Effect of Temperature on the Surface Tension and Density of Trifluoroacetic Acid.

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Orthobaric surface tension and density measurements of trifluoroacetic acid have been determined at twelve temperatures over a range of 24° to 68°. The method of least squares was applied to formulate equations relating the density, corrected capillary rise, and surface tension to the temperature.

A RELATED INVESTIGATION in progress in this laboratory required accurate surface tension data for the halogenated acetic acids so that the surface properties of these compounds in the liquid state could be compared. A search of the literature failed to reveal the existence of such data for most of these compounds, especially over any appreciable temperature range. As a consequence, surface tension measurements were made with the monofluoro-, monobromo-, and mono-iodoacetic acids. Data for the first of these (*2*) and of the last two (*1*) have been reported in the literature. Of special interest to the Authors were the fluorinated acetic acids. The present paper is concerned with the surface tension of trifluoroacetic acid and the variation of this property with the temperature.

Because of the difficulty of preparing difluoroacetic acid, measurements of its surface tension are not available.

EXPERIMENTAL

Materials. The trifluroacetic acid used in this investigation was the purest obtainable from the Eastman Organic Chemicals Corp. Subsequent density measurements, when compared with available literature values, showed a difference of two parts in the third place of decimals at 0° C., while the boiling point, which was 72.1°, represents a variation of 0.3°. These very small differences, together with results of gas chromatographic tests, were regarded as sufficient evidence of satisfactory purity of the compound for the measurements under consideration. The overall error in each derived surface tension values is ±0.05 dyne cm.$^{-1}$.

APPARATUS

The density of the liquid compound was determined with a pycnometer consisting of a bulb of about 10 ml. capacity, to which was sealed a capillary tube of small bore and about 30 cm. in length, into which the enclosed liquid could expand. The bulb and capillary tube were calibrated separately with mercury to a common reference mark which encircled the capillary tube near the point where it was sealed to the bulb. The calibration procedure for the capillary bore consisted essentially in determining, at constant temperature, the total weight of the pycnometer and contents for various accurately measured lengths of the mercury column in the capillary tube from the reference line. A Gaertner microscope slide cathetometer was used for this purpose. The directly measured property, therefore, was the liquid volume at constant weight for variable temperature.

Since trifluoroacetic acid is extremely hygroscopic, all measurements were made under orthobaric conditions with a capillarimeter designed for orthobaric measurements. The apparatus, designed and tested in this laboratory was described in an earlier report (*3*). Preliminary experiments indicated that the trifluoroacetic acid had a low surface tension and relatively high density. It was evident, therefore, that the capillarimeter had to be constructed with a capillary of fine bore to ensure a significant rise of the liquid in the tube. Accordingly, many feet of capillary tubing were tested using the method proposed by Harkins (*1*) for constancy of bore. The capillary tube finally selected had a bore with an average radius of 0.00555 cm. over a section about 10 cm. in length. The bore varied no more than 10^{-6} cm., which introduces an error no larger then ±0.005 dynes cm.$^{-1}$ in the measured surface tension.

To maintain a constant temperature during the measurements, a glass-wool insulated water bath was designed which had side walls of non-distorting heat resistant (herculite) plate glass. This was enclosed by a fiber-board box with narrow windows cut opposite each other, which permitted a clear view of the capillarimeter and pycnometer within the water bath. With efficient stirring and sensitive temperature control, the temperature was maintained constant at the lower temperatures to ±0.02° and to ±0.05° at the higher temperatures. The temperatures were first tested with an NBS certified platinum resistance thermometer–Mueller bridge system which could be read to 0.005°. The exact temperature of the bath at any given instant was determined with a standardized Beckman thermometer.

