succinic anhydride was obtained 12 g. (80%) of N-succinyl-1-ethylamino-2-methylnaphthalene. It was purified from benzene–petroleum ether (b. p. 60–110°) mixture; white crystals, m. p. 123° (cor.).

Anal. Calcd. for $C_{17}H_{19}NO_3$: C, 71.54; H, 6.72. Found: C, 71.67; H, 6.83.

A salt of the racemic acid suitable for resolution could not be found.

Summary

1. N-Succinyl-1-methylamino-2-methylnaphthalene and N-succinyl-1-methylamino-4-chloro-2-methylnaphthalene have been synthesized and resolved. N-Succinyl-1-ethylamino-2-methylnaphthalene was synthesized but no salts suitable for resolution were found.

2. The half-life periods of the active forms were smaller than those of the corresponding bromomesitylene derivative when determined in boiling *n*-butanol, thus indicating the interference of a —CH= group to be less than that of a CH_3—.

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The Molal Electrode Potential of the Silver–Silver Chloride Electrode in Ethyl Alcohol–Water Mixtures[1]

BY ANDREW PATTERSON[2] WITH W. A. FELSING

Harned and his co-workers have demonstrated in a number of papers[3,4] the feasibility of determining the ionization constants of weak acids in water–alcohol solutions. In this Laboratory it was desired to study the effect of the lengthening of the aliphatic chain of the alcohol used in the solvent medium (and of the acid) upon this method of determining the ionization constants of weak acids. In such determinations, the value of the molal electrode potential of the silver–silver chloride electrode in the solvent used is necessary for the calculation of the ionization constant.

These molal electrode potential values are available for ten and twenty per cent. methyl alcohol–water mixtures.[5] The purpose of this investigation was the determination of the molal electrode potential of the silver–silver chloride electrode in 10 and 20% *ethyl* alcohol–water mixtures. The method used was essentially that of Harned and Thomas.[5]

Materials Used

Hydrochloric Acid.—Reagent grade stock was purified by repeated distillation in an all-glass still; the final fractions resulting from several distillations were combined and distilled at a constant pressure of 750 mm. corresponding to a concentration of 20.245% hydrogen chloride.[6] Ethyl

Alcohol.—Commercial ethyl alcohol was agitated with silver oxide to remove aldehydes and was dried by refluxing with calcium oxide for about one week. The dried alcohol was distilled through a packed tower one meter long, the middle portions being collected and protected against moisture; immediately before use, the alcohol was further dried by passing in vapor form over heated anhydrous calcium sulfate. **Hydrogen.**—Cylinder hydrogen was passed over heated copper wire to remove the oxygen it might contain. **Solutions.**—Concentrated stock solutions of hydrochloric acid in the desired alcohol–water mixtures were made gravimetrically from the necessary amounts of the purified acid, alcohol, and water, using proportions such as to make the resultant solution approximately one molal in hydrochloric acid. Five hundred gram portions of such stock solutions were prepared; the weight of each constituent was known to within one milligram.

Five-liter quantities of stock alcohol–water mixtures, containing either 10 or 20% ethyl alcohol, were prepared by weight on a balance sensitive to 0.1 g. The alcohol was weighed on a more sensitive balance in order that the weights of alcohol and water would be known to the same comparable degree of accuracy (*i. e.*, to at least one part in 10,000).

Experimental Procedure

The Silver–Silver Chloride Electrodes.—These electrodes were prepared by a method similar to that employed by Keston[7] in preparing silver–silver bromide electrodes. Platinum spirals were coated with a paste of 10% silver chlorate and 90% silver oxide, both highly purified. The spirals and their coating were then heated in a quartz furnace at 650° for seven minutes. After undergoing an initial aging period, these electrodes proved highly satisfactory. **Hydrogen Electrodes.**—These electrodes consisted of platinized platinum strips one centimeter wide and two and one-half centimeters long. **The Cells.**—The cells were constructed of Pyrex glass in U-shape, equipped

(1) Constructed from a portion of a dissertation presented to the Graduate Faculty of The University of Texas by Andrew Patterson in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1942.

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(3) Harned and Owen, THIS JOURNAL, **52**, 5079 (1930).

(4) Harned and Embree, *ibid.*, **57**, 1669 (1935).

(5) Harned and Thomas, *ibid.*, **57**, 1666 (1935).

(6) Foulk and Hollingsworth, *ibid.*, **45**, 1220 (1923).

