due to steric hindrance in the ortho position. We found a value of +0.26 for the moment of the group in the ortho compound. The o-nitrophenyltrimethylsilane gives a resultant group moment of +0.62 which is about what we would expect.

If structure IV existed to any appreciable extent in the unsubstituted phenyltrimethylsilane, we would expect the moment of the trimethylsilyl group in this compound to be less than it is in benzyltrimethylsilane since resonance of the silicon group with the ring is not possible in the latter compound. We find, however, a moment of +0.47 for the group in the benzyl compound, a value which is the same as that in the phenyl

derivative within experimental error. We are therefore led to believe that structure IV makes practically no contribution to the structure of phenyltrimethylsilane itself but becomes important in derivatives of this compound due to group interaction.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

The Temperature–Interfacial Tension Studies of Some Alkyl Esters of Monofluoroacetic and Monoiodoacetic Acids Against Water

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This is the third in a series of interfacial tension studies involving the lower esters of the monohalogen acetic acids with water. The present paper reports the results obtained from the ethyl and n-propyl esters of monofluoroacetic acid, and the methyl, ethyl, n-propyl and n-butyl esters of monoiodoacetic acid over an appreciable range of temperature. The method of least squares was applied in formulating empirical equations relating the interfacial tensions to the temperature, and the equations were used to calculate the temperature coefficients, the latent heats, and the enthalpy attending the formation of each sq. cm. of interfacial surface. The data and calculated results are presented in two tables.

Although interfacial tension studies have proved to be of fundamental importance in the interpretation of the behavior of systems having great specific surfaces, the subject has not received nearly as much study as surface tension. This may be due to (a) the experimental difficulties attending accurate measurements, and (b) the failure to understand the significant role that it plays in numerous aspects of theoretical and industrial chemistry. Interfacial tension is undoubtedly a complex phenomenon which is probably capable of resolution and interpretation through experimentally established relationships among the factors which determine the properties of the transition region.

The purpose of this investigation was to obtain interfacial tension data for a series of esters of monofluoroacetic and monoiodoacetic acids with water over an appreciable temperature range, and to formulate empirical equations relating the interfacial tension and temperature. With these data it was possible to determine several thermodynamic properties of the interfacial region. This is the third of a series of such studies which will eventually include other homologous series containing substituted halogen groups.

Experimental

Preparation and Purification of the Esters.—Six esters were studied in this investigation. Owing to experimental difficulties, only the ethyl and n-propyl esters of monofluoroacetic acid were used. The remaining four were the methyl, ethyl, n-propyl and n-butyl esters of monoiodoacetic acid. The two esters of monofluoroacetic acid were prepared from sodium fluoroacetate, sulfuric acid and the corresponding alcohols. For final purification, the esters were subjected to the vacuum fractionation method described by Morton.[2]

A 15-inch column was used. This was packed with single-turn glass helices and fitted with a total reflux variable take-off head. The middle third boiled at a constant temperature and was collected for use.

The methyl, ethyl and n-butyl esters of monoiodoacetic acid were prepared by the method of Fisher as described by Fieser and Fieser,[3] and the n-propyl ester by halogen exchange. In the latter preparation sodium iodide, n-propyl alcohol and n-propyl chloroacetate were used. This method gave a very good yield of the n-propyl iodoacetate.

The esters of monoiodoacetic acid were purified by fractional distillation in an atmosphere of nitrogen with the aid of an 8-inch column. Since the esters tended to decompose in the light, the fractionations were carried out in the dark. Under these conditions the esters distilled over at a constant temperature with a slight yellow color. Distillation through a Claisen head was then carried out with a small globule of mercury in the receiving flask.[4] The final products obtained were colorless. During the interfacial tension measurements which followed, a small globule of mercury was kept in constant contact with the organic liquids in the receiving container where the tips delivered the drops. The mutually saturated liquids were tested spectroscopically for the presence of mercury, but no traces were detected. Because of their instability, all subsequent operations involving these esters were carried out as rapidly as possible in subdued light.

