Surface Chemistry in Biomedical and Environmental Science
NATO Science Series

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Surface Chemistry in Biomedical and Environmental Science

edited by

Jonathan P. Blitz
Eastern Illinois University,
Charleston, IL,
U.S.A.

and

Vladimir M. Gun’ko
Institute of Surface Chemistry,
Kiev,
Ukraine

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and executed on a computer system, for exclusive use by the purchaser of the work.
Professor A. A. Chuiko, NATO ARW co-director from which these proceedings are derived, died on the 16th of January, 2006. His outstanding contributions to the fields of physical chemistry, physics, chemistry and solid surface technologies will be a lasting legacy. Professor Chuiko obtained his Doctorate in Chemical Sciences in 1972. Since 1988 he was an academician of the National Academy of Sciences of Ukraine. Some activities and awards during his career include being an active member of the Academies of Technological Sciences of Ukraine and Russian Federation, an Honored Scientist and Technologist of Ukraine, a laureate of the State Prize of UkrSSR in Science and Engineering and the Pisarzhevsky Prize, and the President of the Ukrainian Chemical Society. Professor Chuiko in 1986 was a founder and permanent Director of the Institute of Surface Chemistry of the National Academy of Sciences of Ukraine, a world renowned research organization in which he was a driving force.

A. A. Chuiko expended considerable effort to the training of young scientists, having trained more than 100 Ph.D. and Doctors of Sciences students.

A. A. Chuiko and his co-workers developed fundamentals of modern surface chemistry of ultra-dispersed solids, new types of functional nanomaterials, and founded a new direction in pharmacology based on nanomaterials. His comprehensive creative activity was characterized by deep intuition and understanding of new and perspective directions in chemical science. Many of his projects led to industrial materials production.

Prof. Chuiko was a positive force in many people’s lives. He is remembered as an outstanding and talented scientist, a man of deep erudition possessing a sharp and ever active mind. He was a man of inexhaustible energy, initiative, and wisdom. His sincere generosity will remain in the hearts of his colleagues.
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preface</td>
<td></td>
<td>xi</td>
</tr>
<tr>
<td>xi</td>
<td>List of Contributors</td>
<td>xiii</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Fundamentals</strong></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Water structuring at colloidal surfaces</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>M. Chaplin</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Microgels and core-shell particles</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>B. Vincent</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Microencapsulation: fundamentals, methods and applications</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>D. Poncelet</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>The molecular layering method: progress in science and practical</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>works for creation of functional nanomaterials</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A. A. Malygin</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Analysis of surface structures using XPS with external stimuli</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>G. Ertas, S. Suzer</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Modification and coating of polymer surfaces</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>O. Gershevitz, P. Silickas, C. N. Sukenik</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Is it possible to generalize the problems of porous materials</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>formation, study and exploitation?</td>
<td></td>
</tr>
<tr>
<td></td>
<td>M. S. Mel’gunov, V. B. Fenelonov</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>Theoretical analysis of surface pressure of monolayers formed by</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>nano-particles</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V. B. Fainerman, V. I. Kovalchuk, D. O. Grigoriev, M. E. Leser,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R. Miller</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>Oxide, carbon, and carbon/mineral adsorbents for toxic, explosive,</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>and narcotic compounds – synthesis, properties, and applications</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V. Gun’ko, R. Leboda, V. Turov, V. Zarko, A. Chuiko†</td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>Porous polymeric nanocomposites filled with chemically modified</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>fumed silicas</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Y. Bolbukh, V. Tertykh, B. Gawdzik</td>
<td></td>
</tr>
</tbody>
</table>
11. Ion-electrostatic interaction in systems of inorganic nanoparticles and biological cells in electrolyte solution

12. Structural and adsorption characteristics of pyrocabon-mineral adsorbents
J. Skubiszewska-Zięba, R. Leboda, V. M. Gun’ko, B. Charmas

13. Synthesis and structural/adsorption characteristics of unmodified and modified hybrid carbon/mineral adsorbents
J. Skubiszewska-Zięba, R. Leboda, V. M. Gun’ko, O. Seledets

Biomedical Applications of Nanomaterials

14. Surface Functionalization for Biomedical Applications
H. J. Mathieu, X. Gao, Y. Chevolot, D. J. Balazs

15. Surface modifications to influence adhesion of biological cells and adsorption of globular proteins
W. Norde

16. Fundamentals of nanosilica applications for human protection
V. M. Gun’ko, V. V. Turov, A. A. Chuiko†

17. Medical aspects of application of highly disperse amorphous silica
A. Chuiko†, A. Pentyuk, E. Shtat’ko, N. Chuiko

18. The interaction of nanostructured biomaterials with human cell cultures. The choice of cell cultures for use as biocompatibility probes
S. L. James, M. Illsley, S. E. James, E. Mendoza, S. R. P. Silva, P. Vadgama, P. Tomlins, S.V. Mikhalovsky

19. Physical characterisation of a polycaprolactone tissue scaffold
P. V. Grant, C. M. Vaz, P. E. Tomlins, L. Mikhalovska, S. Mikhalovsky, S. James, P. Vadgama

20. Nanostructured and nanocomposite hydrogels for biomedical applications
# Table of Contents

21. *An overview on the toxicity of inhaled nanoparticles*  
B. Fubini, I. Fenoglio, G. Martra, R. Ceschino, M. Tomatis, R. Cavalli, M. Trotta  
241

22. *Detection of V-type nerve agent degradation products using a polypyrrole/pyrroloquinoline quinone-modified electrode*  
O. V. Shulga, C. Palmer  
253

23. *Biological applications of functionalized carbon nanoparticles*  
J. Barkauskas  
265

24. *Interaction of cells with nanoparticles*  
V. A. Pokrovskiy, N. P. Galagan, A. A. Chuiko†  
277

25. *The role of nature and structure of surface sites in the biological response to silica particles*  
I. Fenoglio, M. Ghiazza, R. Ceschino, F. Gillio, G. Martra, B. Fubini  
287

26. *Magnetically sensitive nanocomposites for medical and biological applications*  
P. P. Gorbik, L. P. Storozhuk, A. A. Chuiko†, L. Yu. Vergun, V. F. Chekhun  
299

27. *Hydrophobized silica nanocomposites with immobilized antioxidants (vitamins C and E)*  
P. Kuzema, O. Stavinskaya, O. Kazakova, I. Laguta  
307

28. *Interaction of some biomolecules with modified nanosilica surfaces studied by quantum chemistry*  
O. Tsendra, A. Datsyuk, V. Lobanov, A. Grebenyuk, A. Chuiko†  
315

