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The Surface Tension of Unassociated Organic Liquids: A Simple Method of Interpolation

BY A. R. CARR AND T. WOLCZYNSKI

Several methods have been proposed to interpolate and extend surface tension data for various normal or unassociated organic liquids. Van der Waals,[1] Ferguson,[2] Sugden[3] and others have developed these formulas.

It is the purpose of this paper to suggest a simple method of interpolation of surface tensions of unassociated organic liquids which will hold over wide ranges of temperature. This may be derived from the Ferguson equation, which is

$$\gamma = K(T_c - t)^n$$

where γ is the surface tension, T_c is critical temperature, K is a constant depending upon the solution tested and n is equal to 1.2 for normal organic liquids.

The method is analogous to Duhring's rule as applied to vapor pressure. It consists of plotting the temperatures at points of equal surface tensions of a standard liquid and an unknown liquid. The result is a straight line. To apply this rule one needs only to know the surface tension of a standard liquid over a fairly wide range of temperature and two temperatures at which the two liquids have equal surface tensions. If the critical temperatures of the two liquids are known, only one temperature at which the two liquids have equal surface tension is required, for at the critical temperature the surface tension of all liquids is zero.

This rule may be expressed mathematically as

$$\frac{T_2 - T_1}{\Theta_2 - \Theta_1} = K$$

where T_2 and T_1 are the temperatures of the unknown liquid which has the same surface tensions as the standard liquid at the temperatures Θ_2 and Θ_1, respectively, and K is the slope of the line. If the critical temperature Θ_c and T_c of the liquids are substituted for T_2 and Θ_2, respectively, only one other pair of temperatures need be known to determine the slope of the line. Once the slope K is determined the line may be drawn and interpolation for surface tension is possible at all temperatures in this range by the following method. Through any temperature draw a line parallel to the horizontal axis and intersecting the line drawn through points of each surface tension. Through this point of intersection draw a line parallel to the vertical axis and read the temperature of the reference substance under the same surface tension as that of the liquid in question. From the table for the standard liquid read the surface tension corresponding to this temperature. This will be the surface tension of the unknown liquid at the temperature originally chosen. In like manner the surface tension of the unknown liquid may be determined at any temperature within the range of the experimental data.

Chlorobenzene was chosen as the standard liquid and its surface tension over the range 10–333° was calculated by the formula $\gamma = 72.2\,(1 - (T/632.3))^{1.23}$ as given in the "International Critical Tables."

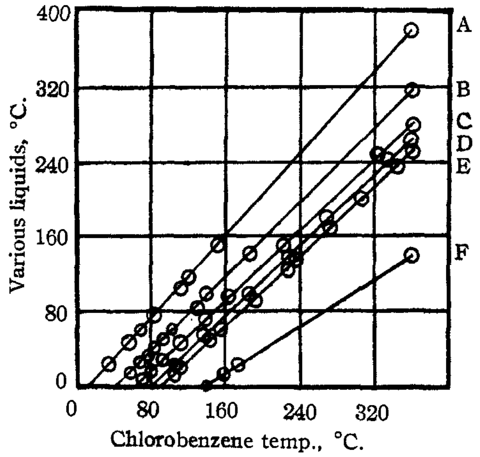

Fig. 1.—A chlorotoluene, B toluene, C carbon tetrachloride, D propyl acetate, E methyl isobutyrate, F methyl chloride.

Figure I gives the lines of equal surface tensions for a number of unassociated organic liquids. The points at the right on each line give the critical temperatures for these liquids. Thus it may be seen that the method is applicable for checking critical temperatures. All normal liquids gave straight lines to the critical temperature. Such associated liquids as *o*-, *m*- and *p*-cresol, acetone, ethyl, methyl, propyl and butyl alcohols, and aniline gave straight lines only over

(1) Van der Waals, *Z. physik. Chem.*, **13**, 716 (1894).

(2) Ferguson, *Science Progress*, **9**, 445 (1915).

(3) Sugden, *J. Chem. Soc.*, **125**, 32 (1924).

a small range of temperature. The surface tension data for the above liquids were taken from "International Critical Tables."

