investigating gas imperfection and were the essential element in the solution of this long baffling problem.

While it has been shown that the thermodynamic data are consistent with these spectroscopic constants, other values of the spectroscopic quantities within certain limits are allowed. It seems hardly worth while to investigate this extensively at present. Nevertheless, even though the principal dilemma concerning the potential barrier and entropy of methanol is now removed, the exact 932 cal./mole value for the barrier is only as certain as the spectroscopic data indicate. Considering the uncertainty in the vibration frequency assignment, the thermodynamic data might be consistent with any barrier within a few hundred calories of this 932 cal. figure. Moreover, if the moment of inertia of the OH group (for torsion) is substantially larger than the 1.01×10^{-40} here assumed, then an appreciably higher barrier would be indicated. This moment of inertia requires either an abnormally large C–O–H angle or an abnormally short O–H distance.

Acknowledgments.—We wish to acknowledge the great assistance of Dr. Gordon M. Barrow in the construction of the calorimeter and in making available to us the second set of thermometer calibrations mentioned above. We also wish to thank Professor W. D. Gwinn for his helpful advice and guidance, particularly while one of us (K. S. Pitzer) was away from Berkeley.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

The Temperature–Interfacial Tension Studies of Some Alkyl Esters of Monobromoacetic Acid against Water[1]

BY JOSEPH J. JASPER AND WILLIAM J. MAYER

This is the second of a series of interfacial tension studies of the methyl, ethyl, *n*-propyl and *n*-butyl esters of the monohalogenated acetic acids against water. The present paper involves the interfacial tension measurements of the above esters of monobromoacetic acid at four temperatures between 26.8 and 70.4° against water, the two liquids being mutually saturated. With the aid of least squares, empirical equations were formulated which relate the interfacial tensions to the temperature. The data are tabulated in density–temperature and interfacial tension–temperature tables. The empirical equations were used to calculate the latent heat and enthalpy of formation per sq. cm. of interfacial surface. These are presented in a table.

Although the interfacial tensions of many organic liquid compounds measured against water have appeared in the literature, such data are generally inadequate since they include no appreciable temperature ranges nor present any correlation with the properties of the molecular species involved. As a consequence, interfacial tension data, of potentially great usefulness in numerous aspects of theoretical and industrial chemistry, are meager or non-existent.

The purpose of this investigation was to obtain interfacial tension data for the lower esters of monobromoacetic acid with water over an appreciable temperature range, and to formulate empirical equations relating these variables. The present study represents the second of a series[2] which will eventually include the corresponding esters of other monohalogen acetic acids, and also other homologous series containing substituted halogen groups.

Experimental

Preparation and Purification of the Ester.—The methyl, ethyl, *n*-propyl and *n*-butyl esters of monobromoacetic acid were used in this study. The methyl and ethyl esters were obtained from the Eastman Kodak Company, while the *n*-propyl and *n*-butyl esters were prepared by us. The method of preparation was that of Fisher as described by Fieser and Fieser.[3] The esters were subjected to vacuum fractionation for their final purification. The apparatus and procedure were exactly the same as previously described for the four alkyl esters of monochloroacetic acid.[2]

Determination of the Densities.—The densities play an important role in the determination of interfacial tension. Since they appear in the equation as explicit variables, they must be determined directly and accurately. A modified form of the "type D" pycnometer described by Weissberger[4] was used. Three pycnometers were constructed as nearly alike as possible in form and dimensions. Two of these were used for the respective mutually saturated liquids and the third as a counterpoise. Repeated trials showed a deviation in the densities no greater than 0.05 per cent. even

TABLE I

DENSITY DATA FOR THE MUTUALLY SATURATED LIQUID COMPOUNDS

Ester	Temp., °C.	Density	
		Ester saturated with water	Water saturated with ester
Methyl	26.8	1.6408	1.0159
	42.6	1.6135	1.0103
	55.2	1.5902	1.0047
	70.4	1.5628	0.9972
Ethyl	26.8	1.4947	1.0028
	42.6	1.4695	0.9972
	55.2	1.4501	.9918
	70.4	1.4254	.9835
n-Propyl	26.8	1.4024	.9984
	42.6	1.3796	.9929
	55.2	1.3615	.9875
	70.4	1.3394	.9800
n-Butyl	26.8	1.3366	.9974
	42.6	1.3158	.9921
	55.2	1.2994	.9867
	70.4	1.2789	.9787

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(1) Presented before the Division of Physical and Inorganic Chemistry at the Chicago meeting of the American Chemical Society, September 1950.

(2) J. J. Jasper and W. J. Mayer, THIS JOURNAL, **72**, 4767 (1950).

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

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

at the higher temperatures where the least accuracy might be expected. The procedure employed was similar to that described previously.[2] Four thermoregulators, each set at a different temperature, facilitated rechecking of data. The exact temperatures were read from NBS certified thermometers. The densities are shown in Table I.

Determination of Interfacial Tension.—For measuring the interfacial tensions, a modification of the drop-weight method of Harkins and Brown was used.[5] The method involved drop volumes rather than weights because of the greater experimental convenience of the former. The apparatus consisted essentially of a glass spring, a series of glass tips upon which the drops formed, a series of measuring pipettes, a receiving tube, and a device for actuating the spring-pipet system. The experimental procedure was exactly the same as previously described.[3] To test for possible decomposition of the esters, measurements were repeated with the same identical mutually saturated liquids over the same temperature range for three consecutive days. The results were constant.