## Environmental Applications of Nanomaterials

29. *Synthesis and characterization of ordered mesoporous materials for removal of heavy metal ions*  
M. Jaroniec, O. Olkhovyk  
325

30. *Functionalized surfaces: silica structure and metal ion adsorption behavior*  
I. P. Blitz, J. P. Blitz, V. M. Gun’ko, D. J. Sheeran  
337
31. Heterogeneously catalyzed alkane isomerization – towards 100% selectivity
H. Knözinger

32. Low temperature oxidation of carbon monoxide over alkali-metal promoted palladium-tin oxide catalysts
B. Mirkelamoglu, G. Karakas

33. Nanoparticles of aluminium salts hydrolysis products in water treatment and disinfection
S. Barany, J. Gregory, A. Shcherba, I. Solomentseva

34. Co-adsorption of the low molecular carboxylic acids and cadmium ions at the metal oxide/electrolyte interface
W. Janusz, M. Matysek

35. Interaction of Phenolic Pollutants with PNIPA hydrogels
K. László, K. Kosik, E. Wilk, E. Geissler

36. Nanoscale oxides as destructive sorbents for halogenated hydrocarbons
A. M. Volodin, A. F. Bedilo, D. S. Heroux, V. I. Zaikovskii, I. V. Mishakov, V. V. Chesnokov, K. J. Klabunde

37. Dynamic adsorption of tert-butylbenzene, cyclohexane and water vapours on fixed activated carbon/molecular sieve beds
D. Palijczuk, R. Szmigielski, V. M. Gun’ko, R. Leboda

38. Influence of pre-adsorbed NaCl on breakthrough dynamics of TBB and DMMP on activated carbon at different airstream humidities
R. Szmigielski, D. Palijczuk, R. Leboda, V. M. Gun’ko, J. Skubiszewska-Zieba

39. Influence of the nature of active surface sites of highly disperse oxides on adsorption of heavy metal ions
V. I. Zarko, V. M. Gun’ko, L. S. Andriyko, E. V. Goncharuk, M. Matysek, E. Skwarek, W. Janusz
PREFACE

This volume details work presented at the NATO Advanced Research Workshop entitled “Pure and Applied Surface Chemistry and Nanomaterials for Human Life and Environmental Protection” held in Kiev, Ukraine, September 14-17, 2005. A total of 39 selected works have been compiled detailing research in three categories all related to the surface chemistry of nanomaterials: fundamentals, biomedical applications for human life, and environmental protection.

There exists great hope throughout the scientific community for the application of nanotechnologies to solve myriad technological problems. Nanomaterials and nanoparticles exhibit unique properties which are now being explored for potential uses, as well as hazards. Given the scale of nanomaterials surface chemistry inevitably plays a huge role in their properties, since most of these materials are largely comprised of surface. The synthesis of nanomaterials ranging from core-shell particles, microencapsulation techniques, molecular layering of nanoparticles, mixed oxide nanoparticles, carbon nanoparticles, hybrid carbon/mineral nanoparticles, and functionalized materials, as well as artificial polymer biomaterials filled by modified nanoparticles, catalysts, etc. are all topics that are discussed.

A common theme throughout this volume involves the adsorption and interfacial, especially biointerfacial, behaviour of all of the above mentioned nanomaterials. For environmental and human protection, the adsorption of heavy metal ions, toxins, pollutants, drugs, chemical warfare agents, narcotics, etc. is often desirable. A healthy mix of experimental and theoretical approaches to address these problems is described in various contributions. In other cases the application of materials, particularly for biomedical applications, requires a surface rendered inactive to adsorption for long term biocompatibility. Adsorption, surface chemistry, and particle size also plays an important role in the toxicological behaviour of nanoparticles, a cause for concern in the application of nanomaterials. Each one of these issues is addressed in one or more contributions in this volume.

We believe this volume holds a special niche in describing the current state of the art in the fundamentals and applications of a variety of nanomaterials. We thank all of the authors for their fine contributions, which make us proud to be editors of this book. We also thank the NATO Security Through Science Program for making the workshop and this series volume possible, for which we are most grateful. We sincerely hope you will find this volume useful.

January, 2006
Professor Jonathan Blitz – Charleston, IL, USA
Professor Vladimir Gun’ko – Kiev Ukraine
Co-editors
LIST OF CONTRIBUTORS

1. M. CHAPLIN
   London South Bank University, Borough Road, London SE1 0AA, UK

2. B. VINCENT
   School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK

3. D. PONCELET
   ENITIAA, Rue de la Géraudière BP 8225, 44322 Nantes Cedex 3, France

4. A. A. MALYGIN
   Saint-Petersburg Institute of Technology (Technical University), 26 Moskovskii pr.,
   Saint-Petersburg, Russia

5. G. ERTAS, S. SUZER
   Bilkent University, Department of Chemistry and the Laboratory for Advanced
   Functional Materials, 06800 Ankara, Turkey

6. O. GERSHEVITZ, P. SILICKAS, C. N. SUKENIK
   Department of Chemistry, Bar-Ilan University, Ramat Gan, ISRAEL 52900

7. M. S. MEL’GUNOV, V. B. FENELONOV
   Boreskov Institute of Catalysis SB, RAS, Prospekt Akad. Lavrentieva 5, Novosibirsk,
   630090, Russian Federation

8. V. B. FAINERMAN,1 V. I. KOVALCHUK,2 D. O. GRIGORIEV,3 M. E. LESER,4
   AND R. MILLER5
   1Medical Physicochemical Centre, Donetsk Medical University, 16 Ilych Avenue, 83003 Donetsk, Ukraine
   2Institute of Biocolloid Chemistry, 42 Vernadsky avenue, 03680 Kyiv (Kiev), Ukraine
   3Max-Planck-Institut für Kolloid- und Grenzflächenforschung, 14424 Potsdam/Golm, Germany
   4Nestec Ltd., Nestlé Research Centre, Vers-chez-les-Blanc, CH-1000 Lausanne 26, Switzerland

9. V. GUN’KO,1 R. LEBODA,2 V. TUROV,1 V. ZARKO,1 A. CHUIKO†
   1Institute of Surface Chemistry, 03164 Kiev, Ukraine,
   2Maria Curie-Sklodowska University, 20031 Lublin, Poland

