[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

An Azeotropic Mixture of Secondary Butyl Alcohol and Secondary Butyl Bromide[1]

BY DAVID F. HOUSTON

An azeotropic (constant boiling) mixture of secondary-butyl alcohol and secondary-butyl bromide recently encountered in our work apparently is not recorded in the literature. The following study of this mixture has been made.

Experimental

Sec-butyl Alcohol.—Commercial *sec*-butyl alcohol[2] was fractionated in a six-plate bubbling-cap still,[3] without a Cottrell boiler, but with a thermometer immersed in the vapors. The fraction boiling at 99.4 to 100.5° was dried over anhydrous sodium sulfate, distilled over freshly ignited lime, and the constant boiling fraction collected. The refractive index and boiling point of the product are shown in Table I.

Sec-butyl Bromide.—A 50% excess of phosphorus tribromide was added dropwise to the commercial alcohol, cooled in ice water. The mixture was heated for one-half hour on the steam-bath, cooled and poured onto cracked ice. The oily layer was separated, distilled, thoroughly washed with water and 10% sodium carbonate solution, and dried over calcium chloride. The bromide was fractionated in the bubbling-cap still. The refractive index and boiling point of the constant boiling fraction are given in Table I.

Azeotropic Mixture.—A mixture of 150 ml. each of the alcohol and the bromide was distilled slowly from the bubbling-cap still. During a fore-run of about 20 ml., the temperature rose to 87.2°, where it remained while 155 ml. of the mixture was obtained. It then rose to the boiling point of the alcohol and again became constant. The refractive index and boiling point of the azeotropic mixture are given in Table I.

Composition of the Azeotropic Mixture.—From a curve drawn by plotting the refractive indices, at 20°, of a series of alcohol–bromide mixtures against the mole per-

TABLE I

BOILING POINTS AND REFRACTIVE INDICES

Material		n_D^{20}	B. p., *corr.*, °C., at 760 mm.
Sec-butyl alcohol	Present material	1.3983	99.5 ± 0.1
	Previously reported	1.3970[a]	99.50[b]
Sec-butyl bromide	Present material	1.4370	91.3 ± 0.1
	Previously reported	1.4372[c]	91.25[d]
Azeotropic mixture		1.4256	87.2 ± 0.1 (749 mm.)

[a] J. Timmermans and F. Martin, *J. chim. phys.*, **25**, 432 (1928). Calculated from value at 15° and the coefficient $\Delta n/\Delta t$ 0.00049 given in this reference. [b] *Ibid.*, p. 431. [c] G. V. Wendell, *Am. Chem. J.*, **26**, 318 (1901). Calculated from value given at 25.25° and the coefficient $\Delta n/\Delta t$ 0.00054 determined on the present material. [d] J. Timmermans, *Bull. soc. chim. Belg.*, **36**, 504 (1927).

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[1] Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

[2] Stanco Distributors, Inc., New York City, kindly supplied a quantity of this alcohol. Their assistance is hereby gratefully acknowledged.

[3] J. H. Bruun and S. T. Schicktanz, *Bureau of Standards Journal of Research*, **7**, 851–882 (1931).

centages of the bromide, the azeotropic mixture was found to contain 70.7 mole per cent. of *sec*-butyl bromide. Data for the series of mixtures are shown in Table II.

Bromine was directly determined in the constant boiling fraction by the method of Lemp and Broderson.[4] These determinations gave values of 71.0 and 71.4 mole per cent. of bromide in the mixture.

TABLE II

REFRACTIVE INDICES OF MIXTURES OF SEC-BUTYL ALCOHOL AND BROMIDE

Weight per cent. of bromide....	....	15.02	27.39	39.08	51.70	60.06
Mole per cent. of bromide......	....	8.51	16.94	25.75	36.67	44.86
n_D^{20}........................	1.3983	1.4013	1.4042	1.4073	1.4117	1.4138

Weight per cent. of bromide............	70.41	79.25	84.85	93.34	100
Mole per cent. of bromide..............	56.27	67.36	75.20	88.33	100
n_D^{20}..............................	1.4192	1.4242	1.4275	1.4329	1.4370

Conclusion

Secondary-butyl alcohol and secondary-butyl bromide form an azeotropic mixture boiling at 87.2° at 749 mm., having a refractive index n_D^{20} of 1.4256, and containing 71.0 ± 0.4 mole per cent. of the bromide.

[4] J. F. Lemp and H. J. Broderson, THIS JOURNAL, **39**, 2069–2074 (1917).

WASHINGTON, D. C.

RECEIVED JULY 31, 1933
PUBLISHED OCTOBER 6, 1933

Note

Copper Selenate Tetrammine Dihydrate

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We recently described a method for preparing copper selenate tetrammine dihydrate in large crystals.[1] Slight variations in the procedure, however, often result in failure and occasionally no crystals at all are deposited from the ammoniacal solution. We have now perfected two new procedures which are entirely dependable.

(1) Fifteen grams of crystalline copper selenate (Kahlbaum) is dissolved by boiling in 25 cc. of 25% aqueous ammonia and, after filtering and cooling with ice, alcohol is added, the precipitate filtered off, washed with acetone and ether, and dried on a porous plate. Ten grams of this product is dissolved, for the greater part, by warming in 8 to 10 cc. of 25% aqueous ammonia and the hot solution is filtered as quickly as possible but without suction. The hot filtrate is then placed in a closed Erlenmeyer flask partially submerged in a large amount of hot water so that it will cool slowly. It is important that the solution be not shaken during this period.

(2) The same procedure is followed except that the hot solution in the Erlenmeyer flask is rapidly chilled to room temperature, whereupon needles of monohydrate precipitate. These are redissolved, for the greater

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[1] THIS JOURNAL, **53**, 4013 (1931).