intensity of 10 when similarly treated. Phosphors developed from mixtures of calcium phosphate with certain organic compounds have been studied in the light of results from the purely inorganic cases.

These experiments have led to the general conclusion that, in the absence of a specific metallic activator, fluorescence resulting from heat treatment of inorganic compounds is due to formation of complexes of critical composition through partial decomposition or of critical physical condition through modification of crystal structure.

SCHENECTADY, NEW YORK RECEIVED MARCH 11, 1938

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE AND COLUMBIA UNIVERSITY]

Acid Dissociation Constants in Dioxane–Water Mixtures by Potentiometric Titration

BY CECIL C. LYNCH AND VICTOR K. LA MER

While potentiometric acid–base titrations in aqueous solutions have been examined exhaustively both with respect to theory and practice by many workers,[1–9] comparatively few investigations have been made in non-aqueous and mixed solvents. In this connection the work of Bishop, Kittredge and Hildebrand[10] in ethyl alcohol, of Clark, Wooten and Compton,[11] and Wooten and Hammett,[12] in *n*-butyl alcohol should be mentioned. Likewise, La Mer and Downes[13] have shown the possibility of acid–base titration in benzene, and Tomicek[14] has made titrations of weak acids in several mixed solvents. Since dioxane–water mixtures offer a continuous transition from a polar aqueous to non-polar solvent, a study of the titration of weak acids in such mixtures presented a significant problem.

The unusual and complicated conductivity titration curves obtained by La Mer and Downes[13] for electrolytes in benzene and the equally complicated conductivity dilution curves obtained by Fuoss and Kraus[15] for salts in dioxane–water mixtures stimulated us to investigate whether or not the e. m. f. titration curves would be simple or complex in low dielectric solvents.

Dioxane–water mixtures were selected for several reasons. This cyclic ether mixes with water in all proportions, giving a wide range of dielectric constant; it is becoming more and more important as a solvent for many substances which are practically insoluble in water: for example, the commercially important resin acids, like abietic acid. Also, many related physical properties[16,17] of the aqueous mixtures are rapidly becoming available in the literature.

In preliminary work on potentiometric titrations of weak acids in dioxane–water mixtures, the titration curves did not yield results in agreement with the Nernst relation. This finding encouraged further investigation and led to the results here presented.

Theory of Acid–Base Titrations.—Auerbach and Smolczyk[1] employed the relation

$$K = m_{\text{H}}(X/1 - X) \qquad (1)$$

for monobasic acids for the acid region, where K is the dissociation constant (classical); m_{H} is the concentration of the hydrogen ion; X is the fraction of the acid neutralized. They assumed that all salts were completely dissociated and that the concentrations were so low that the activity coefficients for univalent ions could be taken as unity. Söderbäck[2] in an elaborate and thorough treatment modified this relation by introducing the activity coefficient and the thermodynamic dissociation constants. His relation is

$$K^0 = fm_{\text{H}}\,(B/(B - 1)) \qquad (2)$$

where $B = (mx/cv_0) + (m_{\text{H}}/c)\,(1 + x/v_0)$; m is molarity of the base; x is volume of base used; c is initial concentration; v_0 is initial volume of acid solution; f is activity coefficient of univalent ions. Eq. (2) is not significantly different from

$$K^0 = fm_{\text{H}}(X/(1 - X)) \qquad (3)$$

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(1) Auerbach and Smolczyk, *Z. physik. Chem.*, **110**, 65 (1924).

(2) Söderbäck, *Arkiv. Kemi. Min. och. Geol.*, **11A**, 1 (1934).

(3) Brönsted, *Z. physik. Chem.*, **169**, 52 and 361 (1934).

(4) Larsson, *ibid.*, **156**, 352 and 381 (1931): **157**, 342 (1931); **159**, 306 and 315 (1932): **165**, 53 (1933).

(5) Hahn, *Ber.*, **62B**, 727 (1929); *Z. angew. Chem.*, **43**, 712 (1930); *Z. physik. Chem.*, **127**, 1 (1927).

(6) Gane and Ingold, *J. Chem. Soc.*, 1594 (1928); 2158 (1931).

