

that more than one water molecule may occupy a position in the "lattice" vacated by a soap molecule leads to negative deviations of a_2/N_2 from constancy. a_2/N_2 for the liquid crystalline phases except for the middle soap of sodium palmitate, does go through a minimum, but it is quite possible that factors other than those here considered are responsible for this behavior. As in the case of curd fibers, any attempt at a more quantitative formulation of the behavior of these liquid crystalline solutions must wait until more has been learned about their internal structure.

Although Raoult's law is a fair first approximation for the liquid crystalline solution, the equation for regular solutions¹⁴ which has as its principal feature a correction term to Raoult's law arising from dissimilarity in the molecular fields of the components, is not applicable. This failure may be due to the fact that a fundamental step in the derivation of the equation is the counting of the number of pairs of interacting spheres—an approximation that cannot be valid for soap-water systems. It seems likely that an equation derived in a similar manner in which differences

(14) J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).

in geometrical form of the molecules and in their arrangement in the solution are considered, might be satisfactory. Note that a different basic model may be required for each phase in contrast to the behavior of regular solutions, where a single model is applicable over the whole concentration range even though two liquid phases may be formed.

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Summary

The vapor pressure of aqueous sodium laurate at 90° has been measured as a function of its concentration and the existence of waxy soap as a separate phase has been confirmed.

The activities of sodium palmitate and sodium laurate have been calculated for each of the phases present in aqueous systems at 90°. Possible models of each of these phases are described. The models proposed account qualitatively for the experimental activity concentration curves of middle soap and neat soap.

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The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. VIII. Extrapolations in 82% Dioxane Mixtures and Standard Potentials

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In the previous communications in this series, the standard potentials of the cells, H_2 HCl(*m*), Dioxane(*X*), H_2O (*Y*) | AgCl-Ag in mixtures containing 20,^{2,4,5} 45^{2,3,6} and 70%^{2,7,8} dioxane have been evaluated. In addition, the thermodynamic properties of hydrochloric acid in the mixtures have been determined from 0 to 50° and throughout wide acid concentration ranges. These mixtures possess dielectric constants of approxi-

mately 60, 40 and 20. In this communication, similar results have been obtained in a dioxane-water mixture containing 82% by weight of dioxane which has a dielectric constant of approximately 10. Measurements were obtained at acid concentrations from 0.001 to 0.01 *M*, inclusive, and at 5° intervals from 5 to 45°.

The evaluation of the standard potential in solutions of dielectric constant as low as these cannot be carried out at the present time with the certainty obtainable in the media of higher dielectric constant. There are a number of reasons for this. The Gronwall, La Mer and Sandved extension of the Debye and Hückel theory is not satisfactory in media of dielectric constant of the magnitude, 10. This is due to the fact that the second term of the extended term series is large,

(1) This communication contains some of the experimental material from a dissertation presented by Fletcher Walker to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1936.

(2) Harned and Morrison, *THIS JOURNAL*, **58**, 1908 (1936).

(3) Harned and Calmon, *ibid.*, **60**, 334 (1938).

(4) Harned, *ibid.*, **60**, 336 (1938).

(5) Harned and Donelson, *ibid.*, **60**, 339 (1938).

(6) Harned and Donelson, *ibid.*, **60**, 2128 (1938).

(7) Harned and Calmon, *ibid.*, **60**, 2130 (1938).

(8) Harned, Donelson and Calmon, *ibid.*, **60**, 2133 (1938).

