The solution became somewhat viscous during this time. The solution was poured into ethanol to precipitate the polymer. A white powdery product which did not darken, decompose or melt below 300° was obtained in 10% yield. This product was insoluble in benzene, chloroform, ethyl acetate, dioxane, dimethyl formamide, ether and hot trichloroethylene. It was soluble in ethyl cinnamate.

Anal.[8] Calcd. for $C_{11}H_{12}O_2$: C, 75.02; H, 6.87. Found: C, 74.95; H, 7.04; N, 0.37.

This nitrogen content is equivalent to the nitrile nitrogen in 0.087 g. of 2,2'-azobisisobutyronitrile.

Polymer of a similar nature was obtained in low yield in cyclohexane solution.

Ten grams of ethyl cinnamate, 0.12 g. of benzoyl peroxide and 0.025 g. of technical lauryl mercaptan were heated at 60° for about a week. On isolation as before an 11.3% yield of polymer was obtained.

Polymethyl Cinnamate.—Twenty grams of methyl cinnamate and 0.10 g. of 2,2'-azobisisobutyronitrile were heated at 60° for about 10 days and then to 85° for 3 days. When the solution was poured into ethanol a white powder was obtained in 2% yield. This product was insoluble in common solvents and did not darken, melt or decompose when heated to 300°.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.04; H, 6.22. Found: C, 71.08; H, 6.43; N, 1.17.

The nitrogen content corresponds to that of 0.055 g. of initiator.

A sample of fibrous polymethyl cinnamate was isolated from an old sample of methyl cinnamate. Its physical properties and infrared spectrum were similar to those of the material made by 2,2'-azobisisobutyronitrile polymerization, except that it was obviously of higher molecular weight. Its low solubility has interfered with proper evaluation of this material.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.04; H, 6.22. Found: C, 73.46; H, 6.37.

Attempts to use standard emulsion polymerization procedures for making these products are contemplated.

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(8) We are indebted to Mrs. Ester Fett and Mr. Joseph Nemeth for the microanalyses reported here.

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Anion Exchange Studies. VIII.[1,2] Separation of Iron and Aluminum in Sulfate Solutions

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It had been shown in an earlier paper that Fe(III) can be strongly adsorbed from chloride solutions by the quaternary amine polystyrene divinyl benzene "strong base" anion-exchange resin Dowex-1.[3] A similar study of the adsorbability of Fe(III) from sulfuric acid and ammonium sulfate solutions has now been carried out. For these media, conditions of strong adsorption were found. However, in contrast with the behavior in chloride solutions, the maximum adsorption found was considerably smaller for sulfate than for chloride solutions, and adsorption was found to decrease greatly with acidity and slightly with sulfate concentration.

The sulfate form of the resin was prepared by washing the chloride form with 1–2 M H_2SO_4 until the effluent was chloride-free and then washing the resin with distilled water until the *p*H of the effluent was larger than 5. Since elution of the acid from the resin tends to tail strongly,[2] large volumes of water are necessary.

The adsorbability of Fe(III) was investigated by determining distribution coefficients D (amount Fe per kg. of resin/amount Fe per l. of solution) by shaking iron sulfate solutions with known amounts of resin, and determining the change in iron concentration spectrophotometrically.

In the sulfuric acid solutions significant adsorption was found only for M $H_2SO_4 < 0.1$. This adsorption increased rapidly with decreasing sulfuric acid concentration reaching values of $D =$ *ca.* 100 in 0.001 M H_2SO_4.

Adsorbabilities in ammonium sulfate solutions were measured with some acid added (initially 0.01 M H_2SO_4) to prevent extensive hydrolysis of Fe(III) and possible hydrolytic polymerization. D was found to decrease from *ca.* 35 in 0.01 M $(NH_4)_2SO_4$ to *ca.* 10 in 4 M $(NH_4)_2SO_4$, and to be essentially independent of iron concentration in the range 10^{-5} to 10^{-3} M Fe(III) under conditions where loading of the resin with respect to iron is small.