10. Y. BOLBUKH,1 V. TERTYKH,1 B. GAWDZIK2
    1Institute of Surface Chemistry of National Academy of Sciences of Ukraine, Gen.
     Naumov Str. 17, 03164 Kyiv, Ukraine
    2Faculty of Chemistry, Maria Curie-Sklodowska University, M.C. Sklodowska Sq. 3, 20031 Lublin, Poland
List of Contributors

11. L. G. GRECHKO, L. B. LERMAN, O. YA. POKOTYLO, N. G. SHKODA, A. A. CHUIKO, K. W. WHITES
   Institute of Surface Chemistry, 17 General Naumov Street, Kyiv 03164, Ukraine
   South Dakota School of Mines and Technology, Rapid City, South Dakota 57701-3995, USA

12. J. SKUBISZEWSKA-ZIĘBA, R. LEBODA, V. M. GUN’KO, B. CHARMAS
   Maria Curie-Sklodowska University, Maria Curie Sklodowska Sq.3, 20-031 Lublin, Poland
   Institute of Surface Chemistry, 17 General Naumov Street, 03164 Kiev, Ukraine

13. J. SKUBISZEWSKA-ZIĘBA, R. LEBODA, V. M. GUN’KO, O. SELEDETS
   Maria Curie-Sklodowska University, Maria Curie Sklodowska Sq.3, 20-031 Lublin, Poland
   Institute of Surface Chemistry, 17 General Naumov Street, 03164 Kiev, Ukraine

14. H. J. MATHIEU, X. GAO, Y. CHEVOLOT, D. J. BALAZS
   École Polytechnique Fédérale de Lausanne (EPFL)-IMX, Station 12, CH-1015 Lausanne, Switzerland
   Equipe Biotechnologie, UMR 5512 CNRS/ECL, Lyon/France
   Swiss Federal Lab. of Materials Testing and Research, EMPA-St. Gallen/Switzerland

15. W. NORDE
   Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, and University Medical Centre Groningen, Antonius Deusinglaan 1, Groningen, The Netherlands

16. V. M. GUN’KO, V. V. TUROV, A. A. CHUIKO
   Institute of Surface Chemistry, 17 General Naumov Street, 03164 Kiev, Ukraine

17. A. CHUIKO, A. PENTYUK, E. SHTAT’KO, N. CHUIKO
   Institute of Surface Chemistry, 17 Generala Naumova Str., Kyiv 03164, Ukraine
   Vinnitsa State Medical University, 56 Pirogova Str., Vinnitsa 21018, Ukraine
   Institute for Occupational Health of the Academy of Medical Sciences of Ukraine, 75 Saksaganskogo Str., Kyiv 01033, Ukraine

18. S. L. JAMES, M. ILLSLEY, S. E. JAMES, E. MENDOZA, S. R. P. SILVA, P. VADGAMA, P. TOMLINS, S.V. MIKHALOVSKY
   School of Pharmacy and Biomolecular Science, University of Brighton, Moulsecoomb, Brighton BN2 4GJ, UK
   Blond McIndoe Centre, Queen Victoria Hospital, East Grinstead RH19 3DZ, UK
   Nano-electronics centre, Advanced Technology Institute, University of Surrey, Guildford GU2 7XH, UK
   Materials Centre, National Physical Laboratory, Queens Road, Teddington, Middlesex TW11 0LW, UK
   IRC in Biomedical Materials, Queen Mary, University of London, Mile End Road, London E1 4SN, UK
19. P. V. GRANT,1 C. M. VAZ,1 P. E. TOMLINS,1 L. MIKHALOVSKA,2
S. MIKHALOVSKY,2 S. JAMES,2 P. VADGAMA3
1Division of Engineering and Process Control, National Physical Laboratory, Hampton Road, TW11 0LW, United Kingdom
2Department of Pharmacy and Biomolecular Sciences, University of Brighton, Cockcroft Road, Brighton, BN2 4GJ, United Kingdom
IRC in Biomedical Materials, Queen Mary, University of London, Mile End Road, London, E1 4NS, United Kingdom

20. A. SPANOUDAKI, D. FRAGIADAKIS, K. VARTZELI-NIKAKI, P. PISSIS, J. C. RODRIGUEZ HERNANDEZ†, M. M. PRADAS†
Department of Physics, National Technical University of Athens, 15780 Athens, Greece
†Center for Biomaterials, Universidad Politécnica de Valencia, E-46071 Valencia, Spain

21. B. FUBINI, I. FENOGLIO, G. MARTRA, R. CESCHINO, M. TOMATIS, R. CAVALLI, M. TROTTA
1Dip. di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali and Interdepartmental Centre “G. Scansetti” for Studies on Asbestos and Other Toxic Particulates, University of Torino, via Pietro Giuria 7, 10125 Torino, Italy
2Dip. di Scienza e Tecnologia del Farmaco, University of Torino, via Pietro Giuria 9, 10125 Torino, Italy

22. O. V. SHULGA, C. PALMER
Department of Chemistry, University of Montana, Missoula, MT 59812, USA

23. J. BARKAUSKAS
Vilnius University, Naugarduko 24, 03225 Vilnius, Lithuania

24. V. A. POKROVSKIY, N. P. GALAGAN, A. A. CHUIKO†
Institute of Surface Chemistry, 17 General Naumov Street, 03164 Kiev, Ukraine
†Department of Chemistry, Inorganic and Physical Chemistry and Interdepartmental Centre “G. Scansetti” for Studies on Asbestos and Other Toxic Particulates and Centre of Excellence of Nanostructured Interfaces and Surfaces (NIS) University of Torino, via Pietro Giuria 7, 10125 Torino, Italy

25. I. FENOGLIO, M. GHIAZZA, R. CESCHINO, F. GILLIO, G. MARTRA, B. FUBINI
Dip. di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali and Interdepartmental Centre “G. Scansetti” for Studies on Asbestos and Other Toxic Particulates and Centre of Excellence of Nanostructured Interfaces and Surfaces (NIS) University of Torino, via Pietro Giuria 7, 10125 Torino, Italy

1Institute of Surface Chemistry 17 General Naumov Street, Kyiv 03164, 2Institute of Hematology and Transfusionology, 12 Berlinskiy Street, Kyiv 04060, 3Kavetsky Institute of Experimental Pathology, Oncology and Radiobiology, 45 Vasyl’kivska Street, Kyiv 03022, Ukraine
List of Contributors

27. P. KUZEMA, O. STAVINSKAYA, O. KAZAKOVA, I. LAGUTA
Institute of Surface Chemistry of National Academy of Sciences of Ukraine, 17 General Naumov Street, Kyiv, 03164, Ukraine

