The Critical Point of Heterogeneous Polymers

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and if $C_B{}^0$ be kept equal to zero, it reduces to

$$\ln(1-N_A)+(1-KD_B/D_A)N_A=-(\Sigma D_B KC_A{}^0/El)t. \quad (14)$$

Since N_A no longer remains small, the correction term in (9) cannot be neglected and its effect may be maximized further by choice of a system for which KD_B/D_A is large (e.g., Cs$^+$—H$^+$ exchange). These conditions can be met experimentally, and this means of testing the validity of the film diffusion mechanism is currently under investigation, as well as the more obvious approach of varying the particle sizes and flow or stirring rate.

[1] F. C. Nachod and W. Wood, J. Am. Chem. Soc. 66, 1380 (1944).
[2] H. A. Thomas, J. Am. Chem. Soc. 66, 1664 (1944).
[3] W. Juda and M. Carron, J. Am. Chem. Soc. 70, 3295 (1948).
[4] Boyd, Adamson, and Myers, Jr., J. Am. Chem. Soc. 69, 2836 (1947).

Availability of Radioantimony-Beryllium Neutron Sources

OAK Ridge National Laboratory has developed a relatively inexpensive radioantimony-beryllium neutron source which is now available for distribution to users in the United States. These sources will be allocated through the Isotopes Division, U. S. Atomic Energy Commission.

The sources use a core of 32 grams of antimony metal surrounded by a $\frac{3}{16}$ in.-thick beryllium metal cup, the assembly being enclosed in an aluminum jacket. The outside dimensions of this jacket are as follows:

Cylinder containing source	$1\frac{3}{16}$ in. diameter $\times 1\frac{3}{16}$ in. long
Aluminum plate protruding from one end	$\frac{5}{8}$ in.
Hole in plate for handling	$\frac{1}{4}$ in.
Over-all length of assembly	$1\frac{3}{4}$ in.

The entire unit is placed in the pile and the antimony activated to the desired level. Antimony 122 (half-life 2.8 days) and antimony 124 (half-life 60 days, gamma-ray energy 1.72 Mev) are both formed in this irradiation, but the source can stand for two weeks before shipment to allow the Sb 122 to decay. Saturation activity of the Sb 124 is approximately 3.5 curies; however, normally an activation time of 120 days will be used which will give an activity of about 2.6 curies. A source activated for 69 days and cooled for 16 days gave an unshielded gamma-radiation reading of about 20 roentgens/hour at one foot. Other readings followed the inverse square very closely. Shorter activation periods may be arranged if a lower activity is satisfactory. After the activity of the Sb 124 has decayed, it may be reactivated by re-insertion in the pile.

It has been found that the saturated source will emit a total of about 8×10^6 neutrons per second or 9.8×10^4 neutrons/cm^2/second at one inch, if it is assumed that the source behaves as a point source. The neutrons are approximately monoenergetic.*

The shipping container for the source will weigh approximately 350 pounds and should be returned to Oak Ridge National Laboratory within three weeks after date of shipment. A customer will have to make arrangements beforehand to provide a suitable storage space for the source; a lead pig with walls four inches thick would probably be sufficient.

It is planned to charge for the source and the irradiation separately, thus allowing the requestor to choose one, two or more months' irradiation time. The itemized costs of the source are as follows:

Antimony-beryllium Source	$44.00
Service Irradiation of Source	$43.00/month
Returnable Deposit on Container	$400.00.

* The following are references to articles dealing with the subject of the energy of the neutron: Collins, Waldman and Guth, Phys. Rev. 56, 878 (1939); D. J. Hughes and C. Eggler, Phys. Rev. 72, 902 (1947); A. Wattenberg, Phys. Rev. 71, 497 (1947).

The Critical Point of Heterogeneous Polymers

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IN a recent note Stockmayer[1] derived equations giving the concentration of the solvent and the value of the interaction constant at the critical point of solutions of heterogeneous polymers which conform to the Flory-Huggins theory. Stockmayer's conclusion is that the critical point depends on the weight- and z-average molecular weights and not on the number-average molecular weight as previously believed.[2]