The color of the adsorbed iron complex varies somewhat with concentration in the resin phase, becoming red-brown at high concentrations. The adsorbed species cannot readily be identified since, as pointed out in an earlier paper,[2] the resin adsorbs sulfuric acid, hence causing significant changes in the acidity of the solutions and in the composition of the resin phase. The strong dependence of adsorption on acidity suggests that a basic sulfate complex is involved.

The adsorption of Fe(III) can be utilized for separations. The principles of these separations are illustrated in experiments with Al(III) which is only weakly adsorbed under conditions where Fe(III) is strongly adsorbed. Thus, an Fe(III)–Al(III) solution containing 0.005 M $Fe_2(SO_4)_3$, 0.005 M $Al_2(SO_4)_3$ and 0.010 M H_2SO_4 was passed through a 0.488 cm.^{2} × 15.9 cm. Dowex-1 column in the sulfate form with flow rate 0.34 cm. min.$^{-1}$. Aluminum appeared in the effluent after *ca.* 4.2 cc. of solution had been passed through the column. The iron concentration of the solution was $< 10^{-6}$ M. Iron was adsorbed at first at the top of the column, slowly moved through it, and appeared after *ca.* 95 ml. in the effluent. Since the interstitial volume of the column is *ca.* 3.3 cc., while Al(III) appeared in the effluent after 4.2 cc., it appears that Al(III) is slightly adsorbed under these conditions. Possibly for these reasons Fe(III) appears in the effluent somewhat earlier when the same separation is carried out with more concentrated Al(III) solutions (*e.g.*, after 44 ml. with a 0.005 M $Fe_2(SO_4)_3$–0.48 M $Al_2(SO_4)_3$–0.005 M H_2SO_4 solution in a similar though slightly shorter column (15.0 cm.)).

Fe(III) can be eluted from the column by increasing the sulfuric acid concentration of the eluent. The experiments described in Fig. 1 illustrate the procedure. In these experiments, iron was adsorbed from 0.5-ml. samples of 5 × 10^{-3} M $Al_2(SO_4)_3$–5 × 10^{-3} M $Fe_2(SO_4)_3$–10^{-2} M H_2SO_4 solutions on 0.187 cm.^{2} × 9.3 cm. columns,

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(1) This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous paper, K. A. Kraus, F. Nelson and J. F. Baxter, THIS JOURNAL, **75**, 2768 (1953).

(3) G. E. Moore and K. A. Kraus, *ibid.*, **72**, 5792 (1950).

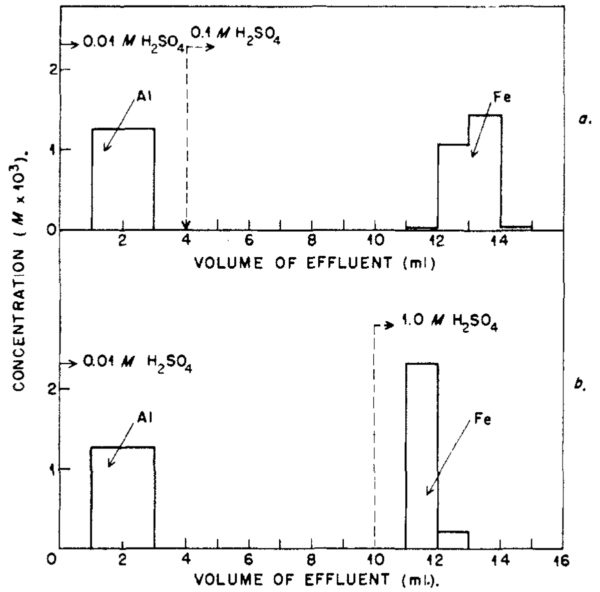

Fig. 1.—Separation of Al(III) and Fe(III) by anion exchange in sulfate solutions (0.187 cm.^{2} × 9.3 cm. Dowex-1 column).

Al(III) rapidly appeared in the effluent while Fe(III) was adsorbed (iron concentration in effluent $< 10^{-6}$ M). The appearance of Fe(III) in the effluent is considerably delayed when elution is carried out with 0.1 M H_2SO_4, (Fig. 1a) but is quite rapid when elution is carried out with 1.0 M H_2SO_4. In both experiments, the Fe(III) band is narrow and shows little tailing. The long delay in the appearance of the Fe(III) band in the effluent with 0.1 M H_2SO_4 is probably connected with the adsorption of sulfuric acid by the resin and its partial conversion to the bisulfate form. The sulfuric acid concentration thus remains considerably less than that of the eluent until the column has been equilibrated with the new medium.

