periodica polytechnica

Chemical Engineering
52/2 (2008) 71–74
doi: 10.3311/pp.ch.2008-2.04
web: http://www.pp.bme.hu/ch

ABSTRACTS

Conference of MSc students – abstracts of the best contributions October 2007

Krisztina László (ed.)

Received 2008-09-07

Langmuir and Langmuir-Blodgett films of bidisperse silica particles

Ádám Detrich

Supervisor: Zoltán Hórvölgyi
Department of Physical Chemistry
and Material Sciences,
e-mail: zhorvolgyi@mail.bme.hu

Nanostructured coatings on solid surfaces can influence advantageously the properties of the substrate (optical, electric, magnetic, etc). Using the Langmuir - Blodgett (LB) method, we can regulate the thickness, structure and composition of the coatings. The process of the preparation, however, is very complicated and the structure of the films is influenced by many factors. For this reason, model investigations are necessary to reveal the conditions which determine the structure of the coatings. The nanoparticles, basic elements of LB coatings, can be polydisperse and the effect of polydispersity on the structure and properties of the Langmuir and LB films has not been investigated yet. On the other hand, it might be desirable to use particles with different size to fabricate films with special properties.

My purpose in the present work is to prepare and characterize nanoparticulate Langmuir and LB films by using well-defined bidisperse model materials.

Three different alcosols of nearly monodisperse silica particles with 37, 61 and 100 nm diameters were used for the experiments (polydispersity ca. $\pm$ 10%). Two bidisperse systems (61 nm-100 nm and 37 nm-100 nm, respectively) at three different compositions were used to study the effect of size difference on the structure formation.

The structure of the one- and two-component (bidisperse) particulate Langmuir films was studied in Wilhelmy film balance. The resultant surface pressure (Π) vs. surface area (A) isotherms were analysed in terms of the surface covering ability of the particles. The Langmuir films of particles were transferred onto glass supports. The structure of the monoparticulate LB films was studied by scanning electron microscopy (SEM) and UV-Vis spectroscopy methods.

The SEM investigation revealed a statistical ordering of different sized particles, no segregation by size was observed. The transmittance curves spectra of the LB films showed antireflection properties in a broad visible wavelength range for each sample. However, both the maximum of light transmittance and its position were strongly dependent on the composition of the mixed films. The transmittance curves were analysed in terms of an inhomogeneous optical model which provided film thickness and average refractive index values. Refractive index gradient across the film was also assessed. Significant differences were found in case of the 37 nm-100 nm bidisperse systems at certain film compositions. I came to the conclusion that the smaller particles can be situated both at the substrate or at the air side of the layer depending on their concentration in the film. In case of lower rate number of smaller particles they can be in the outer side of the layer but at higher concentration they can be at the substrate. The analysis of the Π-A isotherms and SEM investigations also confirmed this hypothesis.

Acknowledgement

I thank Dr. Erzsébet Hild for the useful pieces of advice. The financial support of the Hungarian Scientific Research Fund (OTKA T049156) is gratefully acknowledged. This work was accomplished in the scope of a specific support action of EU FP 6 (Hungarian Network of Excellent Centers on Nanosciences).

Krisztina László
Faculty of Chemical Enginering, Budapest University of Technology and Economics, H–1521 Budapest,, Hungary

Approximating distillation column profile based on composition-dependent relative volatility

Csaba I. Farkas

Supervisor: Endre Rév
Department of Chemical and
Environmental Process Engineering,
e-mail: lepenyhalus@gmail.com

Several methods have been developed in the last decades for solving the large scale, strongly non-linear, equation systems forming the model of multistage multicomponent distillation processes. These methods range from the stage by stage calculation of Lewis - Mattheson, through the multitude versions of the boiling point (BP) and sum of rates (SR) decomposition methods, to the numerous variants of simultaneous Newton iteration. The proper solution method should be selected with respect to the type of the mixture.

Convergence of any such method depends on the initial values given to the state variables. Flow rates are usually approximated with constant molar overflow but estimation of the temperature and the composition is not easy in case of strongly non-ideal mixtures. Initializing a column with azeotrope forming mixture is really difficult. The simplest initial estimation, a linear profile, frequently gives rise to divergence even if there is a reasonable solution with the given specifications. Constant relative volatility is sometimes applied to calculate an initial profile but using this model does not help in case of azeotropes. The usual practice in such cases is initializing with engineering insight, i.e. anticipating the results.

A composition-dependent relative volatility model is developed in the present work and applied successfully to approximate the composition and temperature profiles of distillation columns. The applied model computes the logarithm of the relative volatility as a second degree polinomial of liquid mole fractions. Two parameters are fitted to the infinite dilution in case of binary mixtures. The model can be extended to multicomponent mixtures referring to the parameters of the lower dimension mixtures.