28. O. TSENDRA, A. DATSYUK, V. LOBANOV, A. GREBENYUK, A. CHUIKO
Institute of Surface Chemistry, 17 General Naumov Street, Kiev 03164, Ukraine

29. M. JARONIEC, O. OLKHOVYK
Department of Chemistry, Kent State University, Kent, Ohio 44242, USA

30. I. P. BLITZ, J. P. BLITZ, V. M. GUN’KO, D. J. SHEERAN
Eastern Illinois University, Charleston, IL 61920 USA
1Institute of Surface Chemistry 03164 Kiev, Ukraine

31. H. KNÖZINGER
Department Chemie und Biochemie, Universität München, Butenandtstrasse 5-13, Haus E, 81377 München, Germany,

32. BURCU MIRKELAMOGLU, GURKAN KARAKAS
Department of Chemical Engineering, Middle East Technical University, 06531 Ankara, Turkey

33. S. BARANY, J. GREGORY, A. SHCHERBA, I. SOLOMENTSEVA
1University of Miskolc, Institute of Chemistry, H-3515 Miskolc-Egyetemváros, Hungary
2University College London, Gower Street, London, WC1E 6BT, UK
3Institute for Electrodynamics, National Academy of Sciences of Ukraine, Kiev, Ukraine

34. W. JANUSZ, M. MATYSEK
Department of Radiochemistry and Colloid Chemistry, Maria Curie Skłodowska University, pl. M. C. Skłodowskiej 3, 20-031 Lublin, Poland

35. K. LÁSZLÓ, K. KOSIK, E. WILK, E. GEISSLER
1Department of Physical Chemistry, Budapest University of Technology and Economics, Budapest 1521, Hungary
2Laboratoire de Spectrométrie Physique CNRS UMR5588, Université J. Fourier de Grenoble, BP 87, 38402 St Martin d’Hères, France

36. A. M. VOLODIN, A. F. BEDILO, D. S. HEROUX, V. I. ZAIKOVS’KIY, I. V. MISHAKOV, V. V. CHESNOKOV, K. J. KLABUNDE
1Boreskov Institute of Catalysis, Novosibirsk, 630090, Russia;
2Department of Natural Sciences, University of Maine at Farmington, Farmington, ME, USA;
3Department of Chemistry, Kansas State University, Manhattan, KS, USA, 66506
List of Contributors

37. D. PALIJCZUK, R. SZMIGIELSKI, V. M. GUN’KO, R. LEBODA
Military Institute of Chemistry and Radiometry, 00-910 Warsaw, Poland
Institute of Surface Chemistry, 17 General Naumov Street, 03164 Kiev, Ukraine
Faculty of Chemistry, Maria Curie-Sklodowska University, 3 Maria Curie-Sklodowska Square, 20-031 Lublin, Poland

38. R. SZMIGIELSKI, D. PALIJCZUK, R. LEBODA, V. M. GUN’KO, J. SKUBISZEWSKA-ZIEBA
Military Institute of Chemistry and Radiometry, 00-910 Warsaw, Poland
Faculty of Chemistry, Maria Curie-Sklodowska University, 3 Maria Curie-Sklodowska Square, 20-031 Lublin, Poland
Institute of Surface Chemistry, 17 General Naumov Street, 03164 Kiev, Ukraine

Institute of Surface Chemistry, 17 General Naumov Street, 03164 Kiev, Ukraine
Faculty of Chemistry, Maria Curie-Sklodowska University, 20031 Lublin, Poland
WATER STRUCTURING AT COLLOIDAL SURFACES

MARTIN CHAPLIN*
London South Bank University, Borough Road, London SE1 0AA, UK

Abstract. Colloids in contact with water exert control over the arrangement of the first shell of the surrounding water by means of polar, dispersion and directed hydrogen-bonding effects. The preferred orientations of this first shell water are affected by the favored orientations of the second and more distant aqueous shells. If the colloid surface is flexible, it enables greater freedom of movement within the surface water molecules whereas if the surface is fixed, the adjacent water is more static and more extensively structured. The surface structuring of water is affected by, and will affect, the thermodynamics and kinetics for the binding of other molecules to the surface. In this paper, examples of the organization of water at colloidal surfaces are described and general conclusions drawn. These examples include \((C_{60}^-I_0)[5,6]\) fullerene, \(\beta\)-helix antifreeze proteins, and oxomolybdate clusters.

Keywords: antifreeze protein; \(\beta\)-helix; \(C_{60}\); fullerene; hydration; hydrophilic surface; explicit water model; ice crystal; icosahedral water cluster; polyoxomolybdate; colloid

1. Introduction

Water consists of small molecules \((H_2O)\) with significant dipole moment. The hydrogen atoms are positively charged with depleted electron density away from the electron dense oxygen atom. The charge effect alone would cause water molecules to be attracted to each other, but the attraction has added directionality due to the location of the electron depletion, away from the oxygen atom and in line with the O-H covalent bond. Increased directionality results from the partial covalency of the resultant hydrogen bonding which is most evident when the three atoms O-H···O are linearly arranged with the O-atoms close to 0.28 nm apart. Liquid water possesses a unique set of

* To whom correspondence should be addressed. Martin Chaplin, London South Bank University, Borough Road, London SE1 0AA, UK; email: martin.chaplin@lsbu.ac.uk

properties due to the high density of this hydrogen bonding, almost equivalent to the density of covalent bonding, and their preferred tetrahedral organization. Although hydrogen bonds are weak, if compared to covalent bonds, they form cooperatively with the result that most water molecules act as within clusters rather than individually. The size and density of these water clusters is determined by the temperature, pressure, solutes and the presence of surfaces; low density water with more extensive tetrahedral clustering being most evident at low temperatures and pressures. It has previously been shown that there is a sufficient and broad evidential base for the tendency of such water to ideally form icosahedral water clusters (Figure 1a), which accommodates the unique properties of water.\(^1,2\)

2. Liquid Water Clustering at Surfaces

The colloidal solid-liquid water surface shows complex structuring that may involve several water layers. It depends on the direct surface-water interactions, polarization effects, the extent, charge and shape of the surface, rotational diffusion and interactions with secondary hydration layers and solutes. The structuring has both binding enthalpic and breaking entropic contributions, with the main difference between these surface-water interactions and bulk water-water interactions being due to the unchanging nature of the surface compared with the shifting nature of bulk water. This lowers the entropic penalty for the surface binding of water.

There are several (equivalent) ways of describing what happens to the structure of water at surfaces:

1. Water molecules at hydrophobic surfaces lose hydrogen bonds and therefore have increased enthalpy. They compensate for this by doing pressure-volume work, i.e. the network expands to form low-density water with lower entropy (e.g. see Ref. 3).

