Volume 110 (1998)

Progress in Colloid & Polymer Science

Trends in Colloid and Interface Science XII

Guest Editors:
G. J. M. Koper (Leiden)
D. Bedeaux (Leiden)
W. F. C. Sager (Twente)
C. Cavaco (Leiden)

The 11th Conference of the European Colloid and Interface Society (ECIS) was held in September 1997 in Lunteren, The Netherlands. The scientific program covered theoretical, experimental, and technical aspects of modern colloid and interface science. This volume contains a selection of contributions in the following fields:

- New topics in colloid science
- Polymer colloids
- Rheology
- Surfactant colloids
- Polymers and surfactants at interfaces

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F. Kremer (Leipzig)
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Springer

ISBN 3-7985-1117-9
ISSN 0340-255 X

Die Deutsche Bibliothek –
CIP-Einheitsaufnahme

Progress in colloid & polymer science. –
Darmstadt : Steinkopff ; New York :
Springer
Früher Schriftenreihe
Reihe Progress in colloid & polymer
science zu: Colloid & polymer science
ISSN 0340-255X

Trends in colloid and interface science ... :
... European Colloid and Interface Society
(ECIS) conference ... – Darmstadt :
Steinkopff ; [New York] : Springer
12 (1998)
(Progress in colloid & polymer science ;
Vol. 110)
ISBN 3-7985-1117-9

Chemistry Editor:
Dr. Maria Magdalene Nabbe;
Production: Holger Frey, Ajit Vaidya.

Typesetting and Copy-Editing:
Macmillan Ltd., Bangalore, India

Printing: Druckhaus Beltz, Hemsbach

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PREFACE

The 11th Conference of the European Colloid and Interface Society (ECIS 97) was held September 1419, 1997 in the Congress Center *De Blije Werelt*, Lunteren, The Netherlands. The conference was attended by 205 scientists from 24 different countries. The scientific program contained 50 oral and 142 poster contributions and covered theoretical, experimental and technical aspects of modern colloid and interface science. This volume contains a selection of the contributions presented at the conference and is divided into the following sections:

- New topics in colloid science,
- Polymer colloids,
- Surfactant colloids,
- Polymers and surfactants at interfaces,
- Rheology.

In the Overview (page XXX) various contributions to the conference are discussed. During the conference three poster contributions were selected that, according to the Organizing Committee, were of outstanding quality. The contributors, H. Behrens (see page XXX), T. Iwanaga (see page XXX), and K. Marinova (see page XXX), received the Poster Prize in the form of a book of choice from the exhibition at the conference site.

The Organizing Committee wishes to thank all participants for their scientific contributions which resulted in a very successful conference. We are especially grateful to the members of the Scientific Committee:

Peter Schurtenberger, ETH Zürich, Switzerland
Otto Glatter, Universität Graz, Austria
Dominique Langevin, Centre de Récherche Paul Pascal, France
Thomas Zemb, CEN Saclay, France
Vittorio Degiorgio, Università di Pavia, Italy
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Martien Cohen Stuart, Agricultural University, The Netherlands
Jaap Leyte, University of Leiden, The Netherlands
Jorrit Mellema, University of Twente, The Netherlands
Grégoire Porte, Université Montpellier II, France

who helped us in the difficult task of selecting the contributions for oral presentations.

We gratefully acknowledge the financial support from the European Colloid and Interface Society, the Royal Academy of Sciences, the Leiden Institute of Chemistry, the Faculty of Mathematics and Science of the Leiden University, Shell Nederland, DSM Research, Akzo Nobel, Unilever, and the Institut für Terrestische Ökologie of the Eidgenössische Technische Hochschule in Zürich. Their support enabled us to give 13 grants covering the conference fee and accommodation to young researchers and scientists from Eastern European countries.

On behalf of the Organizing Committee:
Ger J. M. Koper, Leiden Institute of Chemistry, The Netherlands, chair
Dick Bedeaux, Leiden Institute of Chemistry, The Netherlands
Wiebke F. C. Sager, University of Twente, The Netherlands
Carolina Cavaco, Leiden Institute of Chemistry, The Netherlands

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Wiebke F. C. Sager
University of Twente

ECIS 97 – an overview

This volume contains contributions presented at the 11th Conference of the European Colloid and Interface Society *(ECIS 97)* held in the Congress Center De Blije Werelt, Lunteren, The Netherlands, on September 14–19, 1997. Topics covered at the conference were: *New topics in colloid science, Rheology, Surfactant colloids, Polymer colloids, Surfactants at interfaces, and Polymers at interfaces.* Each topic formed a separate section of the conference comprising a 45 minute key note lecture (KL), a 35 minute invited lecture (IL), five or six 15 minute contributed talks, and a dedicated part of the poster session. In the evenings, informal scientific lectures were given by leading Dutch scientists related to the field. These proceedings comprise 40 % of the oral and 25 % of poster contributions presented at the conference. A somewhat larger number of papers were submitted for the topics *New topics in colloid science and Polymer colloids.* The contributions are ordered according to the conference topics of which *Surfactants at interfaces and Polymers at interfaces* have been merged into one section. In the following, a brief overview of selected talks which are not published in this volume is given. In order to facilitate the access to recent publications for interested readers we include a reference list of the subjects presented. The conference started with the topic:

