A Boiling Point Tensiometer

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A tensiometer is described for the measurement of the surface tension of boiling liquid mixtures. Nitrogen is forced at a very low flow rate alternately through two capillary tubes submerged in the boiling liquid. The diameter of one of these capillaries is accurately known. The surface tension of the liquid is calculated from the maximum pressure difference occurring as each bubble of gas breaks away from the capillary tubes. The accuracy of the equation used is 0.1%. The tensiometer has been used with the systems methylcylcohexane-toluene, benzene-methylcyclohexane, and water-acetic acid.

THE EXPERIMENTAL determination of the surface tension of boiling liquid mixtures is of considerable importance in distillation studies as such data are difficult to calculate and are subject to considerable error. The change of surface tension with concentration can influence the foam structure and the stability of liquid films. The plate pressure drop is also influenced by this change.

Sugden (*4*) developed a tensiometer for use at ambient temperatures which was reported (*1*) to provide greater speed, simplicity, and accuracy than any other. One of its advantages is the formation of a fresh liquid surface for each determination. With small modifications, this tensiometer has proved quite satisfactory for the determination of surface tension at the boiling point for organic and aqueous mixtures.

APPARATUS

Nitrogen (or air) from a gas cylinder is passed through a drying tower containing $CaCl_2$ and via a regulating valve and manometer to the tensiometer. A Hone high-pressure stainless steel 0.25-inch needle valve proved satisfactory for controlling the small required gas rate. The manometer is immersed in a constant temperature water bath at 20° C. so that the density of the manometer liquid is maintained constant. The manometer liquid used with organic liquid mixtures is a kerosine fraction (ρ = 0.7733 gram per ml. at 20° C.), and for aqueous systems carbon tetrachloride (ρ = 1.595 gram per ml. at 20° C.). The pressure drop recorded by the manometer is measured with a cathetometer mounted on a vertical pillar. Micrometer adjustment and vernier scales in the vertical plane enable the measurement of differences in liquid level to 0.01 mm.

The tensiometer, Figure 1, consists of a glass vessel 1.5 inches in diameter provided with a 40-watt external electric heating coil, a side arm condenser, and a drain tap for the withdrawal of liquid samples. Into the top of the vessel is fitted a ground glass stopper through which are sealed two tubes and a thermometer pocket. One tube ends in a short length of precision bore capillary tube of known diameter (in this case 1.25 mm.), and the other tube is drawn out until its diameter is 0.1 to 0.2 mm. The actual diameter of this drawn out tube need not be known. The length of the two tubes must be the same, to ensure that they are both immersed to the same depth in the liquid. A two-way tap in the tube containing the capillary bore section is used to divert the gas flow from one tube to the other, the gas passing preferentially through this tube if the tap is open.

OPERATING PROCEDURE

The liquid mixture is introduced to the tensiometer through the side arm condenser until the tube tips are submerged to a depth of 1 to 2 cm. A small amount of mercury is also added to fill the drain line, and thus prevent the liquid sample from containing any "dead space" liquid. The electric heater is switched on, and the power input varied to maintain an even, but not vigorous, boiling action within the liquid. The gas flow rate is then adjusted with the needle valve to maintain a rate of bubbling from an immersed tube of approximately one bubble in five seconds. The manometer level fluctuates, registering a maximum pressure as the bubble breaks away from the tube. This maximum difference is measured with the cathetometer, first when the gas is bubbling through the capillary tube, (h_1), and then when bubbling through the other tube, (h_2).

The empirical equation formulated by Sugden (*4*), and accurate to 1 part in 1000 for the surface tension, δ (dyne/cm.), provided $0.2 > r_2 > 0.1$ cm. & $r_1 < 0.01$ cm. is:

$$\delta = A\,\rho\,g(h_1 - h_2)\left[1 + \frac{0.69\,r_2 D}{\rho\,(h_1 - h_2)}\right]$$

