The Conductance and Ionization Constants of Propionic and Normal Butyric Acids in Water at 25°

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The modern theories of interionic attraction, which are now accepted in the form of limiting laws, are particularly useful in the interpretation of weak electrolytes. It has been shown by several investigators[1–3] that accurate conductance measurements of a weak binary electrolyte should suffice in theory to yield values of the limiting conductance and thermodynamic ionization constant. In media of high dielectric constant, such as water, there is strong evidence for the complete dissociation of the salts of weak acids (or bases) and therefore the limiting conductance of the weak electrolyte may be obtained by use of the additive law of Kohlrausch. But in nonaqueous solvents of low dielectric constant there are no strong electrolytes and hence to determine the limiting conductance it is necessary to apply methods of extrapolation to conductance data on the weak electrolyte alone.

For the additive method it is sufficient to determine the limiting conductance of the sodium salt of the weak acid, since the other necessary data are obtainable from the work of Shedlovsky.[4]

The extrapolation methods are based on a solution of the three simultaneous equations

$$K = \frac{C\theta^2 f_{\pm}^{\,2}}{1 - \theta} = K^1 f_{\pm}^{\,2} \qquad (1)$$

where K and K^1 are the thermodynamic and stoichiometric ionization constants, respectively, θ is the degree of dissociation, C is the total concentration of the acid in equivalents per liter, and $f_{\pm}$ is the mean activity coefficient of the ions. The activity coefficient of the undissociated acid is assumed to be unity.

$$-\log f_{\pm} = a\sqrt{C\theta} \qquad (2)$$

where a is the Debye–Hückel coefficient.

$$\theta = \frac{\lambda}{\lambda_0}\left[\frac{1}{1 - \frac{A}{\lambda_0}\sqrt{C\theta}}\right] \qquad (3)$$

where λ is the equivalent conductance of the acid at the total concentration C, λ_0 is the limiting conductance of the acid, and A is the Onsager coefficient for uni-univalent ions in water at 25°.

If the right-hand side of (3) is expanded, and terms of order higher than $\sqrt{C}$ discarded, the simple quadratic expression used by Shedlovsky[5]

$$\theta = \frac{\lambda}{\lambda_0}\left[1 + \frac{A}{\lambda_0}\sqrt{C\theta}\right] \qquad (4)$$

is obtained. A combination of (1), (2), and (4) leads to a simultaneous solution which is much easier to use and, moreover, equation (4) has been shown to fit conductivity data over a much longer range of concentration than the original Onsager expression.

When λ_0 is not known, a trial value is assumed and adjusted until the equations are self-consistent.

With these considerations in mind I have determined accurately the conductance of propionic and normal butyric acids in water at 25°. An examination of this data by the extrapolation method made it clear that data on the salts of these acids were necessary. The determinations of conductances of sodium propionate and sodium butyrate, given later in this paper, were made in collaboration with Dr. Theodore Shedlovsky.

Experimental Assembly and Technique.—The apparatus and technique used follow so closely the practice of Jones and his associates[6,7] and of Shedlovsky[8] that only the briefest description is necessary.

The bridge, of the Jones and Josephs type (with shielding, following the practice of Shedlovsky[8]), was constructed by the Cambridge Instrument Company to order.

A two-stage audio amplifier and telephones of 2000 ohms resistance formed the detector circuit.

A vacuum tube oscillator of the "push-pull" type, constructed as described by Shedlovsky,[8] supplied current to the bridge. The frequency could be varied in steps over a range of 850 to 4000 cycles by a bank of condensers in parallel. The frequency for various condenser settings was determined roughly by audio comparison with a General Radio oscillator which in turn was calibrated by a tuning fork. Several times in each series of measurements the frequency was varied, but since the conductances were found to be independent of frequency an accurate knowledge of the latter was unnecessary.

A shielded decade resistance box, supplied by the Cambridge Instrument Company, permitted direct reading to 11,111 ohms, to the nearest 0.01 ohm. It was calibrated by the National Physical Laboratory with direct current. None of the coils was thermostated, but the box was enclosed in a lagged wooden case and the temperature was known to the nearest degree.

