

It is striking that the molar increment of surface tension of the hydrochloride or sodium salt of ϵ -aminocaproic acid is very much less negative than that of isoelectric α -aminocaproic acid and therefore *a fortiori* presumably less negative than that of its salts. This is an illustration of the fact pointed out by Cohn⁵ on the basis of a systematic study of solubilities that the effect of a CH₂ group situated between polar groups (whether or not they bear a free charge) is different from that of one located in a hydrocarbon residue in the molecule.

As a result of the application of a new and exceedingly accurate method of measuring surface tension Jones and Ray¹⁹ report a very curious phenomenon shown by aqueous solutions of inorganic salts. The surface tension-concentration curves, which are linear at ordinary concentrations, do not continue straight back to the ordinate axis, but dip down so as to show negative surface tension increments when the solutions are very dilute. It

(19) Jones and Ray, *THIS JOURNAL*, **57**, 957 (1935).

would be of importance in any theoretical interpretation of surface tension to know whether or not dipolar ions behave in the same way, and it is hoped in the future to study the problem by this more accurate method.

Summary

Measurements of the surface tension of aqueous solutions of seven amino acids of differing size and moment and of glycine betaine have been made with the drop weight method. In the case of four of the amino acids the surface tension is greater than that of water; in the other cases it is less. In these dipolar ions there appears to be an antagonism between the effect of the electric moment which tends to increase the surface tension, and the size and number of organic groups in the molecule which tend to lower it. The effect of converting an amino acid into its hydrochloride or its sodium salt is to lower the surface tension of the solution.

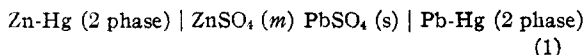
CAMBRIDGE, MASS.

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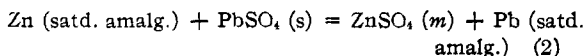
The Electromotive Force of the Cell Zn-Hg (2 phase) | ZnSO₄ (m) PbSO₄ (s) | Pb-Hg (2 phase) and its Temperature Coefficient at 25° and Concentrations from 0.05 to 1.5 Molal¹

BY JACOB KIELLAND²

Determinations of the e. m. f. of the cell



corresponding to the chemical reaction



have been reported by Bray³ at 25° for molalities from 0.0005 to 3.5, and by Cowperthwaite and La Mer⁴ at 0, 12.5, 25, 37.5 and 50° for molalities from 0.0005 to 0.01, also 0.02 and 0.05 molal at 0, 25 and 50°.

In the present paper are given some e. m. f. measurements on cell (1) for the molalities 0.0512, 0.150, 0.510 and 1.501 at the temperatures 15, 25 and 35°.

Experimental Part

Preparation of Materials.—Lead sulfate of definite crystalline form was prepared from *pro*

(1) This work was aided by a grant from "Anna Paus's Legat."

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(3) U. B. Bray, *THIS JOURNAL*, **49**, 2372 (1927).

(4) I. A. Cowperthwaite and V. K. La Mer, *ibid.*, **53**, 4333 (1931).

analysis reagents in the way recommended by Bray³ and stored under doubly distilled water until needed. Zinc sulfate stock solution was made up from Kahlbaum "zur analyse" reagents and doubly distilled water, and analyzed by the zinc ammonium phosphate method as well as by weighing in the form of zinc sulfate after evaporation and heating on addition of some drops of sulfuric acid.

Four per cent. lead amalgam and 4% zinc amalgam were made up with *pro analysis* metals and redistilled mercury as described by Cowperthwaite and La Mer,⁴ filtered hot through capillary tubings and stored under a slight excess pressure of purified nitrogen.

Tank nitrogen was purified from oxygen by the wet combustion method described by Van Brunt,⁵ using a nitrogen lift pump to circulate the ammonia-ammonium carbonate solution over the copper wire gauze filling of the absorption tower.

Experimental Method.—The cell was similar to that used by Cowperthwaite and La Mer,⁴ with

(5) C. Van Brunt, *ibid.*, **36**, 1448 (1914).

the exception that the electrodes were inserted at the top, using well ground glass joints. The solutions and the cell were freed from oxygen by running purified nitrogen through the whole system for four hours. The method of filling the cell with amalgams and solutions, and sealing off with mercury, was essentially the same as used by Cowperthwaite and La Mer.

The cleaning of cells and electrodes was effected by washing with concentrated sulfuric acid, distilled water, and then with a weak alcoholic solution of potassium hydroxide. They were then rinsed ten times with doubly distilled water, steamed out for an hour and subsequently dried at 110°.