Results and Discussion

The tables contain the data for the four bromoesters. The empirical temperature–interfacial tension equations were formulated by using the method of least squares. The observed values, from which the empirical equations were determined, were averages of at least five independent measurements for each temperature in the range employed. The interfacial tension values of the esters against water, together with the empirical temperature equations for the temperature range 26.8 to 70.4°, are shown in Table II.

TABLE II

INTERFACIAL TENSIONS OF THE ORGANIC LIQUIDS AGAINST WATER (ERGS./CM.^{2})

Bromoacetate	Temperature 26.8°	42.6°	55.2°	70.4°
Methyl	13.3 ± 0.28	13.0 ± 0.28	12.3 ± 0.26	11.2 ± 0.26
Ethyl	17.6 ± 0.23	16.7 ± 0.22	16.0 ± 0.22	15.0 ± 0.21
n-Propyl	21.9 ± 0.20	21.3 ± 0.19	20.6 ± 0.16	19.6 ± 0.17
n-Butyl	23.8 ± 0.17	23.3 ± 0.16	22.8 ± 0.16	22.0 ± 0.15

Methyl bromoacetate: $\gamma_i = 13.15 + 0.0249t - 7.63 \times 10^{-4}t^2$

Ethyl bromoacetate: $\gamma_i = 18.72 - 0.0375t - 2.18 \times 10^{-4}t^2$

n-Propyl bromoacetate: $\gamma_i = 22.28 - 1.85 \times 10^{-3}t - 5.10 \times 10^{-4}t^2$

n-Butyl bromoacetate: $\gamma_i = 24.13 - 4.8 \times 10^{-4}t - 4.3 \times 10^{-4}t^2$

From reference to these equations, it is clear that the decrease in the interfacial tensions with temperature is not linear. Since the interfacial tension is influenced by mutual solubility of the respective liquid compounds, and the solubility, in turn, increases with the temperature, departure from linearity is due, at least in part, to the solubility factor.

With the aid of the empirical equations, it was possible to calculate the entropy ($d\gamma/dt$), latent heat (L), and the enthalpy (H) attending the formation of each sq. cm. of interfacial surface over the temperature range employed. The last two of these are shown in Table III.

TABLE III

VALUES OF SOME THERMODYNAMIC PROPERTIES OF THE ESTER–WATER INTERFACES (ERGS./SQ. CM.)

Temp., °C.	Methyl bromoacetate *L*	*H*	Ethyl bromoacetate *L*	*H*	*n*-Propyl bromoacetate *L*	*H*	*n*-Butyl bromoacetate *L*	*H*
26.8	4.8	18.1	14.8	32.4	8.8	30.7	7.1	30.9
42.6	12.7	25.6	17.7	34.4	14.3	35.6	11.8	35.1
55.2	19.5	31.8	20.2	36.2	19.1	39.7	15.8	38.6
70.4	28.4	39.7	23.4	38.4	25.4	45.0	21.0	43.0

For a saturated surface the latent heat L is related to the temperature coefficient by the equation, $L = -T(d\gamma/dt)$. Thus, L may have either a positive or a negative value. Since the interfacial tensions of the bromoesters have negative temperature coefficients, the corresponding values of L are positive, indicating that energy is utilized in the formation of the interface. The entropy, and also the temperature derivative of the latent heat, is positive.

DETROIT, MICHIGAN

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(5) A. Weissberger, ref. 4, p. 172.

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

Dissociation Constants of Adrenergic Amines[1]

BY ESTHER B. LEFFLER,[2] HUGH M. SPENCER AND ALFRED BURGER

Basic dissociation constants of a representative group of twenty-seven adrenergic amines have been determined. No obvious correlation between pressor activity and basicity has been found.

An attempt to correlate pharmacodynamic and electropolar properties might shed some light on the mode of action of adrenergic amines. We are reporting basic dissociation constants for twenty-seven adrenergic amines as a contribution to this question.

Experimental

Most of the compounds used in this study were kindly supplied by Smith, Kline and French Laboratories, Philadelphia, Pa.; six were obtained from Sterling-Winthrop Research Institute, Rensselaer, N. Y. Most of them were in the form of salts. Free bases were converted into the hydrochlorides by neutralization of an ethereal solution of the amine. The salts were recrystallized from absolute ethanol, precipitating with absolute ether, unless otherwise noted. The compounds were considered to be sufficiently pure when they had been recrystallized to constant melting point, and their analyses agreed with the calculated values.

The apparent dissociation constants of the amines were determined by measuring the *p*H of a solution containing equivalent concentrations of the amine and its salt. These solutions were obtained by adding to a solution of the salt the calculated amount of sodium hydroxide solution required for half-neutralization. The concentrations ranged from 0.0003–0.001 molal in salt and free base at the half-neutralization point. The *p*H values were measured with a hydrogen electrode or a *p*H meter. With the several com-

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(1) Part of a dissertation presented to the Graduate Faculty of the University of Virginia by Esther B. Leffler in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1950.

(2) Philip Francis du Pont Senior Fellow, 1947–1948, Department of Chemistry, Randolph-Macon Women's College, Lynchburg, Virginia.