

electrical resistance higher than a critical value which he believes is about 3 ohms, it becomes effective in inhibiting further attack whereas a thinner film with a smaller resistance is not effective. The data of Fig. 1 are at least qualitatively consistent with these general views because it is evident that in the range of higher concentration (pressure) the amount adsorbed at a given concentration (pressure) is greater on the reduced surface. That is, any fresh iron exposed by acid attack in a pickling bath may become covered with a relatively thick layer of inhibitor whereas the oxide surfaces are covered with a thinner film. Moreover, if there is orientation on the iron surface the exposed part may be the relatively inert ethyl group. This suggests that dipole moment and polarizability may be significant factors in inhibitor action and that a study of these properties may show some correlation with the effectiveness of different organic compounds.

Summary

The adsorption of ethyl iodide on a plane surface of unreduced and reduced iron has been determined at 20° over the pressure range 10⁻⁶ to 1

mm. The adsorption isotherms fit Langmuir's equation and Palmer's relation only at intermediate pressures. The coverage at apparent saturation is about 100% based on the geometric area of the sample, which indicates that the iron surface is substantially plane.

Force-area curves for the two surfaces are quite different; that on the unreduced surface resembles the curves for insoluble films on water and shows a break at an area of about 30 sq. Å. per molecule whereas that on the reduced surface shows no such break. Comparison of the curves with that for an ideal two-dimensional gas suggests that on the unreduced surface the intermolecular forces are predominantly of the van der Waals type whereas on the reduced surface dipole repulsion seems to be the primary factor.

The molar heat of adsorption calculated from the isotherms is 11,800 cal. for the reduced iron and 12,200 cal. for the unreduced surface.

Although the temperature of measurement was well below the critical temperature, no critical phenomena were observed.

The possible bearing of the results on the action of inhibitors is discussed.

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RECEIVED NOVEMBER 9, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Boiling Point Elevation. III. Sodium Chloride 1.0 to 4.0 *M* and 60 to 100°¹

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The activity coefficient of sodium chloride has been determined at 0° from measurements of the freezing point depression,³ and at 25° from electromotive force^{4,5} and isopiestic vapor pressure measurements.^{6,7} In 1932 Harned and Nims⁸ extended the electromotive force measurements over the temperature range 0 to 40°. Harned and Cook⁹ have reconsidered the calculation of the activity coefficient from the data of Harned and Nims,⁸ and shown that the activity coefficients

so obtained are consistent with the values given by other investigators at 0 to 25°. The data for sodium chloride have been extended further to cover the temperature range 60 to 100° by a determination of the boiling point elevation.¹⁰ These results have been shown to be consistent with those of Harned and Cook⁹ for the concentration range 0.05 to 1.0 *M*. To complete the measurements we have determined the boiling point elevation of sodium chloride solutions for the concentration range 1.0 to 4.0 *M* and at temperatures between 60 and 100°. It has been pointed out by Harned and Cook⁹ that the values of \bar{L}_2 derived from the temperature coefficients of the electromotive force measurements appear to change too rapidly with the temperature. A consideration of all of these results not only allows a more reliable estimation of \bar{L}_2 and $\bar{C}_p - \bar{C}_{p0}$, but

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(3) Scatchard and Prentiss, *THIS JOURNAL*, **55**, 4355 (1933).

(4) Harned, *ibid.*, **51**, 416 (1929).

(5) Brown and MacInnes, *ibid.*, **57**, 1356 (1935).

(6) Robinson and Sinclair, *ibid.*, **56**, 1830 (1934).

(7) Scatchard, Hamer and Wood, *ibid.*, **60**, 3061 (1938).

(8) Harned and Nims, *ibid.*, **54**, 423 (1932).

(9) Harned and Cook, *ibid.*, **61**, 495 (1939).

(10) Smith, *ibid.*, **61**, 500 (1939).

also permits their determination over a much greater range of temperature.

The boiling point elevations were determined with an apparatus essentially the same as the one described by Smith.¹¹ The e. m. f. of the 26-junction thermel was read to $\pm 1.0 \mu v.$ ($\pm 0.001^\circ$ in temperature) with a "Queen" potentiometer.

