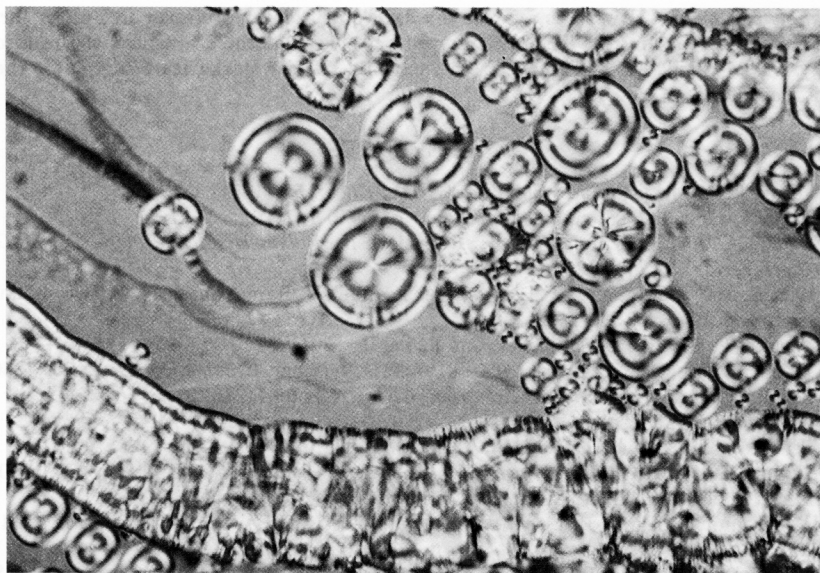
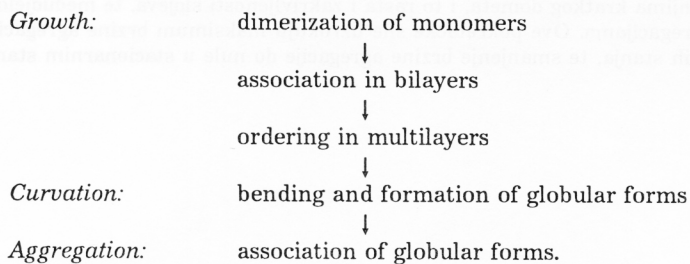


Figure 8. Photomicrograph from the polarizing microscope of AIDBS liquid crystal phase. Concentrations in mol dm^{-3} : $\text{Al}(\text{NO}_3)_3 = 1 \times 10^{-2}$, HDBS = 4×10^{-2} , $\text{HNO}_3 = 9 \times 10^{-3}$, λ -plate, total magnification $150\times$.

Macro-spherulites undoubtedly show their association character, *i.e.* in the middle of the picture the spherulite gets suddenly disintegrated into many small ones. They can also be very easily attracted into a sticky viscous mass with strong surface tension.

Emphasis on the Dynamics of the Lamellar Liquid Crystalline Phases

The aggregation dynamics of a lamellar phase formation in the described experiments can be assumed as a series of consecutive processes, which can be mainly divided in the time periods of elementary short-range interactions of growth and curvation of multilayers and in the time periods of consecutive aggregations. Schematically, the primary particles formation can be presented as:



Although the macrospherulites appear in a size range of 40 000 to 150 000 Å, the basic interplanar distances remain strictly the same, emphasizing the distinction between the basic processes of growth and secondary processes of aggregation, due to the short- and long-range forces, respectively.

Acknowledgement. – I wish to express my deep gratitude to Professor C. Führer for useful discussions and for having the TEM micrographs prepared at the University of Braunschweig, Germany. I also thank Dr. S. Popović from Institute »Rugjer Bošković«, Zagreb for the X-ray diffraction studies.

REFERENCES

1. B. Težak, E. Matijević, and K. Schultz, *J. Phys. Chem.* **55** (1951) 1557.
2. A. S. C. Lawrence, *Mol. Cryst. Liquid Cryst.* **7** (1969) 1.
3. H. Bader, K. Dorn, B. Hupfer, and H. Ringsdorf, in »*Polymeric Membranes*«, Ed. M. Gordon, Springer Verlag, Berlin 1985, pp. 1-62.
4. H. Lamparski, U. Liman, J. A. Barry, D. A. Frankel, V. Ramaswami, M. F. Brown, and D. F. O'Brien, *Biochemistry* **31** (1992) 685.
5. M. Mirnik, P. Strohal, M. Wrischer, and B. Težak, *Kolloid-Z.* **160** (1958) 146.
6. D. Težak, V. Hrust, S. Heimer, B. Težak, and M. Wrischer, *Croat. Chem. Acta* **53** (1980) 397.
7. D. Težak, N. Batina, and B. Čosović, *Croat. Chem. Acta* **59** (1986) 813.
8. D. Težak, to be published.
9. D. Težak and F. Strajnar, *Period. Biol.* **93** (1991) 333.
10. D. Avnir, Ed.: »*The Fractal Approach to Heterogeneous Chemistry*«, J. Wiley & Sons, 1990, Great Britain, Courier Intern. Ltd., Tiptree, Essex, pp. 69-72.
11. P. W. Schmidt, D. Avnir, D. Levy, A. Höhr, M. Steiner, and A. Röhl, *J. Chem. Phys.* **94** (1991) 1474.
12. P. Pfeifer, D. Avnir, and D. Farin, in »*Large Scale Molecular Systems – Quantum and Stochastic Aspects*«, Eds. W. Gans, A. Blumen, and A. Amann, NATO ASI Series, B, Plenum Press, New York 1991, pp. 215-229.
13. D. Težak, S. Popović, S. Heimer, and F. Strajnar, *Progr. Colloid Polym. Sci.* **79** (1989) 293.
14. B. Težak, *Disc. Faraday Soc.* (1966) No 42, 175.
15. D. Težak, F. Strajnar, D. Šarčević, O. Milat, and M. Stubičar, *Croat. Chem. Acta* **57** (1984) 93.
16. W. Jahn and R. Strey, *J. Phys. Chem.* **92** (1988) 2294.

SAŽETAK

Dinamički pristup stvaranju agregata lamelarnih tekućih kristala

Đurđica Težak

Pomoću mjerenja raspršenja svjetla, difrakcije X-zraka i mikroskopije prikazana je neobična kinetika agregacije amfifilnih micela u vodenim otopinama.

Dinamika stvaranja lamelarnih mezofaza objašnjena je kao konsektivni proces, uzrokovan međudjelovanjima kratkog dometa, i to rasta i zakrivljenosti slojeva, te međudjelovanjima dugog dometa – agregacijama. Ove pokretačke sile uzrokuju maksimum brzine agregacije u periodima neravnotežnih stanja, te smanjenje brzine agregacije do nule u stacionarnim stanjima.