the zero moment of this compound in dioxane, is of importance in connection with the mechanism of the hydrolysis of silicon tetrachloride. This reaction has been interpreted[12] as resulting from the formation of ${}^+$O-Si${}^-$ bonds with the subsequent splitting off of hydrogen chloride. A mechanism involving the formation of Cl–H bonds would appear more probable unless the smaller size of the water molecule, compared to dioxane, makes the formation of an ${}^+$O-Si${}^-$ bond possible in this special case.

The low moment of germanium tetrachloride in dioxane reveals that only a small amount of interaction takes place between these compounds in solution. Efforts to isolate a solid dioxanate of germanium tetrachloride have been unsuccessful and this confirms the view that very little tendency exists for germanium to expand its valence shell in forming coördinate bonds with dioxane. A comparison of the behavior of germanium and titanium tetrachlorides toward dioxane is of interest. While the solubility of the complex of titanium tetrachloride in dioxane is too small to permit determination of its moment in dioxane, the existence of the crystalline complex indicates that coördination readily occurs, at least in the solid state. The greater size of the titanium atom is probably responsible for the difference in the behavior of titanium and germanium tetrachlorides.

The effect of atomic radius is further shown in the case of stannic chloride. A solid coördina-

(12) Sidgwick, J. Chem. Soc., 125, 2672 (1924).

tion complex having the composition $SnCl_4 \cdot 2C_4H_8O_2$ has previously been reported.[13] That coördination persists in solution is evident from a comparison of the zero moment obtained for stannic chloride in benzene[3] with the value, 3.82, in dioxane. The values[14] reported for $(C_2H_5)_2O \cdot SnCl_4$ and $2(CH_3)_2CO \cdot SnCl_4$ are 3.60 and 7.7, respectively. The possible arrangements of the chlorine atoms and dioxane molecules in the octahedral complexes would permit various configurations having moments ranging from 0 to about 6. For this reason it is not possible to estimate from the data the degree of coördination of stannic chloride with dioxane, but it is evident that dioxane coördinates to a greater extent with stannic chloride than with germanium tetrachloride.

Summary

Electric moments have been determined for boron chloride, aluminum chloride, ferric chloride, silicon tetrachloride, germanium tetrachloride and stannic chloride in dioxane. Coördination between dioxane and boron chloride in solution is almost complete. Ferric chloride appears to interact only slightly with dioxane. The extent of coördination of the group IV B elements increases with increasing size of the central atom, silicon tetrachloride having a zero moment and stannic chloride a moment of 3.8 in dioxane.

(13) Rheinboldt and Boy, J. prakt. Chem., 129, 268 (1931).
(14) Ulich, Hertel and Nespital, Z. physik. Chem., B17, 21 (1932).

The Effect of Temperature on the Surface Tension and Density of Some Halogen Substituted Acetic Acids

BY JOSEPH J. JASPER AND LEWIS ROSENSTEIN

In a recent investigation carried out in this Laboratory, accurate surface tension–temperature data were required for the comparison of certain physico-chemical properties of the halogen substituted acetic acids. Search of the literature revealed the apparent unavailability of such data for most of the compounds involved. To supply this deficiency, the surface tension–temperature data for monobromoacetic acid and monoiodoacetic acid were determined over an appreciable temperature range in their molten states.

Experimental

Materials.—The compounds were Eastman Kodak Company reagent quality. The melting point of the monobromoacetic acid was 49.7° and that of monoiodoacetic acid 81.9°. No decomposition of the latter was observed below 130° during the measurements. The decomposition of this compound below its boiling point is believed to be dependent upon traces of mineral acids and moisture present[1]; therefore, great care was used to prevent traces of those impurities from reaching the molten monoiodoacetic acid.

(1) Eastman Kodak Company, private communication.

Procedure.—Because of the relative simplicity of the process and the necessity of excluding moisture from the molten compounds, the capillary rise method was employed for the surface tension measurements. The apparatus used was a slight modification[2] of that described by Richards and Coombs.[3] To ensure a plane reference liquid surface, the dimensional specifications suggested by Richards and Carver[4] were adopted. The diameter of the reference surface was 45 mm. The capillary tube of the apparatus was calibrated according to the method suggested by Harkins and Brown,[5] in which the focusing method described by Wolff, Shoemaker and Briggs[6] was employed, using a "cold" fluorescent light source. The radius of the capillary was found to be 0.019168 cm.