Osmotic Coefficients.—The osmotic coefficient at a temperature $T_0 + \theta$, and at the saturation pressure of steam at a temperature T_0 , is given as a function of the boiling point elevation θ by the equation¹⁰

$$\varphi' = 55.5074 \Delta H_0 \theta / \nu RT_0^2 m (1 - b'\theta / 2\Delta H_0 + \dots) \quad (1)$$

The osmotic coefficient as a function of the activity coefficient is given by

$$\varphi = 1 - 1/m \int_0^m m d \ln \gamma \quad (2)$$

In Fig. 1 the values of φ' as determined from the boiling point elevations and equation (1) are plotted together with φ as determined by equation (2) from the activity coefficients of Harned and Nims⁸ relative to $\gamma_{0.1}$ as given by equation (3) of Harned and Cook.⁹ The circles, diameter

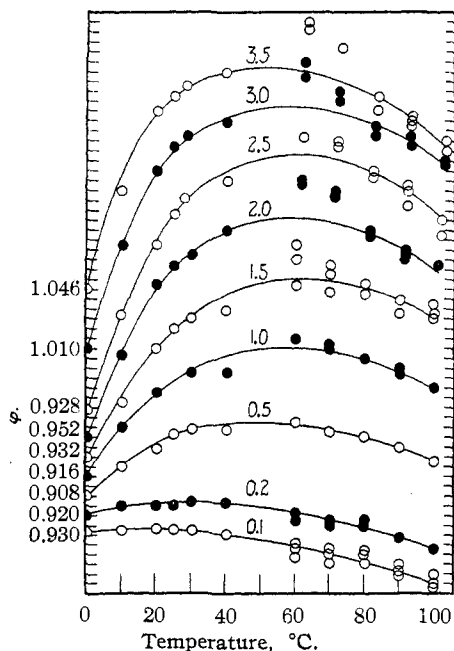


Fig. 1.—Osmotic coefficients; 0 to 40° electromotive force, 60 to 100° boiling point elevation; \circ , ± 0.001 .

± 0.001 , for the temperature range 60 to 100° represent φ' as determined from the experimental values of θ . The smooth curves represent our

(11) Smith, *THIS JOURNAL*, **61**, 497 (1939).

estimate of the probable values of φ . The reproducibility of the boiling point elevations was of the order of 0.005° . From equation (1) for $T_0 = 333.16$, $m\Delta\varphi'$ is approximately equal to $1.3\Delta\theta$, thus the derivations of our experimental results from the smooth curve at 60° correspond to about 0.02° at concentrations of 3.5 and 4.0 M , and decrease to 0.005° at 1.5 M . The deviations at 70° are about one-half their value at 60°. This trend toward a high value for θ at the lower temperatures also exists in the more accurate results at the lower concentrations.¹⁰ The reproducibility of the elevation for the 1.0 M solution at 60° was of the order of 0.0003° , the deviation in θ as shown by the φ plot is about 0.0006° . The reason for this trend in θ at the lower temperatures is not apparent. The maximum error in the electromotive force results at 40° as judged from the corresponding plot of the activity coefficients amounts to 0.3 mv. The smoothed values of φ as read from a large scale plot of Fig. 1 are given in Table I.

TABLE I

OSMOTIC COEFFICIENTS

m	φ_{60}	φ_{70}	φ_{80}	φ_{90}	φ_{100}
1.5	0.968	0.968	0.966	0.963	0.960
2.0	.999	.998	.995	.991	.986
2.5	1.031	1.029	1.026	1.022	1.016
3.0	1.061	1.059	1.057	1.053	1.048
3.5	1.092	1.090	1.086	1.082	1.077
4.0	1.130	1.127	1.120	1.113	1.105

Activity Coefficients.—The activity coefficients in the temperature range 60 to 100° were determined from the relation¹⁰

$$\ln \gamma' = \varphi' - 1 + \int (\varphi' - 1) d \ln m \quad (3)$$

The experimental values of γ are given in Table II.

TABLE II

ACTIVITY COEFFICIENTS

m	γ_{60}	γ_{70}	γ_{80}	γ_{90}	γ_{100}
1.5	0.662	0.656	0.646	0.638	0.629
2.0	.683	.672	.663	.651	.641
2.5	.707	.697	.685	.674	.659
3.0	.736	.724	.709	.700	.687
3.5	.771	.758	.742	.730	.716
4.0	.811	.794	.777	.763	.746

Figure 2 shows a comparison of the activity coefficients, for the concentration range 1.5 to 4.0 M , with those determined from the data of Harned and Nims⁸ relative to $\gamma_{0.1}$ as given by Harned and Cook.⁹ The circles, diameter ± 0.001 , represent the experimental values. The deviations from the smooth curves indicate that γ as determined

