

# INTERFACIAL PHENOMENA FOR ENGINEERS

## A Bridge Between Engineering and Life Sciences

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**D**URING RECENT YEARS it has become increasingly evident that the principles and techniques of chemistry and physics of surfaces are of considerable importance in chemical engineering. Theoretical and experimental research in this area have appeared in the chemical engineering journals under the general title of "Interfacial Phenomena." Therefore, it is not surprising that many chemical engineering departments have included in their curriculum courses on interfacial phenomena or surface and colloid chemistry. In the winter of 1972 I was asked to present three lectures on the principles and techniques of surface chemistry to undergraduate students in chemical engineering as a part of the course on "Materials of Chemical Engineering." I presented an introduction to surface tension, interfacial tension, miscibility of liquids, foams, emulsions and wettability of surfaces. Surprisingly, about 15 undergraduate chemical engineering students submitted a petition to the department requesting that an undergraduate course on interfacial phenomena be offered. At the suggestion of the department, I formulated a course to be given beginning the spring quarter of 1972.

My main objective in teaching this course was not to make every student an expert in surface and colloid science. Rather, the course would offer them a better understanding and appreciation of the principles and applications of surface-active molecules, the properties of surfactant solutions at various interfaces, and also a number of applications such as foams, emulsions, lubrication and flotation of minerals. Among the textbooks available, I suggested *Physical Chemistry of Sur-*

*faces* by A. W. Adamson. *Interfacial Phenomena* by J. T. Davis and E. K. Rideal was suggested as a reference book. However, it is important to mention that these books were not appreciated by most of the students. The fact that most of the material presented to the class was derived from a number of research papers, review articles, and other specialized books, contributed to their poor appreciation of these books. The course was designed for 3 credit hours and was taught three lectures per week. Instead of giving numerical examples as homework problems, I decided to provide them a number of reprints related to the topics being discussed in the class as required reading material.

### TOPIC OUTLINE

The following is a brief outline of the topics followed during the quarter.

**1. Introduction:** surface-active molecules and five major interfaces; i.e., gas/liquid, liquid/liquid solid/liquid, solid/solid, solid/gas.

**2. Properties of surfactant solutions:** surface tension, CMC, Gibb's adsorption isotherms, surface excess concentration, solubilization, pH near a charged surface (i.e., surface pH *vs.* bulk pH), effect of salts, chain length, temperature and additives on CMC; cylindrical and lamellar liquid-crystalline structures of surfactants.

**3. Spreading of a liquid on another liquid:** spreading coefficient, effect of surfactants on spreading of oils, interfacial instability and interfacial tension, surface pressure, Marangoni effect.

**4. Spreading of liquids on solids:** work of cohesion and adhesion, contact angle and wettability, critical surface tension of solids.

**5. Insoluble Monolayers:** surface pressure-area curves, cross-sectional area of molecules, effect of temperature on phase-transitions in monolayers,



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reactions in monolayers, surface potential, surface radioactivity, surface absorption spectra measurements, surface viscosity and two-dimensional Newtonian and Non-Newtonian liquids, equation of state for monolayers, electrical double layer and Gouy potential, effect of pH and salts on monolayers, surface  $pK$  vs. bulk  $pK$  for monolayers, mixed monolayers and molecular associations in 1:1, 1:2 and 1:3 molecular ratios. Monolayers of biological lipids and the correlations with membrane phenomena.

**6. Foams:** stability of soap bubbles, rate of drainage, surface viscosity and molecular packing, foam stabilizing and antifoaming agents, foam fractionation and other applications.

**7. Macro- and Microemulsions:** oil-water-surfactant systems, effect of structure, concentration and chain length of surfactant on emulsion properties, HLB values, spontaneous emulsification, phase-inversion, emulsion rheology and stability, various applications of emulsions.

**8. Flotation of Minerals:** collectors, frothers, activators, and depressors, selective flotation, absorption of collectors on minerals, contact angle

and flotability, use of oppositely charged collectors, ion-flotation.

**9. Friction and Lubrication:** Boundary and hydrodynamic lubrication, coefficient of friction, scuff load, percent metallic contact, wear rate, biolubrication, synovial fluid, structure of lubricant additives.

**10. Gas/Solid Interface:** Physical and chemical adsorption, catalysis, various types of adsorption isotherms, monolayer-multilayer adsorption and capillary condensation, pore volume, hysteresis.

**11. Artificial Organs:** Nonthrombogenic surfaces, blood-clotting, Heparin, biomaterials, transplants and implants, biological and model membranes, surface chemical aspects of lungs and cornea.

## EXPLANATION BY DEMONSTRATION

On several occasions, I gave experimental demonstrations to make concepts clear and interesting. For example, two dimensional liquid and solid monolayers of stearic acid, respectively, on subsolutions of  $\text{NaCl}$  and  $\text{CaCl}_2$  were distinguished by sprinkling talc particles and blowing air toward the particles. For monolayers in the liquid state, the particles move freely in the surface, whereas for solid monolayers, the particles do not move at all. In another experiment on the use of a wetting agent for wettability of surfaces, I dipped a polished teflon bar into aqueous  $\text{KMnO}_4$  solution, and pulled it out. The teflon rod remained white because water did not wet the teflon. However, upon adding a few drops of soaps or detergents, when the same process was repeated the teflon became pink when removed from the  $\text{KMnO}_4$  solution, suggesting that soap molecules caused water to wet the teflon surface. Many such demonstrations on foams and emulsions made students appreciate the importance of surface chemistry in many engineering applications.

