Simplified Technique for Surface Area Determination by Adsorption of Nitrogen

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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.

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[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.
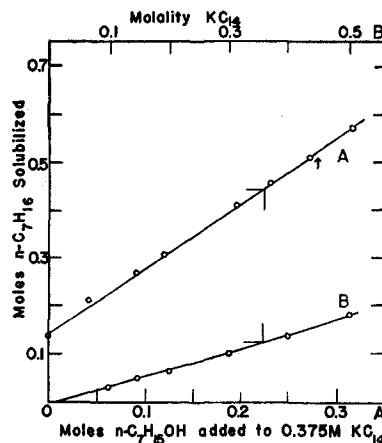

FIG. 1. Comparison of the solubilization of n-heptane in n-tetradecanoate (B) and in 0.375 M n-tetradecanoate with added n-heptanol (A). Arrow indicates saturation point of n-heptanol in 0.375 M potassium n-tetradecanoate.

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.

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

a determination than with the conventional method and without sacrifice of accuracy. The proposed assembly is adaptable to a portable piece of equipment for surface area measurements.

The apparatus includes a U-shaped adsorption tube, one arm of which is capillary tubing and the other contains the sample. A gas entering the tube has intimate access to all parts of the sample before leaving. Calibrated gas burets of approximately equal volume are connected to each of the two arms of the adsorption tube. Both burets are equipped with hand-operated mercury leveling bulbs.

The sample contained in the adsorption tube is freed from conflicting impurities, such as air and moisture, by heating in a continuous stream of helium. Before making the dead-space-calibration, the exit connection is closed and the furnace surrounding the adsorption tube replaced by a Dewar flask containing liquid oxygen. A quantity of helium is next drawn into the system filling the sample tube and only one of the burets. The resultant pressure is designated as p_1. When the helium is expanded so as to include the second buret, as well, its pressure becomes p_2. The "dead-space" volume may be calculated according to the easily derivable relationship:

$$V/T = [p_2/(p_1-p_2)](V_2/T_0) - V_1/T_0,$$

where V = geometrical volume of dead space, T = temperature of liquid O_2 or N_2 bath, V_2 = volume of buret No. 2, V_1 = volume of buret No. 1, p_2 = pressure of helium in the system including both burets and dead space, p_1 = pressure of same quantity of helium when compressed into the volume of No. 1 buret and the dead space, and T_0 = room temperature.

A measured amount of nitrogen is then introduced and the helium-nitrogen mixture is passed from one gas buret through the sample to the other buret. This process is repeated until a constant pressure reading is obtained. The liquid oxygen bath is not removed between the time of calibration and nitrogen adsorption. An additional quantity of nitrogen is added for each subsequent adsorption point. In the calculation it is necessary to subtract the partial pressure of the helium from the total pressure to obtain that due to the nitrogen. The surface area may be then calculated from the adsorption data in the well-known procedure of Brunauer, Emmet, and Teller.

It has been shown that for a number of adsorbents, such as silica gel, coconut-shell charcoal, an activated clay, titania, and bone char, that the pressure of helium has very little, if any, influence on the adsorption of nitrogen at liquid oxygen temperature. For example, values for surface area of 60, 61, 61 m^2/g were obtained for a sample of bone char with the respective partial pressure of helium of 80, 79, and 405 mm Hg. The value obtained for the same sample in the absence of helium in a conventional system was 59 m^2/g.

Carrier-Free Radioisotopes from Cyclotron Targets. I. Preparation and Isolation of Sn113 and In114 from Cadmium*

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THE cyclotron is the only practical source of many carrier-free[1] radioisotopes. The preparation and radiochemical isolation of a number of these activities, produced in the 60-in. cyclotron of Crocker Laboratory, will be presented in this paper

and in subsequent papers of this series. In most cases the carrier-free radioisotopes were prepared for use in biological systems and the final preparations were in the form of isotonic saline solutions at a range of pH from 5 to 8.

The present paper reports the radiochemical isolation of carrier-free Sn113 and In114 produced by bombarding cadmium with 38-Mev alpha-particles. At this energy, Sn113 and In114 are produced in a thick target by the nuclear reactions:[2] $Cd^{110}(\alpha, n)Sn^{113}$, $Cd^{111}(\alpha, 2n)Sn^{113}$, $Cd^{112}(\alpha, 3n)Sn^{113}$, $Cd^{111}(\alpha, p)In^{114}$, $Cd^{112}(\alpha, pn)In^{114}$. The shorter-lived tin and indium activities, together with the possible radioisotopes of silver produced by (n, p) reactions, were allowed to decay out prior to the chemical separations.

The target, a block of C.P. cadmium metal, soft-soldered to a water-cooled copper plate, was bombarded with 38-Mev alpha-particles for a total of 450 μa-hr. at an average beam intensity of 3.4 μa. After aging for one week, the bombarded surface was milled off and dissolved in a minimum volume of 16N HNO_3.

A 0.2 g of target cadmium nitrate was dissolved in 25 ml of water, and the tin and indium activities were carried quantitatively on 10 mg of $Fe(OH)_3$ precipitated with NH_4OH. The $Fe(OH)_3$ was dissolved in 15 ml of 36N H_2SO_4 and transferred to an all-glass distilling flask.[3,4] The 9N HBr was added dropwise while a stream of CO_2 was bubbled through the solution at 220°C. The distillate containing the carrier-free Sn113, HBr, Br_2, and traces of H_2SO_4 was caught in a series of traps filled with 12N HCl; the indium activity remained in the residue. Carrier-free radio-tin collected in HNO_3 or H_2SO_4 forms a radiocolloid[5,6] and is adsorbed onto the walls of the containing vessel. The 12N HCl keeps the radio-tin in solution, presumably as the chlorostannate complex. The trap contents were treated with 5 ml of 16N HNO_3 to destroy HBr, 15 mg of citric acid were added and the solution was evaporated on a steam bath to the 1- to 2-ml volume of H_2SO_4 carried over in the distillation. Citric acid prevents the formation of radiocolloid after removal of HCl.

The H_2SO_4 solution was diluted with 25 ml of water and the radio-tin was carried down on $Fe(OH)_3$ precipitated with NH_4OH. The $Fe(OH)_3$ was dissolved in 8N HCl and iron was extracted with isopropyl ether. The aqueous phase, containing HCl, Sn113, and equilibrium amounts of the In113 daughter, was evaporated to dryness on 10 mg of sodium citrate. The activity dissolved quantitatively in distilled water.

The carrier-free Sn113 was identified by its 105-day half-life and by the 0.39-Mev conversion electron of the In113 daughter.[7] The indium fraction from a chemical separation of an equilibrium mixture using tin and indium carriers, showed the 105-min. period of In113.

The residue from the tin distillation, containing Fe^{+++} and In114, was neutralized with NH_4OH. The $Fe(OH)_3$ plus indium activity was dissolved in 8N HCl, and extracted with isopropyl ether. The HCl solution of In114 was evaporated to dryness on 10 mg of NaCl. The activity dissolved quantitatively with the addition of distilled water. The In114 was identified by the assigned 48-day half-life and by the 0.19-Mev conversion electron.[7,8]

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[1] This term is used to indicate that no stable isotopic carriers have been intentionally added. In a "carrier-free" separation the specific activity is determined by the chemical purity of the reagents.
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