(7) Keston, *ibid.*, **57**, 1671 (1935).

with the usual hydrogen entry tube and bubbler exit, and were provided with connections for filling when evacuated. **The Thermostat.**—The kerosene-filled thermostat was equipped with a mechanical refrigerating system, controlled heaters, and an effective stirrer. Temperatures could be controlled to better than 0.01°. **Electromotive Force.**— The electromotive force measurements of cells of the type

$$H_2(1 \text{ atm.}), \text{ HCl } (m \text{ in } 10 \text{ and } 20\% \text{ } C_2H_5OH-H_2O),$$
$$\text{AgCl(s) + Ag(s)} \quad (1)$$
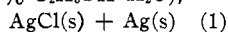
were made over a concentration range of 0.005 to 0.1 molal and at six different temperatures: 0, 10, 20, 25, 30, and 40°. For each dilution of the stock solution, one set of three cells was used over the range 0 through 25°, and a second set of three cells containing the same concentration over the range 25 through 40°. Thus three measurements of the electromotive force were made for each concentration at each temperature except 25°, where a total of six values were obtained.

Since the evaluation of the molal electrode potential required a knowledge of the molarity, c, as well as the molality, m, of the solutions, density determinations were made at each temperature.

In order to correct the observed cell potentials to one atmosphere pressure of hydrogen, the total vapor pressures

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS H_2 (1 ATM.), HCl (m IN 10 AND 20% ETHYL ALCOHOL-WATER), AgCl(s) + Ag(s) AT 25°C.

10% Ethyl alcohol		20% Ethyl alcohol	
Molality	E. m. f. volts	Molality	E. m. f. volts
0.093092	0.35020	0.114389	0.33569
.066462	.36590	.082072	.35125
.063229	.36878	.076389	.35426
.055045	.37502	.065376	.36212
.049673	.38034	.059216	.36612
.033673	.39874	.048326	.37590
.026429	.41035	.037328	.38798
.009431	.46019	.028773	.40055
.008296	.46644	.019551	.41965
.003159	.51373	.008936	.45709

presented in this paper by means of equations relating these potentials to the temperature.

Table II lists the densities and vapor pressures of the solvents used.

The molal electrode potential was obtained from these data by plotting the values of E_0 as a function of the molarity. E_0 was calculated from the equation

$$E_0 = E_{obs.} - 4.606 \frac{RT}{F} \log m - 4.606 \frac{RT}{F} uc^{1/2} - 2 \frac{RT}{F} Bc$$
$$(2)$$

where E_0 is the apparent molal electrode potential, $E_{obs.}$ is the observed voltage of the solution whose molality is m and molarity c, and u is the Debye–Hückel constant.

At any one temperature the true molal electrode potential E_0' is related to E_0 by the function

$$E_0 = E_0' - Bc \quad (3)$$

which is the equation of a straight line of which B is the slope. Plots of E_0 were made as a function of c and E_0' was then easily determined. The values of E_0' calculated by this method from data of the type exemplified by those obtained at 25° are presented in Table III. Using the method of least squares, an equation relating E_0' to the temperature has been derived in the form

$$E_0' = a + b(t - 20) + c(t - 20)^2 \quad (4)$$

which represents the results to within ±0.05 mv. The calculated constants are:

	a	b	c
10% Ethyl alcohol	0.21898	4.89247×10^{-4}	-1.40006×10^{-6}
20% Ethyl alcohol	.21011	4.08604×10^{-4}	-5.57748×10^{-6}

TABLE II

DENSITIES AND VAPOR PRESSURES OF SOLVENT MIXTURES

°C.		0	10	20	25	30	40
Densities, g./ml.	10%	0.9841	0.9839	0.9818	0.9804	0.9787	0.9747
	20%	0.9772	0.9725	0.9686	0.9664	0.9639	0.9585
Vapor press., mm.	10%	6.1	12.4	23.5	38.0	51.5	78.5
	20%	7.7	15.3	28.5	45.5	61.9	91.1

of the solvent mixtures were determined over the same temperature range by the method of Felsing and Thomas.[8] The measurements were accurate to 0.1 mm.

Experimental Data and Calculated Results.—

The data obtained at 25° are presented in Table I as illustrative of the data obtained; the data at the other temperatures, too numerous for presentation here, are found elsewhere.[9] The calculated values of the molal electrode potentials are

(8) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

(9) Andrew Patterson, Ph.D. Thesis, University of Texas, June, 1942.

TABLE III

THE MOLAL ELECTRODE POTENTIAL OF THE SILVER–SILVER CHLORIDE ELECTRODE

Temp., °C.	E_0' (in 10% ethyl alcohol)	E_0' (in 20% ethyl alcohol)
0	0.22726	0.21606
10	.22328	.21367
20	.21901	.21013
25	.21467	.20757
30	.21383	.20587
40	.20783	.19962

Summary

1. Electromotive force measurements have

been made on cells H_2(1 atm.), HCl(m in 10 and 20% C_2H_5OH — H_2O), AgCl(s) + Ag(s).