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(1) Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

(2) Shedlovsky and Uhlig, *J. Gen. Physiol.*, **17**, 549 (1934).

(3) Fuoss, THIS JOURNAL, **57**, 488 (1935).

(4) Shedlovsky, *ibid.*, **54**, 1411 (1932).

(5) Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(6) Jones and Josephs, THIS JOURNAL, **50**, 1049 (1928).

(7) Jones and Bollinger, *ibid.*, **51**, 2407 (1929); **53**, 411 (1931).

(8) Shedlovsky, *ibid.*, **52**, 1793 (1930); **52**, 1806 (1930).

The thermostat was filled with Mineral Colza Oil and controlled to ± 0.001° by a Thyratron relay.

Two pipet cells of Jena glass were used for the more concentrated solutions. They were calibrated with 0.1 demal potassium chloride, using the recent values of Jones and Bradshaw.[9] The temperature of the thermostat was set to 25 ± 0.005° by using a thermometer recently calibrated by the National Physical Laboratory.

Two flask cells, one of Pyrex and one of clear quartz, were used for the more dilute solutions. The electrodes were lightly platinized. After each run the cells were cleaned with redistilled alcohol and ether, and occasionally with hot chromic acid.

Conductivity water was obtained from a still which followed the general design of Ellis and Kiehl.[10] The boiler was of Pyrex and the condenser of fused silica. Purified nitrogen was passed up the column and out through a water trap. A ball and socket joint connected the Pyrex and silica portions of the still and gave great flexibility and freedom from breakage. The boiler was charged with a good grade of distilled water made 0.025 molar in phosphoric acid. The still yielded one liter per hour of fair conductivity water ($k = 5 \times 10^{-7}$ mhos), and about 400 cc. per hour of the best water ($k = 0.8$ to 2×10^{-7} mhos). For the more dilute solutions the water was distilled directly into the flask cells.

Densities were determined with an ordinary Sprengel pycnometer in a water thermostat.

All solutions were made up by weight. The more accurate weighings were performed on an analytical balance which could be read to 0.1 mg. Water and stock solutions were weighed on a large balance to the nearest 10 mg. Weights were calibrated against a set standardized by the National Physical Laboratory.

Materials.—The propionic and normal butyric acids were Kahlbaum "purest." They were further purified by fractional crystallization and distillation. The freezing point of the recovered portion of propionic acid was −22.4°, which may be compared with −20.8° (Timmermans and Hennaut-Roland[11]) and −22.3° (Broughton[12]). The final portion of butyric acid melted at −5.37°, very close to the value given by Timmermans and Hennaut-Roland.[11] As a check on the purity of the acids they were analyzed by weight titrations against carbon dioxide free sodium hydroxide. By using phenolphthalein and a technique which excluded carbon dioxide it was possible to titrate with a precision of 0.04%. Several titrations gave the purity of the propionic acid as 100.02%, and that of the butyric acid as 99.96%. Accordingly the acids were assumed to be pure within the experimental error. The sodium hydroxide was standardized against a standard brand of benzoic acid.

The molecular weights of the acids were taken from the "International Critical Tables."

Several determinations of the densities of solutions of both acids checked so well with the data of Drucker[13] that the latter's measurements were used to compute concentrations.

Results.—Tables I and II give the data for the two acids. The columns are, respectively, the concentration in equivalents per liter, the equivalent conductance, the degree of dissociation, the mean activity coefficient of the ions; the stoichiometric ionization constant, and the thermodynamic ionization constant. These ta-

