A Course in

APPLIED SURFACE CHEMISTRY

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Few undergraduate or graduate curricula contain a course in applications of surface phenomena, yet the need for background in *applied* surface chemistry arises daily in the industrial production of foams, detergents, emulsions, paper, and textile fibers, as well as in processes involving adsorption, such as reinforced plastic and rubber systems, heterogeneous catalysts, and crystallization. The properties of the material surface are also important in lubrication problems of certain types and in the selection of materials to be used for biological applications, and in numerous other situations. Since such systems are encountered so frequently in almost any manufacturing process or, in fact, in most experimental research projects, there appears to be a need for the teaching of a few fundamental concepts combined with practical applications.

My own interest in this area began with graduate courses in colloid chemistry and polymer chemistry. But it was not until I was involved in industrial research that I realized the need for a more practically-oriented type of approach. I was working for what was then called the Silicones Division of Union Carbide Corporation, and, of course, most silicone products are sold because of some beneficial surface property. Also at that time I noticed that the same fundamental ideas were applicable to many different kinds of products such as fibers, rubber, foams, and waxes. I'm sure that this is obvious to someone knowledgeable in the area of surface chemistry, but it was quite a revelation to me at the time.

When I came to the University of Virginia there was a course called, appropriately enough, Applied Surface Chemistry. So after I expressed an interest in developing a course which would apply certain fundamentals in many broad areas, this seemed the perfect place to do it, although the course had previously emphasized somewhat different aspects. I felt that the only prerequisite necessary for the student should be a course in physical chemistry, and that the course should be offered as an elective for seniors and graduate students. I see no need for differentiating between undergraduate and graduate students in such a course as both really have the same background in surface chemistry (i.e., relatively little).

The reception of the course at the University of Virginia has been both encouraging and somewhat enthusiastic. A number of students take the course each year, both seniors and graduate students, and from other departments as well as from Chemical Engineering. The students usually quickly find an application for the material. A number of graduates have written me that they were finding numerous uses for the course material in their subsequent jobs, whether in production, development, or research. The course is also a natural one for a short-course because it can be shortened without deleting any of the important concepts simply by not covering as many applications. I have taught it both as a one-week course and as a two-day course in the Today Series of the AIChE.

With this background, then, let me now describe the content. But first, let me stress again my belief in having a little knowledge go a long way; that is, using many applications which really involve the same fundamental ideas. This philosophy will be quite evident in the outline of the course, and is also a criticism one might make. Some people may feel that it is better to go into some areas deeply, and, of course, that is a good approach in many instances. However, I feel that the survey approach is better for this course, which is, after all, only the first one in a possible series of surface phenomena courses.

In general my course outline follows the Table of Contents of the book "Physical Chemistry of Surfaces" by A. W. Adamson, Second Edition, Interscience, 1967. In fact, I assign

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that book as the text for the course, although I really do not use it to any great extent. Some of the students feel that perhaps I should not assign it as an official textbook, but instead make it an optional reference. My reasons for not doing so are based on two observations: (1) students rarely refer to suggested reference books, and (2) I think that it is quite valuable to have a good compilation of experimental methods for measuring surface phenomena, which Adamson certainly is. Thus by becoming at least somewhat familiar with the material in the book, the students will know in the future how to go about setting up a given type of apparatus. In order to accomplish this familiarity, I usually suggest short reading assignments every day in Adamson. There are other books which one could use for such a course, but the variety of experimental apparatus covered in Adamson is much greater than in other texts, thus making it a valuable reference book for future use.

An Outline of Applied Surface Chemistry

I. Introduction concerning the importance of knowing surface characteristics.
II. Thermodynamics of Surfaces
  A. Concept of surface free energy
  B. Derivation of surface thermodynamic properties from surface tension.
III. Capillarity
  A. Physical definition of surface tension
  B. Fundamental equation of capillarity, and influence of surface geometry on surface tension.
  C. Ways to measure surface tension, and ways to estimate it from other data.
  D. Influence of surface tension and size on thermodynamic properties of small drops.
IV. Concentration Effects on surface tension
  A. Gibb's adsorption and surface excess concentration
  B. Surface active agents
    1. Levelling agents
    2. Detergents
  C. Micelle formation
V. Films and Monolayers
  A. Formation of monolayers on liquid surfaces
    1. Surface pressure
    2. Surface viscosity
    3. Use as evaporation supressants
  B. Formation of a liquid film on a liquid surface
    1. Work of adhesion and of cohesion
    2. Spreading coefficients
    3. Antifoaming agents
VI. Liquid–Solid Interfaces
  A. Development of Young–Dupré equation
  B. Definition of work of cohesion, work of adhesion, and spreading coefficient
  C. Wetting agents
  D. Coatings for water repellency
  E. Further discussion of detergency
  F. Ore flotation
VII. Liquid–Liquid Interfaces
  A. Emulsions
    1. Factors affecting stability
    2. Emulsifying agents
  B. Microencapsulation
  C. Emulsion polymerization
VIII. Foams
  A. Gibb's theory of elasticity
  B. Marangoni effect
IX. Solid–Solid Interfaces
  A. Lubrication, stressing boundary lubrication in particular
X. Fluid–Solid Interfaces
  A. Adsorption
    1. Isotherms, with special emphasis on Langmuir, B–E–T, Temkin, Freundlich.
    2. Physical adsorption versus chemisorption
    3. Heterogeneous catalysts
      a. Models for unimolecular and bimolecular reactions
      b. Temperature dependency
  B. Adsorption from solution
    1. Ordinary monomeric solutes
    2. Polymers
      a. Reinforced plastics and rubber
XI. Miscellaneous
  A. Nucleation and crystal growth
  B. Membranes
  C. Electrical properties of surfaces.