New topics in colloid science

Chairman: Otto Glatter, Universität Graz

KL Mode selective optical receivers: Application to colloidal systems. J. Ricka, University of Berne [1, 2, 3]

IL Quantitative real-space analysis of colloidal structures and processes. A. van Blaaderen, Utrecht University [4, 5, 6]

Ricka started his lecture by discussing the advantages of replacing the classical pair of pinholes in optical devices by a single mode fiber, thus, selecting a single mode [1, 2, 3]. After introducing the principles of optical single mode receivers, he focused on two techniques whose performance improved due to the superior sensitivity and simplicity of single mode fiber set-ups, namely, dynamic light scattering and confocal scanning microscopy. In the last part of his talk, he presented new results on an interesting coil-globule transition occurring in aqueous solutions of the mixed polymer/surfactant system PNIPAM (poly(N-isopropylacrylamide))/SDS. Phenomena observed upon addition of SDS to a solution of the thermosensitive polymers, which collapse from the coil state into the globular state upon increasing temperature, are more complex than expected from polymer/surfactant couples studied previously. Below the coil-globule transition temperature polymer-bound SDS micelles that incorporate the polymer backbone as well as quasi-free micelles form, depending on the SDS concentration. In the course of the temperature-induced coil-globule transition of the macromolecules, the mixed polymer surfactant aggregates undergo a profound restructuring. The surfactant remains firmly associated with the polymer and above the transition temperature the polymeric globules seem to be coated with a surfactant layer, stabilizing the globules against aggregation observed in SDS free systems.

Van Blaaderen showed how fluorescence confocal scanning light microscopy can be used to obtain 3D coordinates in optically matched dispersions of, e.g., fluorescently labeled core-shell particles [4, 5, 6]. Examples were given for real-space structures of hard-sphere glasses, crystals grown by colloidal epitaxy, electrorheological fluids, and binary structures. At the end of the lecture he demonstrated that so far fast temporal information can only be obtained in a 2D plane albeit in the bulk of a dispersion.

Rheology

Chairman: J. Mellema, University of Twente

KL The rheology of strongly interacting colloidal suspensions: Experimental elucidation of reversible shear thickening. N. Wagner, University of Delaware, Newark [7, 8, 9]

IL The role of disorder in emulsion rheology. F. Lequeux, Université Louis Pasteur, Strasbourg [10, 11]

Among a variety of interesting phenomena observed for concentrated suspensions under shear, Wagner discussed the reversible shear thickening transition in the context of interparticle interaction and the underlying microstructure on a colloidal level [7, 8, 9]. He demonstrated that combining rheological measurements with optical and neutron scattering is a versatile approach to reveal the mechanism of shear thickening and its dependence on the type of colloidal stabilization employed.

In the invited lecture, Lequeux demonstrated that quenched disorder can explain complex phenomena observed in the rheological behavior of concentrated oil-in-water emulsion [10, 11]. The non-linearity and the frequency dependence of the loss modulus cannot be understood in terms of the classical Princen models which, over the last 2 decades, have been successfully applied to describe yield stress and the elastic modulus. The mechanical response of an emulsion can, in fact, be divided in at least three domains: The first regime is characterized by very small strains and a linear response which can be related to thermal fluctuations. In the second regime, for intermediate strain values below the yield stress, the response is non-linear, but the elastic modulus is apparently linear. Above the yield stress, in the third regime, the system flows with fracture. To demonstrate the origin of non-linearities a new technique, the position echo technique, was developed which allows one to measure the motion of the oil droplets in a periodic macroscopic flow. The results demonstrate that in the second and third mechanical regime, only some of the droplets contribute to the irreversibility of the flow.