It is well, however, to consider carefully the significance of the critical point. By definition a critical point is a point in the phase diagram at which two coexisting phases become identical. The point derived by Stockmayer satisfies this condition. But while for a two-component system a small change of concentration, at constant temperature and pressure, leads one into the homogeneous region, it must not be assumed that this is necessarily the case for a multi-component system, and, in fact, it will not be so in general. The thermodynamic reason for this is that for a two-component system such a change is one at which the intensive variables remain constant, while for a multi-component system even at the critical point changes at constant temperature and pressure are possible in which the chemical potentials are not constant. In general, a change along a line in the phase diagram joining the point representing the pure solvent and the point representing a given heterogeneous polymer involves changes of chemical potentials even at the critical point and leads in one direction into the heterogeneous region. In other words, even if such a line may pass through a critical point, it is not necessarily a tangent to the binodial there, but cuts the two-phase boundary there and at another point, and passes through the two-phase region between these points. Solutions of the given polymer will separate into two phases in a certain range of concentrations even for values of the interaction constant μ which are below that given by Stockmayer; the minimum value of μ for which this holds is the one at which the line touches the two-phase boundary, but the point of contact is not, in general, a critical point, and the coexisting phase has a different composition.

These conditions are brought out in the diagrams given by the author in a recent publication[3] for the case in which the heterogeneous polymer consists of two species only (Figs. 6 and 7). It is easily confirmed that Stockmayer's Eqs. (6) and (7) reduce to those given by the author for the case of two-polymer components,
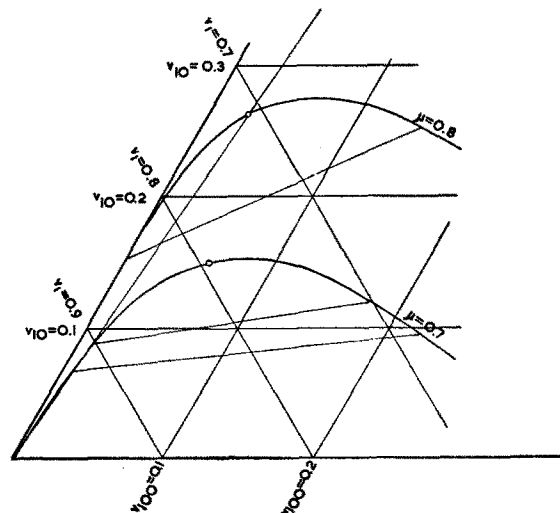

FIG. 1. Corner of phase diagram of the system solvent and two polymers of chain-lengths 10 and 100, with binodials for $\mu = 0.7$ and 0.8. o critical points, v volume fractions.

Eqs. (15) and (16).[3] The part near the solvent corner of the triangular diagram for the case of two polymers of chain-lengths 10 and 100 is shown in Fig. 1, together with the binodials for $\mu=0.7$ and 0.8. The critical points are also shown, as well as several tie lines. The line joining the pure solvent ($v_1=1$) to the point representing a polymer of composition $v_{10}{}^0=0.9105$, $v_{100}{}^0=0.0895$, passes through the critical point of the binodial for $\mu=0.8$ ($v_1=0.7096$, $v_{10}=0.2644$, $v_{100}=0.0260$) and cuts this binodial again near $v_1=1$. It also cuts the binodial for $\mu=0.7$ at about $v_1=0.920$, $v_{10}=0.073$, $v_{100}=0.007$, and again near $v_1=1$, and the least value of μ for which separation into two phases is possible, is somewhat below 0.7. For this polymer Stockmayer's equation for the critical point gives 0.8; on the assumption that the critical point is determined by the number average molecular weight, the critical value would be 0.849, even further from the minimum value.

[1] W. H. Stockmayer, J. Chem. Phys. 17, 588 (1949).
[2] Robert L. Scott, J. Chem. Phys. 13, 178 (1945).
[3] H. Tompa, Trans. Faraday Soc. (submitted for publication).

Solubilization in Swollen Micelles*

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RECENTLY, additional evidence to indicate that there are at least two different loci of solubilization in soap micelles has been obtained. Previous indications were based on the fact that there were characteristic differences observed when solubilization data (moles oil dissolved vs. moles soap) were plotted. In the case of non-polar solubilization, the curves were convex toward the concentration axis; for dyes or polar compounds, curves were linear or concave toward this axis.[1] Long-chain alcohol solubilization (as n-heptanol) show this latter effect.[2] Micelles were found to increase in size in the presence of hydrocarbons[3] and it has been indicated that long-chain alcohols do not swell micelles.[4] It is apparent that the hydrocarbons are solubilized by being incorporated in the micelle center while the polar molecules upon solubilization are oriented, in the micelle, as are the soap molecules, with their hydrocarbon chains lying roughly parallel to those of the soap molecules and their polar-hydrogen-bonding head toward the water.[1,2] If this hypothesis is correct, it should be possible to prepare a swollen micelle (soap solution essentially saturated with polar compound such as a long-chain alcohol) which would solubilize more hydrocarbon than the same concentration of soap alone.