Determination of the Densities.—Since the density factor appears in the interfacial tension equation as an explicit variable, densities must be determined as accurately as possible. The pycnometers used were a modified form of the "type D" instrument described by Weissberger.[5] Three pycnometers, each having a volume of about 20 ml., were constructed as nearly alike as possible with respect to dimensions and shape. Two of these were used for the respective mutually saturated liquids, and the third as a counterpoise. Repeated trials showed no deviation in the densities greater than 0.05% over the temperature range employed. Several thermoregulators were used, each of which was set at a different temperature. This made it possible and convenient

(1) Present address: Park Forest, Illinois.

(2) A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, Chapters IV and V.

(3) L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 133.

(4) A. H. Blatt, "Organic Syntheses," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 402.

(5) A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, New York, N. Y., 1945, p. 79.

to compare the data from time to time at exactly the same temperatures previously used. Although the thermoregulators controlled the temperature of the water-bath within a narrow range, the exact temperatures were read from a NBS certified thermometer. Details of technique and procedure were the same as described in an earlier study involving the esters of monochloroacetic acid.[6] The densities of the organic liquids saturated with water (d_o) and water saturated with the organic liquids (d_w) are shown in Table I.

Determination of the Interfacial Tensions.—A modification of the drop-weight apparatus of Harkins and Brown[7] was used for measuring the interfacial tensions in this in-

TABLE I

Density and Interfacial Tension Data for the Ester-Water Systems

Ester	Temp., °C.	d_o	d_w	γ_i (Ergs/cm.²)
Ethyl	24.6	1.0848	1.0100	9.8 ± 0.08
fluoro-	26.8	1.0824	1.0057	9.7 ± .08
acetate	42.6	1.0614	0.9995	9.4 ± .08
	55.4	1.0443	.9936	8.9 ± .08
	60.3	1.0378	.9911	8.6 ± .08
	70.4	1.0238	.9850	8.0 ± .07
n-Propyl	24.6	1.0402	1.0018	14.1 ± 0.12
fluoro-	26.8	1.0377	0.9990	14.0 ± .13
acetate	42.6	1.0183	.9936	13.7 ± .12
	55.4	1.0026	.9878	13.1 ± .20
	60.3	0.9974	.9858	12.7 ± .20
	70.4	0.9841	.9803	....
Methyl	24.6	1.9935	1.0105	16.2 ± 0.43
iodo-	42.6	1.9596	1.0046	15.9 ± .41
acetate	55.4	1.9365	0.9995	15.4 ± .44
	60.3	1.9274	0.9960	15.2 ± .40
Ethyl	24.6	1.7980	1.0016	18.2 ± 0.22
iodo-	42.6	1.7665	0.9956	17.9 ± .21
acetate	55.4	1.7436	.9903	17.5 ± .21
	60.3	1.7345	.9875	17.3 ± .21
n-Propyl	24.6	1.6757	0.9987	23.0 ± 0.31
iodo-	42.6	1.6465	.9926	22.8 ± .31
acetate	55.4	1.6264	.9870	22.5 ± .26
	60.3	1.6190	.9842	22.4 ± .29
n-Butyl	24.6	1.5860	0.9979	26.1 ± 0.18
iodo-	42.6	1.5555	.9919	25.4 ± .17
acetate	55.4	1.5365	.9864	24.5 ± .17
	60.3	1.5290	.9840	24.1 ± .16

Ethyl fluoroacetate: $\gamma_i = 9.7221 + 0.01737t - 5.889 \times 10^{-4}t^2$

n-Propyl fluoroacetate: $\gamma_i = 13.7003 + 0.03778t - 8.9196 \times 10^{-4}t^2$