TABLE I

EQUIVALENT CONDUCTANCES AND IONIZATION CONSTANTS OF PROPIONIC ACID AT 25°. $\lambda_0 = 385.47$

Concn. $C \times 10^3$	λ	θ	$f_\pm$	$K^1 \times 10^5$	$K \times 10^5$
0.033831	177.94	0.46212	0.9954	1.343	1.331
.035330	174.76	.45377	.9953	1.332	1.320
.072197	134.25	.34880	.9942	1.349	1.333
.16091	96.690	.25136	.9926	1.358	1.338
.24142	81.209	.21116	.9917	1.365	1.342
.26595	77.812	.20234	.9915	1.365	1.342
.35702	68.283	.17761	.9908	1.369	1.344
.37303	66.895	.17400	.9907	1.367	1.342
.56685	55.320	.14395	.9895	1.372	1.343
.72479	49.385	.12853	.9888	1.374	1.343
.87116	45.348	.11805	.9883	1.378	1.345
1.8650	31.657	.082480	.9856	1.383	1.343
2.8788	25.717	.067042	.9839	1.387	1.343
4.8026	20.099	.052440	.9817	1.394	1.343
6.9117	16.852	.043990	.9799	1.399	1.343
6.9880	16.764	.043761	.9798	1.400	1.344
8.8839	14.903	.038920	.9786	1.400	1.341
10.342	13.844	.036164	.9777	1.403	1.341
12.208	12.763	.033351	.9768	1.405	1.340
15.347	11.375	.029738	.9753	1.407	1.338
15.401	11.373	.029732	.9754	1.403	1.335
49.876	6.3628	.016681	.9670	1.411	1.320
75.352	5.1598	.013543	.9635	1.401	1.301
101.64	4.4283	.011633	.9607	1.392	1.285
152.87	3.5375	.0083126	.9544	1.344	1.228
192.95	3.1576	.0064011	.9494	1.279	1.153

TABLE II

EQUIVALENT CONDUCTANCES AND IONIZATION CONSTANTS OF NORMAL BUTYRIC ACID AT 25°. $\lambda_0 = 382.40$

Concn. $C \times 10^3$	λ	θ	$f_\pm$	$K^1 \times 10^5$	$K \times 10^5$
0.029576	193.29	0.50622	0.9955	1.535	1.521
.055746	154.28	.40418	.9945	1.529	1.512
.082109	132.99	.34851	.9938	1.531	1.512
.10606	120.01	.31451	.9933	1.530	1.510
.29695	77.368	.20293	.9910	1.534	1.507
.33908	72.904	.19124	.9907	1.534	1.505
.43277	65.335	.17142	.9901	1.535	1.505
.78715	49.671	.13040	.9883	1.539	1.503
.83817	48.242	.12666	.9881	1.540	1.503
.93748	45.846	.12038	.9877	1.545	1.507
1.0096	44.319	.11638	.9875	1.548	1.509
1.5818	35.848	.094184	.9859	1.549	1.506
2.1506	30.961	.081378	.9848	1.550	1.504
2.1754	30.817	.080999	.9847	1.553	1.506
2.7827	27.394	.072024	.9837	1.556	1.505
2.8099	27.253	.071653	.9837	1.554	1.504
3.6043	24.184	.063609	.9826	1.557	1.504
4.1450	22.610	.059482	.9819	1.559	1.504
5.2881	20.102	.052905	.9808	1.563	1.503
6.4110	18.312	.038209	.9798	1.565	1.503
8.5822	15.893				
17.350	11.247				
99.879	4.6414				
149.96	3.7317				
189.92	3.2776				
240.10	2.8631				
295.42	2.5398				

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[9] Jones and Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

[10] Ellis and Kiehl, *ibid.*, **57**, 2145 (1935).

[11] Timmermans and Hennaut-Roland, *J. chim. phys.*, **27**, 401 (1930).

[12] Broughton, *Trans. Faraday Soc.*, **30**, 367 (1934).

[13] Drucker, *Z. physik. Chem.*, **52**, 641 (1905).

bles are based on λ_0 values obtained from salt conductances by the additive method. Furthermore, the values of $\theta, f_{\pm}$, etc., have been computed by the new and more convenient method due to Shedlovsky.[5] It should be noted that for the present data the various extrapolation methods give identical results in the range of concentration where K is reasonably constant. No water correction has been made in computing the equivalent conductances since the specific conductivity of the water used never exceeded 0.2×10^{-6} mho, and is due largely to the presence of carbon dioxide.

