[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF EDGEWOOD ARSENAL.]

THE INTERSOLUBILITY OF BETA-BETA DICHLORO-ETHYL SULFIDE AND ETHYL ALCOHOL.

BY THOS. G. THOMPSON J. H. BLACK AND G. T. SOHL.[1]

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The purpose of this investigation was to determine the intersolubility of β,β′-dichloro-ethyl sulfide and ethyl alcohol in order to ascertain the feasibility of using the latter substance for the purification of the sulfide.

Preparation of Materials.

β,β-Dichloro-ethyl sulfide was obtained from the commercial product by double distillation at pressures of 13 to 14 mm. The product after purification had a melting point of 13.6°.

The absolute alcohol was prepared by treatment with lime until no test for water was obtained.

The "95% Alcohol" used in the experiments reported below, upon analysis was found to contain only 92.5% ethyl alcohol.

The Intersolubility of β,β′-Dichloro-ethyl Sulfide and 92.5% Ethyl Alcohol.

The apparatus used in the determination of the solubilities consisted of a glass cylinder, sealed at one end, and fitted at the other with a 2-holed rubber stopper. A thermometer was placed through one hole of the stopper and a small glass tube, the length of the stopper, through the other, into which was introduced a glass stirring rod. The solubilities of the alcohol and the sulfide were determined by heating together the two substances in the proportions given in the table until a clear solution was produced. The temperatures at these points were noted. Upon

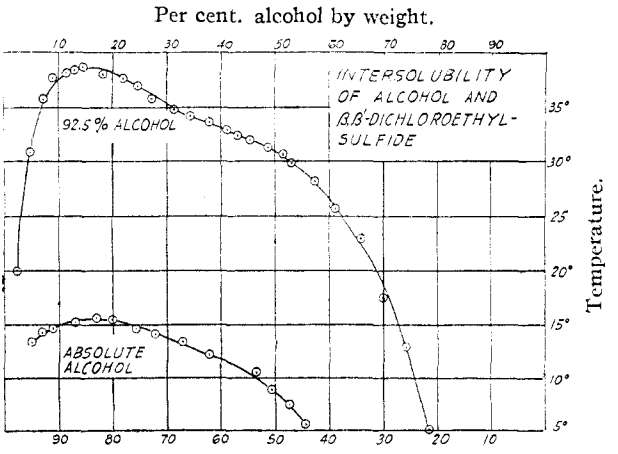

Fig. 1.

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cooling the solution very slowly a characteristic cloudiness appeared, resulting from the formation of 2 liquid phases. The temperatures at which the cloudiness first appeared were noted. The mutual solubilities of β,β′-dichloro-ethyl sulfide and 92.5% alcohol are given in Table I, the data being illustrated by the solubility curve in Fig. 1. The temperatures given in the table, in each case, is the mean obtained from the temperature at which the solution cleared and that at which the cloudiness was produced. Above the curves in Fig. 1 a homogeneous system exists and below the curve there is a heterogeneous system of two liquid phases.

TABLE I.

Temp. ° C.	β,β′-Dichloro-ethyl sulfide. G.	92.5% ethyl alcohol. G.	β,β′-Dichloro-ethyl sulfide. %.	92.5% ethyl alcohol. %.
19.9	31.97	0.81	97.53	2.47
30.9	...	1.62	95.18	4.82
35.7	...	2.43	92.93	7.07
37.8	...	3.24	90.80	9.20
38.4	...	4.05	88.75	11.25
38.5	...	4.86	86.80	13.20
38.6	...	5.67	84.93	15.07
37.9	...	7.29	81.42	18.58
37.6	...	8.91	78.20	21.80
36.7	...	10.53	75.22	24.76
35.8	...	12.15	72.45	27.55
35.2	...	14.58	68.67	31.33
34.4	...	17.02	65.27	34.73
33.6	...	19.45	62.18	37.82
33.0	...	21.88	59.37	40.63
32.5	...	24.31	56.76	43.24
31.0	...	26.74	54.45	45.55
31.4	...	29.17	52.29	47.71
30.6	...	32.42	49.66	50.34
29.9	28.13	...	46.47	53.53
28.3	24.30	...	42.84	57.16
25.6	20.46	...	38.70	61.30
21.7	16.62	...	33.91	66.09
17.6	14.06	...	30.26	69.74
12.8	11.51	...	26.20	73.80
5.1	8.95	...	21.64	78.36

The Intersolubility of β,β′-Dichloro-ethyl Sulfide and Absolute Alcohol.

The results obtained from the study of the intersolubilities of β,β′-dichloro-ethyl sulfide and absolute alcohol at varying temperatures are given in Table II and illustrated by the curve in Fig. 1. The procedure was the same as that reported above.

The effect of water upon the critical point of solubility is very decided. With 92.5% ethyl alcohol a critical temperature of solubility of 38.6° was secured, but with absolute alcohol, the critical temperature was 15.6°.

TABLE II.

Temp. ° C.	β,β′-Dichloro-ethyl sulfide. G.	92.5% ethyl alcohol. G.	β,β′-Dichloro-ethyl sulfide. %.	92.5% ethyl alcohol. %.
13.6	31.90	1.57	95.31	4.69
14.5	...	2.35	93.13	6.87
14.8	...	3.14	91.04	8.96
15.3	...	4.71	87.13	12.87
15.6	...	6.48	83.12	16.88
15.5	...	7.85	80.25	19.75
14.8	...	10.20	75.76	24.24
14.2	...	12.56	71.75	28.25
13.6	...	15.70	67.00	33.00
12.2	...	19.62	61.91	38.09
11.8	...	23.55	57.52	42.48
10.6	...	27.47	53.73	46.27
9.1	...	31.40	50.39	49.61
7.5	...	35.32	47.45	52.55
5.6	...	39.25	44.83	55.17

Purification of Crude Mustard Gas by Means of Alcohol.

From the above data it is evident that crude mustard gas, providing the rate of hydrolysis was not too rapid, could be purified by treatment with alcohol. A few experiments were conducted using equal volumes of 92.5% ethyl alcohol and the crude material containing 71% β,β′-dichloro-ethyl sulfide. Yields varying from 19 to 31.8% of an excellent product were obtained. These experiments were performed as follows. (*a*) The crude material was extracted at a temperature slightly above the critical point of solubility. Most of the sulfur together with a tar-like mass remained insoluble. (*b*) The supernatant solution was removed and cooled considerably below the critical temperature, causing the formation of two liquid phases, the upper phase being primarily a solution of β,β′-dichloro-ethyl sulfide in alcohol and the lower phase a solution of alcohol in β,β′-dichloro-ethyl sulfide. The concentrations are a function of the temperature. (*c*) Crystals of the solid sulfide were obtained by sufficient lowering of the temperature.

Conclusions.

1. The critical temperature of solubility of β,β′-dichloro-ethyl sulfide and absolute ethyl alcohol was found to be 15.6° and with 92.5% ethyl alcohol, 38.6°. The addition of water to the alcohol increases the critical temperature of solubility.

2. Crude mustard gas may be purified by extraction with ethyl alcohol, yielding a very good product.

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UNIVERSITY OF WASHINGTON,
SEATTLE, WASHINGTON.