Surfactant colloids

Chairman: J. C. Earnshaw, The Queens University of Belfast

KL Structure and phase equilibria of microemulsions. U. Olsson, University of Lund [12, 13, 14]

IL Recent advantages in cryogenic transmission electron microscopy. D. Danino, Israel Institute of Technology, Haifa [15]

Olsson first reviewed state-of-the-art knowledge on the stability and the phase behavior of microemulsions introducing the Helfrich free energy concept and emphasized the crucial role of the spontaneous curvature, H_0, of the surfactant monolayer [12, 13, 14]. The invariance of the curvature energy with respect to the transformation $H_0 \rightarrow -H_0$ and ϕ_0 $(1-\phi_0)$, ϕ_0 being the volume fraction of oil, implies a symmetric phase diagram, as observed with nonionic surfactants of the C_iE_j type, for which H_0 is found to be a strong and approximately linear function of temperature. At constant ϕ_s/ϕ_0, ϕ_s being the surfactant volume fraction, plates, cylinders, spheres, and spheres plus excess oil form when H_0 deviates further from zero. He focused in particular on features of spherical o/w droplets and the L_3 or sponge phase. For the droplet phase, characterized over a large volume fraction essentially by hard sphere interactions, new osmotic pressure measurements were presented for the ternary system as well as for droplets charged up by the addition of SDS. While the binodal corresponds to $\Pi = 0$, Π being the osmotic pressure, it might be possible to identify the spinodal from $\partial\Pi/\partial\phi = 0$ inside the coexistence region. When H_0 is near zero, the phase diagram reveals also an L_3 phase, which joins up with the bicontinuous microemulsion upon bilayer swelling and may crystallize into a cubic phase at higher surfactant concentrations. The L_3 phase has a finite swelling and exists with excess solvent.

De Vries (Delft University of Technology) gave an interesting presentation on undulations in lamellar charged fluid membranes [16, 17]. He first introduced a theoretical account for the interplay between electrostatic interactions and thermal undulations, both in the presence and absence of added electrolyte. In the second part of his talk he showed that this theoretical description can quantitatively explain backscattering experiments obtained on dilute lamellar $C_{12}E_5$ phases, which were charged up by the addition of small amounts of SDS.

Pedersen (Risø National Laboratory) presented Monte Carlo simulation studies on semidilute solutions of semiflexible polymers and worm-like micelles [18, 19]. The simulations were performed to calculate the scattering functions for the full system as well as the single chains including excluded-volume effects.

Appell (Université Montpellier II) presented results of a small angle neutron scattering study of oil swollen micelles to which hydrophobically endgrafted hydrosoluble polymers were added. Successive addition of polymers grafted at only one end induces an increasing repulsive interaction between the micelles leading to the occurrence of a pronounced peak in the scattering curves. For double sided grafted polymers attenuation of the introduced repulsion was explained by bridging occurring between the micelles.

In the invited lecture Danino showed recent advances in cryogenic transmission electron microscopy [15]. Special attention was given to the vitrification of viscous and oil-continuous phases which allows to follow directly microstructural

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changes induced by, e.g., temperature or concentration changes.

Polymer colloids

Chairman: V. Degiorgio, Università di Pavia

KL Charge, structure, and stability of aqueous polymer-colloid suspensions. M. Borkovec, ETH Zürich [20, 21, 22]

IL Light scattering studies of adsorption of surfactant and polymers on colloids. R. Piazza, Università di Pavia (see page 89)

After reviewing the different mechanisms that can lead to the build-up of charges on macromolecules and colloidal particles, Borkovec showed how these concepts can be applied to the understanding of electrostatic forces, which determine the structure and aggregation behavior of colloidal particle suspensions [20, 21, 22]. In the low salt region the properties of the stable suspensions are mainly determined by effective charges derived from the far limit of the electrostatic potentials. The suspensions thus display fluid-like structures, aggregation processes are slow and colloidal crystals may form. At higher salt concentrations the suspensions become unstable, aggregation processes are fast and lead initially to the formation of doublets and at the later stages to larger clusters, and ultimately to gelation.

Surfactants at interfaces

Chairman: U. Olsson, University of Lund

KL Forces between surfactant monolayers adsorbed at oil-water interfaces. P. D. I. Fletcher, University of Hull [23, 24]

IL Light scattering from surfactants at interfaces. J. C. Earnshaw, The Queens University of Belfast [25, 26, 27, 28]

Fletcher reported the first results obtained with a newly developed liquid surface force apparatus, which allows direct determination of the interaction force exerted, the film radius, and thickness, when a micrometer sized oil droplet coated with a surfactant monolayer approaches a surfactant monolayer adsorbed at an oil/water interface [23, 24]. The measurements also yield results for the disjoining pressure as a function of separation between the monolayers interacting across the thin oil-water-oil emulsion film formed when the apex of the oil drop is close to the oil/water interface. Results for a range of ionic and nonionic surfactant monolayers showing repulsive interactions were presented. The films formed have a film thickness greater than approximately 15 nm. The variation of disjoining pressure with film thickness is found to be in accordance with electrostatic theory. In addition SDS monolayers have been studied at various salt concentrations to modify the attractive forces between the monolayers. Such monolayers show a short range adhesive interaction and exhibit a strong hysteresis in their force-distance behavior as the surfaces are pushed together and pulled apart indicating that additional forces are required to unstick the oil droplet from the interface. Measurements of forces between surfaces at small separation is of central importance in attempting to gain a fundamental understanding of many aspects of the complex behavior of colloidal systems, such as factors controlling emulsion stability.