Density determinations were made with a 20-ml. Pyrex pycnometer, which was provided with an expansion bulb and a ground-glass stopper. This was calibrated with mercury.

The constant-temperature system consisted of a thick-wall Pyrex jar of eighteen liters capacity and an electronic relay controlled by a mercury regulator having a bulb of 250-ml. capacity. The Pyrex jar was insulated with magnesia-asbestos, one inch thick. Two small openings in the insulation, cut diametrically opposite, provided the necessary observation windows. Petroleum oil, the liquid medium of the bath, was found to provide a slower heat transfer than water. Although this effect was largely overcome by increasing the efficiency of stirring, the best temperature precision obtainable was ±0.2°.

The capillary rise was measured with a short range cathetometer. To ensure thermal equilibrium between the measured liquid and the surrounding oil-bath, at least thirty minutes were allowed. During this time the apparatus was agitated constantly. To equalize the pressure within the system with that of the prevailing atmosphere, the stopcock with which the apparatus was equipped was opened to the air from time to time through a calcium chloride drying tube. Between readings, the capillary was wet by drawing the liquid to the full length of the bore and allowing it to recede spontaneously to its static equilibrium position.

Experimental Results

The equation[7]

$$\gamma = \frac{(h + (r/3))(d_1 - d_a)gr}{2}$$

was used to calculate the surface tension γ. In this equation, h is the capillary rise, r the capillary radius, and d_1 and d_a, respectively, the densities of the liquid and air during the experiment. Each

(2) J. R. Bright and J. J. Jasper, THIS JOURNAL, **63**, 3486 (1941).

(3) T. W. Richards and L. B. Coombs, *ibid.*, **37**, 1656 (1915).

(4) T. W. Richards and E. K. Carver, *ibid.*, **43**, 827 (1921).

(5) W. D. Harkins and F. E. Brown, *ibid.*, **41**, 499 (1919).

(6) Wolff, Shoemaker and Briggs, *Bull. Bureau of Standards*, **12**, 432 (1915).

(7) N. E. Dorsey, "National Research Council Bull.," No. 69, p. 56.

recorded measurement is the average of ten to fifteen readings. Experimental results are presented in Tables I and II.

TABLE I

DENSITY AND SURFACE TENSION DATA FOR MOLTEN MONOBROMOACETIC ACID

Temp., °C.	Density, g./ml.	$(h + (r/3))$, cm.	$(d_1 - d_a)$	Surface tension, dynes/cm.
55	1.9017	2.2561	1.9007	40.30
70	1.8778	2.1870	1.8768	38.57
85	1.8531	2.1230	1.8522	36.96
100	1.8286	2.0454	1.8277	35.13
120	1.7955	1.9648	1.7947	33.14
145	1.7542	1.8446	1.7535	30.40
170	1.7123	1.7237	1.7117	27.72

TABLE II

DENSITY AND SURFACE TENSION DATA FOR MOLTEN MONOIODOACETIC ACID

Temp., °C.	Density, g./ml.	$(h + (r/3))$, cm.	$(d_1 - d_a)$	Surface tension, dynes/cm.
85	2.2694	1.8119	2.2685	38.63
90	2.2606	1.7908	2.2597	38.03
95	2.2519	1.7653	2.2510	37.35
100	2.2430	1.7488	2.2421	36.85
110	2.2250	1.7161	2.2242	35.87
120	2.2070	1.6659	2.2062	34.54
130	2.1893	1.6278	2.1886	33.41

These data give straight line relationships. Using the method of least squares, the equations for the best curves were calculated and are given in the following:

For monobromoacetic acid

$$d = 1.93302 - 0.0016482t \tag{1}$$
$$\gamma = 46.20552 - 0.10901t \tag{2}$$

For monoiodoacetic acid

$$d = 2.42118 - 0.0017837t \tag{3}$$
$$\gamma = 48.35779 - 0.11483t \tag{4}$$

The average deviation of the data from these curves is as follows: (1) 0.024%; (2) 0.15%; (3) 0.024%; (4) 0.14%.

Summary

The effect of the temperature on the density and the surface tension of monobromoacetic acid and monoiodoacetic acid in the molten state was determined over an appreciable temperature range. The data obtained gave straight line relationships. The equations were calculated by using the method of least squares.