The model describes the implicite temperature dependence through composition dependence. Equi librium plots computed with the new model well approximate the measured data of strongly non-ideal mixtures, and cross the diagonal at the azotropic composition. Even heterogeneous azeotropes are well modelled. The initial column profiles computed with the new model are rather similar to the final solution. Processes can be modelled with the new initial profile when the solution algorithms do not converge with the conventional initialization.

The alternatives of conventional lactic acid production in grain biorefinery

András Pásztor

Supervisors: Áron Német,
Béla Sevella
Department of Applied Biotechnology and
Food Science
e-mail: bsevella@mail.bme.hu

Nowadays the lactic acid (LA) has various utilizations, therefore it is one of the most promising chemical raw materials of our time. The polymerized lactic acid could replace oil-based plastics, its production causes less CO_2 emission, and furthermore it is biocompatible and totally biodegradable. LA could be produced by chemical synthesis or it can be prepared by fermentation of microbes from renewable resources like starch.

The first alternative of the conventional fermentation was the use of thermophilic strains like *Clostridium thermocellum, Geobacillus stearothermophilus, Lactobacillus delbruki bulgaricus, Thermus thermophilus*. The advantage of this technology is the lower risk of contamination due to the applied higher temperature (approx. 60˚C). The four strains were screened on Lac-2 medium (120 g/l glucose, 30 g/l corn steep liquor (CSL), 6 g/l yeast extract (YE), 0,5 g/l KH_2PO_4, 0,3 g/l $MgSO_4 \cdot 7H_2O$, 0,01 g/l $FeSO_4 \cdot 7H_2O$, 0,01 g/l $MnSO_4$), which was optimized for industrial lactic acid production. In addition a thermostable, Gelrite-based solid medium was developed for the *T. thermophilus*, which can be used at 80˚C. *T. thermophilus* achieved the highest productivity (0,026 g/l·h), but this rate was far lower than expected from industrial strains.

Using amylolitic bacteria in mesophilic fermentation makes the use of amylase and glucoamylase unnecessary in production. *Lactobacillus amylophilus* and *Lactobacillus amylovorus* were tested and the latter was selected and studied in batch fermentation (B. Braun Biostat Q 1/0,8L). The bacteria achieved 96% conversion on the optimized Cheng-medium [1] with 100 g/l starch, the productivity was 1,35 g/l·h. The planned biorefinery would use a wheat flour based, gluten-free starch solution, which contains approx. 160 g/l carbohydrate. *L. amylovorus* attained 1,65 g/l·h productivity in the mentioned medium, containing 30 g/l YE. It was obvious that YE must be replaced with a cheaper N-source. A 4 × 4 statistical experimental design was performed on the quality and quantity of N-sources, which showed that CSL would be the best alternative. Process simulations made with Super Pro Designer showed that reducing the concentration of YE from 20 g/l to 5 g/l lowered the price of lactic acid by more than 50%.

References

1 **Zhang Ch**, *Direct fermentation of starch to lactic acid by L. amylovorus*, Biotech. Lett. **13** (1991), 733-738. 10.

Investigation of nanoparticulate LB films by optical spectroscopy and scanning angle reflectometry methods

Örs Sepsi

Supervisors: Zoltán Hórvölgyi,
Erzsébet Hild
Department of Physical Chemistry,
and Material Sciences,
e-mail: zhorvolgyi@mail.bme.hu,
hild@goliat.eik.bme.hu

The preparation of nanostructures raises the claim for new methods to characterize precisely their electrical, magnetic and optical properties. In the elaboration of new characterization methods, samples prepared by the Langmuir-Blodgett (LB) technique may serve as adequate models [?1–2].

My work presents a method for the investigation of the optical features of solid supported thin films fabricated from nanometer-sized particles. The model samples consist of thick transparent quartz glass supports, covered symmetrically by identical non-absorbing, nanoparticulate thin films on both sides.

UV-Vis transmittance spectra and reflectance vs. angle of incidence curves of homogeneous, slightly inhomogeneous and periodic structures were simulated to analyse the applicability of the investigation methods.

Solid supported mono- and multilayers of ZnO and SiO_2 particles were studied by scanning angle reflectometry and optical spectroscopy. The scanning angle reflectometry is a novel method for the investigation of solid supported nanoparticulate films and, to the best of my knowledge, this is the first attempt to use it for thin films of nanoparticles on transparent substrate of finite thickness.

Homogeneous and hexagonal models of the layer structure were used to evaluate the experimental results. The homogeneous model provides the effective refractive index and film thickness. The hexagonal model assumes hexagonal close-packed arrangement of monodisperse spherical particles. The in depth inhomogeneity in this model was taken into account with the effective medium approach. The results of the hexagonal model are the refractive index of the particles and the particle diameter.

Both the experimental results and the simulations suggest that the scanning angle reflectometry is an adequate method to investigate thin particulate films (below 100 nm) on transparent substrates of finite thickness.

