

layers under various conditions are shown in Table I.

TABLE I
ABSOLUTE SURFACE VISCOSITY OF CHLOROPHYLL MONO-LAYERS ON WATER

pH	F	μs
5.8	1.5	0.001
5.8	5	.001
5.8	7	.001
5.8	16	.305
3.0	9	.002
5.8	9	.002
10.0	9	.002
3.0	30	.242
5.8	30	7.8
10.0	30	40.7

Excellent multilayers (up to 600 layers) are easily built up as Y-films on glass or chromium, using a piston oil of tricresyl phosphate ($F = 9$ dynes cm.^{-1}) on distilled water. Built-up films of this type when measured by sodium light³ give a thickness of 14.2 Å. using the value of the refractive index 1.64 as determined by Dr. Katharine B. Blodgett of this Laboratory. When higher piston oil pressures were used the monolayer was found to be easily compressible with $F = 16$. A-B hydrous films are formed with water separating the A- and B-monolayers, the thickness of the double layer being about 35 Å. When $F = 30$ the double layer shows a thickness of 59 Å. at pH 3.0 and 5.8 and 68 Å. at pH 10.0. By drying the successive layers, dehydrous multilayers can be built up.

A chlorophyll Y-multilayer is non-wettable by water, giving a contact angle of 80°, but is wettable and soluble in hydrocarbons such as hexadecane which becomes fluorescent when placed on the built-up film. A single layer of chlorophyll molecules will produce fluorescence in a drop of benzene placed in contact with it.

Monolayers of chlorophyll may be deposited on top of barium stearate multilayers as PRA, PRB or PRAB films. The A-monolayer and the B-monolayer both give a contact angle of 90° against water and the drop will flow over the surface when the slide is tilted about 25°. A PRAB film, however, shows a contact angle of only 70° with very great hysteresis when the slide is tilted.

Chlorophyll Y-films of thicknesses ranging from one to 600 layers were examined with a beam of blue light. No detection of fluorescence could be

(3) Katharine B. Blodgett and Irving Langmuir, *Phys. Rev.*, **51**, 964 (1937).

observed in any instance involving a built-up film. When a small amount of chlorophyll was dissolved in Petrolatum and a drop placed on a clean water surface, it showed distinct fluorescence but the small area to which the drop spread indicated that little of the chlorophyll had become adsorbed at the interface between the oil and the water. When enough was added to the oil to cause it to spread to a monolayer the fluorescence disappeared.

A minute amount of chlorophyll added to molten paraffin exhibits strong fluorescence. This property instantly disappeared upon the solidification of the paraffin. Chlorophyll mixed with heptadecanol and hexadecane and spread as monolayers on water or transferred to solids shows no fluorescence.

A monolayer of chlorophyll deposited on a substrate of pure barium stearate or egg albumin when immersed into benzene is completely dissolved, indicating the absence of strong adsorption forces between the substrate and the chlorophyll.

The absence of chlorophyll fluorescence when spread as a homogeneous or dispersed monolayer on water or when deposited as homogeneous or dispersed single or multi-layers on solids indicates that the fluorescent property of chlorophyll involves more than dispersion alone.

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The Ternary System Methyl Alcohol, Toluene and Water

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In continuation of a series of earlier investigations of related binary and ternary systems¹ the solubility curve for the ternary system methyl alcohol, toluene and water at 25° has now been determined and the distribution of methyl alcohol between various proportions of water and toluene has been calculated. Incidentally, the refractive indices of various saturated solutions in this system have also been measured.

Materials.—Synthetically prepared methyl alcohol was desiccated over lime and fractionated from an all glass still. The relative density of the material used was d_{25}^{25} 0.78672 and the refractive index was n_D^{25} 1.32660.

(1) E. R. Washburn and others, *THIS JOURNAL*, 1931-1935; *J. Phys. Chem.*, 1936-1937; See *J. Phys. Chem.*, **41**, 457 (1937).

Mallinckrodt reagent toluene was fractionated after repeated treatments with sodium wire. The purified product had a density of d_4^{25} 0.86216, and a refractive index of n_D^{25} 1.49375.

The water was distilled from alkaline permanganate through a block tin condenser.