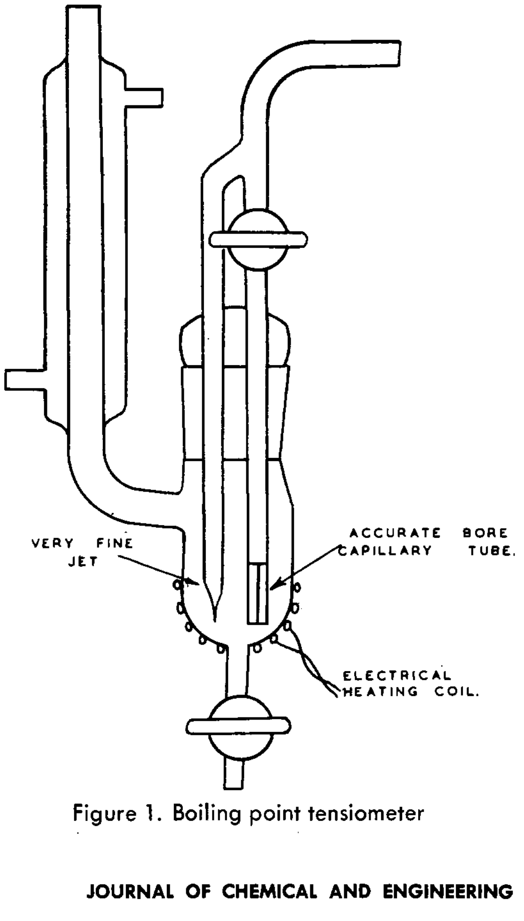

Figure 1. Boiling point tensiometer

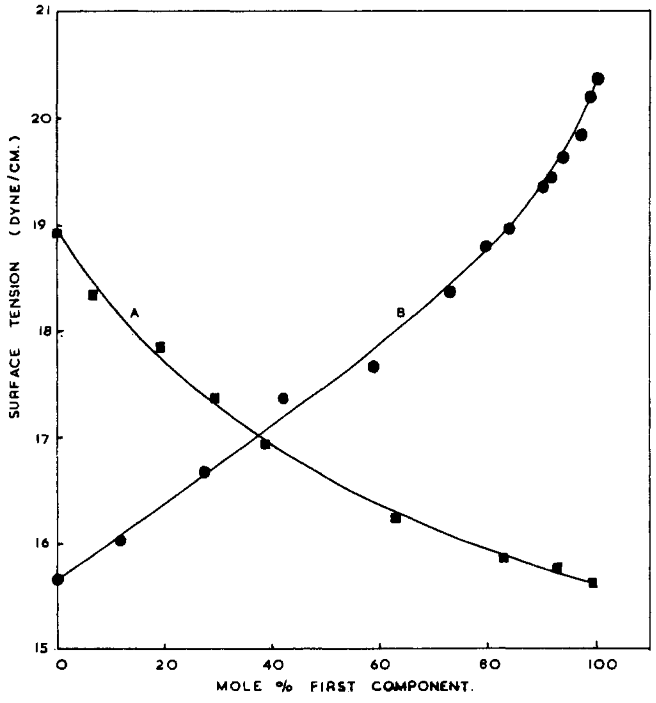

Figure 2. Surface tension at b.p. vs. composition for organic systems
A. Methylcyclohexane-toluene
B. Benzene-methylcyclohexane

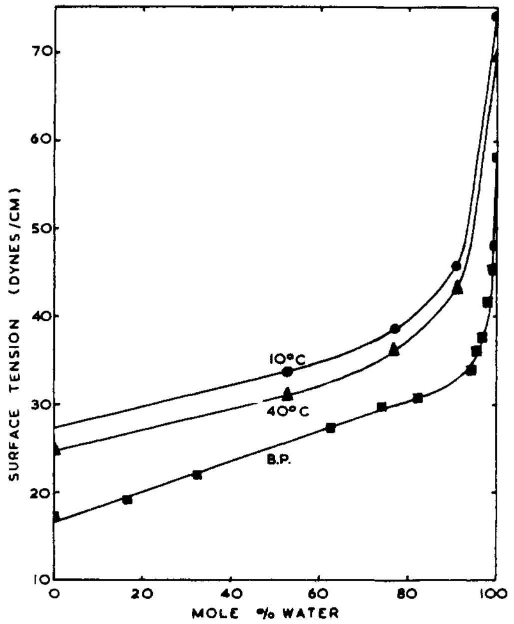

Figure 3. Surface tension vs. composition for water–acetic acid at different temperatures
● ▲ Literature values (5)
■ Experimental

where

A = constant of apparatus, determined by calibration
r_2 = radius of larger capillary tube (cm.)
D = density of liquid sample (grams/ml.)
ρ = density of manometer liquid (grams/ml.)
g = 981 (cm./sec.^{2}).

The apparatus constant, A, was determined by calibration of the tensiometer with benzene at 20° C. ($\delta = 28.88$ dyne/cm.), and found to be 0.003712.

The density of the liquid sample, D, does not need to be known accurately, as an error of 1% in its value causes an error of less than 0.1% in the surface tension. In consequence, the values of D for boiling liquid mixtures could be obtained by linear interpolation of values for the pure boiling liquids available from the literature (*3*).

The factor in large brackets in the equation never exceeded 1.015.

EXPERIMENTAL RESULTS

Values of the surface tension of the five pure components at the boiling point are given below.

Table I. Surface Tension at Boiling Point Dyne/Cm.

Liquid	Experimental	Literature (3)
Water	58.14	58.85 ± 0.2
Acetic acid	17.27	18.1 ± 0.3
Benzene	20.39	21.26 ± 0.15
Toluene	18.91	17.5 ± 0.3
M.C.H.	15.62	...

These.are compared with values taken from the literature (*3*) giving an assessment of the reliability of the tensiometer.

The variation of surface tension at the boiling point with composition was measured for three binary systems methylcyclohexane–toluene, benzene–methylcyclohexane, and water–acetic acid (*2*). The results are shown graphically in Figures 2 and 3.

No published data could be found of the variation of surface tension with composition at the boiling point for these systems. However, a comparison with published values for one system is contained in Figure 3, where the surface tension of water–acetic acid mixtures at 10° C. and 40° C. taken from the literature (*5*) is included with the experimental results at the boiling point.

The tensiometer gives values of the pure components to within ±1.0 dyne/cm. of those found in the literature and values repeatable to ±0.05 dyne/cm. for boiling liquid mixtures.

LITERATURE CITED

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RECEIVED for review July 27, 1962. Accepted March 8, 1963. One of the authors (J.P.C.) received financial support from the Directors of British Oxygen Research and Development Department, England.