2. Vapor pressure and density measurements of the solvent have been made and tabulated

for the temperature range 0 through 40°.

3. The molal electrode potentials of the silver–silver chloride electrode have been calculated.

The Ionization Constants of Propionic Acid in Methyl and Ethyl Alcohol–Water Mixtures from 0 Through 40°[1]

BY ANDREW PATTERSON[2] WITH W. A. FELSING

The purpose of this investigation was the determination of the ionization constants of a weak acid in solvent media of lower dielectric strength than that of water. Harned and Embree[3] have shown that the electromotive forces of cells of the type

H_2 (1 atm.), (HA(m_1), NaA(m_2), NaCl(m_3)) in

x alcohol–water, AgCl(s) + Ag(s)

may be used to calculate the ionization constants of weak acids in water–alcohol mixtures, provided the dielectric strength does not become low enough to permit ionic association.

For this study, propionic acid in solution with 10 and 20% methyl and ethyl alcohol–water mixtures was chosen; measurements were proposed at 0, 10, 20, 25, 30, and 40°.

Materials Used

Propionic Acid.—C. P. Eastman Kodak Co. propionic acid was separated into fractions by distillation through a two-meter column packed with berl saddles, the first and last portions being discarded. The middle portions selected for use had a refractive index n^{20}D 1.3874 (literature[4] value, $n^{19.9}$D 1.38736), and an analysis confirmed their purity. **Sodium Propionate.**—This salt was prepared from purified propionic acid and sodium carbonate by the method of Watson and Felsing[5]; analysis of the product indicated high purity. **Sodium Chloride.**—Reagent grade material was precipitated thrice with hydrogen chloride, washed with cold distilled water, and centrifuged. **Methyl Alcohol.**—A high grade stock material was fractionated three times through a one-meter packed column, the first and last portions being discarded each time. The final fractionation yielded material having a refractive index n^{20}D 1.3288 (literature[6] value, n^{20}D 1.329). **Ethyl Alcohol.** —The preparation of this alcohol was described in a previous paper.[7]

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(2) Present address: Department of Chemistry, North Texas Agricultural College, Arlington, Texas.

(3) Harned and Embree, THIS JOURNAL, **57**, 1669 (1935).

(4) "International Critical Tables," Vol. 7, p. 35.

(5) Watson with Felsing, THIS JOURNAL, **63**, 410 (1941).

(6) "International Critical Tables," Vol. 7, p. 79.

(7) Patterson with Felsing, THIS JOURNAL, **64**, 1478 (1942).

Solutions.—Concentrated stock solutions were prepared by choosing the relative amounts of dry alcohol, water, propionic acid, sodium propionate, and sodium chloride to yield a solution which was approximately molal in each of the three solutes, while the solvent consisted of either 10 or 20% of methyl or ethyl alcohol in water. All solutions were made by weight. From these stock solutions, the cell solutions were prepared by dilution. All solutions were kept from contact with air as nearly as possible; hydrogen was bubbled through all solutions immediately prior to their introduction into the cells. The concentrations m_1, m_2, and m_3 were known to an accuracy of 0.1%; the cell solutions were introduced by a vacuum technique to avoid contact with air. The total vapor pressures of all solutions were determined experimentally.[7]

Experimental Results.—Each recorded electromotive force in Tables I and II is the average of three separate cell values at each temperature except at 25°, where six measurements were made. The temperature range was covered by two sets of cells containing solution of the same concentration: one from 0 through 25° and the other from 25 through 40°. All electromotive forces were corrected to a partial pressure of one atmosphere of hydrogen; the observed voltage of one cell remained constant within ±0.05 mv. after attaining equilibrium, and the voltages of a set of cells were reproducible to within 0.2 mv.

Ionization Constant.—The equation for the electromotive force of the cells measured may be written

$$\left(E_{obs.} - E_0' - \frac{RT}{F} \ln \frac{m_{HPr} m_{Cl^-}}{m_{Pr^-}} \right) = \left(-\frac{RT}{F} \ln \frac{\gamma_H \gamma_{Cl^-} \gamma_{HPr}}{\gamma_H \gamma_{Pr^-}} - \frac{RT}{F} \ln K_{HPr} \right)$$

where E_0' is the molal electrode potential of the silver–silver chloride electrode in the particular solvent medium, K is the ionization constant of the acid and γ and m are the respective activity coefficients and molalities. By inspection it is seen that $m_{HPr} = (m_1 - m_H)$ and $m_{Pr^-} = (m_2 - m_H)$; however, these quantities may be replaced with m_1 and m_2, since propionic