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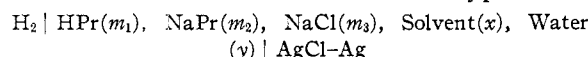
The Ionization Constants of Propionic Acid in Isopropyl Alcohol-Water Mixtures from 0 to 40°¹

BY ROBERT LEE MOORE² WITH W. A. FELSING

Introduction

The object of this investigation was the determination of the value of the ionization constant of propionic acid in propyl alcohol-water mixtures. The investigation of the effect of a change in solvent media upon the ionization of weak acids was instituted by Harned³ and his co-workers at Yale University and has been extended in this Laboratory by Patterson and Felsing.⁴ The latter measured the ionization constants of propionic acid in 10 and 20% methyl alcohol-water and ethyl alcohol-water mixtures. It was intended, therefore, to extend the study to *n*-propyl alcohol-water and isopropyl alcohol-water mixtures as solvents for the propionic acid. However, as was pointed out in a previous paper,⁵ it was found that the hydrogen electrode in *n*-propyl alcohol-water mixtures did not yield reproducible behavior. The results attained with isopropyl alcohol-water mixtures are presented in this paper.

The ionization constants were determined from the electromotive force of cells of the type



where *x* was 5, 10 or 20 weight per cent. isopropyl alcohol and the weight molalities *m*₁, *m*₂ and *m*₃ were approximately equal. The measurements were made over the temperature range 0 to 40° in 5° intervals.

Experimental

The preparation of the materials used and an account of the experimental procedure are given briefly below.

Propionic Acid.—Eastman Kodak Co. "White Label" propionic acid was fractionated through a meter-long packed column and the middle portion retained for use (n.b.p., 140.6°; *n*_D²⁰ 1.3871).

Sodium Chloride.—Reagent grade salt was precipitated twice from solution with hydrogen chloride and once from water alone. The product was dried at 500°.

Sodium Carbonate.—Reagent grade sodium bicarbonate was recrystallized twice from conductivity water, dried and heated to 280° for one hour to convert to the carbonate.

Solutions.—Concentrated stock solutions of propionic acid, sodium propionate, and sodium chloride in the desired isopropyl alcohol-water solvent were prepared by weighing the required amounts of the purified propionic acid, sodium carbonate, sodium chloride, conductivity

water and anhydrous isopropyl alcohol. The weights of the carbon dioxide evolved and of the water formed were accounted for in the calculations. The solutions, on which voltage measurements were to be made, were prepared by weight dilution of the stock solutions with the corresponding 5, 10 or 20% isopropyl alcohol. The concentrations *m*₁, *m*₂ and *m*₃ were known to better than 0.1%, and the ionic strength (*m*₂ + *m*₃) ranged in value from about 0.01 to 0.1 molal. Six to eight dilutions were prepared in each solvent mixture.

Experimental Procedure.—The apparatus and the techniques of manipulation and measurement were described in a previous paper⁵ dealing with the determination of the standard electrode potential of the silver-silver chloride electrodes in these solvent mixtures. Three separate cells were filled with each mixture and their voltages determined; also two series of such measurements on each mixture were made, a low temperature series (0 through 25° in 5° steps) and a high temperature series (25 through 40° in 5° steps). Each series constituted a fresh filling of the three cells. Thus, six independent voltage measurements were obtained on each solution mixture at 25° and three at each of the other temperatures. The average agreement between the voltages of cells containing the same solution and the agreement between the high and low temperatures series was about 0.05 millivolt.

No evidence of any change in the composition of the solution due to ester formation was observed. It was found that the cell voltages obtained at 25° for the low and the high temperature series on the same solution carried out as much as several weeks apart were in excellent agreement. In addition, the rapid titration of samples of the stock solutions with sodium hydroxide solution gave the expected titer of propionic acid. It thus appears that appreciable ester formation did not occur.