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The Photochemical Reaction between Chlorine and Formaldehyde. The Preparation of Formyl Chloride

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The thermal reaction between Cl_2 and CH_2O has been studied by Spence and Wild[1] who find that the two gases do not react appreciably at 100°, but form carbon monoxide and hydrogen chloride quantitatively at 150°. The only photochemical process involving gaseous formaldehyde which has been reported is its slow decomposition by ultraviolet light into carbon monoxide and hydrogen, a reaction studied by Bredig and Goldberger[2] and more completely by Norrish and Kirkbride.[3] Spence[4] has found that the polymerization of formaldehyde is unaffected by light of any wave length.

Material and Apparatus

Chlorine was prepared by heating cupric chloride. The gas was stored in a large glass bulb, and was admitted to the reaction vessel by means of stopcocks greased with a mixture of dextrin, glycerin and mannitol. Chlorine so obtained was sufficiently pure to react with carbon monoxide with only a very slight induction period. In a few runs chlorine was evolved from a copper chloride tube sealed directly to the reaction vessel, but no greater purity was obtained by this method.

Of several methods which were used for the preparation of formaldehyde, the one recommended by Spence[4] proved most satisfactory. Dry nitrogen was passed over dried paraformaldehyde (Eastman) or α-polyoxymethylene kept at 120°, and the monomeric vapor was condensed in liquid air and fractionally distilled. To prevent polymerization, it was necessary to keep the formaldehyde frozen in liquid air at all times. Enough of the gas for a run could be obtained by removing the liquid air for a few minutes.

Other gases used in these experiments were obtained by conventional methods. Carbon monoxide was made by dehydrating formic acid with sulfuric acid, and was bubbled through concentrated sodium hydroxide and concentrated sulfuric acid. Hydrogen chloride, prepared by dehydrating a hydrochloric acid solution with sulfuric acid, was frozen in liquid air, fractionally distilled once and stored over anhydrone. Phosgene was distilled from a bomb into a liquid-air trap, fractionally distilled three times and kept as a liquid in a trap surrounded with ice.

The reaction vessel used was a spherical quartz bulb of about 200-cc. capacity, connected to the line by means of a quartz–Pyrex graded seal. For illumination a mercury arc was used in the earlier experiments and a 300-watt tungsten lamp in the later ones.

The strong tendency of formaldehyde to polymerize made it necessary to carry out these experiments at elevated temperatures. Some of the work was done at 60°, but better results were obtained at 80°. To maintain these temperatures, a thermostat with a quartz window was used; tubes leading to the reaction vessel were wrapped with chromel wire and heated electrically. Considerable difficulty was encountered in finding a stopcock grease serviceable at these temperatures and able to withstand the action of chlorine. Apiezon grease was used for a time, but the glycerin–mannitol–dextrin mixture mentioned above proved more satisfactory. It is slowly attacked by chlorine, but apparently no volatile products are formed capable of inhibiting the reaction. The great disadvantage of this grease was the necessity of renewing it after every three or four runs.

The reaction was followed by observing the accompanying pressure change, but the polymerization of formaldehyde made an indirect method of measuring pressures necessary. For this purpose a "click gage" was employed, a thin glass diaphragm on the side of a small bulb, deformed so as to snap into a new position with an audible click when a certain pressure difference is established on its two sides. The gage was connected directly to the reaction vessel, and pressures were read simply by noting the pressure on the outer surface of the gage necessary to make it click. Thus the reaction mixtures were kept entirely within the thermostat, except for one heated side-tube leading to the pumps and gas reservoirs. Click gage readings are reproducible to well under 0.1 mm., but this method of pressure measurement has several disadvantages. The gages, of course, are very fragile; one follows the reaction not directly but by measuring pressures after intervals of illumination; and considerable time is required to make each reading.

Pressures outside the click gage were measured on an α-bromonaphthalene manometer two meters in length. Pressure readings in the following pages will be given in cm. of α-bromonaphthalene; since this substance has a density approximately one-tenth that of mercury, the pressure readings will correspond nearly to mm. of mercury.

Results and Discussion

The primary process in this reaction, whatever source of illumination is used, is the dis-

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(1) Spence and Wild, *Nature*, **132**, 170 (1933).

(2) Bredig and Goldberger, *Z. physik. Chem.*, **110**, 521 (1924).

(3) Norrish and Kirkbride, *J. Chem. Soc.*, **135**, 1518 (1932).

(4) Spence, *ibid.*, 1193 (1933).