in acid solution. These data support the suggestion that the uncharged dye is bound to the protein by hydrogen bond formation in which the dye acts as an electron donor, as proposed for binding by albumin.[10] The hydrogen bonded dye would be expected to have a spectrum intermediate between that of the free base and that of the hydrochloride. We cannot explain at the present time why albumin, which has been shown by equilibrium dialysis methods to bind chrysoidin,[10] does not produce such a spectral shift.

To test the possibility that the dye is bound to the lipoprotein by "solution" in the lipid portion of the protein a spectrum of the free base in petroleum ether was obtained. It can be seen from Fig. 4 that this spectrum is quite different from that obtained in the presence of the protein, indicating that the environment of the dye is not entirely hydrophobic when bound. It has also been suggested[24] that the spectral shift could be a result of hydrogen bonding with the lipid portion of the protein molecule. The similarity of the spectrum in dodecyl alcohol to that in the presence of lipoprotein supports this point of view.

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(24) By a referee.

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NOTES

Non-exchange of F^{18} between HF and Fluorinated Methanes

BY JAMES E. BOGGS, E. R. VAN ARTSDALEN AND A. R. BROSI

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The exchange of isotopic chlorine between HCl and the series of compounds CH_3Cl, CH_2FCl, CHF_2Cl and CF_3Cl in the gas phase recently has been studied[1] in an attempt to obtain information regarding the effect of fluorine on the reactivity of such compounds. We have now attempted to obtain similar data for fluorine exchange between HF and the compounds CH_3F, CH_2F_2, CHF_3, CF_4, and CF_2Cl_2.

The longest-lived isotope of fluorine, F^{18}, has a half-life of only 112 minutes, and there is only one stable isotope, F^{19}. For this reason we have conducted a few experiments attempting to prepare F^{21} in the hope that it might have a longer half-life, although crude calculations indicate that its half-life may be only on the order of seconds or minutes.

Experimental

Materials.—Methyl fluoride was synthesized by the reaction between KF and CH_3SO_4K.[2] Traces of acetone were removed by repeated distillation from a trap at −100°. The authors would like to express their appreciation to Dr. W. B. McCormack of E. I. du Pont de Nemours and Co. for supplying us with samples of CH_2F_2, CHF_3 and CF_4. The compound CF_2Cl_2 was purchased from the Matheson Co. We are grateful to Dr. H. A. Bernhardt and Dr. W. Davis, Jr., of the K-25 Plant, Carbide and Carbon Chemicals Co., Oak Ridge, for supplying us with highly purified HF and for valuable suggestions relating to the experimental techniques we have used. All compounds were fractionally distilled *in vacuo* and vapor pressure measurements used to establish purity.

Radioactive F^{18}.—Several methods were tried for the production of F^{18}. Irradiation of NH_4F in the Low Intensity Test Reactor for two hours produced about 10 microcuries of F^{18} per gram of NH_4F by the reaction $F^{19}(n,2n)F^{18}$. Irradiation of LiF containing 10 mole % Al_2O_3 in the Graphite Reactor for two hours gave about one microcurie of F^{18} per gram of starting material by the reactions $Li^6(n,\alpha)H^3$, $O^{16}(t,n)F^{18}$. Bombardment of $LiNO_3$ in the Graphite Reactor for two hours produced about 50 microcuries of F^{18} per gram by the same process. There was some chemical decomposition of the nitrate. Bombardment of NaF with 22 mev. protons at low beam intensity in the 86-inch cyclotron for only one minute produced about 50 microcuries of F^{18} per gram by the reaction $F^{19}(p,pn)F^{18}$.

The F^{18} produced in the cyclotron was radiochemically pure, while all of the pile methods produced a mixture of other activities. The F^{18} was identified by its γ-spectrum, γ,γ-coincidence count (from positron annihilation), half-life and chemical separation. The method finally adopted was the $LiF-Al_2O_3$ bombardment in the pile, because of greater convenience for the purpose intended and with the facilities available.

Attempts to Produce F^{21}.—Several attempts were made to produce F^{21} by the sequence $Li^6(n,\alpha)H^3$, $F^{19}(t,p)F^{21}$. Lithium fluoride was bombarded in the Low Intensity Test Reactor for periods ranging from 10 minutes to 45 hours. No activity which could be ascribed to fluorine (other than F^{18}) was observed.

Apparatus and Procedure.—An all-nickel vacuum line was constructed using heliarc-welded joints. This consisted of a manifold with several fixed and removable traps and storage vessels. A Booth-Cromer gage was used to measure pressure.

After the $LiF-Al_2O_3$ mixture was irradiated in the pile, it was placed in a nickel exchange vessel and attached to the vacuum line. Hydrogen fluoride was condensed onto it, allowed to warm to room temperature for a few minutes, then distilled off. The F^{18} in the resulting HF was radiochemically pure and sufficiently active to allow tracer studies to be conducted over 10–12 hours.

Equal amounts of radioactive HF and one of the fluorinated methanes were transferred to a nickel reaction vessel of 70-ml. capacity. The total pressure ranged from 350 to 550 mm. at room temperature. The mixture was heated for the desired length of time in a Marshall furnace, the temperature of which was maintained constant by an Electromax controller. The products were then separated by fractional distillation in the vacuum line and the F^{18} activity in the two products compared with that in the original HF. The gas to be counted was contained in a nickel vessel which could be placed in a well-type scintillation counter.

Results

No exchange of fluorine was observed between HF and the compounds CH_2F_2, CHF_3, CF_4 or

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(1) J. E. Boggs and L. O. Brockway, THIS JOURNAL, **77**, 3444 (1955).