Methyl iodoaetcate: $\gamma_i = 15.564 + 0.04527t - 8.63 \times 10^{-4}t^2$

Ethyl iodoacetate: $\gamma_i = 18.2513 + 0.01075t - 4.324 \times 10^{-4}t^2$

n-Propyl iodoacetate: $\gamma_i = 23.11 - 0.0012t - 1.65 \times 10^{-4}t^2$

n-Butyl iodoacetate: $\gamma_i = 27.08 - 0.0353t - 2.25 \times 10^{-4}t^2$

vestigation. The method involved the volumes of drops rather than their weights, owing to the greater experimental convenience of the former. The apparatus assembly consisted essentially of a glass helical spring made of 4-mm. Pyrex tubing, which connected a calibrated measuring pipet with the tip upon which the drops formed. The spring consisted of 7 coils of 30 cm. diameter and had a total vertical uncoiling range of 15 cm. The liquids were caused to flow from the measuring pipet through the spring to the tip by uncoiling the former, thereby increasing the hydrostatic head. A screw device actuated the movable spring-pipet portion of the system vertically and enabled the operator to control

the rate of drop formation with great exactness. A series of interchangeable tips and measuring pipets permitted the measurement of a wide variety of liquids representing a considerable range of densities. Since the aqueous phase wetted the tip the best, it was chosen as the drop-forming liquid. The experimental procedure was exactly the same as previously described.[6]

In previous studies the four lowest esters of the monohalogen acetic acids were measured. It was not possible, however, to measure all of the corresponding esters of monofluoroacetic acid. The methyl ester is completely miscible with water in all proportions and, therefore, forms no interface with the latter. When water and n-butyl fluoroacetate are mutually saturated, their densities closely approach each other and are identical at 43.3°. As a consequence, the drops which formed, even from very small tips, were very large and failed to break away from the tip at such extreme temperatures as 8 and 90°, which are the limits at which measurements are possible. When the drops become too large, they tend to rotate slowly and erratically about and above the tip in the liquid medium. Under these conditions, it is impossible to maintain a condition of approximate static equilibrium during the final stages of the formation of the drop. It was only possible, therefore, to measure the interfacial tensions of the ethyl and n-propyl esters against water. Due to the actinic effects on the esters of monoiodoacetic acid, the interfacial tension measurements were carried out as rapidly as possible in subdued light.

Results and Discussion

The equation applied in calculating the interfacial tensions[8] follows

$$\gamma_i = vg(d_o - d_w)/2\pi r F$$

where γ_i is the interfacial tension in ergs per sq. cm., v the drop volume in ml., d_o the density of the organic liquid saturated with water, d_w the density of the water saturated with the organic liquid, g the gravity factor, r the radius of the tip in cm., F the Harkins correction factor. The interfacial tension data are tabulated in Table I. The table is followed by the empirical temperature–interfacial tension equations which were formulated from least squares. For a given tip at a constant temperature, the above equation may be reduced to the form

$$\gamma_i = kv(d_o - d_w)$$

It is evident that the magnitude of γ_i is directly proportional to the drop volume v and to the effective density $(d_o - d_w)$. Since the drop volume is proportional to the mass, large drops should give large values of γ_i. This effect, however, may offset by a small effective density, a fact clearly shown by the data of the fluoroesters which formed large drops. The volumes of the drops decreased progressively from the ethyl fluoroacetate to the n-butyl iodoacetate. This necessitated the substitution of larger tips as the molecular weights of the organic compounds increased, in order to maintain the Harkins correction factor within the optimum range of maximum accuracy. In this, as in previous interfacial tension studies,[6,9] involving the esters of the monohalogen acetic acids, the authors have found that within an homologous series for a given temperature, the effective densities decreased and the interfacial tensions increased with increasing molecular weights of the organic compounds.

The data given in Table I for the two esters of monofluoroacetic acid are the average of at least

(6) J. J. Jasper and W. J. Mayer, This Journal, **72**, 4767 (1950).

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

(8) W. D. Harkins and Y. C. Cheng, ibid., **43**, 35 (1921).

(9) J. J. Jasper and W. J. Mayer, ibid., **73**, 2610 (1951).