Discussion of Results.—Table I shows that the measured conductances of the four most dilute points are in error. This is undoubtedly due to the use of a Pyrex flask cell. The effect of glass on the conductivity of very dilute solutions of weak acids was noted many years ago by Kraus and Parker.[14] The data of Table II do not show this effect since the butyric acid measurements were made in quartz.

A plot of the logarithm of the stoichiometric ionization constant against the square root of the ionic strength for these two acids gives straight lines for total acid concentrations not exceeding 0.01 normal. These lines have very nearly the Debye–Hückel slope (1.013), and the intercepts give the logarithm of the thermodynamic ionization constant. At higher concentrations log K^1 falls off rapidly with increasing ionic strength, an effect noted by MacInnes and Shedlovsky[15] for acetic acid. Davies[16] showed that this so-called "medium effect" is largely due to viscosity in the case of acetic acid, and I propose to discuss the effect of viscosity in a forthcoming paper.

The extrapolation method yields a thermodynamic ionization constant of 1.343×10^{-5} for propionic acid, in fair agreement with the value 1.332×10^{-5}, obtained by Harned and Ehlers[17] from electromotive force measurements. The latter figure has been reduced from a molar to a concentration basis.

For normal butyric acid extrapolation gives 1.508×10^{-5}, in excellent agreement with the value 1.510×10^{-5}, obtained by Harned and Sutherland[18] from electromotive force measurements.

The Conductance of the Sodium Salts of Propionic and Normal Butyric Acids in Water at 25°

Materials.—Kahlbaum acids were used, but no further purification was attempted since the salt concentrations of stock solutions were known accurately from titrations.

Preparation of Solutions.—A carbonate-free solution of sodium hydroxide was prepared and standardized by weight titrations against Bureau of Standards acid potassium phthalate. The latter was dried before using. Phenolphthalein was used as indicator and nitrogen was passed through the titration vessel for some time before the alkali was added and during the titration. It so happens that the phenolphthalein end-point corresponds very closely to the pH of neutralized acid phthalate so that it is possible to titrate to an accuracy of 1 or 2 parts in 10,000. As a check, however, the pH of the final solution was determined with the glass electrode and if necessary a small correction applied. The acids were titrated in a similar manner, but since in this case the pH of the neutralized solutions does not correspond to the phenolphthalein end-point, the correction was important. By applying the correction it was possible to titrate the acids to a precision of 3 parts in 10,000. This method has the advantage of being much more rapid and convenient than the method of differential electrometric titration of MacInnes and Dole.[19]

When a sufficient number of titrations had established the strength of the acids, stock solutions were made up without indicator. To suppress hydrolysis about 0.5% excess acid was added. The salt concentration was known accurately from the amount of alkali used.

The densities of several solutions of sodium butyrate were measured and it was found that the agreement with sodium acetate solutions was very close in the dilute range. Accordingly it was considered justifiable to use the same density–concentration relationship in the case of sodium propionate.

Table III gives the conductances of sodium propionate and sodium butyrate at 25°.

TABLE III

Sodium Propionate		Sodium Butyrate	
C	λ	C	λ
0.0021779	82.53	0.0012132	80.14
.0041805	81.27	.0025811	78.27
.0078705	79.72	.0071049	76.72
.014272	77.88	.011963	75.21
.025973	75.64	.016858	74.04
		.029336	71.86
		.063417	68.03
		.106195	64.86
$k_{H_2O} = 0.269 \times 10^{-6}$		$k_{H_2O} = 0.467 \times 10^{-6}$	

The specific conductances of the solutions were corrected by 1×10^{-7} mho, that amount of the conductance of the water being estimated as due to salt impurity. The remaining conductance of the water was considered as due to its carbon dioxide content. In the slightly acid solutions

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(14) Kraus and Parker, THIS JOURNAL, **44**, 2429 (1922).

