and bismuth oxyiodide in liquid ammonia at room temperature may be represented by the equation $BiOI + KNH_2 \rightarrow BiONH_2 + KI$.

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[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Ternary System: Ethyl Alcohol, Toluene and Water at 25°

BY E. ROGER WASHBURN, ALBERT E. BEGUIN AND ORVILLE C. BECKORD

In order to have solubility and distribution data for this system at 25° to compare with the systems already studied[1] and others which are soon to be described, it has been found necessary to carry out this investigation. Ormandy and Craven[2] and Tarasenkov and Poloznintzeva[3] have studied this system but their studies did not include determinations of the distribution of alcohol between the toluene-rich and water-rich layers or refractive indices of the saturated solutions, and the temperatures at which they worked were not those at which our earlier studies have been made.

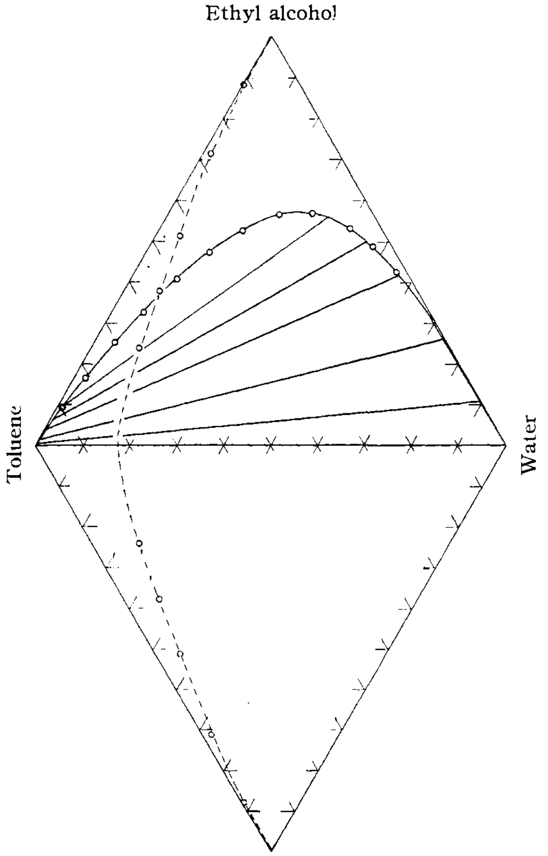

Fig. 1.—Solubility and conjugation curves at 25.0°.

Materials.—Carefully purified water was used. It was distilled from alkaline permanganate and collected while hot. A commercial grade of absolute ethyl alcohol was refluxed over lime for many hours and carefully fractionated. Its specific gravity d^{25}_4 was 0.7851 ± 0.0001, while its refractive index n^{25}_D was 1.35940 ± 0.00001.

Toluene of "analytical reagent grade" was dried over sodium and fractionated. This material had a specific gravity d^{25}_4 of 0.8608 ± 0.0002 and an index of refraction

TABLE I

SOLUBILITIES AND REFRACTIVE INDICES AT 25.0°

Wt. % toluene	Wt. % alcohol	Wt. % water	Refractive index
*89.84	9.36	0.81	1.4779
85.54	13.04	1.42	1.4719
*81.13	16.74	2.13	1.4660
76.33	20.66	3.01	1.4595
*70.46	25.29	4.25	1.4520
*60.61	32.66	6.73	1.4381
*49.26	40.83	9.91	1.4233
*39.40	47.37	13.23	1.4108
*29.52	52.89	17.59	1.3980
24.67	54.96	20.37	1.3920
*19.96	56.42	23.62	1.3860
17.66	56.76	25.58	1.3830
*12.94	56.66	30.39	1.3770
9.41	55.46	35.12	1.3720
* 6.37	53.04	40.59	1.3679
5.33	51.78	42.89	1.3660
* 3.72	48.89	47.39	1.3630
* 1.75	42.48	55.76	1.3585
	Toluene saturated with water		1.4923
	Water saturated with toluene		1.3320

TABLE II

REFRACTIVE INDICES AND CONCENTRATIONS OF ALCOHOL IN CONJUGATE SOLUTIONS AT 25.0°

Water-rich layer		Toluene-rich layer		
Refractive index	Wt. % alcohol	Refractive index	Wt. % alcohol	Distribution ratio
*1.3389	11.0	1.4920	0.2	0.02
1.3440	19.2	1.4912	.7	.04
*1.3480	25.7	1.4903	1.3	.05
1.3540	35.2	1.4882	2.7	.08
*1.3581	41.7	1.4850	4.7	.11
1.3616	46.9	1.4841	5.3	.11
*1.3641	50.0	1.4822	6.5	.13
1.3683	53.3	1.4796	8.2	.15
*1.3724	55.6	1.4778	9.4	.17

(1) E. R. Washburn and others, THIS JOURNAL, **53**, 3237 (1931); **54**, 4217 (1932); **56**, 361 (1934); **57**, 303 (1935); **59**, 2076 (1937).