TABLE I
ELECTROMOTIVE FORCES OF THE CELL
 $\text{H}_2 \mid \text{HCl}(m), \text{dioxane}(X), \text{H}_2\text{O}(Y) \mid \text{AgCl}-\text{Ag}$
 $X = 82\%$ by weight

t	$m \dots 0.001$	0.0015	0.002	0.003	0.005	0.007	0.01
5	0.37475	0.36154	0.35260	0.34095	0.32656	0.31705	0.30700
10	.37169	.35818	.34907	.33728	.32257	.31280	.30254
15	.36837	.35469	.34544	.33346	.31823	.30831	.29788
20	.36488	.35097	.34158	.32923	.31384	.30385	.29330
25	.36088	.34682	.33731	.32472	.30906	.29886	.28844
30	.35684	.34262	.33298	.32016	.30433	.29415	.28345
35	.35241	.33800	.32827	.31514	.29932	.28893	.27843
40	.34762	.33310	.32326	.31019	.29426	.28390	.27301
45	.34271	.32805	.31818	.30509	.28893	.27853	.26765

in fact, greater than the first term in solutions of lower acid concentration ($\sim 0.001 M$). In the second place, as shown by Harned and Calmon,⁷ reliable electromotive forces at concentrations of acid below $0.001 M$ cannot be obtained with the present technique. For an empirical extrapolation independent of these extended terms, results in the region of concentrations as low as $0.00005 M$ or less would be required. Because of these difficulties, we have employed a method of extrapolation which utilizes the mass action law and the ionization constant of hydrochloric acid computed from conductance measurements. Although the use of extraneous data is not so satisfactory as making all the computations from electromotive forces only, we regard this method as the best available at present.

Experimental Results

The methods of preparation of the solutions and electrodes, and the operation of the cells have been described previously.⁹ The silver-silver chloride electrode made by heating nine parts of dry silver oxide and one part of dry silver chlorate to 450° for ten minutes, was found to be more satisfactory in hydrochloric solutions or concentrations 0.001 to $0.01 M$ than those prepared by electrolysis. At $0.01 M$ and higher concentrations no difference in performance was noted between these two types of electrodes. The acid concentration in the mixture was known to within 0.03% . The temperature control was kept within $\pm 0.01^\circ$. Rather close control was necessary because the cell was found to have a comparatively high temperature coefficient. A type K potentiometer and high sensitivity galvanometer were employed.

The cells required twelve hours or somewhat more to reach equilibrium at the initial tempera-

ture of 25° . After this was attained, equilibrium at another temperature (*e. g.*, 20 or 30°) was reached in one hour. Two series of measurements were made at each concentration. Triplicate cells were first measured at 25° . One series was made by raising the temperature by 5° intervals to 45° , and after the measurements were made at this temperature, the temperature was lowered to 25° and the final readings taken. The second series was carried out in a similar manner. Measurements were made at 25° , then at 5° intervals until 5° was reached and finally at 25° . Solutions of 82% dioxane-water mixtures freeze between 0 and 5° .

Agreement of the initial and final readings at 25° was taken as the criterion of the proper operation of a cell. The average reproducibility in this concentration range was found to be ± 0.2 mv., the maximum deviation ± 0.3 mv. This indicates that the present results are not quite so reliable as those obtained in media containing less dioxane where the accuracy was within ± 0.1 mv.

Table I contains the electromotive forces corrected to one atmosphere pressure of hydrogen. The vapor pressure of this mixture was obtained from the work of Hovorka, Schaefer and Dreisbach.¹⁰ The mole fraction of dioxane in 82% dioxane-water mixtures is very nearly one-half: so the values of the vapor pressure employed are those reported for this concentration. These investigators give the vapor pressure at 10° intervals from 10 to 80° . In order to obtain values at 5° intervals from 5 to 45° , Newton's interpolation formula was used. The measurements were made at acid concentrations very near the round concentrations given in the table. The results given were obtained from suitable large scale graphs of the results.

(9) Harned and Morrison, *Am. J. Sci.*, **37**, 161 (1937).

(10) Hovorka, Schaefer and Dreisbach, *THIS JOURNAL*, **58**, 2264 (1936).