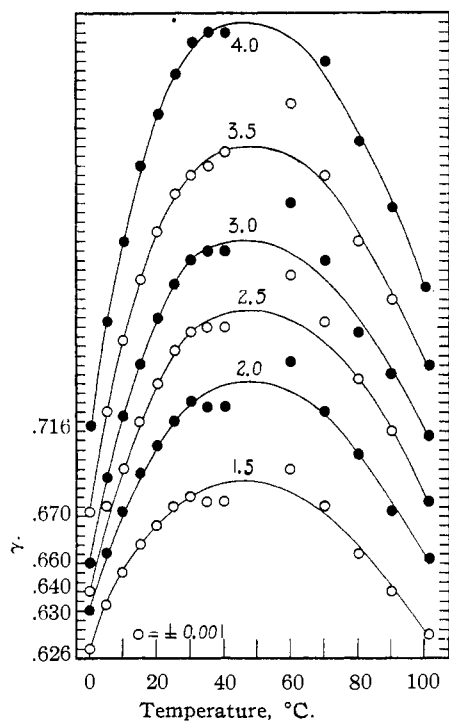


Fig. 2.—Activity coefficients; 0 to 40° electromotive force, 60 to 100° boiling point elevation; ○, ● ± 0.001 .

from the electromotive force data is too low at 35 and 40°, while γ determined from the boiling point elevation is too high at 60 and 70°. At 40° the maximum difference in γ is 0.004, which corresponds to 0.3 millivolt in electromotive force. At 60° the deviation in γ is about 0.01 at concentrations of 3.5 and 4.0 M , and 0.005 at 1.5 M . At 70° the deviations from the smooth curves are about 0.004 for concentrations of 2.5 to 4.0 M , while at the higher temperatures the experimental points fall on the curve to within ± 0.001 .

Relative Partial Molal Heat Content.—By definition this quantity is given by the equation

$$d \ln \gamma / d(1/T) = \bar{L}_2 / \nu R \quad (4)$$

The values of \bar{L}_2 given in Table III were determined from the slopes of the tangents to the curves of $\ln \gamma$ plotted against $1/T$. The results at 0° are practically the same as those given by Harned and Cook,⁹ those near 100° are not as reliable since the slope near the end of a curve is not well defined. These results together with the

calorimetric results of A. L. Robinson,¹² Gulbransen and Robinson¹³ and of Rossini¹⁴ are plotted in Fig. 3. The former are represented by open circles, diameter 50 cal., the latter by dots, diameter 30 cal. The dotted line represents the values given by Rossini¹⁵ for 18°. An inspection of Fig. 3 shows that when both the electromotive force and boiling point results are considered the agreement of \bar{L}_2 determined from these results with those determined from calorimetric measurements is quite satisfactory. The 15, 20, and 25° curves fit the calorimetric data better, and the 18 and 40° curves appear to be more reasonable than the corresponding curves given by Harned and Cook⁹ as determined from the electromotive force results alone. This is quite conclusive evidence that the maxima in the γ vs. t curves of Fig. 2 occur at higher temperatures than would be anticipated from the electromotive force data. The curves for the higher temperatures can only be considered as an indication of the nature of the change in \bar{L}_2 with temperature and concentration.

Relative Partial Molal Heat Capacity of the Solute.—This quantity is given by the equation

$$\bar{C}_p - \bar{C}_{p_0} = d \bar{L}_2 / d(T) \quad (5)$$

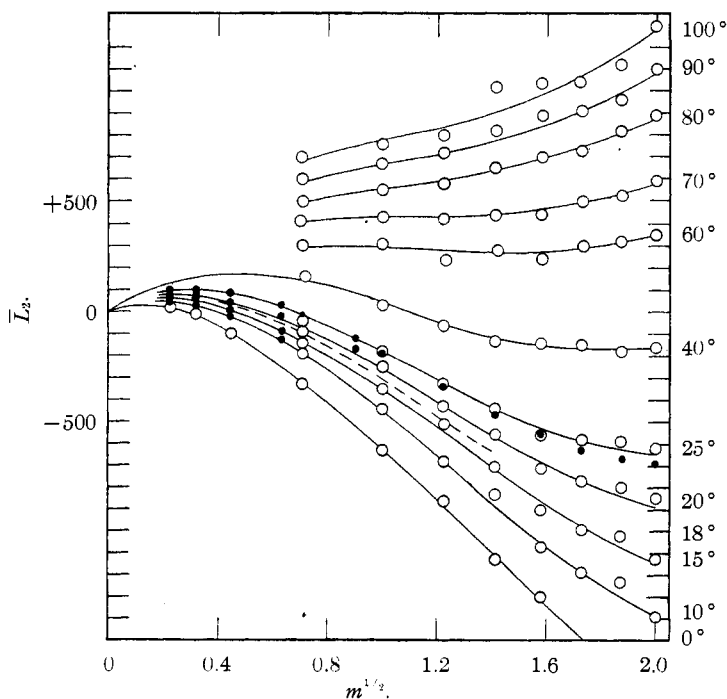


Fig. 3.— \bar{L}_2 versus $m^{1/2}$; ○, 50 cal.; ●, 30 cal.