2. Water covers a hydrophobic surface with clathrate-like pentagons in partial dodecahedra. This minimizes the loss of most of the hydrogen bonds, maximizes the van der Waals contacts between the hydrophobic solute and the water, while reducing the hydrogen bonding between the surface water molecules. The rotational restriction of the hydrogen bonds at such hydrophobic surfaces may be partially responsible for their increased strength.

3. The chemical potential of water is raised due to the bonds left dangling if water cannot directly interact with the surface. The potential of water is decreased by expanding the water network. This expansion has been verified experimentally.\(^4\)
4. Water molecules at hydrophilic surfaces form hydrogen bonds to the surface. These develop because either (a) they are enthalpically stronger than water-water hydrogen bonds and so energetically able to break water-water bonding, or (b) because otherwise water’s hydrogen-bonding sites may be left ‘dangling’ at the surface or (c) because the entropic cost is low so allowing enthalpically weaker bonding for the same free energy change. Clearly if more than one of these factors is operational then the bonding will appear much stronger. The primary surface-water will tend to orient to facilitate hydrogen-bonded connections amongst them. Secondary water-water hydrogen bonding then tends to mutually form the most stable preferred clustering; this extensive clustering being determined by polarization, hydrogen bond cooperativity and the favored tetrahedral stereochemistry.

If the colloid surface possesses conformational flexibility, the water structuring will have reciprocated effects on the surface structure. This enables greater freedom of movement within such surface water molecules and increases the entropic cost of hydration and so reduces the extent, duration and degree of order within the surface hydrogen bonding. Although often apparently little regarded, sometimes ignored and frequently poorly or misleadingly modeled, the surface structuring of water will affect, and is affected by, the thermodynamics and kinetics for the binding of other molecules to the surface. When there is significant rotational diffusion, such as with small proteins, then hydrogen bonds will break and water molecules will be cast off within the volume corresponding to secondary hydration.

The icosahedral cluster model offers a structure on which large molecules can be mapped in order to investigate their interaction with water within a three-dimensional hydrogen-bonded network, and here offers new insights into the ways fullerene and polyoxomolybdate molecules interact with water in aqueous solution.

3. Fullerene Hydration

An interesting, if lesser-known fact concerning \( \text{C}_{60} - I_6 \)[5,6] fullerene, is that it can be dissolved in water on transference from an organic solvent using sonication without the need of stabilizers or chemical modification.\(^5\) The result is a molecular colloidal solution containing a variety of negatively charged clusters. This \( \text{C}_{60} \) fullerene is an electronegative molecule showing some aromatic behavior in its twenty six-membered (but not its twelve five-membered) rings, with the \( \pi \)-orbitals biased outwards.\(^6\) The solubility of individual \( \text{C}_{60} \) molecules may be explained if the fullerene sits (ideally) within an icosahedral water cluster (Figure 1) missing its inner water dodecahedron. All twenty remaining next-to-inner water molecules are ideally situated to form...
HO-H···π hydrogen bonds to each of the twenty six-membered rings in the fullerene, by the positioning of O-H orthogonally over these aromatic rings; the optimum positioning for the hydrogen bond to a benzene molecule. Such HO-H···π hydrogen bonds are known to possess about half the binding energy of HO-H···O hydrogen bonds with O-H atoms centrally and vertically placed and the distances from the oxygen atom to the aromatic centroid of about 3.1-3.7 Å (c.f. 3.2 Å for all 20 such bonds to fullerene in this model, Figure 1b). These twenty water molecules can then be further linked through their remaining three hydrogen bonds to the twelve water pentagons formed from the sixty fully triply hydrogen-bonded water molecules in the outer shell. The fullerene thus presents a negatively charged surface to the environment and thus the positively charged H-atoms of water, as found experimentally. In such a structure, the carbon atoms become centers of electron-deficiency and capable of interacting with lone pair electrons donated by extra water molecules. These extra water molecules have room to sit under the outer shell water molecules without unrealistic close contacts. An increased tendency to ionize by these carbon-linked water molecules increases the negative charge on the C_{60} molecules and makes the C_{60} solution acidic, as found experimentally. The resultant positioning of up to six hydroxide ions (0.184 nm and 0.28 nm from the nearest C and O atoms respectively) increases the aromatic electron density so strengthening the HO-H···π hydrogen bonding in the surrounding inner aqueous shell. The corresponding hydrogen ions may be associated with the water in the immediately surrounding shell or the bulk. It is clear that (C_{60}^\text{−})[\text{I}_0][5,6] fullerene interacts with water via weak π-hydrogen bonds, which enable an unstrained surface coating with water molecules, so promoting the fullerene’s unexpected aqueous solubility.

The structure is also compatible with findings by Andrievsky using piezogravimetry (20-24 H_2O per C_{60}) and agrees with low temperature differential calorimetry where two types of water were evident, fully hydrogen bonded water melting at 0°C (~60 H_2O per C_{60}) showing a necessary hydrogen-bonding to hydrogen-bond deficient water, melting at ~2.3°C (19 ± 1 H_2O per C_{60}) with 30% less enthalpy change. In icosahehdral hydrates C_{60} (Figure 1b), there are 20 inner sphere H2O and 60 outer (second) sphere H2O molecules. C_{60} molecules in water also form colloidal clusters based on 3.4 nm diameter (carbon atoms) icosahehdral arrangements of thirteen C_{60} molecules. Here the C_{60} molecules are necessarily separated by water molecules to form clusters with this diameter. Such an arrangement is shown in Figure 2 within an expanded, but now strain-free, cluster of water icosahehdral clusters. The water network is formed by tetrahedral tricyclo decamer (H_2O)_{10} structures connecting groups of four C_{60} molecules. The modeled diameter of the cluster
Figure 1. (a) The inner 100 molecules of water from the expanded icosahedral \((\text{H}_2\text{O})_{280}\) network.\(^1\) (b) A \(\text{C}_{60}\) molecule sitting inside this icosahedral water network by replacing the inner 20 molecules.

Figure 2. A tessellated network of icosahedral water clusters, \((\text{H}_2\text{O})_{1020}\), surrounding and separating an icosahedral cluster of thirteen \(\text{C}_{60}\) molecules, shown black. The tetrahedral network of water’s oxygen atoms is shown white.

