The behavior of 2-fluoroquinoline in acid solution suggested that the other 2-halo derivatives might react similarly. However, identical spectra of 2-chloroquinoline were obtained in neutral and 0.01 *M* HCl solutions. These results led to the measurement of the spectrum of the compound in 6 *M* HCl in an effort to obtain evidence of hydrolysis in a strongly acid solution. A marked shift of the spectrum was evident, but it bore no resemblance to that of carbostyril. However, since the solution was so strongly acid, the curve could represent the absorption of the hydrochloride of either 2-chloroquinoline or carbostyril. To distinguish between the two, the solution was neutralized with calcium carbonate; the excess calcium carbonate was filtered off and washed, the washings being added to the filtrate. The solution was then diluted to twice its original volume, after having added enough hydrochloric acid to make the final concentration of the solution 0.01 *M* with acid. The spectrum of this solution was measured, and a curve which was almost identical with that of 2-chloroquinoline in neutral and 0.01 *M* HCl solutions was obtained. Consequently, it is concluded that 2-chloroquinoline is not hydrolyzed in acid solution at normal temperatures as is 2-fluoroquinoline, but that the former compound will form a hydrochloride if made strongly acid.

Experimental

Absorption Spectra.—The spectra were measured and plotted using the same technique as previously described[1]; the haloquinolines and the solvents were also the same.

***p*H Measurements.**—The *p*H measurements were made with a Beckman Glass Electrode *p*H Meter, Model M, Serial No. 17082, with a saturated calomel electrode as reference electrode. The *p*H meter was standardized at *p*H 3.57 with a saturated solution of potassium hydrogen tartrate.[6]

Acknowledgment.—This work is part of a study of the preparation and properties of heterocyclic fluorine compounds being carried out at this Laboratory, and was supported in part by the Office of Naval Research.

Summary

1. Spectrophotometric evidence has indicated that 2-fluoroquinoline is hydrolyzed to 2-hydroxyquinoline in acid solution, the rate of hydrolysis increasing with increasing acid concentration; the spectrum undergoes further change in very strongly acid solution, probably caused by the formation of the salt of 2-hydroxyquinoline.

2. Spectral measurements have indicated that 2-chloroquinoline is not hydrolyzed in acid solution at normal temperatures but will form a hydrochloride if made strongly acid.

(6) Lingane, *Anal. Chem.*, **19**, 810 (1947).

CHAPEL HILL, N. C. RECEIVED APRIL 26, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

The Effect of Temperature on the Thermodynamic Properties and Interfacial Tension of Water with Some Alkyl Esters of Monochloroacetic Acid[1]

BY JOSEPH J. JASPER AND WILLIAM J. MAYER

The interfacial tensions of many organic liquids against water have been determined and reported in the literature. Such data, however, are not available, especially for ranges of temperature. Neither is there appreciable evidence of systematic study and correlation of interfacial tension data with properties of the two molecular species involved in the formation of the interface, regardless of its numerous applications in theoretical and industrial chemistry. The purpose of this investigation was to obtain the interfacial tensions of a series of esters of monochloroacetic acid with water over an appreciable temperature range, and to formulate empirical equations relating these variables. With these data it was possible to calculate the entropy, latent heat and total energy attending the formation of the interfacial surface. This is the first of a series of such studies which will subsequently include the same esters of different monohalogen acetic acids—compounds which possess groups of variable electronegativity at the ends of the molecules.

Experimental

Preparation and Purification of the Esters.—The methyl, ethyl, *n*-propyl and *n*-butyl esters of monochloroacetic acid were used in this investigation. Eastman Kodak Company white label grades of the methyl and ethyl esters were obtained, while the *n*-propyl and *n*-butyl esters were prepared by the method of Fieser.[2] For final purification of the esters, the vacuum fractionation methods described by Morton[3] were employed. A 15-inch column was used, which was packed with single-turn glass helices and fitted with a total reflux variable take-off head. The middle third, the fraction which boiled at constant temperature, was collected for use.

To test the purity of the esters, time–temperature cooling curves were constructed according to the method described by Morton.[4] Purity was judged by the flatness of the temperature horizontal since the weight per cent. purity can be determined only if the nature of the impurity

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Detroit meeting of the American Chemical Society, April, 1950.

[2] L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, 1944, p. 133.

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

[4] A. A. Morton, *ibid.*, p. 40.

is known. All esters had a constant-temperature horizontal of 2.5 to 3 minutes, and these horizontals were comparable with that given by a sample of bromobenzene of known purity under equivalent conditions.

Determination of the Densities.—Densities were determined with a slightly modified form of the "type D" pycnometer recommended and described by Weissberger.[5] Three pycnometers were used, each having a volume of about 20 ml. One was reserved for the ester saturated with water, the second for the water saturated with ester, and the third as a counterpoise. These were calibrated with water specially prepared for this purpose.[6] The esters and water were mutually saturated by vigorously shaking 25 ml. quantities of each together, after which they were kept in contact for at least 24 hours.