Constant e. m. f. was ordinarily obtained one to four hours after the cell was prepared, and was controlled by readings after fifteen to twenty hours. It was found that a constant potential was far more rapidly obtained by passing from higher to lower temperatures than *vice versa*,

Apparatus.—The measurements were carried out with an Otto Wolff Potentiometer 5881 and a Hartmann and Braun Reflecting Galvanometer No. 1528. A Weston element calibrated by "Polytechnisches Reichsanstalt" served as the standard cell. The regulation of the thermostat temperature was maintained to a precision of $\pm 0.02^\circ$ by means of mercury regulators.

Results

The observed values of e. m. f. ($E_{\text{obsd.}}$) and of E^0 , computed from the equation

$$E^0 = E_{\text{obsd.}} + (\nu RT/nF) \ln m \quad (3)$$

are given in Table I. The corrections necessary

TABLE I

OBSERVED E. M. F. AND COMPUTED VALUES OF E^0

Molality, m	$E_{\text{obsd.}}$	$(\nu RT/nF)$ in m	E^0
Temperature 15°			
0.0512	0.53425	-0.07378	0.46047
.150	.51955	- .04710	.47245
.510	.50551	- .01671	.48880
1.501	.49195	+ .01008	.50203
Temperature 25°			
0.0512	0.52830	-0.07635	0.45195
.150	.51350	- .04873	.46477
.510	.49915	- .01729	.48186
1.501	.48500	+ .01043	.49543
Temperature 35°			
0.0512	0.52215	-0.07891	0.44324
.150	.50740	- .05037	.45703
.510	.49285	- .01787	.47498
1.501	.47800	+ .01078	.48878

owing to the solubility of lead sulfate at the concentrations stated in the present paper, are less than 0.01 mv., and are therefore not taken into account.

The values of the mean practical⁶ stoichiometric activity coefficient for zinc sulfate, given by the equation

$$\ln \gamma_{\pm} = \frac{E^0 - E_{\text{obsd.}}}{\nu RT/nF} - \ln m = \frac{E^0 - E^0'}{\nu RT/nF} \quad (4)$$

are collected in Table II, using the best values for E^0 obtained by Cowperthwaite and La Mer.⁴

TABLE II

MEAN PRACTICAL STOICHIOMETRIC ACTIVITY COEFFICIENTS OF ZINC SULFATE

Molality, m	$t = 15^\circ$ ($E^0 = 0.4215_{\text{g}}$)	$t = 25^\circ$ ($E^0 = 0.41086$)	$t = 35^\circ$ ($E^0 = 0.3992$)
0.0512	0.209	0.202	0.190
.150	.128	.123	.113
.510	.0667	.0631	.0569
1.501	.0392	.0372	.0342

Discussion

The agreement between the values presented here and those given by the measurements of Cowperthwaite and La Mer⁴ up to 0.05 molal is very good.

The activity coefficients given previously by Bray⁵ are all higher than those found by Cowperthwaite and La Mer and by the present author. This discrepancy can be traced back to Bray's measurements in the most dilute concentration range.⁷ Using Cowperthwaite and La Mer's $E^0_{298.1} = 0.41086$, which hitherto is the most reliable value given for the normal potential of the cell (1), the activity coefficients given by Bray were recalculated. The results are shown in Table III.

TABLE III

MEAN PRACTICAL STOICHIOMETRIC ACTIVITY COEFFICIENTS OF ZINC SULFATE AT 25°, RECALCULATED FROM BRAY'S MEASUREMENTS

m	0.005	0.01	0.02	0.05		
γ_{\pm}	0.477	0.387	0.298	0.202		
m	0.08	0.1	0.2	0.3	0.5	0.8
γ_{\pm}	0.162	0.148	0.104	0.0837	0.0634	0.0491
m	1.0	1.5	2.0	2.5	3.0	3.5
γ_{\pm}	0.0439	0.0368	0.0354	0.0368	0.0409	0.0476

(6) Cf. practical and rational activity coefficients by F. A. Guggenheim, *Phil. Mag.*, **19**, 588 (1935).

(7) The uncertainty of Bray's extrapolation was already pointed out by Gronwall, La Mer and Sandved [*Physik. Z.*, **29**, 390 (1928)], who found a somewhat different value, with " a " = 4.0 Å. Cowperthwaite and La Mer's " a " = 3.64 is however the most reliable, since cryoscopic measurements also give " a " = 3.6. Bray's measurements at the highest dilutions consequently should not be taken into account.

These recalculated coefficients are in good agreement with Cowperthwaite and La Mer's at concentrations 0.005 to 0.05 *m*, and with the author's at 0.05 to 1.5 *m*. $\log \gamma_{\pm}$ vs. \sqrt{m} are shown in Fig. 1.

