acetylene–alcohol mixtures boil slightly higher than those of the other classes of aliphatic hydrocarbons. This may prove to be significant should the problem of separating acetylenes from hydrocarbon mixtures ever present itself.

Analysis of the constant boiling acetylene–alcohol mixtures was accomplished both by refractive index and density. A sufficient number of mixtures was prepared in each case to establish both isotherms. All distillations were done at atmospheric pressure when the barometer read 745 ± 5 mm.

The acetylenes form ternary alcohol–water heteroazeotropes also. These were not analyzed although some of the data for them were recorded (Table II).

TABLE II

TERNARY HETEROAZEOTROPES OF ALKYLACETYLENES WITH ETHYL ALCOHOL AND WATER

Acetylene	Constant b. p., °C.	Vol. % lower layer[a]	Upper layer $n^{25}D$	Upper layer d^{25}	Lower layer $n^{25}D$	Lower layer d^{25}
n-Butyl	59.9	5.6	1.3921	0.7202	1.3598	0.8597
Diethyl	64.4	14.8	1.4025	.7290	1.3674	.8539
Isoamyl	69.0	17.4	1.3955	.7371	1.3672	.9519
n-Amyl	71.0	28.6	1.3970	.7436	1.3680	.8329

[a] These values are approximate and were measured at 25°.

Experimental

The acetylenes were prepared in the usual way from the alkyl bromides and sodium acetylide in liquid ammonia.[4] Absolute ethyl alcohol (Commercial Solvents Corp.) was redried with magnesium ethoxide immediately before use; d^{25} 0.7852, $n^{25}D$ 1.3594.

A carefully purified sample of each acetylene was mixed with an excess of amount of absolute alcohol and slowly distilled through a helix packed column having an efficiency of 15 plates as determined with an ethylene bromide–benzene mixture. The distillate was collected in fractions and those of nearly the same boiling point, density and refractive index were combined and redistilled. The process was repeated until successive fractions of the distillate showed practically the same composition, not altered by redistillation.

The ternary mixtures were obtained in substantially the same way, except that water was added to the still charge and the column was provided with a special head to prevent premature phase separation. The material which distilled at constant temperature was collected separately but was not redistilled since analysis was not intended.

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[4] Vaughn, Vogt, Hennion and Nieuwland, *J. Org. Chem.*, **2**, 1 (1937).

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Relative Association of Hydrogen and Deuterium Fluorides in the Liquid State

BY JOEL H. HILDEBRAND AND ALLEN GEE

Claussen and Hildebrand[1] found that the vapor pressure of deuterium fluoride is greater than that of hydrogen fluoride, the ratio, P_{DF}/P_{HF} varying from 1.150 at 240° K. to 1.049 at 290° K. The vapor pressure of the deuterium compound is greater than that of the hydrogen compound also in the case of the acetic acids, but it is less in the case of the two kinds of water and ammonia and with deuterium and hydrogen chloride. It was pointed out that the first two pairs are alike in being highly associated in the gaseous phase while the last three are not.

Long, Hildebrand and Morrell[2] determined the variation in the association factors of gaseous hydrogen fluoride and deuterium fluoride with pressure and temperature, showing deuterium fluoride to be more associated. They confirmed the earlier results of Simons and Hildebrand[3], who found that the association of hydrogen fluoride could be reproduced over a wide range by assuming the single equilibrium, $6HF = (HF)_6$, with evidence for smaller polymers below a degree of association represented by the association factor, 1.3. It has been recognized that polymers other than $(HF)_6$ may be present also in the range of higher association, and that the single equilibrium that has been assumed may represent only an average of a more complex scheme of association. The only reason for a preponderance of a hexamer would appear to be a closed ring with its additional hydrogen bond and with corresponding preferred bond angles.[4] However, no independent evidence for ring structure has yet been discovered, and the recent measurements of dielectric constant by Benesi and Smyth indicate linear polymers.[5]

This does not interfere with the purpose of this communication, which is to calculate the partial pressures of the monomers, p_{HF} and p_{DF}, in the saturated vapors in order to learn whether, in the liquid state, the hydrogen compound is less strongly associated than the deuterium compound, as in the cases of water and ammonia.

The following table gives the total pressures at saturation according to Claussen and Hildebrand together with the corresponding partial pressures of the monomers, calculated by the aid of the equations of Long, Hildebrand and Morrell. The ratio, p_{HF}/p_{DF}, is greater than unity, indicating stronger association of the deuterium compound in the liquid, and bringing these com-

TABLE I

T, °K.	Total pressure P_{HF}	Total pressure P_{DF}	Monomer pressure p_{HF}	Monomer pressure p_{DF}	Ratios P_{HF}/P_{DF}	Ratios p_{HF}/p_{DF}
270	314.0	340.1	140.7	133.0	0.923	1.057
280	468.9	499.5	232.8	220.5	.939	1.056
290	681.1	714.2	371.1	351.8	.953	1.055

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[1] Wm. M. Claussen and J. H. Hildebrand, THIS JOURNAL, **56**, 1820 (1934).

[2] R. W. Long, J. H. Hildebrand and W. E. Morrell, *ibid.*, **65**, 182 (1943).

[3] J. H. Simons and J. H. Hildebrand, *ibid.*, **46**, 2138 (1924).

[4] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 298.

[5] H. A. Benesi and C. P. Smyth, *J. Chem. Phys.*, **15**, 337 (1947).

pounds into line with the corresponding waters and ammonias.

