TABLE II

RELATIVE STRENGTH OF BASES IN ACETIC ACID AND WATER

	E_m	$pH_{(HAc)}$	$pK_{H(H_2O)}$
Biuret (first equiv.)	0.700	−2.61	−0.88
1-Amino-5-phenyltetrazole	.685	−2.35	− .62
1-(*p*-Nitrophenyl)-5-aminotetrazole	.628	−1.39	+ .34
1-(*m*-Nitrophenyl)-5-aminotetrazole	.620	−1.26	.47
1-(*m*-Chlorophenyl)-5-aminotetrazole	.606	−1.03	.70
1-(*p*-Chlorophenyl)-5-aminotetrazole	.602	−0.95	.78
1-(*m*-Tolyl)-5-aminotetrazole	.584	− .65	1.08
1-Phenyl-5-aminotetrazole	.582	− .61	1.12
1-(*o*-Tolyl)-5-aminotetrazole	.575	− .50	1.23
1-Benzyl-5-aminotetrazole	.563	− .29	1.44
1-*n*-Propyl-5-aminotetrazole	.541	+ .07	1.80
1-Methyl-5-aminotetrazole	.540	.09	1.82
5-Aminotetrazole	.540	.09	1.82
1-Isopropyl-5-aminotetrazole	.535	.18	1.91
Biguanide (second equiv.)	.478	1.13	2.86
3-Aminotriazine-1,2,4	.465	1.36	3.09
5-Guanylaminotetrazole	.455	1.53	3.26
Guanylurea (first equiv.)	.426	2.03	3.76
Diaminobiuret (first equiv.)	.401	2.45	>4.00
Aniline	.394	2.57	>4.00
Biguanide (first equiv.)	.379	2.82	>4.00
1,4-Dimethyl-5-iminotetrazole	.368	3.01	>4.00

and the effect of the particular 1-substituent on the pK_H of 5-aminotetrazole seems to be what one would expect from the inductomeric influence of that group.

CHEMICAL RESEARCH SECTION
PICATINNY ARSENAL
DOVER, NEW JERSEY

The Effect of Temperature on the Density and Surface Tension of Monofluoroacetic Acid

BY JOSEPH J. JASPER AND PHILOMENA G. GRODZKA

RECEIVED NOVEMBER 13, 1953

In one of a series of related investigations carried out in this Laboratory, accurate surface tension data were required for the comparison of certain physico-chemical properties of the monohalogenated acetic acids at several temperatures. Search of the literature revealed the apparent unavailability of such data for most of these compounds and to correct this deficiency surface tension measurements were undertaken with the monofluoro-, monobromo- and monoiodoacetic acids. The last two of these were reported in the literature,[1] but due to difficulties of preparation data for the first of these could not be obtained. Since surface tension data for monofluoroacetic acid are still missing from the literature, the purpose of this investigation was to supply these data, together with corresponding densities, for an appreciable range of temperature.

Experimental

Preparation and Purification of the Compound.—The starting compound, sodium monofluoroacetate, was obtained from the Monsanto Chemical Company, and the monofluoroacetic acid prepared from it as follows[2]: 300 g. of the sodium salt was added to 800 ml. of water in a 3-liter erlenmeyer flask. To this was added slowly and with constant stirring, a solution containing 294 g. of sulfuric acid in 800 ml. of water. The resulting mixture was filtered and the filtrate extracted four times with 50-ml. portions of ether. The combined ether extracts were then dried with anhydrous sodium sulfate and the supernatant solution decanted. The ether was then removed by distillation, leaving a white crystalline solid which melted at 33°. The crystalline compound was then purified by repeated fractionations, first under partial vacuum and finally under high vacuum. The final product which was selected for use solidified into white transparent needles which melted at 35.3°. This value agrees closely with that of Swarts[3] who reported a melting point of 35.2° for this compound. The melting point was determined from a time–temperature diagram with a 150-g. sample, and the observed freezing time was approximately 50% of the total time of cooling. Since the monofluoroacetic acid was extremely hygroscopic, this operation, as well as all subsequent ones except the surface tension measurements, were carried out in an atmosphere of dry nitrogen.

