The Surface Tension of Chloroform

BY R. FANELLI

The surface tension of chloroform has been determined previously by numerous investigators using various methods. With few exceptions, the determined values fall on two straight lines which differ by less than one dyne per cm.[1] as shown in Fig. 1.
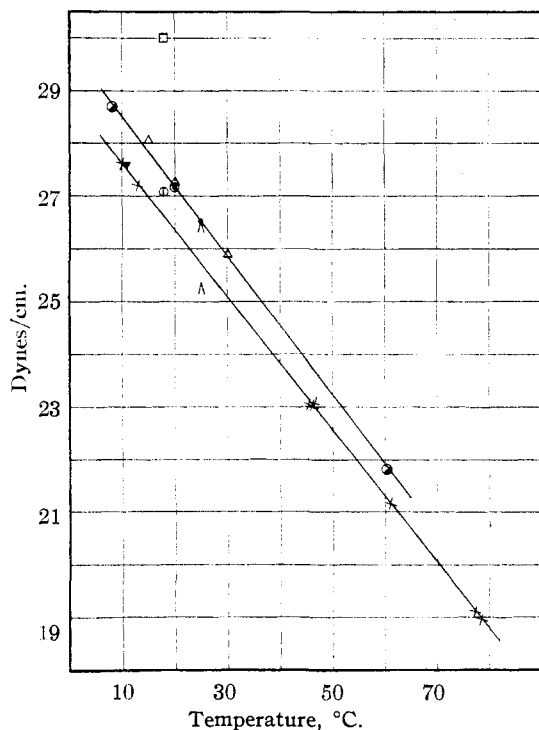
With the exception of Akhamatov's[2] value, all

Fig. 1.—Surface tension of chloroform determined by various investigators: O, Richards and Carver[3] (capillary rise); △, Hennaut-Roland and Lek[4] (capillary rise); X, Ramsay and Aston[5] (capillary rise); ◑, Schiff[6] (differential capillary rise); ▼, Akhamatov[2] (differential pressure corresponding to differential capillary rise); O, Harkins, Clark and Roberts[7] (drop weight); □, Tyler[8] (ripple); O, Addison[9] (vibrating jet); ◑, Whatmough[10] (maximum bubble pressure, single capillary); ∧, Cupples[11] (maximum bubble pressure, single capillary); ●, Fanelli (maximum bubble pressure, Sugden's double capillary).

of the earlier data on the lower curve are due to Ramsay and Aston[5] while the upper curve encompasses almost all other values save that of Tyler[8] which obviously is too high. Because of the novel and less well established methods employed by Akhamatov and Tyler, their values may be justifiably disregarded.

Explanation of Ramsay and Aston's low values probably lies in their failure to correct for the capillary rise in the wide tube (bore not given) and in other errors inherent in the method followed in 1894. Ramsay and Shields[12] using the same method and procedure (bore of wide tube, 1 cm.) and correcting for capillary rise in the wide tube in the case of water, obtained four values in the range 10 to 40°. They are 2.3 to 2.1 (av. 2.2) dynes per cm, too low, indicating that the method and procedure in that period tended to give low results. A correction factor for Ramsay and Aston's values may be approximated by multiplying the ratio of their chloroform value at 25° (25.7 dynes per cm.) to Ramsay and Shield's result for water at 25° (69.9 dynes per cm.) by the above average, 2.2. This factor, 0.8 dyne per cm., is equivalent to the discrepancy shown by the curves in Fig. 1. Richards and Coombs[13] using the capillary rise method attribute the low values of the early investigators to failure to correct all factors which tend to give low results.

At the time Cupple's paper appeared, Sugden's[14,15] form of maximum bubble pressure apparatus employing two capillaries was being standardized against chloroform. Therefore, the effect of saturating the inlet gas with chloroform vapor before entering the capillaries was determined.

Experimental

The apparatus and method of calculation employed have been described by Sugden.[15] The bore of the fine capillary was close to 0.2 mm.; the wider capillary was 3.66 mm. A Meriam Micromanometer reading directly to 0.001 in. (±0.001 in.) with water as the gage liquid measured pressure. Dried nitrogen gas forced through the capillaries was used for bubble formation. The bubble rate was varied between 60 per min. and 60 per 140 sec. In the main each result represents a different bubble rate. The constant temperature bath was kept well within 0.1° of the operating temperature.

The instrument was calibrated against benzene at 20 and 25°. Eastman Kodak Co. thiophene-free benzene,

(1) Dr. Cupples discussed these data in a recent article (11) but he was misled by plotting Richards and Carver's data for 20° incorrectly at 25°. This was confirmed by a private communication from Dr. Cupples.

Ramsay's and Aston's value of 19.98 dynes per cm. at 77.6° is misprinted in the original paper. Recalculation of their data gives the corrected value of 19.08 dynes per cm.

(2) A. Akhamatov, Kolloid Z., 66, 266 (1934).

(3) T. W. Richards and E. K. Carver. THIS JOURNAL, 43, 827 (1921).

(4) Hennaut-Roland and M. Lek, Bull. soc. chem. Belg., 40, 177 (1931).

(5) W. Ramsay and E. Aston, Proc. Roy. Soc. (London), 56, 182 (1894); Trans. Roy. Irish Acad., 32A, 93 (1902).

(6) R. Schiff, Ann., 223, 47 (1884).

(7) W. D. Harkins, G. L. Clark and L. E. Roberts, THIS JOURNAL, 42, 700 (1920).

(8) E. Tyler, Phil. Mag., [7] 31, 209 (1941).

(9) C. C. Addison, J. Chem. Soc., 535 (1943).