TABLE II
DATA EMPLOYED IN EXTRAPOLATION AT 25°
 $a = 6 \text{ \AA.}; K' = 2.02 \times 10^{-4}; u = 11.98; D = 9.53$

m	c	γ^a	γ'	α	$\frac{E_\alpha}{(Eq. 5)}$	E'	$E' - E_\alpha$	
0.001	0.001039	0.313	0.358	0.688	0.0123	-0.03265	-0.0449	
.0015	.001558	.268	.313	.666	.0129	-.03298	-.0458	
.002	.002078	.243	.283	.651	.0143	-.03333	-.0476	
.005	.005194	.174	.210	.597	.0168	-.03568	-.0525	
.007	.007272	.153	.189	.575	.0178	-.03756	-.0554	
.01	.01039	.133	.168	.555	.0183	-.03974	-.0581	
	5°	10°	15°	20°	30°	35°	40°	45°
D	10.52	10.27	10.01	9.77	9.29	9.06	8.84	8.62
u	11.47	11.58	11.72	11.85	12.16	12.30	12.46	12.64

^a From Debye and Hückel-Gronwall-La Mer equation. Used for graph.

Evaluation of the Standard Potentials

The ionization constant of hydrochloric acid in 82% dioxane-water mixtures has been determined by Owen and Waters.¹¹ Their values at 15, 25, 35 and 45° are 2.55×10^{-4} , 2.02×10^{-4} , 1.64×10^{-4} and 1.07×10^{-4} , respectively. These results are in agreement with Bjerrum's theory of ionic association according to which the value of the distance of approach of the ions "a" is 6 Å. Further, the results indicate that "a" changes little with the temperature. The value of 6 Å. is in agreement with the value of "a" of 5.6 Å. obtained by us in our previous treatment of the results in dioxane-water mixtures of higher dielectric constant,^{4,7} and will be employed in the subsequent calculations.

The cell electromotive force, E , is given by the equation

$$E = E'_0 - 2k \log m\gamma \quad (1)$$

where E'_0 is the standard potential, k equals $2.3026 RT/F$, m is the molality and γ the stoichiometrical activity coefficient. By introducing the equation for the Debye and Hückel law, we define the function, E' , by the equation

$$E' = E + 2k \log m - \frac{2ku \sqrt{c}}{1 + A \sqrt{2c}} = E'_0 + f(m) \quad (2)$$

where u is the Debye and Hückel constant, c the concentration in moles per liter of solution and A is the parameter which involves the apparent ionic diameter. The term which converts from rational to stoichiometric activity coefficient has been omitted as insignificant. We also define the deviation from the Debye and Hückel equation, $E' - E'_0$, by the equation

$$E' - E'_0 = E - E'_0 + 2k \log m - \frac{2ku \sqrt{c}}{1 + A \sqrt{2c}} = f(m) \quad (3)$$

(11) Owen and Waters, THIS JOURNAL, 60, 2371 (1938).

It is now necessary to compute the deviation factor, $E' - E'_0$, by some theoretical means. To this end, we utilize the ionization constant, K , and the law of mass action. The cell electromotive force may be expressed by

$$E - E'_0 = -2k \log \alpha \gamma' m \quad (4)$$

where α is the degree of ionization, and γ' is the activity coefficient of the acid as strong electrolyte at a concentration, αm . Combining with equation (3), the deviation factor becomes

$$E_\alpha = E' - E'_0 = -2k \log \alpha \gamma' - \frac{2ku \sqrt{c}}{1 + A \sqrt{2c}} = f(m) \quad (5)$$

so that the problem becomes one of computing α and γ' . According to the mass action law, α is given by

$$\alpha = 1/2 \left[-\frac{K}{\gamma'^2 c} \pm \sqrt{\frac{K^2}{\gamma'^4 c^2} + \frac{4K}{\gamma'^2 c}} \right] \quad (6)$$

By employing the Debye and Hückel equation with the extended terms, γ' was computed, and a suitable plot of $\log \gamma'$ versus c drawn. The solution of equation (6) was obtained by arithmetical approximation. A preliminary value of γ' was substituted in (6) and α evaluated using the known value of K . Then γ' was read off the graph at a concentration αc . This was substituted in the equation and α was recomputed. Three or four approximations of this kind were required to satisfy equation (6). After the evaluation of α and γ' , the deviation factor was computed by equation (5). The results of typical calculation of these quantities are given in Table II. This table also contains values of the dielectric constant and the Debye and Hückel function at the other temperatures.