A specially designed and constructed, glass wool insulated, constant temperature bath was used in this investigation. The stirring system was sufficiently efficient, and the thermoregulator sensitive enough to maintain a temperature constant to 0.02° at the lower temperatures and 0.05° at the higher temperatures of the investigation. The exact temperatures were determined with a series of NBS certified thermometers with two-degree ranges and scale divisions of 0.01°.

Measurement of Densities.—The densities were measured simultaneously with the surface tensions. A bicapillary pycnometer of the type described by Bauer[4] was used. It consisted of a 15-ml. bulb and two capillary tubes, each about 5 cm. in length, into which the liquid contents of the bulb could expand. The capillary tubes were equipped with ground-glass stoppers to prevent contamination of the contents from the surroundings. The molten compound was introduced into the pycnometer bulb with the aid of a glass syringe equipped with a hollow glass needle.

Measurement of Surface Tensions.—The surface tensions were measured by the capillary-height method under orthobaric conditions with a capillarimeter constructed according to the design of Jasper and Herrington.[5] The selection of the capillary tube, and the subsequent procedure employed in testing for constancy of bore, was similar to that of Harkins and Brown.[6] The capillary tube finally selected had a section 4.5 cm. in length with a radius which varied no more than one part per thousand. The average radius of this section from eleven measurements was 0.008211 cm. Since it is necessary that the reference surface of the liquid be approximately plane, equal care was taken in selecting the larger tube in which the reference surface was to be established. This tube had an inside diameter of 4.5 cm. which, according to Richards and Carver,[7] gives a surface sufficiently plane for accurate results. Tests for optical distortion through the walls of the apparatus gave negligible results.

The purified monofluoroacetic acid was transferred in the liquid state from the storage container to an all-glass distillation apparatus to which the capillarimeter was sealed. The compound was solidified with liquid nitrogen and the system evacuated to a high degree of vacuum. The first third of the distillate was rejected and the second third distilled into the reservoir bulb of the capillarimeter. The liquid in the capillarimeter was again solidified with liquid nitrogen, the system again evacuated, and the capillarimeter sealed off. The subsequent surface tension measurements were carried out with the compound in contact with its

---

[1] J. J. Jasper and L. Rosenstein, THIS JOURNAL, **64**, 2078 (1942).

[2] This method of preparation was followed by Clark D. Heenan, Director of the Pontiac Testing Laboratories, who prepared the compound for the author.

[3] F. Swarts, *J. chim. phys.*, **17**, 23 (1919).

[4] N. Bauer in Weissberger, "Physical Methods of Organic Chemistry," Vol. 1, 1st. Ed., Interscience Publishers, Inc., New York, N. Y., 1945, p. 80.

[5] J. J. Jasper and K. D. Herrington, THIS JOURNAL, **68**, 2142 (1946).

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

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

vapor only. The liquid meniscus in the capillary tube appeared to be truly hemispherical under high magnification, with a solid–liquid contact angle of zero. The capillary heights were measured with a Gaertner cathetometer which could be read directly to 0.0001 cm. The light which illuminated the reference surface was directed through a narrow horizontal slit cut into a brass plate which was vertically adjustable. With the aid of this apparatus the reference surface was thrown in sharp silhouette and its position readily determined. Thirty minutes was allowed at each temperature for the capillarimeter contents to reach thermal equilibrium with the water-bath. Between readings, the liquid was made to flow the full length of the capillary by tipping the apparatus nearly horizontal. When the vertical position was resumed, the liquid flowed spontaneously to its equilibrium position with a receding contact angle. Each recorded measurement was the average of from 20 to 30 readings made on different days.

Results

The data were applied in the following form of the capillary-height equation

$$\gamma = \frac{r\left(h + \frac{r}{3}\right)(d_l - d_v)g}{2}$$

where r is the radius of the capillary, h the observed capillary height, d_l and d_v the density of the liquid and vapor, respectively, and g the gravitational factor. Although the vapor densities have been accurately measured in this Laboratory, it was found that they were not significant over the temperature range employed, and accordingly were not used in the density correction. The densities and surface tension values for seven temperatures are shown in Table I. The following equations, which relate the density and the surface tension, respectively, to the temperature, were formulated by the method of least squares.