TABLE II

VALUES OF SOME THERMODYNAMIC PROPERTIES OF THE
ESTER-WATER INTERFACES (ERGS/CM.²)

Ester	Temp., °C.	$-(d\gamma_i/d_i)$	(l)	h
Ethyl	24.6	0.0116	3.5	13.2
fluoro-	26.8	.0142	4.3	14.0
acetate	42.6	.0328	10.4	19.7
	55.4	.0479	15.6	24.6
	60.3	.0547	18.2	26.9
	70.4	.0657	22.6	30.6
n-Propyl	24.6	0.0051	1.5	15.6
fluoro-	26.8	.0100	3.0	17.1
acetate	42.6	.0382	12.0	25.8
	55.4	.0612	20.1	33.2
	60.3	.0698	23.3	36.0
Methyl	24.6	0.0000	..	16.2
iodo-	42.6	.0283	8.9	24.9
acetate	55.4	.0505	16.6	32.0
	60.3	.0588	19.6	34.8
Ethyl	24.6	0.0105	3.1	21.4
iodo-	42.6	.0261	8.2	26.2
acetate	55.4	.0372	12.2	29.7
	60.3	.0414	13.8	31.1
n-Propyl	24.6	0.0093	2.8	25.8
iodo-	42.6	.0153	4.8	27.6
acetate	55.4	.0194	6.4	28.9
	60.3	.0211	7.0	29.5
n-Butyl	24.6	0.0464	13.8	39.9
iodo-	42.6	.0545	17.2	42.6
acetate	55.4	.0601	19.8	44.2
	60.3	.0624	20.8	44.9

five independent measurements for each of the temperatures given. Repeated measurements with the same identical ester–water systems over the same temperature range on succeeding days gave the same interfacial tension values as those obtained initially. The interfacial tension of the n-propyl fluoroacetate was determined at three temperatures only. At 55.4° the effective density was 0.0148. Above this temperature the effective density decreased rapidly and the drops became so large that they could not be measured.

Since the esters of monoiodoacetic acid are less stable, the interfacial tension measurements were carried out in subdued light in order to reduce the actinic effects to a minimum. The interfacial tension values tabulated in Table I are the average

of at least four independent measurements. After standing for several days, it was observed that the esters had changed to a faint yellow color. When redistilled with a small globule of mercury in the receiving flask, a clear colorless product was again obtained which gave interfacial tension values the same as the originals.

The form of the empirical equations which relate the interfacial tensions to the temperature, indicate that the decrease in the interfacial tensions with increasing temperature is not linear. This may be attributed to an increasing tendency of the two molecular species to escape through the transition region into the adjacent phases as a result of their increased translational velocities. Therefore, with rising temperature, the contiguous phases become increasingly similar, but, apparently, not at the same rate, as judged by the fact that the curves are concave to the temperature axis. An interpretation of the shapes of these curves unquestionably involves a complex relation between temperature, solubilities and molecular orientation in the transition region.

The empirical equations were applied in calculating the temperature coefficients of the interfacial tensions $(d\gamma_i/d_i)$ for the temperature range employed. On the assumption that the thermodynamics of liquid surfaces apply as well to liquid–liquid interfaces, these coefficients were applied in the two-dimensional form of the Clapeyron equation[10] to calculate the latent heat (l) attending the formation of each sq. cm. of the interfacial surface over the same temperature range. Since the change of the volumes of the liquid components is negligible when the interfacial area is changed by 1 sq. cm. under isothermal and isobaric conditions, it was also possible to calculate the enthalpy (h) from the equation of the total surface energy, since under the given restrictions the two are practically equal.[11] The energy values are found in Table II. It is to be noted that the slopes of all temperature–interfacial tension curves are negative; therefore, the enthalpy values are positive. This indicates that energy is absorbed when the interfacial areas are extended.

(10) R. H. Bogue, "Colloidal Behavior," Vol. I, 1st Ed., McGraw-Hill Book Co., Inc., New York. N. Y., 1924. p. 144.

(11) Ref. 5, p. 153.