(7) Ashton and Partington, *Trans. Faraday Soc.*, **30**, 598 (1934).

(8) Roller, THIS JOURNAL, **54**, 3485 (1932); **50**, 1 (1928).

(9) Eastman, *ibid.*, **47**, 332 (1925).

(10) Bishop, Kittredge and Hildebrand, *ibid.*, **44**, 135 (1922).

(11) Clark, Wooten and Compton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 321 (1931).

(12) Wooten and Hammett, THIS JOURNAL, **57**, 2289 (1935).

(13) La Mer and Downes, *ibid.*, **53**, 888 (1931).

(14) Tomicek, *Coll. Czech. Chem. Com.*, **6**, 408 (1934).

(15) Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

(16) Åkerlöf and Short, *ibid.*, **58**, 1241 (1936).

(17) Hovorka, Schaefer and Dreisbach, *ibid.*, **58**, 2263 (1936),

Hence, in a medium where the ionic environment is kept sensibly constant, eq. 3 reduces to the Auerbach and Smolcyzk expression, where $K = (K^0/f)$. This can be achieved most simply by maintaining a relatively high constant concentration of inert neutral salt.[18–20]

Fuoss and Kraus[15] from conductivity measurements have shown that ion association in the Bjerrum[21] sense occurs in dioxane–water mixtures. If the dielectric strength is not too low, only association to pairs takes place with univalent ions. We shall examine, accordingly, to what extent association of ions in dioxane–water mixtures will modify the interpretation of the results of acid–base titrations.

Consider a solution containing dioxane, water, lithium chloride in relatively high concentration, and a weak acid, acetic acid, being titrated with a strong base, sodium hydroxide. The titration is carried out by weighing the amounts of sodium hydroxide solution added. We are concerned with the equilibria

(a) $\mathrm{LiCl} \rightleftarrows \mathrm{Li}^+ + \mathrm{Cl}^-$

$$K_1 = (m_{\mathrm{Li}^+} \cdot m_{\mathrm{Cl}^-}/m_{\mathrm{LiCl}})$$

(b) $\mathrm{HA} \rightleftarrows \mathrm{H}^+ + \mathrm{A}^-$

$$K_{\mathrm{HA}} = (m_{\mathrm{H}^+} \cdot m_{\mathrm{A}^-}/m_{\mathrm{HA}})$$

(c) $\mathrm{MA} \rightleftarrows \mathrm{M}^+ + \mathrm{A}^-$

$$K_{\mathrm{MA}} = (m_{\mathrm{M}^+} \cdot m_{\mathrm{A}^-}/m_{\mathrm{MA}})$$

(d) $\mathrm{LiCl} + \mathrm{MA} \rightleftarrows \mathrm{LiA} + \mathrm{MCl}$

$$K_4 = (m_{\mathrm{LiA}} \cdot m_{\mathrm{MCl}}/m_{\mathrm{LiCl}} \cdot m_{\mathrm{MA}})$$

(e) $\mathrm{LiA} \rightleftarrows \mathrm{Li}^+ + \mathrm{A}^-$

$$K_5 = (m_{\mathrm{Li}^+} \cdot m_{\mathrm{A}^-}/m_{\mathrm{LiA}})$$

(f) $\mathrm{MCl} \rightleftarrows \mathrm{M}^+ + \mathrm{Cl}^-$

$$K_6 = (m_{\mathrm{M}^+} \cdot m_{\mathrm{Cl}^-}/m_{\mathrm{MCl}})$$

Electroneutrality requires

(g) $m_{\mathrm{M}^+} + m_{\mathrm{H}^+} + m_{\mathrm{Li}^+} = m_{\mathrm{A}^-} + m_{\mathrm{Cl}^-}$

If m^0 is the initial molality of the acid, then

(h) $m_{\mathrm{MA}} + m_{\mathrm{A}^-} + m_{\mathrm{HA}} + m_{\mathrm{LiA}} = m^0$

Since (mx/w^0) is the stoichiometric molality the base would have at any time if no reaction took place in the solution, we have the relation

(i) $m_{\mathrm{M}^+} + m_{\mathrm{MA}} + m_{\mathrm{MCl}} = (mx/w^0)$

where the m's refer to the molalities of the substances in subscripts; m is the concentration of the base in moles/1000 g. of solution; x is the grams of base solution added at any time; w^0 is the initial weight of the solvent taken; M is the metal ion of the base MOH.