(2) E. Moles and T. Batuecas, *J. chim. phys.*, **17**, 537 (1919).

CF_2Cl_2 in one hour at temperatures up to 500° or between CH_3F and HF up to 400° in one hour. Higher temperatures could not be used because of chemical decomposition or reaction with the wall. No radioactivity was ever observed on the reactor wall, confirming the absence of exchange between HF and NiF_2 reported by Rogers and Katz.[3] Our results emphasize the remarkable stability of the carbon–fluorine bond.

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[3] M. T. Rogers and J. J. Katz, THIS JOURNAL, **74**, 1375 (1952).

[4] Operated by Carbide & Carbon Chemicals Corp. under Contract W-7405 for the U. S. Atomic Energy Commission.

Concentration Profiles in Packed-bed Ion-exchange Systems

BY E. B. BYRNE AND L. LAPIDUS

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In recent years, considerable theoretical effort has been expended to describe the behavior of fixed bed percolation columns. Implicit in all of this work was the assumption of a flat velocity or concentration profile as the solute moves down the bed. Experimental verification or rejection of this assumption has not been considered in any detail. Baddour, *et al.*,[1] and Glueckauf and Coates[2] have briefly mentioned the problem in their ion-exchange studies, while Stewart[3] has shown that adsorption on alumina oxide may produce considerable spreading of the concentration band at any column cross-section. Klinkenberg[4] has also mentioned data collected indicating large variations in fluid velocity in a number of percolation processes.

In this note, the present writers would like to describe briefly a series of experiments in which concentration profiles between acidic and basic forms of an anion-exchange resin, Amberlite IRA-400, were observed.

The main piece of equipment was 10 inches long, 1 inch ID stainless steel column packed with exchange resin to a depth of 8 inches. A 1 inch layer of 1/2 mm. glass beads was placed on top of the resin to act as flow distributor, and glass wall plugs were placed at both ends to retain the beads and the resin. The column was constructed of two milled, semi-cylindrical sections, held together with two pressure clamps. By removing the clamps, the column could be split into two halves. Means were provided for feeding solution at a constant rate to the top of the column as well as for regeneration of the resin and backwashing of the bed proper. Various acids and bases were used both as regenerants and as solutes. These included acetic acid, sulfuric acid and sodium hydroxide. After the concentration profile had progressed to the desired point in the column, the solution was stopped, and 35 ml. of phenolphthalein solution added. The pressure clamps were removed; and the column, including the resin. was slit in a longitudinal direction. As a result, a cross-section of the entire column was available for observation with the acidic and basic portions being colored either a bright red or a neutral color.

The results indicate two distinct types of concentration profiles. The first, occurring when an acid solution percolated through the resin in the basic form, was characterized by a flat profile. This profile maintained its shape throughout the length of the bed. The second, occurring when a basic solution flowed through the acid form resin, resembled sections of an inverted parabaloid or a frustrum of a parabaloid. In the second case, the concentrated wave at the wall was as much as 4 inches ahead of the center section. These two radically different profiles are intimately connected with the swelling and shrinking of the resin as the exchange process takes place. The uniform band occurs when the resin expands during reaction and the non-uniform band when shrinkage occurs. Expansion of the resin tends to flatten the concentration profiles since, as the flow in a localized area advances ahead of the main flow, expansion of the particles reduces the size of interstices between the particles and increases resistance to flow. Shrinkage, on the other hand, tends to accelerate the flow in areas where local flow has advanced ahead of the main flow. This was particularly true near the walls of the column where the resin mass tended to shrink away from the walls, thus producing channels where the flow could advance farther and farther ahead of the main flow. Because of this accelerated flow near the walls of the column, it is possible for basic solution to pass through the entire column almost unreacted, even though the full exchange capacity of the column has not been used.

Thus, the assumption of a flat concentration profile in an ion exchange column would seem to be valid only if the exchange reaction is such that swelling of the resin takes place.

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[1] R. F. Baddour, D. J. Goldstein and P. Epstein, *Ind. Eng. Chem.*, **46**, 2192 (1954).

[2] E. Glueckauf and J. I. Coates, *J. Chem. Soc.*, 1315 (1947).

[3] A. Stewart, *Disc. Faraday Soc.*, **7**, 65 (1949).

[4] A. Klinkenberg, *ibid.*, **7**, 151 (1949).

Equilibrium Constants for the Formation of Complexes between 1,3-Diamino-2-propanol and Various Metal Ions[1]

BY ELY GONICK, W. CONARD FERNELIUS AND BODIE E. DOUGLAS

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Compounds in which 1,3-diamino-2-propanol is present in the form of complexes with metal ions have been isolated.[2,3] However, no data are available to permit comparison of the stability of these complexes with those containing no hydroxyl group. Such data are presented here.

Experimental

1,3-Diamino-2-propanol as obtained from Eastman Kodak Company was refluxed over barium oxide for four hours and distilled at 5 mm. The fraction boiling at 114° melted 40–42° and was found to possess the theoretical equivalent weight on titration.

Details of the experimental procedure are the same as those previously described.[4]

The terms used here and the method of calculation of con-

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[1] Abstracted from a portion of a thesis presented by Ely Gonick in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1951.

[2] F. G. Mann, *J. Chem. Soc.*, 2904 (1927).

[3] J. G. Breckenridge and J. W. R. Hodgins, *Can. J. Research*, **17**, 331 (1939).

[4] E. Gonick, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **76**, 4671 (1954).