Treiner (Université Pierre et Marie Curie, Paris) presented adsorption isotherms at a silica/water interface of nonionic surfactants of the alkylpolyoxyethylated series for pure compounds as well as polydispersed commercial detergents [29, 30]. At low surface coverage polydispersity effects in the alkyl chain length or the ethoxy group number are negligible and the oligomers behave essentially as pure, single surfactants. At higher surface coverage differences in the tendency to form large structures, disks or patched bilayers, which decreases with increasing length of the apolar part, are shown to be cancelled out in the presence of oligomers with longer and shorter alkyl chain lengths.

The question whether first order phase transitions can occur in soluble monolayers at water/air interfaces has been addressed by Lunkenheimer (Max Planck Institute for Colloid and Interface Science, Berlin) who gave a presentation on transitional behavior and phase transitions in soluble adsorption layers [26, 31, 32]. Adsorption of soluble amphiphiles at water/air interfaces is normally characterized by a continuous transition region connecting at least two distinct surface states attributed to the different surface configurations of the amphiphiles. Recently, strong water evaporation retardation and a constant orientation of the amphiphilic layer above the transition concentration has been observed for a still soluble system indicating that even for soluble monolayers surface interactions might become strong enough to meet the conditions for phase separation following the theory of regular surface behavior.

Riegler (Max Planck Institute for Colloid and Interface Science, Berlin) presented a comparative study on the relation between film topology and molecular ordering for rodlike monomers with amphiphilic and purely hydrophobic character at solid/vapor interfaces [33, 34]. Fatty acids as well as alkanes show, at the solid/vapor interface, similar equilibrium film topologies despite their different characters. Below the bulk melting temperature a monolayer forms on the substrate surface which is covered by mesalike islands or a closed film, depending on the surplus concentration. For fatty acids and alkanes with chain length between 14 and 50 C-atoms, small

droplets form out of the surplus material above the melting point. Whereas alkanes with shorter chain lengths or at much higher temperatures show nearly complete wetting.

In the invited lecture Earnshaw demonstrated that the scattering of light by thermally excited capillary waves, which has in the past been successfully applied to study liquid surfaces of pure fluids and spread monolayers, can reveal new phenomena in surfactant solutions [25, 26, 27, 28]. These include demonstrating the existence of transitional effects in adsorbed films associated with the changes in the dynamics of molecular orientation and the subsequent observation of viscoelastic relaxation of the dilatational modulus of such films. Anomalous behavior of the observed capillary waves suggests an electrostatic adsorption barrier.

Polymers at interfaces

Chairman:
M. Cohen Stuart, Agricultural University Wageningen

KL Layer formation and exchange kinetics of adsorbed polymer chains. A. Chakrabarti, Kansas State University (see page 291)

IL Properties of bridging polymer chains. T. van de Ven, McGill University, Montréal [35, 36, 37]

The last lecture of the conference was presented by Van de Ven, who gave an overview on possible mechanisms of polymer bridging [35, 36, 37]. A prerequisite for particle flocculation by polymer bridging is that the adsorbing polymer coats the particles only partly, leaving enough room on the particle surface for bridging to occur. Even particles onto which the polymer does not adsorb can be bridged in the presence of particles onto which the polymer adsorbs, leading to heteroflocculation due to asymmetric polymer bridging. In association induced polymer bridging, non-adsorbing polymers can be turned into adsorbing molecules which are able to bridge colloidal particles. After the bridge is formed, polymers continue to rearrange their configuration, similar to regularly adsorbed polymers, leading usually to an increase in the bond strength with time.

Special lectures

Phase transitions, aggregation, and gelation in colloid polymer mixtures. Henk Lekkerkerker, Utrecht University [38, 39, 40]

Depletion interactions among globular proteins and semidilute polymer. Theo Odijk, Delft University of Technology [41, 42, 43]

Simulating rare events in complex liquids. Daan Frenkel, FOM Institute for Atomic and Molecular Physics, Amsterdam [44, 45]

Poster prizes

During the conference prizes for the three best posters were awarded by a scientific jury and the Organizing Committee. Papers of all three prize winning poster contributions are published in this volume (see pages 66, 245, and 225). The prizes went to:

H. Behrens, M. Schudel, M. Semmler, M. Borkovec, P. Schurtenberger, and H. Sticher
Stability of colloidal suspensions: A DLVO-treatment accounting for surface heterogeneity.

K. G. Marinova, T. D. Gurkov, T. D. Dimitrova, R. G. Alargova, and D. Smith
Oscillatory structural interactions in thin emulsion films containing micelles of ionic surfactant.

T. Iwanaga, Y. Shiogai, and H. Kunieda
Phase behavior of polyoxyethylene modified silicone with water.

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