It is necessary to simplify the problem as follows:

(j) Bjerrum association occurs in the solvent for acids and salts, to the extent of the formation of pairs only.

(k) Sufficient lithium chloride has been added to maintain a constant ionic environment.

(l) That the weight of base solution added to the end-point does not appreciably change the weight of the initial solution.

(m) For MCl and LiA the extent of association is the same and the $m_{\mathrm{Li}^+} = m_{\mathrm{Cl}^-}$ and $m_{\mathrm{LiA}} = m_{\mathrm{MCl}}$. Combining (b), (g), (h), (i), and (m):

$$m_{\mathrm{A}^-} = (K_{\mathrm{HA}}/m_{\mathrm{H}^+})[m^0 - m_{\mathrm{H}^+} - (mx/w^0)] \quad (4)$$

Combining (c), (i), (m)

$$m_{\mathrm{A}^-} \cdot m_{\mathrm{M}^+} = K_{\mathrm{MA}}[(mx/w^0) - m_{\mathrm{M}^+} - m_{\mathrm{LiA}}]$$

But

$$m_{\mathrm{LiA}} = (m_{\mathrm{A}^-}/K')$$

since m_{Li^+} is constant where $K' = (K_5/m_{\mathrm{Li}^+})$. Substituting from (g)

$$m^2_{\mathrm{A}^-} - m_{\mathrm{H}^+} \cdot m_{\mathrm{A}^-} = K_{\mathrm{MA}}[(mx/w^0) - m_{\mathrm{A}^-} + m_{\mathrm{H}^+} - (m_{\mathrm{A}^-}/K')]$$

or

$$m^2_{\mathrm{A}^-} + [K_{\mathrm{MA}} \cdot (1 + K) - m_{\mathrm{H}^+}]\, m_{\mathrm{A}^-} = K_{\mathrm{MA}}[(mx/w^0) + m_{\mathrm{H}^+}]$$

where $K = (1/K')$. Now m_{H^+} is negligible compared with K_{MA} or with (mx/w^0). Thus we obtain

$$m^2_{\mathrm{A}^-} + K_{\mathrm{MA}}(1 + K)m_{\mathrm{A}^-} = K_{\mathrm{MA}}\left(\frac{mx}{w^0}\right) \quad (5)$$

When $m^2_{\mathrm{A}^-}$ is small compared with the remaining terms of eq. (5), a condition true for a weak acid at low concentrations, this expression reduces to

$$m_{\mathrm{A}^-} = \frac{mx}{w^0}\left(\frac{1}{1 + K}\right) \quad (6)$$

That is, the anion concentration is directly proportional to the resulting concentration of added base.

Substituting m_{A^-} of eq. (4) into eq. (6)

$$K_{\mathrm{HA}}\,(1 + K) = m_{\mathrm{H}}\left[\frac{\left(\frac{mx}{w^0}\right)}{m_0 - \left(\frac{mx}{w_0}\right)}\right]$$

or

$$K_{\mathrm{HA}}\,(1 + K) = m_{\mathrm{H}}\left(\frac{X}{1 - X}\right) \quad (7)$$

The right-hand side is identical with K_{HA} as calculated from the classical relation eq. (1). To identify K_{HA} of eq. (7), we will write it as K^0_{HA}, and retain K_{HA} as that constant obtained from

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[18] Brönsted, *Medd. Vet. Akad. Nobel Institute*, **5**, No. 25 (1919); *Kgl. Danske Videnskab. Selskab. Math-fys. Medd.*, III, No. 9 (1920).

[19] La Mer, *Trans. Am. Electrochem. Soc.*, **41**, 507 (1927).

[20] La Mer and Sandved, THIS JOURNAL, **50**, 2656 (1928).