(10) W. H. Whatmough, Z. physik. Chem., 39, 129 (1901).

(11) H. L. Cupples, J. Phys. Chem., 50, 412 (1946).

(12) Ramsay and Shields, J. Chem. Soc., 63, 1089 (1893).

(13) T. W. Richards and L. B. Coombs, THIS JOURNAL, 37, 1656 (1915).

(14) S. Sugden, J. Chem. Soc., 121, 858 (1922).

(15) S. Sugden, ibid., 125, 27 (1924).

m. p. 5°, was fractionally distilled and the middle fraction boiling close to 80° was used. Six determinations were made at varying bubble rates with an average deviation from the mean of less than one part in a thousand. Saturating the nitrogen gas with benzene vapor before entering the capillaries had no effect whatever on the values. Values given by the original unpurified benzene differed but slightly from those given by the purified product.

The chloroform used was prepared from the C. P. analyzed grade by washing with water, drying over calcium chloride, and finally fractionally distilling. The portion boiling close to 61° was used.

The surface tension values obtained at 25.0° using dried nitrogen were: 26.47, 26.49, 26.52, 26.57, 26.56, 26.54; average 26.53 dynes per cm., average deviation from the mean <1/1000.

At 25.0°, using dried nitrogen saturated with chloroform vapor, the following values were obtained: 26.37, 26.47, 26.47, 26.52; average 26.46 dynes per cm., average deviation, <3/2000.

The above values show that saturating the inlet gas with chloroform vapor has little effect upon the surface tension values obtained by using the dried gas alone in Sugden's apparatus.

The values obtained at 20.0° using dried nitrogen were: 27.20, 27.15, 27.16, 27.14, 27.17, 27.14; average, 27.16 dynes per cm., average deviation, <1/1000. These values are very close to Richards and Carver's[3] and with those obtained at 25° fall squarely on the upper curve.

Like benzene, the unpurified chloroform gave essentially the same values as the purified liquid. This confirms Sugden's observation that the normal impurities in water and benzene have but slight effect on their respective surface tension values when the maximum bubble pressure method is used.

Summary

The surface tension of chloroform has been determined at 20 and 25° using Sugden's form of maximum bubble pressure apparatus. The values obtained check Richards and Carver's[3] results very closely.

Using Sugden's apparatus, saturation of the inlet gas with chloroform vapor before entering the capillaries has very little effect on the surface tension values. This confirms Whatmough's[10] observation, contrary to Cupples' findings. The probable explanation for the low values of Ramsay and Aston is reiterated.

75 EAST 45TH STREET
NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA]

The Systems Chromic Ammonium Sulfate–Ferric Ammonium Sulfate–Water and Chromic Ammonium Sulfate–Aluminum Ammonium Sulfate–Water at 25°

BY NORMAN O. SMITH AND CHARLES S. LENNOX

In a summary of the results of a series of isothermal investigations of ternary systems consisting of pairs of isomorphous salts and water Hill, Durham and Ricci[1] showed that the distribution of the salts between liquid and solid solutions obeys the semi-empirical relation

$$\log R_1 = \log K + m \log R_s \qquad (1)$$

where R_1 is the mole ratio of the salts in the liquid, R_s that in the coexisting solid solution, and m and K are constants for a particular system. The distribution constant K was shown to equal $(S_1\gamma_1^0/S_2\gamma_2^0)^{\nu/b}$, where S_1 and S_2 are the aqueous molal solubilities of the component salts, γ_1^0 and γ_2^0 the respective mean ion activity coefficients at these concentrations, ν the total number of ions per molecule of salt and b the number of ions per molecule of the ion which is being interchanged. Originally applied to alums and picromerites equation (1) has since been found to hold also for other isomorphous salt pairs.[2] In the case of alums m, in general, is unity, implying that solid solutions of alums are ideal. Of the five alum pairs reported, however, the ferric ammonium–aluminum ammonium pair did not obey the above relation satisfactorily. It was concluded[1] that this was the result of experimental error, but at the same time it was pointed out that this pair differed fundamentally from the other four in involving an interchange of the trivalent instead of the univalent cation. In order to examine further the effect of interchanging the trivalent cation the distribution studies of the present paper were undertaken.

Experimental

The technique employed was that of the previous alum studies: Complexes of known composition were made up in duplicate from the two alums and water in glass-stoppered test-tubes, glass marbles were added and the tubes rotated in a thermostat at 25 ± 0.03° for many weeks, at the end of which time both the liquid and solid phases were analyzed, the latter after being filtered from the liquid, centrifuged and air-dried for a few minutes. In the chromium–iron system two marbles were used but in the chromium–aluminum system one marble. In most cases the tubes contained about 35 g. of material but in regions of low chromium this was increased to 60 g. The members of each duplicate pair differed only in the order of addition of the components, one alum being dissolved in the water (by slight warming where necessary) before the other was added. In this way each point in the system was approached from two directions thereby establishing the attainment of equilibrium. The fact that a chrome alum was a component of both systems suggested that no less than three months of rotation would be required as it had been shown[3] that well over two months of time is required merely to attain the simple solubility equilibrium of a chrome alum in water. It was found, however, that for the chromium–iron system only nine weeks gave agreement of the duplicates. In

(1) Hill, Durham and Ricci, THIS JOURNAL, **62**, 2723 (1940).

(2) See, for example, Ricci and Smiley, ibid., **66**, 1011 (1944), and Simons and Ricci, ibid., **68**, 2194 (1946).

(3) Hill, Smith and Ricci, ibid., **62**, 858 (1940).