(15) MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

(16) Davies, *Phil. Mag.*, **4**, 249 (1927); "The Conductivity of Solutions," 1933, p. 141.

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

(18) Harned and Sutherland, *ibid.*, **56**, 2039 (1934).

(19) MacInnes and Dole, *ibid.*, **51**, 1119 (1929).

the contribution of carbon dioxide would be negligible.

The limiting conductances were determined by using Shedlovsky's[5] method of extrapolation, in which $1/\lambda$ is plotted against $\sqrt{C}$. This gave $\lambda_0 = 85.92$ for sodium propionate, and $\lambda_0 = 82.70$ for sodium butyrate. These values, combined with the limiting conductances for Na^+ and H^+, as determined by MacInnes, Shedlovsky, and Longsworth[20] (corrected to the Jones and Bradshaw basis) give the λ_0 values for the acids which were used in Tables I and II.

The Limitations of the Extrapolation Method

There are now sufficient accurate conductivity data to permit of a critical examination of the validity of the extrapolation method for determining conductances and ionization constants of weak electrolytes. Table IV gives a comparison of λ_0 and K values as obtained (1) from conductance measurements on the weak acid and its alkali salt, and (2) from conductance measurements of the weak acid alone, using the extrapolation method.

TABLE IV

	From acid and salt conductances		From acid conductances alone, by extrapolation	
Acid	λ_0	K	λ_0	K
Carbonic[21]	394.3	4.31×10^{-7}	424	3.65×10^{-7}
Acetic[22]	390.71	1.753×10^{-5}	395.3	1.705×10^{-5}
Propionic[23]	385.47	1.343×10^{-5}	386.34	1.337×10^{-5}
n-Butyric[23]	382.40	1.508×10^{-5}	386.05	1.475×10^{-5}
Monochloroacetic[24]	389.52	1.396×10^{-3}	389.5	1.396×10^{-3}
o-Chlorobenzoic[25]	380.07	1.197×10^{-3}	380.0	1.197×10^{-3}
Benzoic[26]	382.21	6.312×10^{-3}	382.1	6.312×10^{-3}

Table IV shows that the extrapolation method is reliable if the electrolyte is not too weak ($K \geqq 10^{-3}$), but that if the electrolyte is much weaker ($K \leqq 10^{-5}$) the method may give λ_0 and K values that are seriously in error. Therefore, the statement of some authors[1] that the extrapolation method will give a λ_0 value as accurate as the λ values is unjustified. It is obvious why the extrapolation method may fail if the electrolyte is too weak. Even if the limiting laws are obeyed exactly in the concentration range used for the extrapolation, the correct λ_0 will not be found unless the number of experimental points is very large and the distribution of experimental errors is random. Thus, in the worst case of Table IV, *i. e.*, carbonic acid, accurate extrapolation from λ's of the order of 5 to a λ_0 of 394 would require an unobtainable experimental accuracy. However, the extrapolation methods are valid for determining ionization constants if the λ_0's are known accurately.

It follows from the above that in those cases where it is impossible to measure limiting conductances by the additive principle the extrapolation method may not serve if the electrolyte, is too weak.

I wish to thank Dr. D. A. MacInnes and Dr. Theodore Shedlovsky for continued encouragement and invaluable advice during the progress of this work.

Summary

Measurements are reported on the electrical conductance of solutions of propionic acid, sodium propionate, *n*-butyric acid, and sodium butyrate in water at 25°. From these are derived limiting conductances and ionization constants.

The limitations of the extrapolation method for determining limiting conductances and ionization constants of weak electrolytes are discussed.

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(20) MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, **54**, 2758 (1932).

(21) Shedlovsky and MacInnes, *ibid.*, **57**, 1705 (1935).

(22) MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

(23) Belcher, this communication.

(24) Shedlovsky, Brown and MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1935).

(25) Saxton and Meier, THIS JOURNAL, **56**, 1918 (1934).

(26) Brockman and Kilpatrick, *ibid.*, **56**, 1483 (1934).