The liquids were introduced into the pycnometers by means of a 50-ml. hypodermic syringe equipped with a 12 cm., 20-gage, stainless-steel needle, which could be inserted the whole length of the capillary neck. In each case the liquid was introduced to a point somewhat below the reference mark since expansion into the capillary neck took place after the pycnometer was immersed in the water-bath. The excess liquid above the reference mark was removed with the aid of the syringe after thermal equilibrium was attained. The densities are shown in Table I.

TABLE I

DENSITY DATA FOR THE MUTUALLY SATURATED LIQUID COMPOUNDS

Ester	Temperature, °C.	Density: Ester saturated with water	Density: Water saturated with ester
Methyl	26.8	1.2223	1.0083
	42.6	1.2003	1.0034
	55.2	1.1879	0.9982
	70.4	1.1616	0.9902
Ethyl	25.7	1.1429	1.0019
	42.6	1.1216	0.9960
	55.2	1.1054	.9904
	70.4	1.0859	.9823
n-Propyl	25.7	1.0944	.9978
	42.6	1.0743	.9923
	55.2	1.0590	.9869
	70.4	1.0409	.9791
n-Butyl	26.8	1.0623	.9970
	42.6	1.0450	.9918
	55.2	1.0312	.9862
	70.4	1.0142	.9787

To maintain constant temperature, a specially constructed, glass-wool insulated, water-bath was used. The stirring system was sufficiently efficient, and the thermoregulators sensitive enough, to maintain a temperature constant to 0.02° between 25° and 40°, and to 0.05° up to 90°. Four different temperature regulators were used, each of which was set at a different temperature so that the data could be rechecked at exactly the same temperature previously used.

Determination of Interfacial Tension.—A modification of the drop-volume method of Harkins and Brown[7] was used in this investigation. A series of measuring pipets having capillaries with bores ranging from 1 to 5 mm. and bulb capacities of 3 to 5 ml. were used. The bulbs and attached capillary tubes were calibrated separately, and two reference marks etched on the latter both above and below the bulb.

A spring constructed of 4 mm. pyrex tubing, consisting of 7 coils of 30 cm. diameter, permitted vertical motion of the measuring pipets through a range of 15 cm. with the drop-forming tip stationary. A device for actuating the pipets, similar to that employed by Harkins,[8] effectively controlled the motion of the spring through which the drop-liquid flows, and enabled the operator to vary the rate of drop formation with such accuracy that they broke away from the tip under conditions approaching static equilibrium.

Since the aqueous phase wetted the tip best, it was chosen to form the drops. The tip was arranged, therefore, so that the drops formed vertically upward, subsequently breaking away and passing upward through the more dense organic liquid. The pipet and tip chosen delivered 30 drops, and 4 to 10 complete determinations were made at each temperature over the range employed. Eighteen hours were required to make the measurements for each ester at the four temperatures. To test for hydrolysis, the interfacial tension measurements were repeated on three consecutive days, using the identical ester-water systems over the entire temperature range. The average of the interfacial tension values for each temperature on the third day was the same as those obtained initially. *p*H measurements of the water phases likewise showed no significant change over this same period.

Results and Discussion

The equation used for calculating the interfacial tensions of the organic liquid against water[9] is

$$\gamma_i = V(d_1 - d_2)g/2\pi rF$$

where γ_i represents the interfacial tension in ergs/sq. cm.; V the drop volume in ml.; d_1 the density of the organic liquid phase; d_2 the density of the aqueous phase; g the gravity factor; r the radius of the tip in cm.; $F = \psi(r/V^{1/3})$ the Harkins correction factor.

The Harkins correction factor was determined by plotting a series of $(r/V^{1/3})$ values against F values on a large scale for the range of correction factors needed. After determining the drop volume and the corresponding value of $(r/V^{1/3})$, the correction factor was obtained directly from the graph. The interfacial tension–temperature data are tabulated in Table II. The temperature–interfacial tension relations are shown by the empirical equations

TABLE II

THE INTERFACIAL TENSIONS OF THE ORGANIC LIQUIDS AGAINST WATER (ERGS/SQ. CM.)

Chloroacetate	Temperature 26.8°	42.6°	55.2°	70.4°
Methyl	11.9 ± 0.10	11.0 ± 0.09	10.2 ± 0.09	8.9 ± 0.09
Ethyl	15.9 ± .08	15.4 ± .08	14.8 ± .08	13.9 ± .07
n-Propyl	19.8 ± .09	19.2 ± .08	18.6 ± .09	17.3 ± .09
n-Butyl	22.4 ± .11	21.8 ± .11	21.2 ± .12	20.7 ± .14

Methyl chloroacetate:

$$\gamma_i = 13.25 - 0.0448t - 0.0001950t^2$$

Ethyl chloroacetate:

$$\gamma_i = 16.66 - 0.0206t - 0.0002525t^2$$

n-Propyl chloroacetate:

$$\gamma_i = 20.53 - 0.0130t - 0.0004000t^2$$

n-Butyl chloroacetate:

$$\gamma_i = 23.27 - 0.0303t - 0.0001100t^2$$

From these equations it is seen that the inter-

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

[6] A. Weissberger, *ibid.*, p. 72.