Calculations and Results

The ionization constants of propionic acid were calculated by means of the equation

$$(E - E_0)F/2.3026RT + \log m_{\text{HPr}}m_{\text{Cl}^-}/m_{\text{Pr}^-} = -\log K - \log \gamma_{\text{Cl}^-}\gamma_{\text{HPr}}/\gamma_{\text{Pr}^-} = -\log K'$$

where *E* is the observed cell voltage corrected to 1 atmosphere; *E*₀ is the standard potential of the reference electrode; *m*_{HPr} = *m*₁ - *m*_H; *m*_{Pr⁻} = *m*₂ + *m*_{H⁺}; and *m*_{Cl⁻} = *m*₃. The term containing the activity coefficients vanishes at infinite dilution and is small for small concentrations. If this term is neglected, an apparent ionization constant, *K'*, is obtained; on extrapolation to zero ionic strength, the value of *K'* becomes equal to the true thermodynamic ionization constant *K*. Provisional values of the ionization constants were obtained by ignoring *m*_{H⁺}, calculating values of -log *K'*, and extrapolating the latter to zero ionic strength; this extrapolation yielded a preliminary value of *K*. In a subsequent calculation, *m*_{H⁺} was taken to be approximately equal to the product of this preliminary *K* and the ratio *m*₁/*m*₂ (i.e., *m*_{H⁺} = *K*_{prelim} *m*₁/*m*₂). The ionic strength was then considered to be *m*₂ + *m*₃ + *m*_{H⁺}. This process is repeated until a constant extrapolated value of *K* results; in the investi-

(1) Constructed from a portion of a thesis presented to the Graduate Faculty of the University of Texas by Robert Lee Moore in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1947.

(2) Du Pont Fellow, 1945-1947.

(3) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, N. Y., 1942.

(4) Patterson with Felsing, THIS JOURNAL, **64**, 1480 (1942).

(5) Moore with Felsing, *ibid.*, **69**, 1076 (1947).

gation here described, one such approximation was found to be sufficient.

A buffer ratio (m_1/m_2) of 1.0224 and a range of ionic strength from 0.01 to 0.1 molal were employed in the measurements in 5% isopropyl alcohol solution. Graphs of $-\log K'$ versus the ionic strength were found to be straight lines with only a small slope; the average deviation from the best lines calculated by the method of least squares was less than 0.001 of a pK unit. The values of K obtained from the intercepts of these lines are presented in Table I. Similar results were obtained in 10% isopropyl alcohol; the buffer ratio in these solutions was 1.0228 and the ionic strengths ranged from 0.005 to 0.1 molal. The resulting values of K are also shown in Table I.

As a check on the over-all precision of measurement, two buffer ratios were employed in the 20% isopropyl alcohol solutions. A buffer ratio of 1.007 was found to yield essentially linear extrapolation functions, whereas those for a series of solutions containing an excess of propionic acid (*i. e.*, a buffer ratio of 1.312) exhibited considerable curvature. This departure from linearity was smallest at 0°, where the dielectric constant value of the solvent media is highest; at higher temperatures the deviation became more pronounced. This behavior is shown in Fig. 1, where the two curves at each temperature have been extrapolated to the same point. The values for K in this 20% isopropyl alcohol solution are shown in Table I.

TABLE I

THE IONIZATION CONSTANTS OF PROPIONIC ACID IN ISOPROPYL ALCOHOL-WATER MIXTURES

$t, ^\circ\text{C.}$	$K \times 10^5$			
	0% ^a	5%	10%	20%
0	1.274	1.015	0.7798	0.4315
5	1.305	1.038	.8030	.4483
10	1.326	1.052	.8153	.4588
15	1.336	1.061	.8234	.4658
20	1.338	1.060	.8240	.4664
25	1.336	1.053	.8200	.4660
30	1.326	1.044	.8119	.4622
35	1.310	1.032	.8000	.4542
40	1.284	1.012	.7849	.4441

In Table I, for purposes of comparison, are included the values of the ionization constants of propionic acid in aqueous solution as reported by Harned and Ehlers.⁶ It will be noted that the presence of 20% isopropyl alcohol in the solvent causes approximately a three-fold decrease in the value of the ionization constant. A graph of $\log K$ versus the mole per cent. of isopropyl alcohol in the alcohol yielded a straight line which extrapolated to the value in aqueous solution.