[21] Bjerrum, *Kgl. Danske Videnskab. Selskab. Math-fys. Medd.*, VII, No. 9 (1926).

use of eq. (1); thus we obtain the relation between these constants

$$K^0_{HA}\,(1 + K) = K_{HA} \qquad (8)$$

But $K = (m_{Li^+}/K_5)$ where K_5 is the salt dissociation constant arising from ion-association; we have, then

$$K^0_{HA}\,(1 + m_{Li^+}/K_5) = K_{HA} \qquad (9)$$

This shows that the classical dissociation function of a weak acid as calculated from eq. (1) is a constant in a medium of low dielectric constant, but is different from K^0_{HA}, the idealized dissociation constant freed from effects of ion association, by the factor $(1 + m_{Li^+}/K_5)$. Thus, an extrapolation of K_{HA} to zero lithium chloride concentration gives K^0_{HA}, since K_5 is not zero. Such extrapolations are shown in Fig. 5, employing the log functions of the dissociation constants.

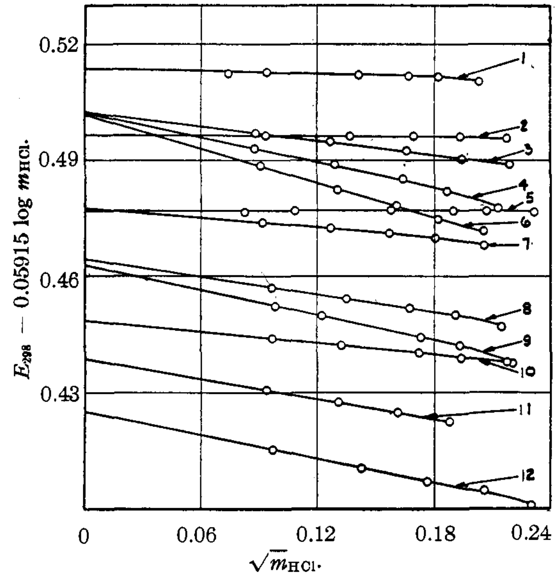

Fig. 1.—Extrapolation plots for E^0 values of the cell.

Dioxane-water ratios		4.040		2.014		1.035
Curves and LiCl molalities	1	0.2827	2	0.6895	5	0.9274
	3	.09607	7	.2121	10	.2379
	4	.04888	8	.08177	11	.1212
	6	.02643	9	.04422	12	.05924

The Reference E. M. F., E^0.—In order to apply the general theory to a titration it is necessary to know the relation between the e. m. f. of the cell measured and the activity of the hydrogen ion, or, for a constant ionic environment, the molality of the hydrogen ion. If we impose the latter condition during titration the relation can be established simply.

Consider the cell in which constancy of the environment has been established by the addition of a relatively high concentration of lithium chloride.

$$\text{Hg, HgCl,} \left\{\begin{matrix}\text{HCl } (m_1)\\ \text{LiCl } (m_3)\end{matrix}\right\}, \text{ Quinhydrone, Au}$$

This cell operates without liquid junction and the following process occurs

$$\text{Hg (1)} + \text{H}^+ + \text{Cl}^- + \text{quinone} = \text{HgCl(s)} + \text{hydroquinone}$$

The e. m. f. is expressed by the relation

$$E_{298} = E^0_1 + 0.05915 \log a_H \cdot a_{Cl}$$

or

$$E_{298} = E^0_1 + 0.05915 \log f^2 \cdot m_H \cdot m_{Cl}$$

and

$$E_{298} = E^0 + 0.05915 \log m_H \qquad (10)$$

where $E^0 = E^0_1 + 0.05915 \log f^2 \cdot m_{Cl}$, since m_{Cl} is effectively equal to the molality of the lithium chloride.

Subtracting 0.05915 log m_{HCl} from each side

$$E_{298} - 0.05915 \log m_{HCl} = 0.05915 \log (m_H/m_{HCl}) + E^0$$

At $m_{HCl} = 0$, we set $\log (m_H/m_{HCl}) = 0$, and $E^0 = (E_{298} - 0.05915 \log m_{HCl})$.