There were two examinations, one mid-term examination and a comprehensive final examination. Here again, instead of giving numerical ex-

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amples to solve, I submitted extensive multiple choice questions during both of these examinations. Each of the questions tested their thorough understanding of the principle involved rather than any memorization of equations. The questions were phrased in such a way that the possibility of guessing the answer was minimized. I should mention that often students took as much as two and one-half hours to answer 20 multiple choice questions. A few of these questions are mentioned as follows:

1. The contact angles of equimolar solutions of hexanoic acid ( $C_6-COOH$ ) and decanoic acid ( $C_{10}-COOH$ ) on a copper plate were found to be respectively \_\_\_\_\_ and \_\_\_\_\_. ( $0^\circ$ ,  $70^\circ$ ,  $110^\circ$ )

2. An off-shore oil spill decreases the surface tension of air/sea interface to 40 dynes/cm. What should be the spreading pressure ( $\pi$ ) of a surface-active agent to push the oil spill away from the shore line?

3. The surface viscosity of monolayers of stearic acid ( $C_{17}COOH$ ) *cis*, oleic acid ( $C_8-CH=CH-C_7-COOH$ ) and elaidic acid ( $C_8-CH=CH-C_7-COOH$ ) *trans* were measured at a surface pressure 10 dynes/cm. The surface viscosities were found to be respectively \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_ centipoises. ( $3.7 \times 10^{-3}$ ,  $4.1 \times 10^{-4}$ ,  $9.7 \times 10^{-4}$ )

4. For two sliding surfaces the coefficient of friction was 0.02 and 0.07, respectively, at the load of 1,000 gm and 2,500 gm. Is this hydrodynamic or boundary lubrication?

5. The palmitic acid monolayers were studied at  $25^\circ C$ ,  $35^\circ C$ , and  $45^\circ C$ . The average area per molecule at a surface pressure 10 dynes/cm were found to be respectively \_\_\_\_\_, \_\_\_\_\_, and \_\_\_\_\_  $\text{A}^2$  molecule. (28, 21, 35)

The numbers in parenthesis were not correct values, but simply indicated the trend or ordering of values. The first question is based on the effect of chain length on adsorption of surfactant on a solid surface. The second is based on the Marangoni effect; i.e., the surface flow occurs

from a high surface pressure region to a low surface pressure region. The third question is based on the effect of *cis* or *trans* double bonds on the area/molecule or molecular packing and hence on the surface viscosity of monolayers. The fourth is based on the definition of hydrodynamic and boundary lubrication from the variation of coefficient of friction with load. The fifth question illustrates the effect of temperature on the average area per molecule in monolayers.

#### STUDENT AND TEACHER EVALUATION

**A**MONG THE 15 STUDENTS who took this course, 12 made more than 85% points on both comprehensive examinations. This was particularly satisfying because more than 60 questions were asked from the materials presented throughout the course. The students were also asked to prepare a term paper on a topic in the general area of interfacial phenomena to be submitted at the end of the quarter. The process of preparing a detailed term paper exposed the students to most of the available sources of information in the area of interfacial phenomena. The quality of the term paper was taken into account in giving the final grade for the course.

I would like to add a note regarding the evaluation of this course by the students in the class. Again, to my great surprise, this undergraduate course on interfacial phenomena brought me the *Excellence in Teaching Award* sponsored by the Standard Oil of Indiana Foundation. The following are a few comments made by students in the teacher's evaluation forms about this course.

"Find a better textbook. . . It would be hard to make improvement in such an excellent course. . . I enjoyed it very much. Best course I ever had in chemical engineering. . . Excellent course and teacher; need better textbook. . . This is the most interesting course I have ever taken. . . One of the most interesting, well taught courses I have ever had. Greatly increased my interest and knowledge. . ."



The course, because of its extreme breadth, could not go into great depth in many of the topics discussed. However, it was successful in giving a bird's eye view of a number of applications of surface chemistry in chemical engineering. This course was successful in balancing a number of mathematically oriented courses, such as transport phenomena, process control, and kinetics, with a descriptive and application-oriented course. The course provided a brief introduction of detergents, foams, emulsions, lubrications, and other biomedical areas to chemical engineering students. I also repeated this course in the spring of 1973

with very similar responses by the students who took it. However, this time I used *Surface Chemistry* by L. I. Osipow (R. E. Krieger Publishing Company, Huntington, New York) as a textbook, which was better received by the students than the previous two books.

I believe a course on interfacial phenomena would be a very desirable part of the undergraduate chemical engineering curriculum, and would contribute greatly in exposing the students to the real systems which chemical engineers are more likely to encounter in their professional careers. □

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## CACHE COMPUTER PROBLEMS



CHEMICAL ENGINEERING EDUCATION, in cooperation with the CACHE (Computer Aides to Chemical Engineering Education) committee, is initiating the publication of proven computer-based homework problems as a regular feature of this journal. Problems should be appropriate for use in an undergraduate or first year graduate chemical engineering course. Problems should be documented according to the published "Standards for CACHE Computer Programs" (September 1971). That document is available now through the CACHE representative in your department or from the CACHE Computer Problems Editor. Because of space limitations, problems should normally be limited to twelve pages total; either typed double-space pages or actual computer listings.

Please submit 5 copies of all contributions to  
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