As is readily apparent from the preceding outline, the scope of the course is quite large. Thus, of necessity, the topics are not covered in great depth. For example, one could easily develop a course merely on electrical properties of surfaces, but, for a first course, I believe that the survey is better. Basically, I try to empha-

size that surface tension is important in various systems, and that it is a function of geometric shape, temperature, concentration, and electrical charge. Most of the topics build on this.

One of the most important aspects of any course, in my opinion, is to have daily problem assignments. There is no easy source of problems for all of these areas. However, I have compiled a large set of what I call "pseudo-industrial applications" which I assign each time. These problems have come from my experiences and reading, and are, for the most part, designed to put the student in a position of a "trouble-shooter" or development engineer. I am listing two examples of such problems at the end of this article. In addition, I ask each student to write a critical review of one article in the literature (of his choice) toward the end of the course. I think that this is quite valuable in demonstrating to the student that he can now understand much of the literature concerning surface phenomena, at least in a superficial sense.

One of the topics I would like to cover in more detail is that of biomaterials. Last year, while I was on leave, another member of our staff taught this course and added a section concerning this, especially in relationship to thrombus formation on implants. This has now been expanded and next year a course will be offered at the University of Virginia covering just biomaterials. Thus the need for me to add material on this subject no longer exists, and the students will be able to learn this area from teachers much more expert than I. However, I believe that it should be kept in mind when developing any general surface phenomena course. □

ChE problems for teachers

Problems from Professor Gainer's course on "Applied Surface Chemistry."

1. A. As Product Manager of Emulsions, Inc., you are responsible for the new product composition. Your laboratory has given you the following data which was obtained at 25°C:

Compound	Density g/ml	Mol. Wt.	Viscosity cp
For dispersed phase:			
A	0.8	100	0.8
B	1.0	150	0.9
For continuous phase:			
C	0.8	200	3.0
D	0.8	210	5.0

A and B are both relatively insoluble in both C and D.

a. Which system of the four possible systems will make the most stable emulsion at 25°C. without the use of an emulsifier?

b. Will this be the most stable emulsion at 50°C? Do you need more data? If so, what?

c. Name two ways to break the emulsion.

B. It has now been decided to use an emulsifier to stabilize the emulsion picked in problem 1A. You have three (3) emulsifiers to choose from:

Emulsifier	Mol. Wt.	Solubility (g/l) in A	B	C	D
E1	150	0.08	0.15	0.25	0.50
E2	150	0.15	0.15	0.25	0.40
E3	250	0.08	0.10	0.35	0.50

a. List the emulsifiers in order of stabilization (list the emulsifier producing the most stable emulsion first, etc.) Why did you choose this order?

b. Are there other factors to be considered in picking the best emulsifier to be used commercially? If so, what data do you need?

2. You have been hired by the Super Detergent Company. It is a small company, and you are their expert in surface chemistry. The boss has an idea for a new detergent which must be commercially competitive. He calls you in his office, hands you a box of the new detergent (Super X) and tells you that he has the following information about the detergent:

- The organic part of the detergent molecule contains approximately 10 carbon atoms. (Molecular weight is 260).
- A surface tension–concentration curve has been obtained as is shown in Figure 1.
- Other commercial detergents of this type sell for 16 cents per pound with recommended use of 1.2 ounces per gallon at 10°C.
- Super X will sell for 18 cents per pound.

It will be your job to evaluate Super X as follows:

a. What minimum concentration of Super X must be used (in ounces per gallon) for maximum detergency? Is Super X competitive with other detergents? Show comparative costs.

b. Would you recommend this amount to be used for washing at higher temperatures? Explain.

c. Can you make any recommendations about making a new detergent, Super XX, which might be cheaper to use than Super X provided that the manufacturing costs of Super XX are the same as for Super X? □