The characteristics of the extrapolation are best illustrated by Fig. 1 where both E' and $E' - E'_0$ are plotted against m . Both of these equal E'_0

when m equals zero. The plot of the Debye and Hückel function E' is deceptive because it is nearly straight and, if the effect of incomplete ionization is not taken into consideration, would be extrapolated as shown by the upper dashed line. This would lead unquestionably to an erroneous E'_0 , in fact a value about 10 mv. too high. The lower dashed line indicates the character of the curve to be expected but, as previously mentioned, we have not been able to obtain reliable results at concentrations low enough to fall on this curve.

The plot of $E' - E_\alpha$ is not all that is to be desired since it possesses considerable slope which decreases the accuracy of the extrapolation. However, the estimation of E'_0 should be fairly close although it is difficult to judge how close. While in media of dielectric constant of 20 or higher, the estimation of E'_0 is of the order of ± 0.1 mv., the absolute error in the present case is roughly of the order of ± 1 mv. Therefore, in computing the thermodynamic properties of these solutions, the results relative to γ equals unity at zero acid concentration may be in error to the above extent although in justice to the experimental work, the values relative to one of the higher concentrations are of a high order of accuracy.

Since Owen and Waters obtained ionization constants at 15, 25, 35 and 45° only, we computed the deviation factor, E_α , at these temperatures, plotted them against temperature and read off values at the other temperatures at which electromotive forces have been determined. With these, extrapolations were made at 5° intervals from 5 to 45°. The values of the standard potentials are given in Table III. These have been expressed by the equation

$$E'_0 = -0.0413 - 23.7 \times 10^{-4} (t - 25) - 8.80 \times 10^{-6} (t - 25)^2 \quad (7)$$

The differences between values computed by this equation and those obtained graphically are given in the last column of the table. Their magnitude indicates the consistency of the extrapolation.

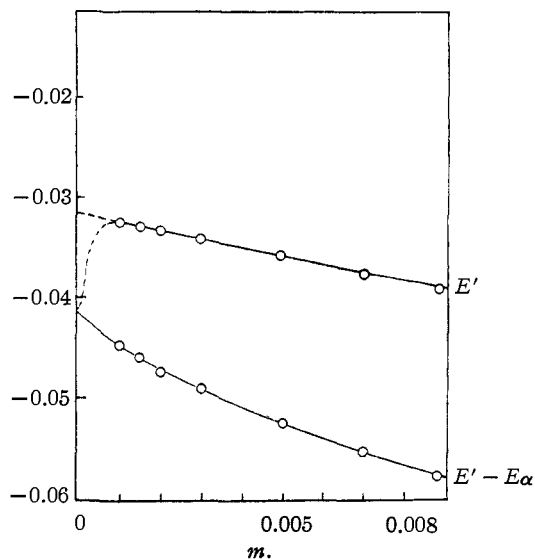


Fig. 1.—Extrapolation functions, E' and $E' - E_\alpha$, versus molality.

TABLE III
STANDARD POTENTIALS

t	E'_0	Δ^a
5	+0.0025	+0.1
10	-.0078	+ .1
15	-.0185	0
20	-.0295	-.1
25	-.0415	+ .2
30	-.0536	+ .2
35	-.0658	-.1
40	-.0787	-.2
45	-.0925	+ .3

^a E'_0 (Eq. 7) - E'_0 (graph).

Summary

1. Measurements of the cells $H_2 | HCl(m)$, dioxane (82%), $H_2O | AgCl-Ag$ from 5 to 45° at 5° intervals, and at seven concentrations between 0.001 and 0.01 M have been made. The dielectric constant of this solvent is approximately 10.
2. From these, the standard potential of the cell has been evaluated by application of the law of mass action and ionization constants derived from conductance measurements.

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