TABLE I

THE DENSITY AND SURFACE TENSION OF MOLTEN MONOFLUOROACETIC ACID

Temp., °C.	Density of molten cmpd. g./cc.	Surface tension, dynes/cm.
36	1.3693	38.21 ± 0.05
40	1.3639	37.76
50	1.3505	36.65
60	1.3372	35.54
70	1.3238	34.43
80	1.3105	33.32
95	1.2905	31.64 ± 0.05

$$d = 1.4173 - 0.00133t$$
$$\gamma = 42.220 - 0.11145t$$

DEPARTMENT OF CHEMISTRY
WAYNE UNIVERSITY
DETROIT 1, MICHIGAN

COMMUNICATIONS TO THE EDITOR

DICHLORO-BIS-(2,2′-DIPYRIDYL)-IRON(II) AND DICHLORO-BIS-(1,10-PHENANTHROLINE)-IRON(II)

Sir:

Calvin and Melchior[1] point out that there is a correlation between the stability of complexes of bivalent metal ions and the second ionization potentials of the gaseous metal atoms. This was also reported independently by Irving and Williams.[2] In a recent detailed treatment of this subject they[3] suggest this stability order follows from considerations of the reciprocal of the ionic radii and the second ionization potentials.

It is well known that salts of the hydrated iron(II) ion are paramagnetic with "ionic" or sp^3d^2 bonds, whereas salts of $[Fe(dipy)_3]^{+2}$ and $[Fe(ophen)_3]^{+2}$ are diamagnetic,[4] indicative of strong covalent d^2sp^3 hybridization. In the stability sequence of complexes of bivalent metals these iron(II) complexes are anomalously high,[3] and furthermore the values of K_3 for the stepwise formation constants[5] in contrast to the usual trend, are greater than K_1 or K_2. Irving and Williams[3] have proposed that these anomalies arise from orbital stabilization, and it is thus of particular interest to determine whether diamagnetism is associated with the addition of the first, second or third chelate molecule.

When solid $[Fe(dipy)_3]Cl_2 \cdot 6H_2O$ was heated in an Abderhalden pistol at 100° over concentrated sulfuric acid *in vacuo* for thirty hours loss of the water and one molecule of 2,2′-dipyridyl resulted.

Anal. Calcd. for $C_{20}H_{16}N_4FeCl_2$: C, 54.70; H, 3.65. Found: C, 54.49; H, 3.80.

At 156°, $[Fe(ophen)_3]Cl_2 \cdot 6H_2O$ also lost the water and one molecule of the base becoming blue.

Anal. Calcd. for $C_{24}H_{16}N_4FeCl_2$: C, 59.16; H, 3.28. Found: C, 58.66; H, 3.22.

On further heating at 156° *in vacuo* $[Fe(dipy)_2Cl_2]$ lost an additional molecule of 2,2-dipyridyl changing from violet-blue to red.

Anal. Calcd. for $C_{10}H_8N_2FeCl_2$: C, 42.44; H, 2.83; N, 9.90. Found: C, 42.75; H, 2.94; N, 10.14.

At 197° *in vacuo* $[Fe(ophen)_2Cl_2]$ was unchanged after several hours.

Magnetic susceptibilities were determined by the Gouy method. A value of 5.2 B.M. was obtained for $[Fe(dipy)_2Cl_2]$ and 5.3 B.M. for $[Fe(ophen)_2Cl_2]$ in agreement with the theoretical value for four unpaired electrons and indicative of "ionic" or sp^3d^2 bonding. These results lend ex-

---

[1] M. Calvin and N. C. Melchior, THIS JOURNAL, **70**, 3270 (1948); first reported in N. C. Melchior, Thesis, University of California, Berkeley, September, 1946.

[2] H. Irving and R. J. P. Williams, *Nature*, **162**, 746 (1948).

[3] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

[4] L. Cambi and A. Cagnasso, *Gazz. chim. ital.*, **63**, 767 (1933); **64**, 772 (1935); F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

[5] T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948); J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 55 (1950).