PROCEDURE

The initial procedure was to seal the capillarimeter and pyconometer to the vacuum line. The trifluoroacetic acid was then placed in borosilicate flask within a dry box which had been flushed continuously for some time with dry air. The trifluoroacetic acid was solidified with liquid nitrogen, after which, the flask was sealed on the vacuum line and the pressure reduced to 0.1 mm. of Hg. The vacuum system then was isolated from the pump and the compound transferred by distillation in vacuo to the pycnometer and then to the capillarimeter, with liquid nitrogen as the coolant. These, in turn, were sealed off from the vacuum system and allowed to stand at room temperature several hours, usually over night, and then placed side by side in the constant temperature bath. During all subsequent measurements the liquid was under its own vapor pressure. The volume of the fluoroacetic acid in the pycnometer was measured as simultaneously as possible with the height of the vertex of the liquid meniscus above the liquid reference surface in the capillarimeter. A series of measurements was made at various temperatures over a range of approximately 24° to 70°. The Gaertner cathetometer used for the linear measurements was mounted for vertical operation and could be read directly to 10^{-4} cm. A minimum of three hours was allowed for the apparatus and contents to reach thermal equilibrium with the water bath. Ten readings were made at each temperature. The average of these is presented in the table.

One important source of error in measuring the height which the vertex of the liquid meniscus reaches in the capillarimeter arises from the difficulty encountered in determining the exact position of the reference surface of the liquid. To minimize this potential error, a fluorescent lighting system was used to illuminate the apparatus within the water bath. A system of shades was arranged between the light source and the window of the box holding the water bath, and these were adjusted until the free reference surface was shown in sharp silhouette. By tilting the capillarimeter between readings, the liquid was made to flow to a point well above the equilibrium heigth, thus wetting the walls of the capillary bore. When the capillarimeter was returned to the vertical position, the liquid flowed spontaneously to its equilibrium height with a receding contact angle.

RESULTS

These data were applied in the following form of the capillary height equation:

$$\gamma = \frac{r(h + r/3)(D_l - D_v)g}{2\cos\theta}$$

in which r represents the radius of the capillary bore, h the measured height of the vertex of the liquid meniscus above the bulk reference surface, $(h + r/3)$ the height corrected for the volume of liquid above the vertex of the meniscus, D_l and D_v the density of the liquid and vapor respectively, g the gravitational factor, and θ the contact angle which the liquid made with the walls of the capillary. Since the meniscus appeared to be hemispherical under high magnification, it was assumed that the contact angle closely approached zero value and, hence, the cosine factor was neglected. The vapor density was calculated with the aid of the following empirical equations proposed by Sugden (5).

$$\log (D_v/D_b(= 5(T/T_b - 1)$$

where,

$$D_b = 0.0122(M/T_b)$$

In these equations, D_v and D_b represent the density of the vapor at the temperatures T and at the boiling point T_b respectively, and M the molecular weight of the liquid.

Table I. Surface Tension of Trifluoroacetic Acid

Temp., °C.	$(h + r/3)$, Cm.	Density of Liquid	Effective Density $(D_l - D_v)$	Surface Tension
24	3.4007	1.4812	1.4732	13.63
26	3.3693	1.4765	1.4679	13.44
28	3.3378	1.4718	1.4625	13.28
30	3.3063	1.4671	1.4572	13.11
35	3.2276	1.4554	1.4437	12.68
40	3.1489	1.4437	1.4300	12.25
45	3.0702	1.4319	1.4158	11.83
50	2.9915	1.4202	1.4013	11.42
55	2.9128	1.4085	1.3861	10.99
60	2.8341	1.3967	1.3700	10.57
65	2.7554	1.3850	1.3536	10.15
68	2.7082	1.3780	1.3433	9.90

In the table, pertinent data and surface tension values are presented as functions of the temperature.

The density, corrected capillary rise (h_c), and the surface tension are linear functions of the temperature. The respective equations, derived with the aid of least squares, are:

$$D = 1.5375 - 0.002346t$$
$$h_c = 3.7785 - 0.01574t$$
$$\gamma = 15.638 - 0.08444t$$

The average deviation of the data from these equations is less than 0.02 per cent.

Since trifluoroacetic acid is markedly hygroscopic, it is possible that water vapor was absorbed from the surroundings during the stages of transfer from the original container to the capillarimeter regardless of the precautions taken. It is doubtful that such a small quantity of water would have any appreciable effect upon the surface tension of the trifluoroacetic acid.

LITERATURE CITED

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