(carbon atoms) is slightly larger at 3.5 nm but well within the experimental error. The required H-bond orientation toward the \(\text{C}_{60}\) molecules is allowed for this cluster size but become problematic as the condensed fully-tessellated cluster grows larger. It would, however, not offer any problem for more porous open tessellated structures. The ratio of inner sphere to outer (second) sphere water molecules varies between 1:3 for single molecules and 2:3 for infinite sized aqueous \(\text{C}_{60}\) clusters. It may be noted that ions that destroy the expanded water network also coagulate such \(\text{C}_{60}\) hydrosols.\(^1\)
4. Water Structuring Around Ice

The growth of hexagonal ice crystals (ordinary ice) shows preference for particular faces. As such, ice formation may be considered as an extreme case of water clustering. Ice crystals may form by (slowly) growing on the basal faces in the direction of the c-axis, as inside vertical freezing pipes or where ice crystals grow down vertically from crystal platelets nucleated on still water with their c-axes vertical, and where sideways growth is prevented but axial growth allowed. Alternatively they may grow more rapidly from the prism faces, as at the disturbed randomly-directed surface of rapidly freezing or agitated lakes. Growth on the \{11–20\} face is even faster but forms new prism faces. The hexagonal crystal structure plus the different growth characteristics of the crystal faces are behind the flat six-pointed shape of snowflakes. The relative speeds of this crystal growth, on the different faces depend on the ability of these faces to form greater extents of cooperative hydration (Figure 3).

Figure 3. Views perpendicular to the faces of the ice (1h) crystal showing the next layer attached (with O-atoms black). (a) Basal face; where only isolated water molecules attach. (b) Prism face, where pairs of newly-attached water molecules may hydrogen bond to each other; one hydrogen bond/two water molecules. The distance between equivalent water molecules are 0.452 nm (marked *) and 0.738 nm (marked **). (c) \{11-20\} face, where chains of newly-attached water molecules may cooperatively hydrogen bond to each other; one hydrogen bond/water molecule. These form ridges which divide and encourage conversion into two prism faces.

Ice inhibitor (antifreeze) proteins achieve their objective in a number of ways. Some antifreeze proteins possess regular arrays of hydrogen-bonding and hydrophobic sites that fit well with the ice lattice. Surprisingly it is not just the hydrophilic hydrogen bonding groups but also the hydrophobic interactions that appear to be of particular relevance in preventing the growth of ice crystals. Amongst these are proteins with \(\beta\)-helix domains that bind to faces of the hexagonal ice crystal. In the *Tenebrio* antifreeze protein there are tandem 12-residue repeats (TCTxSxxCxxAx) that form a \(\beta\)-helix with regularly spaced threonine residues (0.744 nm and 0.464 nm) that make a match to water molecules in the ice prism plane (0.738 nm and 0.452 nm, Figure 3b). Importantly, not only is there a good fit with these hydrophilic hydrogen-bonding
sites but also the associated methyl groups fit into the interstitial spaces in the ice’s hexagonal shells, so creating multiple van der Waals contacts and reducing the free space.

5. Polyoxomolybdate Hydration

The icosahedral water cluster (Figure 1a) is a highly symmetrical idealized structure found in supercooled liquid water. The inner four shells of the cluster, consisting of 160 oxygen atoms (mostly water molecules) have been found experimentally in almost identical positions and orientations within a cavity-encapsulated icosahedral nanodrop of water in a polyoxomolybdate \{(NH_2)_3C\}_20. \{(Mo)Mo_5O_{23}(H_2O)_{12}\}. \{Mo_2O_4(SO_4)\}_{10}. \{Mo_2O_4(H_2PO_2)\}_{20}. 100H_2O (Figure 4a). The water nanodrop is held to the molybdate by its pentagonal (Mo)Mo_5 clusters (Figure 4b).

Recently some properties of a polyoxomolybdate super-cluster have been described. Its most remarkable feature is that it is formed from about 1165 polyoxomolybdate \[{(Mo)Mo_5Mo_5O_{33}(H_2O)_{5}}(H_2O)_n\]_{14} (henceforth abbreviated as \{Mo_{154}\}) clusters that form the surface of the 90 nm diameter spherical super-cluster. The mechanism for such clustering is initially difficult to discern as (a) each \{Mo_{154}\} shows seven-fold symmetry with seven (Mo)Mo_5 groups alternating on each outside edge of a hollow tire-shaped cluster, and (b) the surface density of the \{Mo_{154}\} clusters on the spherical super-cluster is such that they must be separated from each other by several layers of water. The super-cluster model described here presupposes that the wheel-shaped mixed
valence polyoxomolybdate \{Mo\textsubscript{154}\} clusters are hydrated through their pentagonal \((\text{Mo})\text{Mo}_5\) groups as described above for the polyoxomolybdate nanodrop (Figure 4b). This then allows preferential linking between two nanowheels (Figures 5) utilizing similar water clustering arrangement to that found in supercooled water.

![Figure 5](image-url) Two \{Mo\textsubscript{154}\} clusters can be held to each other through a water network involving two pentagonal boxes (one associated with each \(\text{Mo}\text{Mo}_5\)), each with five hydrogen bonded links (as Figure 4b) plus four further hydrogen bonded links from each of the local \((\text{Mo})\text{Mo}_5\text{Mo}_5\text{O}_{33}\) clusters and associated links from neighboring clusters and including 45-plus shared molecules from the partial icosahedral water clusters. Water O-atoms are shown white with the Mo cluster atoms darker. The Mo—Mo distance between the two central surface Mo atoms of the Mo clusters is about 1.59 nm.

These \{Mo\textsubscript{154}\} dimers can themselves dimerize to form tetramers and then link to form octamers eventually forming the pentagons (five tetramers from 20 \{Mo\textsubscript{154}\} clusters) and hexagons (six tetramers from 24 \{Mo\textsubscript{154}\} clusters) on the surface of the super-cluster and further stabilized by the ring closure, as shown in Figure 6.

The route to the supercluster can thus be seen as a number of associations driven by increasing hydrogen bonded links (as Figure 5).

\[
\begin{align*}
\text{Mo}_{154} + \text{Mo}_{154} & \rightarrow \{\text{Mo}_{154}\}_2 \quad 0.5 \\
2 \{\text{Mo}_{154}\}_2 & \rightarrow \{\text{Mo}_{154}\}_4 \quad 1.0 \\
2 \{\text{Mo}_{154}\}_4 & \rightarrow \{(\text{Mo}_{154}\text{Mo}_5\text{O}_{33})\}_2 \quad 1.25 \\
3 \{(\text{Mo}_{154}\text{Mo}_5\text{O}_{33})\}_2 & \rightarrow \{(\{\text{Mo}_{154}\text{Mo}_5\text{O}_{33}\})_2\}_3 \quad 1.375 \\
40 \{(\{\text{Mo}_{154}\text{Mo}_5\text{O}_{33}\})_2\}_3 & \rightarrow \{(\{(\text{Mo}_{154}\text{Mo}_5\text{O}_{33})_2\}_3\}_40 \quad 1.5
\end{align*}
\]

The overall structure of the supercluster has the following topology (Figure 6) where each vertex represents one of the two central Mo atoms (one inside the other relative to the sphere) in the linking \((\text{Mo})\text{Mo}_5\) groups holding the water H-bonded connecting clusters.