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The Refractive Indices and Molecular Dispersion of *cis*- and *trans*-Decahydronaphthalene

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In the course of a series of measurements dealing with the physical–chemical properties of *cis*- and *trans*-decahydronaphthalene it became desirable to ascertain their refractive indices in the temperature range of 0 to 85°.

For this purpose a Pulfrich refractometer was used with two sources of light, a bunsen burner sodium chloride flame for the D line and a guild type of hydrogen tube for the C(Hα) and F(Hβ) lines. The results are given in the form of graphs in Figs. 1 and 2.

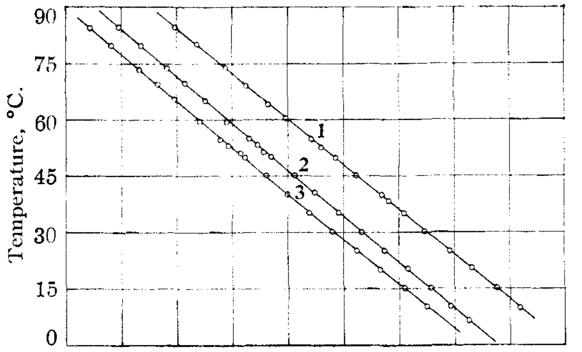

Fig. 1.—Refractive index of *trans*-decahydronaphthalene: 1, n^t_F; 2, n^t_D; 3, n^t_C.

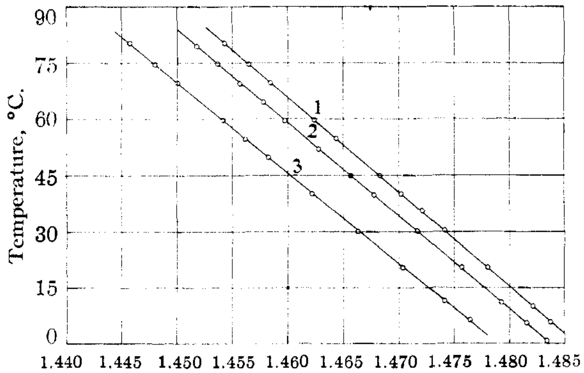

Fig. 2.—Refractive index of *cis*-decahydronaphthalene: 1, n^t_F; 2, n^t_D; 3, n^t_C.

The refractive index–temperature relationship is linear for the *trans* compound within the limits of accuracy obtainable. In the case of the *cis* compound there appeared to be a slight change in slope above 50°. It should be noted that between 50.0 and 50.9° for this compound no readings of the refractive index could be made because of a persistent turbidity, normally associated with all measurements when the temperature of the liquid in the test cup was not constant. This observation appeared significant because other physical properties indicated some change in liquid structure between these temperature regions in the case of the *cis* isomer.

The refractive indices of the *trans* isomer over the temperature interval from 10–90° were used to test the validity of the molar refraction R as calculated from the Gladstone–Dale (R_G), Lorentz–Lorenz (R_L) and Eykman (R_e) equations. The drift in the value of R per degree with rise in temperature for all three wave lengths is shown in Table I.

TABLE I

	n_C	n_D	n_F
$\Delta R_G \times 10^{-3}$	1.6	6.4	5.9
$\Delta R_L \times 10^{-3}$	4.0	6.2	8.1
$\Delta R_e \times 10^{-3}$	52.0	59.0	60.6

Thus for this compound Eykman's empirical equation is far less valid than the other two. Attempts have been made to correlate refractive index with surface tension, notably by Tripathi.[1] However, his equation cannot hold for *trans*-decahydronaphthalene for the molar refraction R increases with temperature while that of the parachor decreases 0.075 unit per degree.[1] Using Eisenlohr's values of carbon and hydrogen the

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(1) R. C. Tripathi, *J. Indian Chem. Soc.*, **18**, 411 (1941).