perature. In the course of some preparative work we have noted the formation, also at room temperature, of striking blue fluorescing substances after treatment of tyrosine, phenylalanine and tryptophan with Denigès reagent.[2]

A fairly stable reagent was prepared by dissolving one part of paraformaldehyde in five parts of concentrated sulfuric acid. The reaction was carried out by dissolving a small sample in 2 ml. of sulfuric acid, adding 1 ml. of reagent and diluting with water after three minutes at room temperature. Fluorescence could be measured with the same filter combinations as are used for thiochrome determinations.

Under these conditions equal weights of the amino acids phenylalanine, tyrosine and tryptophan give intensities in the ratio of 100:4:1. If the acid solution containing tyrosine stood ten minutes before addition of reagent, no fluorescence was observed; this treatment did not affect the reaction with phenylalanine or tryptophan.

The fluorescing solutions are quite stable in the dark, less so in diffuse light, and lose about half their intensity after twenty minutes of ultraviolet irradiation.

Fluorescence is quenched by addition of bromine water, picric acid, hydrogen peroxide, or sodium sulfite, hydrosulfite or nitrite. Cysteine, but not cystine or methionine, inhibits the formation of the fluorescing compounds.

The reaction is also given by N-acetyltyrosine and ephedrine; not by alanine, arginine, asparagine, aspartic acid, cysteine, cystine, glutamic acid, glycine, histidine, isoleucine, lysine, methionine, proline, serine, threonine, valine, thiamine, riboflavin, niacinamide, pteroylglutamic acid, calcium pantothenate, rutin, dextrose, sucrose and maltose.

Crude substances have been isolated from reaction mixtures following treatment of phenylalanine or tyrosine, respectively. These substances react with ninhydrin (Van Slyke method) to yield carbon dioxide virtually equivalent to their total nitrogen content. This is contrary to what might be expected from the tetrahydroisoquinoline or carboline compounds formed with formalin by these amino acids under other conditions.[3] Possibly a reversible condensation product of the triformal glycine ester type[4] is formed. This would fit fairly well with the presently available analytical data on the tyrosine and phenylalanine compounds.

The relation between intensity of fluorescence and concentration of phenylalanine is practically linear over the range from 2–8$\gamma$ per ml. of diluted reaction mixture.

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(2) Denigès, *Compt. rend.*, **136**, 583 (1900).

(3) French and Edsall, "Advances in Protein Chemistry," Vol. II, Academic Press, New York, N. Y., 1945.

(4) Bergmann, *et al.*, *Z. physiol. Chem.*, **131**, 18 (1923).

## REACTIONS OF IONS IN AQUEOUS SOLUTION WITH GLASS AND METAL SURFACES

*Sir:*

Radioactive tracers afford a more direct, sensitive and rapid means than any previously[1] used for studying the sorption of ions in solution on solid surfaces. Using them we have carried out exploratory investigations on some of the variables controlling such reactions. The method consists of immersing small flat samples in a solution of the radioactively tagged ion,[2] removing, rinsing and drying, and determining the intensity of the radioactivity on each with the aid of a Geiger–Mueller counter.

Soft glass samples immersed in 0.05 $M$ sodium carbonate solution show a rapid sorption of sodium ions which approaches an apparent equilibrium value of about 0.5 "monolayers"[3] at 25° and 5 monolayers at 90° after two to three hours immersion. The initial rate of sorption shows an approximately five-fold linear decrease with decrease in $p$H from 12 to 5.

Samples flamed prior to immersion show a much greater rate of sorption than those cleaned only by washing with water and vapor degreasing with carbon tetrachloride. The apparent activation energy[4] was the same, however, *i. e.*, about 10,000 cal. mole$^{-1}$ in neutral solution. This suggests that the flame does not produce new types of reactive centers but uncovers more of the kind already available by cleaning the surface more completely than water and carbon tetrachloride alone. Presoaking of samples in 9 $N$ HCl increased the activation energy for sorption in neutral solution to 13,500 cal. mole$^{-1}$ suggesting that the exchange of sodium ion with an —Si—OH bond may be more difficult than with an —Si—ONa bond.

Sodium ions sorbed on soft glass are removed only very slowly by rinsing in water at room temperature up to ten hours, but are removed somewhat more readily at higher temperature.

The sorpion of silver and cesium ions is qualitatively similar to that of sodium ions. Presoaking of glass in stannous chloride solution, such as used in preparing glass for silvering, caused an increase in the sorption of silver ions.

From 0.2 to 5 monolayers of sodium ion are sorbed by cleaned aluminum, steel, silver and platinum during a few hours immersion at room temperature.

The sorption of carbonate ion on glass or steel is slight, of the order of 0.001 monolayer.