Each vertex, therefore, corresponds to a tetrameric \{Mo\textsubscript{154}\}_4 clusters which also stretch out along the links. The model radius is 45.1 nm which is the same
as the hydrodynamic radius of the supercluster found experimentally by static light scattering (45 nm) and determined from the radius of gyration (45.2 ± 1.4 nm) and by less precise, as somewhat dehydrating, transmission electron microscopy (35-45 nm). This accounts for 960 of the \{\text{Mo}_{154}\} clusters, considered as 12 pentagons each made from five tetramers plus 30 hexagons each made from six tetramers. Additionally, each tetramer has two further equivalent, but exclusive, stabilized sites towards the inside of the tetramer, available for the optional binding of a further single \{\text{Mo}_{154}\} cluster. If these sites are fully decorated, an average cluster size up to 1200 nanowheels may develop, ([\{\{\text{Mo}_{154}\}_3\}_2]\), in line with the Zimm plot value of \(2.54 \times 10^{-7}\) g mol\(^{-1}\) (~1,165 nanowheels at 85% decoration).16

![Figure 6](image)

**Figure 6.** The polyoxomolybdate \{\text{Mo}_{154}\} supercluster showing how 20 nano-wheels may form one of the 12 pentagons and how 24 nanowheels may form one of 80 distorted hexagons. The short links are the Mo—Mo linkages (~1.59 nm) as in Figure 5 and the long links (~12.36 nm) along the octamers are close to the major peak found in the SAXS experimental data (12.9 nm).17

Summing up, various oxomolybdates possess \((\text{Mo})\text{Mo}_5\) ring structures that strongly hydrogen bond to water, forming almost unstrained water clusters that can extend for several aqueous shells and enable extensive colloidal clustering. The organized interfacial water surrounding \{\text{Mo}_{154}\} clusters cause cluster self-association into very large spherical shells with diameter 90 nm and containing a large volume of water. The \{\text{Mo}_{154}\} clusters only contact each other through the water network as evidenced by comparison of the spherical shell size, its mass and the size of its components. This is a clear, if unusual, example of how a relatively small amount of interfacial water can organize very large volumes of liquid water.

## 6. Conclusions

The surface properties of colloids depend on the organization and structuring of their aqueous environment, which is best modeled, at the present time, using explicit water clusters. The orientation of bound water molecules depends on a number of factors including the surface charge distribution, polarization and
optimization of the secondary hydration. Access to this surface by other solutes will depend on the strength and extent of this hydration layer, which will control both the thermodynamics and kinetics of binding.

Further and updated information is available elsewhere.\(^\text{2}\)

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MICROGELS AND CORE-SHELL PARTICLES

BRIAN VINCENT
School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK
e-mail: brian.vincent@bristol.ac.uk

Abstract. An overview of the synthesis and applications of microgels and core-shell particles is provided, with emphasis on work originating from the author’s laboratory. Microgels, which are cross-linked polymer latex particles, can be used for selective uptake of ions or polymers, or the controlled release of various compounds. Various methods for the synthesis of core-shell particles are described such as interfacial polymerization, layer-by-layer deposition, “colloidosomes”, internal phase separation, and silica shells. The release kinetics for controlled (sustained or triggered) release purposes is discussed.

Keywords: microgel particles, core-shell particles, controlled release, triggered release

1. Introduction

Along with the rapid development over the last few decades in our theoretical understanding of colloidal dispersions and experimental techniques to study them, there have been significant advances made in the design and synthesis of colloidal particles of various kinds. The objective has usually been to design particles with a given structure and properties, having some specific function or application in mind. Some parameters which it is now possible to control well include: (a) size and shape (e.g. spheres, ellipsoids, rods, plates), including their distributions; (b) rheological properties (solid, gel, liquid particles); (c) magnetic and electrical properties; (d) porosity; (e) surface properties (charge density, hydrophobicity/hydrophilicity, grafted polymers); (f) non-uniformity, e.g. Janus and patchy particles; and (g) core/shell particles of various kinds.

One widespread application, which has been much researched in recent years, is the use of colloidal systems for controlled uptake and release purposes.
This process is widely-used in a range of technologies, including: pharmaceuticals (drugs); agrochemicals (pesticides, herbicides and fungicides), food processing (flavors); household and laundry products (perfumes); printing (inks). The nature of the colloidal particles used depends on the nature of the uptake/release process and the type of “active” molecules involved. Microgel particles and core/shell particles may both be used for sustained or triggered release. In addition, as described below, microgel particles also may be used for selective uptake purposes.

The purpose of this article is to review the use of microgel particles and of core shell particles, primarily in the context of selective uptake and controlled release applications. Most of the examples will be taken from the work of the author and his coworkers in Bristol, carried out over many years of researching this topic.

2. Microgel Particles

2.1. INTRODUCTION

Microgel particles are cross-linked polymer latex particles which swell in a good solvent environment for the polymer concerned.\(^1\)\(^2\) Swelling and de-swelling of the particles can be induced, therefore, by changes in the local thermodynamic conditions for the polymer chains (e.g. temperature, solvency, osmotic pressure, and for polyelectrolytes pH or ionic strength). The maximum extent of swelling is controlled by the degree of cross-linking co-monomer introduced.