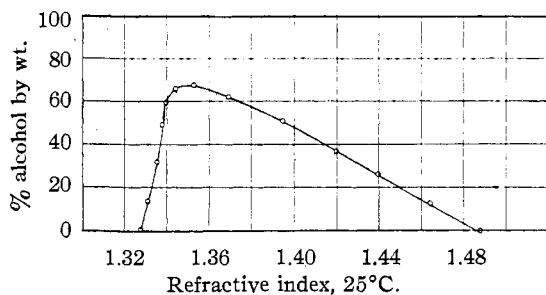


Fig. 1.

Procedure.—A series of solutions of alcohol and toluene was prepared, and water added to each solution to its saturation point at 25°. The refractive indices of these equilibrium solutions were determined at 25° with an immersion refractometer. All solutions were prepared by weight

TABLE I
REFRACTIVE INDICES OF EQUILIBRIUM SOLUTIONS AT 25°

Weight of components			Ref. ind. of solutions
Wt. % toluene	Wt. % alcohol	Wt. % water	
91.28	8.32	0.40	1.47764
86.24	13.02	.74	1.46935
72.40	26.22	1.37	1.44474
60.37	36.84	2.79	1.42537
43.94	50.56	5.51	1.39982
26.99	62.15	10.86	1.37455
14.72	67.35	17.91	1.35771
7.20	65.73	27.06	1.34880
2.83	59.40	37.77	1.34478
1.37	53.12	45.50	1.34331
0.50	41.06	58.43	1.34186
.14	24.00	75.87	1.33860
.06	6.72	93.23	1.33416
Toluene saturated with water			1.49295
Water saturated with toluene			1.33271

TABLE II
REFRACTIVE INDICES OF CONJUGATE SOLUTIONS, AND DISTRIBUTION OF METHYL ALCOHOL BETWEEN THE CONJUGATE SOLUTIONS

Water layer		Toluene layer		Dist. ratio
Wt. % alc.	Ref. index	Wt. % alc.	Ref. index	
2.5	1.33326	0.0	1.49290	
10.1	1.33521	.1	1.49273	0.01
15.4	1.33646	.2	1.49247	.01
22.0	1.33810	.2	1.49236	.01
32.2	1.34026	.4	1.49193	.01
40.6	1.34175	.8	1.49140	.02
42.8	1.34205	2.2	1.48873	.05

and precautions were observed to prevent evaporation during weighing, titration, and measurements of refractive indices. These data are shown in Table I.

The nature of the curve formed by plotting weight percentages of alcohol against refractive indices has been discussed. (1) A ternary solubility diagram for this system reveals that homogeneous solutions exist only in a relatively small concentration area.

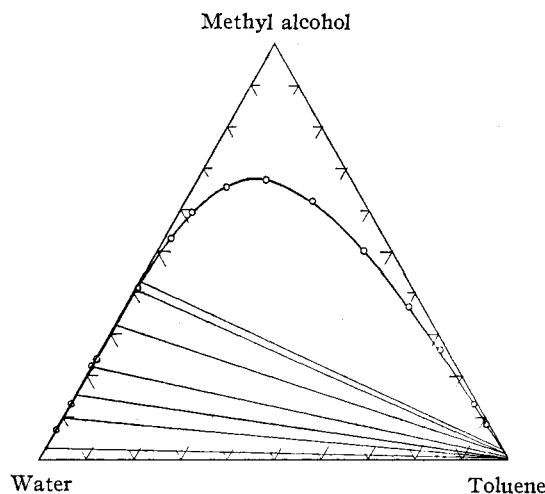


Fig. 2.

A series of mixtures of methyl alcohol, toluene and water which separated into two layers was prepared, and the refractive index of each layer measured at 25°. The measurements of refractive indices served as a measure of the weight percentages of alcohol in the two layers. These observations, together with the calculated distribution ratios of alcohol in the conjugate layers, are recorded in Table II. Lack of constancy in the distribution ratios is probably due, in part at least, to the increased miscibility of water and toluene in the presence of the methyl alcohol.

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Nitroguanyl Hydrazones of Some Aldehydes and Ketones

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Nine new nitroguanyl hydrazones of aldehydes and ketones have been prepared by following the

(1) This note is an abstract of the thesis submitted by Mr. Shoub in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry in June, 1937. Contribution No. 37 from the Department of Chemistry of the Polytechnic Institute of Brooklyn.