Radioautographs have been useful in determining the homogeneity of distribution of sorbed

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(1) W. A. Weyl, "Some Practical Aspects of the Surface Chemistry of Glass," Glass Technology Institute, State College, Pa.

(2) U. S. Atomic Energy Commission Radioisotope Catalog No. 2.

(3) A "monolayer" is arbitrarily defined here as the number of ions required to cover the macro surface area of the sample if each ion covers an area equal to the square of its ionic crystal diameter.

(4) Calculated from the graph of the logarithm of the initial rate of sorption *vs.* $1/T$.

ions on surfaces and may be useful in practical testing of surface cleanliness.

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## SIDE-CHAIN CRYSTALLIZATION IN ALKYL POLYACRYLATES

*Sir:*

Rehberg and Fisher[1] synthesized and polymerized a series of *n*-alkyl acrylates from methyl up to hexadecyl. They reported that the brittle points of these polymers decrease with increasing length of side chain, up to octyl (−65°) after which further increase leads to higher brittle points (*e. g.*, +35° for hexadecyl polyacrylate). In the latter paper it is noted parenthetically that the higher alkyl polyacrylates are crystalline in character.

We have prepared polymers of tetradecyl, hexadecyl and octadecyl acrylate, and copolymers of hexadecyl acrylate with methyl acrylate, and have established the fact that the high brittle points of these polymers are due to crystallization of the *alkyl side chains*. At low temperatures these side chain crystallites bind the polymer into a firm, waxy structure. At a fairly sharp melting point the crystallites melt, and the polymer becomes rubbery. This phenomenon is distinct both from the second order transition phenomenon exhibited by the lower acrylates and from the usual type of polymer crystallization (alignment of the polymer chain itself).

A series of X-ray diffraction photographs were obtained from hexadecyl acrylate polymer which serve to confirm the side-chain crystallinity of these samples. Normal wide angle and small angle Debye–Scherrer patterns were taken. The wide angle diagrams showed the polymeric material to be crystalline, and exhibited a very strong line at 4.2 Å. Small angle patterns were obtained at film-to-specimen distances of 20 cm. with filtered Fe radiation. These diagrams exhibited two sharp diffraction lines at 50 and 150 Å., respectively.

A small angle diagram was also obtained from hexadecyl acrylate monomer. (This material is liquid at room temperature but the specimen was cooled so that it was crystalline.) This diagram showed a diffraction maximum at 28 Å. The length of the polymer side chain is somewhat less than this.

The 150 and 50 Å. spacings found in the polymer may be considered as the first and third orders of a fundamental 150 Å. spacing. If the suggested interpretation of these long spacings as due to a crystallization of side chains is correct, then it would appear that the periodicity in the crystalline side chain packing repeats every six side chain units.

An effort was made to obtain orientation by drawing fibers of the hexadecyl acrylate polymer. X-Ray diagrams of these fibers showed slight orientation effects. The maxima of the long spacings occurred on the equator of these diagrams, which agrees with the interpretation that the crystallization is that of the side chains.

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[1] C. E. Rehberg and C. H. Fisher, THIS JOURNAL, **66**, 1203 (1944); *Ind. Eng. Chem.*, **40**, 1429 (1948).

[2] American Chemical Society Post-Doctoral Fellow 1947–1948.

## POLAROGRAPHIC CURRENT TIME CURVES

*Sir:*

From theoretical considerations, Ilkovič[1] has shown that the average diffusion current for a dropping mercury electrode is given by

$$\begin{aligned} i_d &= knD^{1/2}Cm^{2/3}t^{1/6} \\ &= ICm^{2/3}t^{1/6} \end{aligned}$$

If the "diffusion current constant" ($I$) for a given ion in a given supporting electrolyte is independent of capillary constant, as required by the Ilkovič equation, the performance of practical polarographic analyses can be greatly simplified. Lingane and Loveridge[2] have shown that, for the range of capillaries generally used in analysis, $I$ is not strictly constant. The author recently has shown[3] that it is not possible to properly correct a polarogram, obtained with a large series resistance, by simply subtracting the product of the observed average current and the series resistance from the applied e. m. f. In an attempt to compute the average current for a given applied e. m. f. and series resistance, he was unable to obtain agreement between the calculated and experimental values if he assumed the current during the life of a drop grew as the one-sixth power of the time.

It was, therefore, considered to be of importance both in practical analyses and theoretical studies to examine experimentally the current time relationship for individual drops.

The Brush Development Co. pen recorder, with which recordings can be made over a frequency range of d. c. to 100 c. p. s., was used to determine the relationship on the diffusion region for 0.001 $M$ lead in 1 $M$ potassium chloride (0.01% gelatin),

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[1] D. Ilkovič, *Coll. Czech. Chem. Commun.*, **6**, 498 (1934).

[2] J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **66**, 1425 (1944).

[3] H. A. McKenzie, unpublished work.