EFFECT OF ALCOHOLS ON DECOMPOSITION TEMPERATURE OF CHLOROFORM HYDRATE

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INTRODUCTION. In connection with the work being done on hydrocarbon hydrates in the physical chemistry laboratories of the University of Oklahoma, it became desirable to know what effect 2-propanol might have on the decomposition temperature of chloroform hydrate. The decomposition effect for ethanol had been determined by Sampson (5).

Deaton and Frost (2) report the use of alcohols as inhibitors of hydrate formation in high-pressure natural gas lines. Alcohols are injected into the line to decompose any hydrate present or to inhibit its formation and subsequent closure of the pipes by solid hydrate.

In some preliminary experiments with the system water-chloroform-2-propanol, the question arose as to whether or not 2-propanol would form a hydrate or inhibit its formation. Sampson (5) had determined the decomposition effect ethanol had on chloroform hydrate. Since literature searches and current investigation have indicated that ethanol does not form a lattice type hydrate, it was assumed that a comparison of similar data obtained using 2-propanol with Sampson's data should show correlation. It was further assumed that if the data differed significantly, a hydrate region existed in the system water-2-propanol.

Several authors (1, 3, 4) have reported ethanol hydrates with composition varying from 12 to 1/3 moles of water per mole of ethanol. Since all these decomposed far below 0°C, it was believed that they were not of the lattice type. Present studies indicate that lattice hydrates have 16 moles of water to one of hydrocarbon.

EXPERIMENTAL. The apparatus used to determine the decomposition temperatures consisted of a wide-mouthed, silvered Dewar vacuum flask of one pint capacity fitted with a large cork properly bored to take (a) a "Mix-Master" type stirrer using a single bladed, three segment brass impellor, (b) a calibrated Philadelphia differential thermometer, and (c) a 9 cm. length of 6 mm diameter Pyrex tubing through which the alcohol was introduced. This tube was inclined at a 30° angle from the vertical to facilitate the introduction of the alcohol which was at a temperature of 0-1°C at the time of introduction. The quantity of alcohol was measured with a 1 ml transfer pipette and was added by inserting the pipette into the Dewar through the Pyrex inlet tube.

Three trials with 2-propanol were made; however, data are presented for only the last two because the alcohol was added in increments of 0.1 ml in the first trial, giving a range 0.4 ml over 0.14°C, which is too small a range to be considered for discussion in this paper. 7.0 and 8.0 ml were added to the second and third trials, respectively, in 1.0 ml increments before total decomposition occurred; this is roughly half of the 15 ml. of ethanol added by Sampson (1). During the time in which no alcohol was being added to the system, the inlet tube was kept corked to minimize the vaporization from the Dewar.

The hydrate was prepared by placing 280 gm of ice and 25 ml of washed chloroform in a silvered pint Dewar; sufficient ice was allowed to melt to give a mixture which could easily be stirred. The apparatus was then closed and stirring begun at approximately 1000 rpm.

The temperature of the reaction mixture was carefully observed. This temperature remained at the ice point for about an hour; when all the ice had completely melted, due to heat leakage and energy of stirring, the temperature then rose rapidly to the decomposition temperature of the hydrate and established a plateau. As soon as this condition had been reached, 2-propanol was added in 1.0 ml portions, letting equilibrium be established before the addition of another portion. The condition of equilibrium was ascertained by a new plateau shown by the time-temperature values. A five minute interval of temperature constant to a hundredth of a degree was taken as proof of equilibrium.

INTERPRETATION OF RESULTS. The data obtained using 2-propanol and Sampson's data are presented in Tables I, II, and III.

TABLE I

Second Run. Decomposition of Chloroform Hydrate with 2-propanol.

ML.	M MOLES	ΔM	T °C	ΔT	ΔT ΔM
0			1.68		
1.0	0.0133	0.0133	1.57	0.11	8.27
2.0	0.0267	0.0134	1.50	0.07	5.22
3.0	0.04	0.0133	1.41	0.09	6.77
4.0	0.0533	0.0133	1.34	0.07	5.26
5.0	0.0666	0.0133	1.24	0.10	7.52
6.0	0.08	0.0134	1.21	0.03	2.24
7.0	0.0833	0.0133	1.18	0.03	2.26

TABLE II

Third Run. Decomposition of Chloroform Hydrate with 2-propanol.

ML.	M MOLES	ΔM	T °C	ΔT	$\frac{\Delta T}{\Delta M}$
0			1.62		
1.0	0.0133	0.0133	1.50	0.12	9.02 .
2.0	0.0267	0.0134	1.41	0.09	6.72
3.0	0.04	0.0133	1.32	0.09	6.77
4.0	0.0533	0.0133	1.25	0.07	5.26
5.0	0.0666	0.0133	1.17	0.08	6.02
6.0	0.08	0.0134	1.10	0.07	5.22
7.0	0.0933	0.0133	1.04	0.06	4.51
8.0	0.1066	0.0133	1.00	0.04	3.01

TABLE III

Sampson's Data (1948). Decomposition of Chloroform Hydrate with Ethanol.