It was found possible to express the change in value of the ionization constants with changes in temperature by means of an equation of the form

$$-\log K = A/T + CT - D$$

(6) Harned and Ehlers, *THIS JOURNAL*, **55**, 2379 (1933).

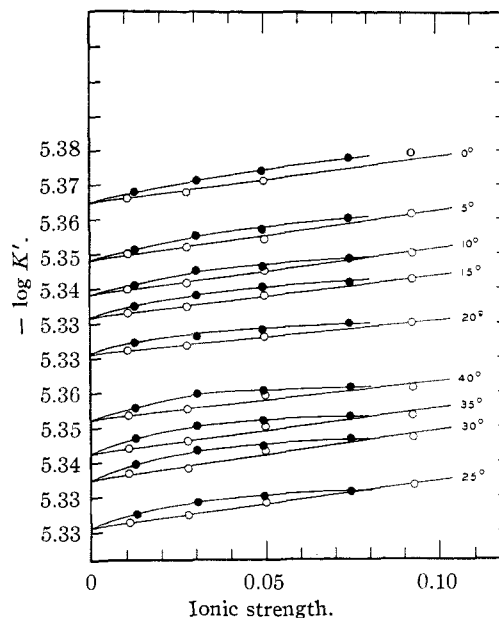


Fig. 1.—Evaluation of the ionization constants of propionic acid in 20% isopropyl alcohol: —●—, $M_1/M_2 = 1.312$; —○—, $M_1/M_2 = 1.007$.

which reproduces the experimental data from 0 to 40° with an average deviation in $-\log K$ of less than 0.0007 pK unit. The values of the con-

TABLE II

CONSTANTS OF THE EQUATION: $-\log K = A/T + CT - D$

$X, \%$	A	B	C
5	1191.0865	0.0139951	3.19088
10	1403.858	.0164058	4.51431
20	1771.125	.0204573	6.70869

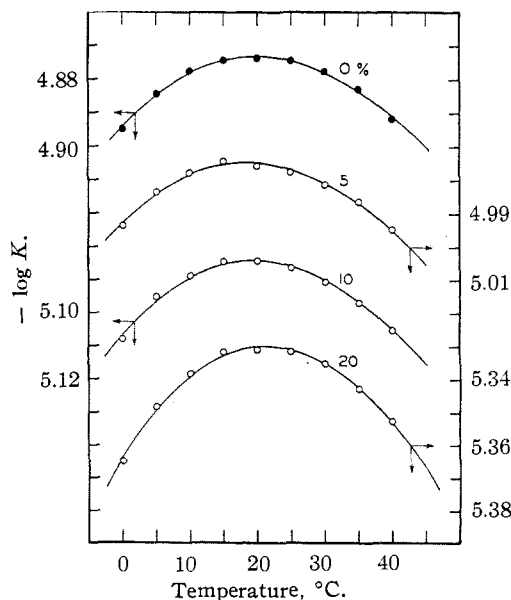


Fig. 2.—Variation of the ionization constants with temperature: —●—, Harned and Ehlers; —○—, this investigation.

stants are presented in Table II. A graph of $-\log K$ versus the temperature shows that the values of the ionization constants reach a maximum in each of the solvent mixtures, as well as in water, at about 20°; this is shown in Fig. 2.

Values of the standard free energy, heat content, heat capacity and entropy of the ionization process may be calculated by means of the equations

$$\Delta F_i^0 = A' + D'T + C'T^2$$

$$\Delta H_i^0 = A' - C'T^2$$

$$\Delta C_{pi}^0 = -2C'T$$

$$\Delta S_i^0 = D' - 2C'T$$

where A' , C' and D' are 2.3026 R times A , C , and D , respectively.