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Chromatography of Some Common Indicators

BY J. V. KARABINOS[1] AND P. M. HYDE

Alumina,[2] calcium carbonate, talc, Super Cel and Hyflo Super Cel have been used successfully as adsorbents for the chromatography of coal tar dyes and indicators.[3] We wish to add to this list Silene EF[4] which has already found extensive use in the carbohydrate series.[5]

The relative degree of adsorption of the indicators on Silene EF–Celite 535[6] (5:1 by weight) was determined as follows. The indicator (0.75 mg.) dissolved in 0.4 ml. of 90% dioxane (90 ml. dioxane–10 ml. water) was put on a Tswett column (10 × 100 mm.) previously wetted with 0.5 ml. of the solvent and the indicator was developed with 5.0 ml. of 90% dioxane. The position of the colored zone was easily determined since the length of the column was calibrated in mm. (0, bottom; 100 mm., top). Checks were obtained in duplicate runs. Comparative data on the relative adsorption of the indicators on Silene EF–Alumina–Celite 535 (5:5:2 by weight) are also presented.

TABLE I

RELATIVE DEGREE OF ADSORPTION OF SOME INDICATORS

Indicator	Position of zone, mm. (color)	
	Silene EF	Silene EF–Alumina
Aurin tricarboxylic acid, ammonium salt	99–100 (Br)	99–100 (Br)
Indigo carmine	99–100 (Bl)	99–100 (Bl)
Alizarin red S	98–100 (R)	98–100 (R)
Alizarin yellow R	98–100 (Y)	98–100 (Y)
Methyl violet	68–100 (Bl)	60–93 (Bl)
Dichlorofluorescein	91–96 (O)	97–98 (Y-O)
Congo red	85–90 (R)	97–100 (O)
Brom phenol blue	73–80 (P)	95–99 (P)
Brom cresol green	62–70 (Bl)	96–99 (Bl)
Chlor phenol red	60–70 (P)	95–98 (P)
Brom cresol purple	15–25 (P)	65–75 (P)
m-Cresolsulfonphthalein	15–25 (Y)	57–63 (O)
Methyl orange	5–20 (Y)	51–60 (Y)
Tropaeolin 00	8–18 (Y)	45–55 (Y)
o-Cresolphthalein	8–18 (Y)	47–55 (Y)
Thymol blue	0–10 (Y)	25–35 (Y)
Cresol red	8–15 (Y)	48–52 (Y)
Brom thymol blue	0–4 (Y)	0–2 (Y)
m-Nitrophenol	0	0
Phenolphthalein	0	0

It is interesting to note that the highly polar dyes, *e. g.*, the sodium salts are more strongly adsorbed.

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(1) Present address: Department of Chemistry, St. Procopius College, Lisle, Illinois.

(2) C. P. grade, J. T. Baker Chemical Company, Phillipsburg, New Jersey.

(3) P. Ruggli and P. Jensen, *Helv. Chim. Acta*, **18**, 624 (1934); **19**, 64 (1936); P. Ruggli and M. Stauble, *ibid.*, **23**, 689 (1940); H. H. Strain, THIS JOURNAL, **61**, 1292 (1939); W. Rieman, *J. Chem. Ed.*, **18**, 131 (1941).

(4) A commercial hydrated calcium silicate generously supplied by the Columbia Chemical Division, Pittsburgh Plate Glass Co., Barberton, Ohio.

(5) L. W. Georges, R. S. Bower and M. L. Wolfrom, THIS JOURNAL, **68**, 2169 (1946).

(6) Johns-Manville Co., New York, N. Y.

Preparation of Resacetophenone

BY JOSEPH R. KILLELEA AND H. G. LINDWALL

The zinc chloride method commonly employed for the preparation of resacetophenone[1] involves a vacuum distillation and yields 65% of colored product. Since the vacuum distillation of high-melting solids is a troublesome process, we have adopted a boron fluoride method which eliminates the necessity of the distillation and gives superior yields of colorless product. Details are given below.

A mixture of resorcinol, 55.0 g. (0.5 mole), acetic anhydride, 54.5 g. (50.0 ml., 0.53 mole) and commercial anhydrous ether, 75 ml., is saturated with gaseous boron fluoride in an ice-bath. The mixture is then stored in a refrigerator for ninety-six hours. The heavy, yellow crystalline mass is broken up with a glass rod and the contents of the flask transferred to a beaker containing 200 g. of crushed ice. The ether is distilled off on a water-bath or allowed to evaporate in a good hood. The light yellow solid is washed with cold water. It weighs 73.0 g. (96%) and melts at 138–142°. It may be recrystallized from 1200 ml. of boiling water (Norit), the recovery being 69.0 g. of colorless solid (91%) melting at 144–145°.

A mixed melting point of this product with a sample prepared by the zinc chloride method showed no depression. The dibenzoate, prepared by Baker's method[2] melted at 80–81° mixed with the dibenzoate prepared from Cooper's product, 80–81°.

The boron fluoride method exemplified above has been employed, with slight modifications, in this Laboratory for the preparation of other polyhydroxyacetophenones.

(1) Cooper, "Org. Syn.," **21**, 103 (1941).

(2) Baker, *J. Chem. Soc.*, 1384 (1933).

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Vanadium Oxide, a Hydrogenation Catalyst[1]

BY V. I. KOMAREWSKY, L. B. BOS AND J. R. COLEY

Vanadium oxide is widely used as an oxidation catalyst. It has also been reported to be an effective catalyst for the dehydrogenation of hydro-

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(1) Presented before the Division of Petroleum Chemistry at the Atlantic City Meeting of the American Chemical Society, April 14, 1947.