- (12) Robinson, *THIS JOURNAL*, **54**, 1311 (1932).
 (13) Gulbransen and Robinson, *ibid.*, **56**, 2637 (1934).
 (14) Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).
 (15) Rossini, *ibid.*, **6**, 791 (1931).

TABLE III

<i>m</i>	RELATIVE PARTIAL MOLAL HEAT CONTENT, \bar{L}_2 , CAL./MOLE										
	<i>t</i> ...0°	10°	20°	25°	30°	40°	60°	70°	80°	90°	100°
0.5	- 330	- 185	- 90	- 45	+ 15	+170	+300	+400	+500	+ 600	+ 700
1.0	- 630	- 440	-250	-180	-100	+ 30	+310	+430	+550	+ 670	+ 760
1.5	- 860	- 680	-430	-330	-260	- 60	+240	+420	+580	+ 720	+ 800
2.0	-1120	- 840	-560	-450	-330	-130	+280	+450	+650	+ 820	+1020
2.5	-1300	-1070	-710	-560	-380	-140	+240	+440	+700	+ 890	+1040
3.0	-1650	-1190	-770	-580	-400	-150	+300	+500	+730	+ 910	+1040
3.5	-1800	-1230	-800	-590	-420	-170	+310	+520	+820	+ 960	+1120
4.0	-1850	-1380	-850	-620	-440	-150	+360	+590	+890	+1100	+1300

TABLE IV

<i>m</i>	THE RELATIVE PARTIAL MOLAL HEAT CAPACITY $\bar{C}_p - \bar{C}_{p_0}$			
	<i>t</i> ...0°	15°	25°	60°
0.5	10	10	10	10
1.0	20	18	16	12
1.5	25	23	20	15
2.0	33	28	24	19
2.5	35	34	32	21
3.0	45	42	35	21
3.5	51	45	38	22
4.0	53	51	41	24

The values given in Table IV were determined from the slopes of the tangents to the curves of \bar{L}_2 plotted against *T*. The greatest relative change

our results can only be considered as approximate, they appear to agree with the results of Gulbransen and Robinson¹³ at the lower concentrations and to show a trend toward those of Rossini¹⁴ at the higher concentrations. This gives further evidence that the suggestion of Harned and Cook,⁹ namely, that the values of \bar{L}_2 determined from the electromotive force measurements change too rapidly with the temperature, is correct. A calorimetric determination of \bar{L}_2 and $\bar{C}_p - \bar{C}_{p_0}$ at the higher temperatures would furnish a valuable guide to the reliability of the activity coefficients as determined from the boiling point elevations.

Summary

1. The activity coefficients and osmotic coefficients of sodium chloride have been determined in the temperature range 60 to 100° for concentrations of 1.0 to 4.0 *M*, and compared with those determined from electromotive force measurements at temperatures between 0 and 40°.

2. The agreement of the relative partial molal heat content as determined from these results together with the electromotive force results is more satisfactory than that obtained from the electromotive force results alone.

3. This indicates that the activity coefficients determined from the electromotive force measurements are low at temperatures near 40°, while those determined from the boiling point elevations are too high at temperatures near 60°.

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RECEIVED FEBRUARY 20, 1939

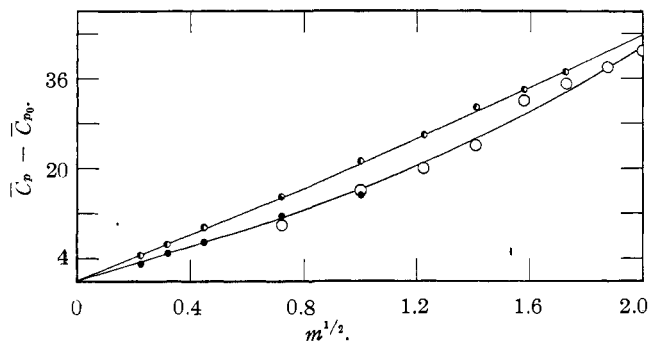


Fig. 4.— $\bar{C}_p - \bar{C}_{p_0}$ versus $m^{1/2}$ at 25°; ○, Rossini; ●, Gulbransen and Robinson.

occurs in the temperature range 0 to 60°; above 60° there is little change with temperature. In Fig. 4 our results at 25° are plotted together with those given by Gulbransen and Robinson¹³ and by Rossini.¹⁴ The former are represented by open circles, diameter 2 cal., the latter by closed and semi-closed circles, diameter 1.2 cal. While