(2) Ormandy and Craven, *J. Inst. Petroleum Tech.*, **7**, 325 (1921).

(3) Tarasenkov and Poloznintzeva, *J. Gen. Chem.* (U. S. S. R.), **2**, 84 (1932).

n^{25}D of 1.49371 ± 0.00001. Although this specific gravity is almost identical with that listed in the "International Critical Tables,"[4] we have reason to believe that the value is a little too low for toluene of highest purity. A small portion of what we believe to be a more nearly pure toluene was used in part of the work. It had a specific gravity d^{25}_4 of 0.86221 ± 0.00003 and a refractive index of 1.49375 ± 0.00003. We were not able to detect any difference in the solubility results obtained with the two grades of toluene.

Procedure.—The solubility curve was determined at 25.0 ± 0.1° in a constant temperature bath by a titration method not greatly different from that previously described.[1] The refractive indices were measured with an Abbe refractometer at the same temperature. An immersion refractometer was used in obtaining the constants for the pure liquids. Large scale curves were plotted for the refractive indices *versus* concentration of each of the three components in the saturated solutions. These curves were used in determining the composition of the conjugate solutions formed when alcohol in insufficient amounts to bring about homogeneity was added to two liquid phase mixtures of water and toluene. Samples were removed from each of the layers, after equilibrium had been reached, for the determination of refractive index. The results are given in Tables I and II. The values marked with a (*) were used in plotting the solubility curve with its tie lines as shown in Fig. 1. The conjugation curve (4) (p. 398), is also indicated. Its intersection with the solubility curve locates the plait point.

(4) "International Critical Tables," Vol. III, p. 29.

Summary

The solubility curve for the ternary system ethyl alcohol, toluene and water has been determined at 25.0°. The refractive indices of the saturated solutions have been recorded. The compositions of various conjugate solutions throughout a large range of concentrations have been measured.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Molecular Freedom and Melting in Alkyl Halides

BY WILLIAM O. BAKER AND CHARLES P. SMYTH

In the course of an investigation relating the structure of organic molecules to their rotational mobility in the solid state, dielectric constant and apparent conductance measurements over a range of temperature and frequency were made on liquid and solid *i*-propyl and *n*-amyl bromides. The crystalline phases were also examined with the polarizing microscope. The *n*-amyl bromide molecule was chosen as less rod-like than long chain compounds,[1] but more anisotropic than the *i*-amyl, *i*-butyl and *i*-propyl derivatives. The latter was selected as intermediate in symmetry between the nearly spherical *t*-butyl halides[2] and the isobromides.[3]

The dielectric measurements with a capacity bridge involved the general procedure previously employed.[4] The usual precautions of pumping off dissolved gases from the liquids, and of slow freezing to reduce void formation, were observed. Temperatures were determined with a platinum resistance thermometer. A small unsilvered dewar tube with a liquid air cooling device was mounted on the microscope stage for observations between crossed nicols.

Purifications of Materials

Final purification was fractionation through a packed jacketed 80 × 2 cm. Pyrex column with still head equipped for variable reflux ratio. Boiling points were measured with Anschütz type short range thermometers calibrated by the Bureau of Standards, and the surface for liquid-vapor equilibrium to give true boiling temperatures was increased by use of a mercury well in the column top. Refractive indices were determined with a Pulfrich refractometer.

i-**Propyl Bromide.**—Material from the Eastman Kodak Co., dried over pure calcium bromide for several weeks, was twice fractionally distilled; b. p. 59.5°; f. p. −90.8°; $n^{20.0}$D 1.42476. "International Critical Tables" values are: b. p. 59.6°; n^{20}D 1.4251, while Skau and McCullough[5] give b. p. 59.41° and f. p. −90.0°. As with the *i*-amyl bromide, the absence of Maxwell–Wagner interfacial polarization on freezing and the low apparent specific conductance values for the liquid assured purity.

i-**Amyl Bromide.**—The Eastman product was dried over calcium bromide for two weeks and twice fractionated; b. p. 128.6°; m. p. −88.7°; $n^{20.0}$D 1.44455; "International Critical Tables" values are: b. p. 127.9°; $n^{20.0}$D 1.4444; whereas Skau and McCullough[5] gave b. p. 129.6°, m. p. −87.9°, and Deese[6] reports m. p. −88.0°.

Experimental Results

The dielectric constants, ϵ, and specific conductances k (ohm^{-1} cm.$^{-1}$) form Table I, in which, also, the temperatures are given in the first column, and the appropriate frequencies in kilocycles are indicated for the other data. Many measurements at intermediate temperatures have

(1) Baker and Smyth, THIS JOURNAL, **60**, 1229 (1938).
(2) Forthcoming publication.
(3) Baker and Smyth, THIS JOURNAL, **61**, in press (1939).
(4) Smyth and Hitchcock, *ibid.*, **54**, 4631 (1932); **55**, 1830 (1933).
(5) Skau and McCullough, *ibid.*, **57**, 2439 (1935).
(6) Deese, *ibid.*, **53**, 3673 (1931).