It would be of great interest to obtain values of the partial molal heat of dilution of zinc sulfate at concentrations here studied, on account of the difference between the calorimetric values given by Lange and collaborators⁸ and the results of La Mer and Cowperthwaite, obtained by application of the Gibbs-Helmholtz equation.⁹ But as \bar{L}_2 in the case of zinc sulfate depends about equally upon the precision with which $(E^{0'} - E^0)$ and $d(E^{0'} - E^0)/dT$ can be determined, it is obvious that more than the three temperatures investigated in the present paper, are necessary to obtain values of \bar{L}_2 which are sufficiently accurate¹⁰ to be compared with those determined calorimetrically. The final answer to the questions must therefore await a more extended investigation.¹¹

Acknowledgments.—The author is indebted to "Norsk Hydro-Elektrisk Kvælstofaktieselskab," Oslo, to "Norges Tekniske Høiskole, Institutt

(8) E. Lange, J. Monheim and A. L. Robinson, *THIS JOURNAL*, **55**, 4733 (1933).

(9) V. K. La Mer and I. A. Cowperthwaite, *ibid.*, **55**, 1004 (1933).

(10) The partial molal heat of dilution varies considerably with the temperature, according to some unpublished calculations of $\bar{C}_p - \bar{C}_p^0$ for zinc sulfate at concentrations studied; hence it is necessary to make use of a sufficient number of temperatures.

(11) According to a communication from Professor La Mer, W. H. Wood, working with Dr. Cowperthwaite, has been reinvestigating the e. m. f. of the cell at 5° temperature intervals from 0 to 50° from high dilution to one molal; the results have not yet been published.

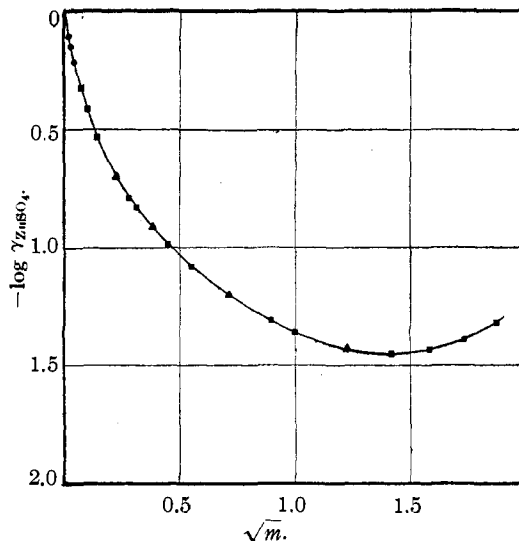


Fig. 1.—Mean stoichiometric activity coefficients of zinc sulfate at 25°: ●, Measurements of Cowperthwaite and La Mer; ■, Bray; ▲, Kjølland.

for Uorganisk Kjemi," Trondheim, and especially to Docent K. Sandved, in whose laboratory this work has been done.

Summary

The electromotive force of the cell Zn (satd. amalgam) | ZnSO₄(*m*), PbSO₄(s) | Pb (satd. amalgam) has been measured at 15, 25 and 35° for concentrations of zinc sulfate of 0.0512, 0.150, 0.510 and 1.501 molal. The activity coefficients of zinc sulfate are given for these concentrations and temperatures.

OSLO, NORWAY

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

Studies in the Phenanthrene Series. XIII. 9,10-Dihydrophenanthrene and Amino Alcohols Derived from It^{1,2}

BY ALFRED BURGER AND ERICH MOSETTIG

The important investigations of Schroeter and his co-workers³ have shown that phenanthrene yields by catalytic hydrogenation (elevated temperature and pressure) and by reduction with sodium and amyl alcohol, three well-defined hydrogenation products, namely, 9,10-dihydro-

phenanthrene, 1,2,3,4-tetrahydrophenanthrene and 1,2,3,4,5,6,7,8-octahydrophenanthrene, in amounts which depend upon the mode of reduction. These investigators determined the structure of the hydrocarbons beyond any doubt by synthetic methods, thus ridding the literature of the great confusion prevailing in the series of hydrogenated phenanthrenes up to that time. While the octahydro⁴ and tetrahydro compounds may be isolated quite conveniently from the

(1) The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

(2) See preliminary note, *THIS JOURNAL*, **57**, 2731 (1935).

(3) Schroeter, *Ber.*, **57**, 2025 (1924); Schroeter, Müller and Huang, *ibid.*, **62**, 645 (1929).

(4) For a convenient preparative method of octahydrophenanthrene, see van de Kamp and Mosettig, *THIS JOURNAL*, **57**, 1107 (1935).