Soap solutions were shaken with n-heptanol for more than 24 hours in sealed ampules and then n-heptane was added. Saturation was determined by an increase in turbidity. The data in Fig. 1 show this enhancement of solubilization in comparing the systems potassium n-tetradecanoate: n-heptanol: n-heptane and potassium n-tetradecanoate: n-heptane. The presence of the long-chain alcohol in potassium tetradecanoate increases the solubilization of n-heptane as much as fourfold. This is much more than would be solubilized if an amount of potassium tetradecanoate equivalent to the alcohol were added to the original soap concentration. The enhancement of solubilization is also much more marked than would be found if an equivalent amount of potassium n-heptanoate in place of n-heptanol were added to the soap solution. Thus, since there is this observed increase in solubilization and since the solubilizations of n-heptane and n-heptanol are independent of each other in the same soap solution (i.e., they are not additive), it must follow that there are at least two loci of solubilization in the soap micelle. Quite similar results have been obtained with added long-chain amines and mercaptans and their effect on the increase of solubilization. These data, with additional results on the alcohol systems, will be reported more in detail in a forthcoming publication.
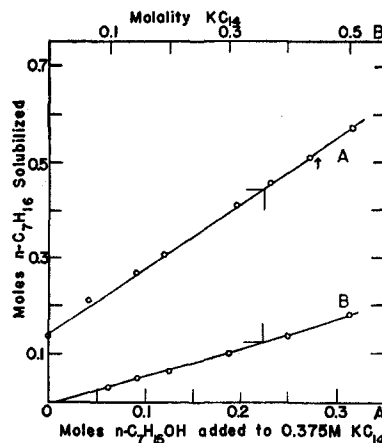

FIG. 1. Comparison of the solubilization of n-heptane in n-tetradecanoate (B) and in 0.375 M n-tetradecanoate with added n-heptanol (A). Arrow indicates saturation point of n-heptanol in 0.375 M potassium n-tetradecanoate.

An explanation of this greatly enhanced solubilization can possibly be found by consideration of the change in the geometry of the micelle. The addition of 0.75 mole n-heptanol per mole n-tetradecanoate (at 0.375 M soap), the chain-length of the alcohol being considerably shorter than that of the soap, would result in a considerable increase in the curvature of the micelle surface. This would result in an increase in the short axis and a decrease in the long axis of the prolate spheroid micelle.[5] More micelles would form and the total volume available for solubilization of the n-heptane would increase. Calculations, based on these assumptions, agree with the experimental findings.

Further, an extremely turbid system is observed when one exceeds the saturation of a long-chain alcohol in a soap solution. Addition of a hydrocarbon to this emulsion results in an enhancement of solubility of the alcohol as evidenced by a marked decrease in turbidity until a transparent system is obtained. A turbid emulsion (a gel at room temperature) is again found upon further hydrocarbon addition. As much as 8–10 times the normal solubilization of n-heptane in soap solutions is possible in such n-heptanol: n-tetradecanoate systems where the initial alcohol concentration exceeds its solubility in the soap solution.

* Paper No. 2498, Sci. J. Series, Minnesota Agricultural Experiment Station.
[1] H. B. Klevens, Am. Chem. Soc. meeting, New York, New York (September 15–19, 1947); J. Am. Oil Chem. Soc. 25 (1949).
[2] W. D. Harkins and H. Oppenheimer, J. Am. Chem. Soc. 71, 808 (1949).
[3] See, for example, review by J. W. McBain, Advances in Colloid Science (Interscience Publishers, Inc., New York, 1942), Vol. I.
[4] W. D. Harkins and R. Mittelman, mentioned in reference 2.
[5] H. B. Klevens, Colloid Symposium, Cambridge, Massachusetts (June 23–25, 1948); J. Colloid Sci. (in press).

Simplified Technique for Surface Area Determination by Adsorption of Nitrogen

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THE determination of surface area of solid adsorbents by the BET method has been one of the most important developments in recent times in the field of surface chemistry. It is based upon the determination of the amounts of nitrogen adsorbed at liquid oxygen or liquid nitrogen temperatures at two or more equilibrium pressures.

A new simplified method has been developed in this laboratory for determining surface areas by nitrogen adsorption. It is based upon the preferential adsorption of nitrogen from nitrogen-helium mixtures at liquid oxygen temperatures. The method proposed has the particular advantage that a vacuum pumping system is not required. Also, less time is consumed in completing