Various types of (heterogeneous) polymerization processes have been described in the literature for making microgel particles, depending on the nature of the polymer involved. Some examples are: (a) dispersion polymerization for making, e.g. poly(N-isopropylacrylamide) [PNIPAM] particles\(^3\) or poly (vinylpyridine) particles [PVP]\(^4\) (the cross-linking (difunctional) monomers used were bisacrylamide and divinylbenzene, respectively); (b) for more water-soluble monomers (and polymers), inverse emulsion polymerization may be used, e.g. for poly (acrylic acid - co - acrylamide) particles [PAAc-co-AM];\(^5\) (c) condensation (step-growth) polymerization, e.g. for cross-linked poly(dimethylsiloxane) [PDMS] microgel particles.\(^6\) Of course, as well as the cross-linking monomer, other co-monomers may also be introduced, in order to introduce specific functional groups into the interior of the microgel particles. A typical example here would be cross-linked poly(N-isopropylacrylamide-co-acrylic acid) [PNIPAM-co-AAc] microgel particles. Such particles will have carboxylic acid groups distributed throughout the interior network of the microgel particles.
One important consideration concerns the distribution of (i) the cross-linker groups and (ii) any co-monomer functional groups, throughout the body of the microgel particles. These distributions are controlled by the reactivity ratios of the various monomers concerned and the nature of the polymerization process (batch, “starve-fed”, etc). Although some small-angle neutron scattering studies have been aimed at determining the cross-link density distributions in swollen microgel particles, more work needs to be carried out to both determine and control these distributions.

Another issue to be addressed concerns the stability of the microgel particle dispersions to aggregation. A significant body of work has now been established on this topic. In the swollen state, i.e. when the microgel polymer is in a good solvent environment, then the particles are thermodynamically stable. This is because of the van der Waals attraction between the particles is insignificant, since the Hamaker constants of the (solvent swollen) particles and of the continuous phase are more-or-less matched. Thus, there is no driving force for aggregation. In terms of the basic thermodynamic relationship governing any physico-chemical process,

\[ \Delta G_{floc} = \Delta H_{floc} - T \Delta S_{floc} \]  

in good solvent conditions, \( \Delta H_{floc} \ll T \Delta S_{floc} \) (both negative terms) and so \( \Delta G_{floc} \) is positive, (Note that \( \Delta S_{floc} \) is associated with loss in translational entropy of the particles when they flocculate). However, as the solvency is made worse, and the particles de-swell, the inter-particle van der Waals attraction starts to increase, and so a point is reached where \( \Delta H_{floc} > T \Delta S_{floc} \) and weak, reversible aggregation is observed.

In order to resist such aggregation, classical electrostatic stabilization of the microgel particles may be introduced. This is achieved, as with normal latex particles, by having a layer of surface charge groups on the microgel particles. Such groups are usually associated with the initiator used in the polymerization process, as in a classical dispersion polymerization. In an inverse emulsion polymerization the surface charge is normally associated with the ionic surfactant molecules used to stabilize the original inverse emulsion droplets. In a condensation polymerization (e.g. of PDMS microgel particles) the surface charge groups come from the terminal, acidic silanol (Si-OH) groups at the ends of the PDMS chains. An alternative procedure to avoid aggregation under deswollen conditions would be to introduce steric stabilization of the microgel particles. This might be achieved, for example, by co-polymerizing in, towards the end of a dispersion polymerization reaction, a suitable macro-monomer (e.g. PEO-methacrylate).
2.2. SELECTIVE UPTAKE

For selective uptake, porous solid or microgel particles are both effective, but the latter give greater flexibility in application, because of their inherent swelling/de-swelling feature. In order to effect entry/penetration of the desired molecules, some driving force (energy gain) is, in general, required to overcome the entropy loss endured by the entering molecules. Examples from the work of this group include the use of designed microgel particles for the selective preferential uptake of harmful ions (e.g. Cd, Pb and Hg species) over more benign ions (e.g. K, Na, Ca and Mg) in potable waters\textsuperscript{10,11} and also the uptake of polymers (e.g. poly(ethylene oxide) [PEO]), with a critical MW cut-off.\textsuperscript{12} In both cases the microgel particles used were based on cross-linked poly(N-isopropylacrylamide-co-acrylic acid) [PNIPAM-co-AAc] polymer latex particles. In the case of the ions, preferential adsorption of the harmful ions occurred at higher pH values (>pH 7), when the AAc groups were in the dissociated, carboxylate ion form. The uptake of PEO, however, was most effective at low pH values (<pH 4) when the AAc moieties were in the undissociated carboxyl acid form. In the case of the cations the primary mechanism of binding was electrostatic, whilst in the PEO case it was relatively strong H-bonding between the ether oxygen atoms of the PEO and the –OH of the carboxylic acid moieties. In order to effect desorption, all that was required, in both cases, was a suitable change in pH to weaken the binding energy.

2.3. CONTROLLED RELEASE

With microgel particles triggered release is more usual than sustained release. Triggered release is usually effected by changing some thermodynamic property of the system which weakens the binding of the active molecule to the functional sites within the microgel particle. Alternatively, a “displacer” molecule, which interacts with the binding site more strongly, may also be used. The release rate for triggered release will normally be first-order (although it may be more complex if a variety of binding sites, having different strengths, are involved). A two-stage triggering method is also a possibility. For example, light could potentially be used as a primary trigger, if its application would induce a secondary (thermodynamic) trigger, such as a temperature rise or a local pH change.

An important aspect to bear in mind with microgel particles is that they may well also change their dimensions (swell/de-swell) when the local thermodynamic conditions are changed. With larger active molecules such as polymers or proteins (or indeed small nanoparticles), this becomes a very important consideration. Swelling/de-swelling will lead to a change in effective pore size,
dramatically affecting the uptake and/or release rate. This principle may actually be utilized to “trap” large molecules (or small nanoparticles) inside the cross-linked network forming the interior of the microgel particles. This might be useful in trying to “protect” vulnerable species (e.g. enzymes or drug molecules) during a multi-stage process, where one stage involves a potentially “harmful” environment. Examples here might be an orally administered drug passing through the very low pH conditions of the stomach into the more benign intestine region, or an enzyme in a laundry formulation surviving the hot wash cycle, before entering the cooler rinse cycle in a typical washing machine process. In cases like these, it is useful to be able to invoke two triggering mechanisms: one to effect swelling/de-swelling of the microgel network, and one to effect adsorption/desorption of the active species. For example, with the PNIPAM-co-AAc microgel particles referred to earlier, the NIPAM groups are temperature sensitive (the lower consolute solution temperature for high MW PNIPAM in water is ~32°C), and the AAc groups are pH sensitive. Hence, temperature changes could be used to trigger the swelling/de-swelling process and pH changes to trigger the adsorption/desorption process.

3. Core-Shell Particles

A typical core-shell particle is illustrated in Figure 1.

![Figure 1.1 Typical core/shell particle.](image)

The core may be a solid or a liquid, or indeed a gas but this is unusual in the context of release applications. Hollow particles have found applications in other areas such as surface coatings, where they offer a high refractive index contrast with film itself, and therefore good light scattering properties. The shell