Acknowledgements

The financial support of the Hungarian Scientific Research Fund (OTKA T049156) is gratefully acknowledged. This work was accomplished in the scope of an Austrian-Hungarian co-operation program (TéT A-3/04) and Osztrák-Magyar Akció Alapítvány (AÖU 67öu15)

References

1 **Naszályi L, Deák A, Hild E, Ayral A, Kovács AL, Hórvölgyi Z**, *Langmuir-Blodgett films composed of size-quantized ZnO nanoparticles: fabrication and optical characterization*, Thin Solid Films **515** (2006), 2587–2595, DOI 10.1016/j.tsf.2006.05.006.

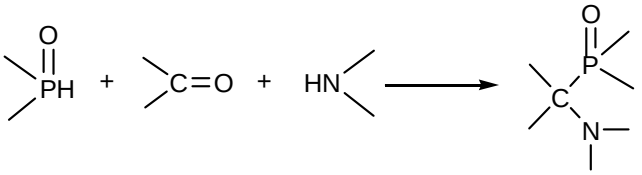
2 **Hild E, Deák A, Naszályi L, Sepsi Ö, Ábrahám N, Hórvölgyi Z**, *Use of the optical admittance function and the WKB approximation to simulate and evaluate transmittance spectra of graded-index colloidal films*, J. Opt. A: Pure Appl. Opt. **9** (2007), 920-930.

Phospha-*Mannich* condensations under microwave irradiation

Anna Szekrényi

Supervisor: György Keglevich
Department of Organic Chemistry and Technology
e-mail: keglevich@mail.bme.hu

In this paper we discuss the phospha-*Mannich* condensations of ternary systems comprising >P(O)H reactants, aldehydes or ketones and secondary or primary amines carried out under microwave irradiation. As the result of these reactions the products are α-aminophosphonates, which form an important class of potentially biologically active compounds due to their structural analogy to α-amino acids.



Emphasis was laid on the usage of heterocyclic compounds, not only as >P(O)H reactant but also as amines. The effects of the different reaction conditions – including solvent-free synthesis – on the outcome of the reaction were examined. In order to find the optimal conditions the mechanism of the condensation was also studied. On the whole nineteen new compounds were produced and were identified on the basis of ^{31}P, ^{13}C and ^{1}H NMR, as well as mass spectrometry.

Application of Raman-microspectroscopy in pharmaceutical developments

Balázs Vajna

Supervisors: György Marosi,
András Szabó
Department of Organic Chemistry and Technology
e-mail: marosi@mail.bme.hu

The formulation of pharmaceuticals is one of the most important and rapidly developing fields in the pharmaceutical industry. However, the formulation processes – unlike chemical operations – frequently lack methods to analyse the intermediate products of the steps of technology.

The aim of my work was to determine the applicability of Raman-microspectroscopy in a 7-step formulation technology,

starting from the raw active pharmaceutical ingredient (API) and ending with the packaging of the product.

Firstly, an API was prepared in amorphous state by several methods. The products were then analysed with XRD, DSC, polarized light microscopy and Raman-microspectroscopy. The latter method was most sensitive to the existence of crystalline contamination, in cases where XRD and DSC did not detect the presence of crystalline contaminants.

In the next step an API solution was deposited from solution onto the surface of an excipient. Raman mapping was shown to be applicable in determining the distribution of the API on the surface of the inactive pharmaceutical ingredient (IPI), which can be useful in selecting the optimal ingredients in a pharmaceutical product. The method was also used after a granulation process, where the distribution of multiple APIs was characterized. Since some compounds are incompatible with others, this may help to answer future questions regarding chemical stability.

Pellets may be coated to improve bioavailability of API. These coating steps of pellets were proved to be controlled subsequently by Raman-microspectroscopy.

Another option after granulation is manufacturing the tablet. Model tablets with the same constitution were prepared with 7 different technologies (each widely used in common practice). With a mapping surface of 600 μm $\times$ 600 μm (20 μm resolution in both axes), all technologies can be distinguished. Quantitative analysis of the accurate contents requires larger maps with at least 1200 μm $\times$ 1200 μm area (with same resolution).

The thickness of PVA tablet coating was also analysed with this method. We used the pure component spectra and classical least squares (CLS) regression to model the measured spectra of the coated tablets. The calculated coating quantity was found to be in good correlation with the real coating thickness, thus, with appropriate calibration, coating thickness can be determined using Raman-spectra of the tablet surfaces.

As the last step, packaged tablets were analysed through a plastic blister. We demonstrated that Raman-microscopy can be used to identify the API in a packed product without opening the packaging.

Raman-microspectroscopy is a fast and convenient method, requiring negligible sample preparation and a short spectrum acquisition time. Since the method can be automated for specific purposes, in the future it may play an important role in pharmaceutical technology, not just in research and development but also in the manufacturing processes.