Summary

1. The tetrabromo-cyclohexadienone formula, which was proposed for the compound resulting from the action of bromine on tribromophenol, is improbable.

2. Facts are brought forward which render very remote the possibility of tribromophenol bromide being a mixture of *ortho-* and *para-*quinoid forms.

3. Benedikt's original structure for tribromophenol bromide accounts for the facts introduced if a partial rearrangement of trihalogenated phenol chlorides, which contain bromine in the *para* position, to the isomeric trihalogenated phenol bromides, is postulated.

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THE INFLUENCE OF TEMPERATURE ON THE RECIPROCAL SOLUBILITY OF THE MONO-ALKYL ETHERS OF ETHYLENE GLYCOL AND WATER

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RECEIVED SEPTEMBER 14, 1925 PUBLISHED FEBRUARY 5, 1926

A considerable number of binary-liquid systems are known, the solubility curves of which approach one another with increasing temperature and meet at an upper consolute point. In relatively fewer cases the curves approach one another with diminishing temperature and meet at a lower consolute point. Only a limited number of systems have been discovered which possess both upper and lower consolute temperatures. The first example, that of nicotine and water, was discovered by Hudson.[1] The other known systems are methylethyl ketone and water,[2] *sec.*-butyl alcohol and water,[3] β-picoline and water, α,α-lutidine and water, 3-methylpiperidine and water, 4-methylpiperidine and water[4] and 2-methylpiperidine and water.[5]

With the exception of the liquid mixtures, methylethyl ketone and water and *sec.*-butyl alcohol and water, which possess completely closed solubility curves only at high pressures, all of the systems previously described have as one component a cyclic nitrogen base.

In an earlier paper from this Laboratory[6] it was stated that the members

[1] Hudson, *Z. physik. Chem.*, **47**, 113 (1903).

[2] Kohnstamm and Timmermans, *Verslag Akad. Wetenschappen Amsterdam*, **21**, 783 (1913).

[3] Timmermans, *Arch. Néerland. sci.*, **6**, 147 (1922).

[4] Flaschner, *J. Chem. Soc.*, **95**, 668 (1909).

[5] Flaschner and MacEwen, *ibid.*, **93**, 1000 (1908).

[6] Cretcher and Pittenger, THIS JOURNAL, **47**, 164 (1925).

of the series *bis*(β-alkoxy)ethyl ether are less soluble in hot than in cold water. The present authors have studied the behavior of the system *bis*(β-ethoxy)ethyl ether and water by the method of Alexejew[7] and have found that it apparently possesses both upper and lower consolute temperatures. Owing to an interaction of the components at the higher temperatures, this system was not studied further.

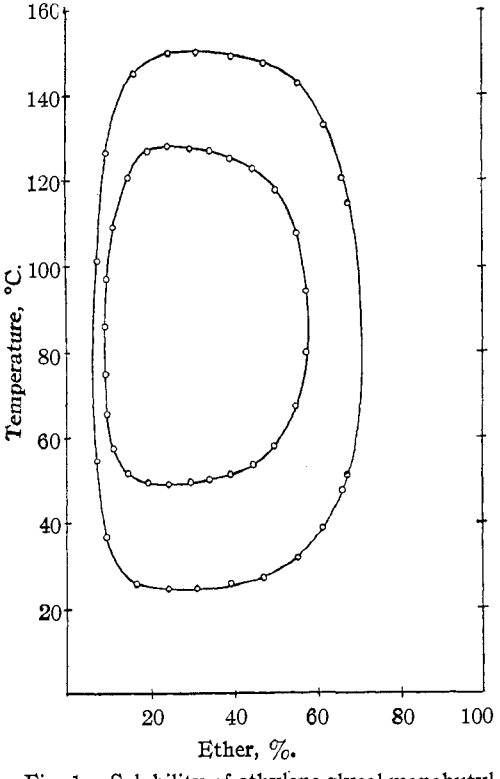

Fig. 1.—Solubility of ethylene glycol monobutyl ethers in water. The outer curve is that of *iso*-butyl ether; the inner, that of *n*-butyl ether.

During an investigation of the properties of the monoalkyl ethers of ethylene glycol, the authors have found that the normal butyl and *iso*butyl ethers possess completely closed solubility curves. So far as it has been possible to determine, the lower members of the series are miscible with water in all proportions and at all temperatures. The addition of a third substance (sodium chloride) insoluble in one component, renders it possible, however, to obtain curves similar to those obtained with the butyl ethers. These curves have not been studied in detail.

The behavior of the monoamyl ethers and of the dialkyl ethers of ethylene glycol, which possess properties of solubility similar to those of the monobutyl derivatives herein described, will be investigated later.

Experimental Part

Method of Procedure.—Weighed amounts of water and glycol ether were sealed in glass tubes. To determine the higher points, the tubes were rocked in a bath of glycerol; the lower points were determined in a bath of water. Each point recorded is the average of at least two readings agreeing to within 0.6° when approached from above and below the temperature of miscibility.

Purity of Materials.—The ethers used in this work were purified by

[7] Alexejew, *Wied. Ann.*, **28**, 305 (1886).

repeated fractional distillation; the boiling range of the samples selected was 0.1° and the boiling points corresponded exactly with the temperatures recorded in a previous paper.[8] The data are recorded in Table I and Fig. 1.

TABLE I

SOLUBILITY OF NORMAL AND ISOBUTYL GLYCOL ETHERS IN WATER

n-Butyl ether			*iso*Butyl ether		
Ether, % by wt.	Lower soln. temp., °C.	Upper soln. temp., °C.	Ether % by wt.	Lower soln. temp., °C.	Upper soln. temp., °C.
8.99	Not on curve		5.07	Not on curve	
9.18	75[a]	86[a]	7.57	54.5[a]	101.5[a]
9.94	65.8	97.0	9.94	36.6	126.1
11.45	57.6	109.3	16.68	25.9	145.0
14.94	51.6	120.4	24.51	24.6	150.0
19.94	49.6	126.8	31.54	24.7	150.2
24.78	49.1	128.0	39.70	25.5	149.3
30.03	49.6	127.7	47.46	27.1	147.9
34.42	50.1	126.8	55.80	31.9	142.6
39.67	51.3	125.3	61.80	38.9	132.9
44.95	53.5	122.9	66.13	47.6	120.6
50.08	58.0	117.8	67.70	51.0[a]	114.5[a]
55.08	67.1	107.7	70.86	Just on curve	
57.87	80[a]	94[a]	72.11	Not on curve	

[a] These points could not be determined with the same degree of accuracy as those on other portions of the curve owing to the minute quantity of one of the phases present.

The curves obtained for these substances are essentially of the same shape as those obtained by other investigators in this general field. The opalescence previously reported for portions of the curves near the consolute points was noticed in these cases.

Summary

1. Three series of aliphatic ethers, namely, *bis*(β-alkoxy)ethyl ether, ethylene-glycol mono-alkyl ether and ethylene-glycol dialkyl ether have been discovered to possess, when in binary mixture with water, properties of solubility similar to those of the system nicotine and water.

2. Complete solubility data for ethylene-glycol mono-*n*-butyl and mono-*iso*butyl ethers and water have been determined.

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[8] Cretcher and Pittenger, THIS JOURNAL, **46**, 1503 (1924).