[7] W. D. Harkins and F. E. Brown, THIS JOURNAL, **41**, 499 (1919).

[8] This apparatus is described and illustrated by Weissberger in his book, p. 174; see ref. 5.

[9] W. D. Harkins and Y. C. Cheng, THIS JOURNAL, **43**, 35 (1921).

TABLE III

VALUES OF SOME THERMODYNAMIC PROPERTIES OF THE ESTER–WATER INTERFACES

Temp., °C.	Methyl chloroacetate			Ethyl chloroacetate			*n*-Propyl chloroacetate			*n*-Butyl chloroacetate		
	$d\gamma_i/dt$	L	E	$d\gamma_i/dt$	L	E	$d\gamma_i/dt$	L	E	$d\gamma_i/dt$	L	E
26.8	−0.0552	16.61	28.51	−0.0341	10.26	26.16	−0.0344	10.35	30.15	−0.0362	10.89	33.29
42.6	− .0614	19.38	29.38	− .0421	13.29	28.69	− .0470	14.84	34.04	− .0397	12.53	34.33
55.2	− .0663	21.77	31.97	− .0484	15.89	30.69	− .0572	18.78	37.38	− .0424	13.92	35.12
70.4	− .0722	24.80	33.70	− .0562	19.30	33.20	− .0693	23.80	41.50	− .0458	15.73	36.43

facial tensions decrease with increasing temperature, but not linearly. Since the interfacial tension is influenced by mutual solubility of the liquid compounds, and the solubility is in turn dependent on the temperature, it is to be expected that departure from strict linearity is due, at least partially, to the solubility factor. With the aid of the empirical equations, it was possible to calculate the entropy ($d\gamma_i/dt$), latent heat (L), and total energy (E) attending the formation of 1 sq. cm. of the interfacial surfaces over the temperature range given. These are shown in Table III, with all energy values expressed in ergs.

Since for saturated surfaces, the latent heat L is related to the temperature coefficients by the equation $L = -T(d\gamma_i/dt)$, the latent heat may be positive or negative—positive when the interfacial tension decreases with the temperature and negative when it increases. The esters of this series have positive values of L, and it is evident, therefore, that energy is utilized when the interface is extended. The effect of increasing the length of the ester chain on the solubility of the compound is clearly reflected in the increasing values of the interfacial tension in passing from the methyl to the butyl ester at any given temperature. It might be expected, therefore, that the methyl ester of the fluorine substituted acetic acid would be completely soluble in water. This was found to be the case.

Summary

The interfacial tensions of the methyl, ethyl, *n*-propyl and *n*-butyl esters of monochloroacetic acid were measured against water at the temperatures 26.8, 42.6, 55.2 and 70.4°, and the procedure briefly described. Density and interfacial tension data for these temperatures are tabulated in respective tables. An empirical equation relating the interfacial tension and temperature was formulated for each of the esters. The equations were applied in the calculation of the entropy, latent heat, and total energy of formation per sq. cm. of the interface, and these values were presented in a table.

DETROIT, MICHIGAN RECEIVED APRIL 18, 1950

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Copolymerization in Emulsion[1]

BY F. T. WALL, R. E. FLORIN AND C. J. DELBECQ

A great many copolymerization systems have been investigated up to the present time, and it appears that in most instances the compositional relationships involved are adequately described by a copolymerization equation[2,3,4] which in differential form is

$$\frac{dM_1}{dM_2} = \frac{M_1(r_1M_1 + M_2)}{M_2(M_1 + r_2M_2)} \qquad (1)$$

In the above equation M_1 and M_2 represent the unreacted amounts of the two monomers and r_1 and r_2 are ratios[5] of certain specific reaction rate constants characteristic of the particular system. From its derivation it might be expected that equation (1) would hold only for single phase polymerizations; it is observed empirically, however, that it also describes emulsion copolymerizations providing r_1 and r_2 are given proper values which are generally different from those observed for single phase reactions. It is a matter of some interest, therefore, to ascertain the reasons for the success of equation (1) in emulsion systems assuming that it has more than empirical validity. Theoretically equation (1) should hold in the immediate environment of the reaction providing M_1 and M_2 are taken as concentrations in that neighborhood. This suggests that an explanation of why the equation works for the over-all system might be obtained by examining such factors as monomer solubilities in those regions of an emulsion which might conceivably serve as reaction loci.

As a result of some earlier work by Wall and co-workers[6] on the emulsion polymerization of rubber-like copolymers, it was suggested that the polymerization reaction might occur in the aqueous phase. Under those circumstances,

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[1] This work was carried out under sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944).

[3] Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

[4] Wall, THIS JOURNAL, **66**, 2050 (1944).

[5] Alfrey, Mayo and Wall, *J. Polymer Sci.*, **1**, 581 (1946).

[6] Wall, Powers, Sands and Stent, THIS JOURNAL, **70**, 1031 (1948).