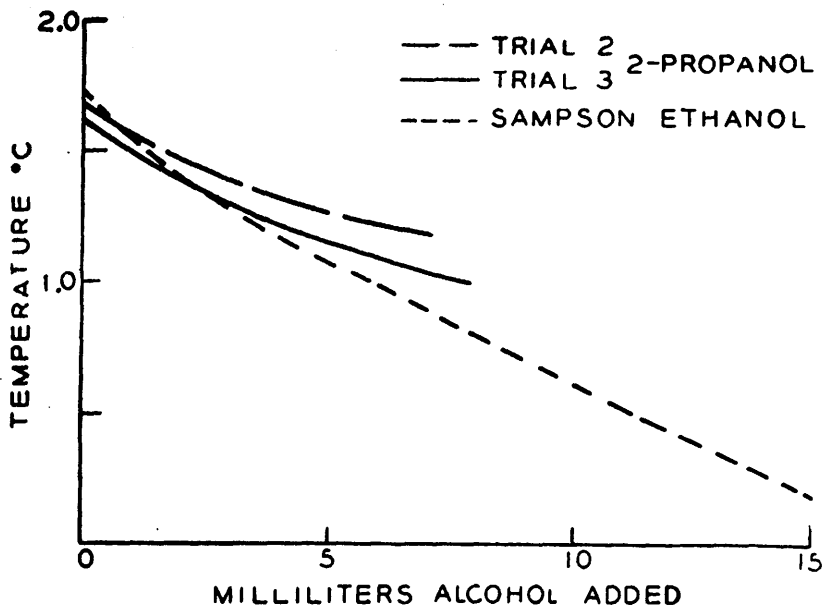| ML.	M MOLES	ΔM	T °C	ΔT	$\frac{\Delta T}{\Delta M}$
0.0			1.72		
0.5			1.65		
1.0	0.0172	0.0172	1.58	0.14	8.14
2.0	0.0344	0.0172	1.45	0.13	7.56
3.0	0.0516	0.0172	1.33	0.12	6.98
4.0	0.0688	0.0172	1.22	0.11	6.40
5.0	0.0860	0.0172	1.11	0.11	6.40
6.0	0.103	0.017	1.01	0.10	5.88
7.0	0.120	0.017	0.90	0.11	6.47
8.0	0.138	0.018	0.80	0.10	5.55
9.0	0.155	0.017	0.70	0.10	5.88
10.0	0.172	0.017	0.60	0.10	5.88
11.0	0.189	0.017	0.51	0.09	5.29
12.0	0.206	0.017 ´	0.42	0.09	5.29
13.0	0.223	0.017	0.33	0.09	5.29
14.0	0.241	0.017	0.24	0.09	5.29
15.0	0.258	0.017	0.17	0.07	4.12

FIGURE 1.

Figure 1 shows the relation between volumes of alcohol added and the resulting plateau temperatures of decomposition. It will be noted that there is some discrepancy between the reported decomposition temperatures of the hydrate itself. The decomposition temperature according to Sampson is 1.72°C for pure hydrate. This variation could be due to an impure sample; i. e., insufficient washing; or an immersion effect of the differential thermometer.

On examining the slope of the lines in Figure 2, it will be noted that all three trials showed nearly the same molal depression effect. No quantative calculations can be made because of insufficient knowledge of the exact composition of the hydrate. It will probably be safe to draw the conclusion that all alcohols which do not form a hydrate will have the same molal freezing point constant against hydrates.

In the absence of any obvious difference between 2-propanol and ethanol, it was concluded that 2-propanol did not form a lattice type hydrate.

The moles of alcohol added were calculated from the volumes using the following formula:

$$M = \frac{VD}{w}$$

where V is the volume of alcohol, D the density, and w the molecular weight. The densities used were as follows: 2-propanol: 0.801 and ethanol: 0.79.
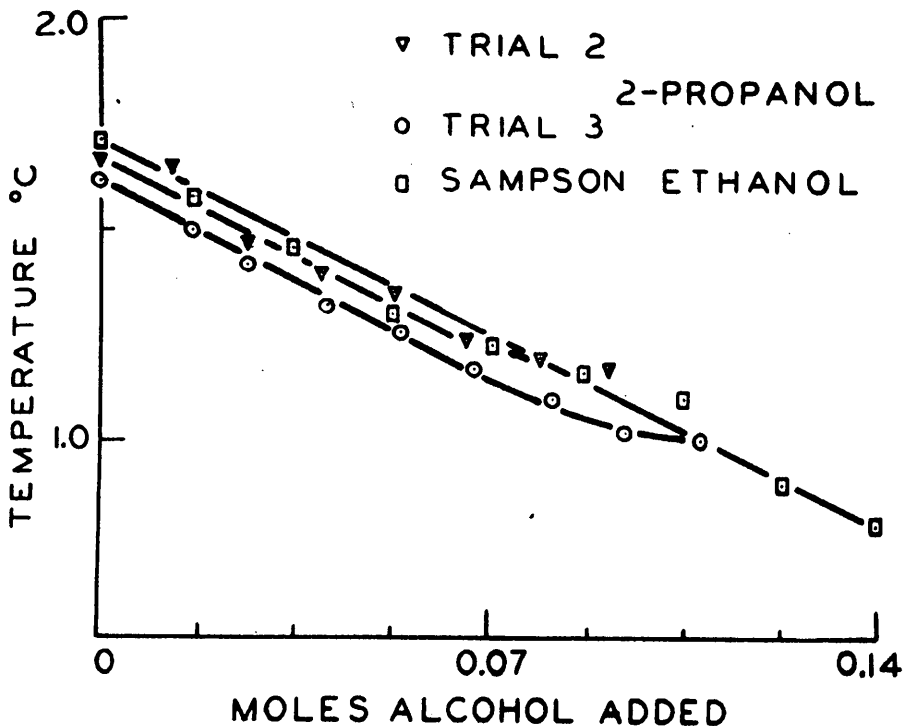
FIGURE 2.

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