A graph of $-\log K$ versus the reciprocal of the dielectric constant was made to test the validity of the Born⁷ equation. The curve obtained differed only slightly from a straight line over the range of dielectric constants involved. The values obtained for the ionization constant of

(7) Born, *Z. Physik*, **1**, 45 (1920).

propionic acid in methyl and ethyl alcohol-water solutions by Patterson and Felsing⁴ and in dioxane-water solutions by Harned and Dedell⁸ were plotted on the same graph and were found to fall very nearly on the same line. Thus, even though the Born equation is not rigorously obeyed, it appears that the dielectric constant of the medium is more important than the nature of the added organic solvent in determining the extent of ionization of this weak acid.

Summary

1. The ionization constants of propionic acid in 5, 10 and 20 weight per cent. isopropyl alcohol solutions have been determined from 0 to 40° by the use of cells without liquid junction.

2. Equations are presented which express the ionization constants as functions of the temperature. From these, the values of the standard thermodynamic quantities may be calculated.

(8) Harned and Dedell, *THIS JOURNAL*, **63**, 3308 (1941).

AUSTIN, TEXAS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

A Photoelectronic Counter for Colloidal Particles¹

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During the Second World War, gas mask filters were developed to such a high state of efficiency that they passed only a small fraction of the most penetrating aerosols (about 0.3 micron (μ) diameter). Recently we have described⁵ an electronic photometer, designed as a smoke penetrometer for the comparisons of concentrations of very dilute aerosols, with a limit of sensitivity of 10^{-9} g./liter. If somewhat coarser test smokes are used, the penetration might be of the order of a few particles per minute, which would be beyond the limit of accuracy of this or any apparatus measuring steady illumination, since the scattered light would come in pulses. In the summer of 1944 we undertook the development of an instrument which would count individual particles and give rapid quantitative tests of the best filters.

(1) This paper is based chiefly upon work done for the Office of Scientific Research and Development under Contract OEMsr-282 with Northwestern University. The later development of the instrument was carried out for the Army Service Forces under Contracts WA-18-064-CWS-137 and -160 with Northwestern University. This paper was presented before the Division of Physical and Inorganic Chemistry at the 111th meeting of the American Chemical Society, in Atlantic City, N. J., April, 1947.

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(5) F. T. Gucker, Jr., Hugh B. Pickard, and Chester T. O'Konski, *THIS JOURNAL*, **69**, 429 (1947), and F. T. Gucker, Jr., *Electronics*, **20**, 107 (1947).

A dioctyl phthalate (DOP) smoke of about 0.8 μ diameter was chosen for the first experiments. Preliminary tests with this smoke in our photoelectric smoke penetrometer showed that the detectable limit of sensitivity corresponded to the light from only ten smoke particles, hence the counting of individual particles of this size did not seem impossible. The change from right-angle light scattering to the more intense forward-angle scattering, and the development of a stable high-gain pulse amplifier seemed a logical line of attack. By June 1945 we had developed a photoelectronic apparatus, with an electrical background of 1 count per minute or less, which would count individual DOP particles down to 0.6 μ diameter. We are describing the apparatus here since, in addition to serving as a supersensitive smoke-filter penetrometer, it can be adapted to many other uses in colloidal chemistry, bacteriology, biology and industry.

Apparatus

The apparatus consists of three parts: (1) a cell in which a stream of the very dilute smoke, passing through an intense light beam, scatters flashes of light forward upon a photosensitive cell, (2) a stable pulse amplifier with a maximum voltage gain of about 300,000, and (3) a thyratron trigger circuit which actuates a mechanical counter. The smoke cell and amplifier are mounted on a chassis base, 7.6 \times 25.4 \times 35.6 cm. (3 \times 10 \times