The limiting value may be obtained by extrapolation, and equation (10) employed for calculation of the hydrogen ion molality from e. m. f. measurements. It is to be noted that a different E^0 is required for each solution in which, either by a variation of the concentration of lithium chloride or of the dioxane, the activity coefficient has been altered.

Experimental

Potentiometric titrations have been made at 25° in three dioxane–water mixtures in which the ratios were 1.035, 2.014 and 4.040, respectively, using acetic, propionic, butyric and benzoic acids, as examples of readily soluble acids, and abietic and stearic acids as representative water insoluble acids. Large additions of lithium chloride produced immiscibility in the dioxane–water system, which sets an upper limit to the permissible concentration of lithium chloride.

A preliminary study of the 25° isotherm for the system: sodium hydroxide–dioxane–water showed that small amounts of sodium hydroxide produced immiscibility. Hence it was necessary to add approximately molal caustic in aqueous solution in the form of the titrating base from a weighing pipet to keep the dilution factor under one per cent.

Preparation of Materials

Dioxane.—Technical 1,4-dioxane from the Eastman Kodak Co. was purified by the method described by Eigenberger.[22] The product was kept over metallic sodium, from which it was distilled when needed.

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[22] Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931).

Acids.—Purified acids: acetic acid from Baker Chemical Co., propionic acid and butyric acid from Eastman Kodak Co., were twice recrystallized and twice distilled at reduced pressure and then analyzed for purity by titration with the sodium hydroxide solution in aqueous solution. All were chemically pure within 0.1%. The benzoic acid was from the Bureau of Standards. Purified abietic acid from the Hercules Powder Company and U. S. P. stearic acid were used without further treatment.

Lithium Chloride.—Merck c. p. Lithium Chloride was used without further treatment. Aqueous solutions of this salt had a *p*H of 6.85.

Solutions.—All solutions were prepared by direct weighing, and all titrations made by weight. Thus, the concentrations are expressed by weight per cent. or by molality.

In order to prepare the dioxane-water-lithium chloride solutions, aqueous solutions of lithium chloride were first prepared and analyzed for chlorine. The aqueous lithium chloride solution was then mixed with dioxane to the proper ratio. This was also the method of obtaining the dioxane-water-hydrochloric acid solutions which were added to the dioxane-water-lithium chloride solutions to give the hydrochloric acid solutions used in determining the E^0 values for the cells. The other acid solutions were prepared by adding the acids directly to the dioxane-water-lithium chloride solutions.

Apparatus.—The titration cell is represented symbolically as

$$\mathrm{Hg},\ \left\{\begin{matrix}\mathrm{HgCl}\\ \mathrm{LiCl}\ (m_3)\end{matrix}\right\},\ \left\{\begin{matrix}\mathrm{HA}\ (m_1)\\ \mathrm{MA}\ (m_2)\\ \mathrm{LiCl}\ (m_3)\end{matrix}\right\},\ \text{Quinhydrone, Au}$$

the solvent, one of the dioxane-water mixtures, extends throughout the cell. This cell also avoids liquid junctions. All measurements were made with the cell in a water thermostat at 25.00 ± 0.03°. The bridge between electrodes was made with a ground-glass joint in the acid portion to avoid mixing and loss by diffusion during titration.

E. m. f. measurements were made with a Leeds and Northrup Type K potentiometer, and a Type P galvanometer, sensitive to 0.00083 microampere. The Weston Normal Cell was checked frequently against other standard cells. The calomel electrodes in dioxane-water-lithium chloride solution were found reproducible to 0.1 mv. over a period of three days. Measurements with the cells were reproducible to within 0.2 mv.

Experimental Data and Results

The E^0 values for the cells were determined by measuring a series of cells of the type

$$\mathrm{Hg, HgCl},\ \left\{\begin{matrix}\mathrm{HCl}\ m_1\\ \mathrm{LiCl}\ m_3\end{matrix}\right\},\ \text{Quinhydrone, Au}$$

in which the solvent medium was dioxane-water. Linear[3] extrapolation of the function $[E^0 - 0.05915 \log (m_{\mathrm{H}}/m_{\mathrm{HCl}})]$ against $\sqrt{m_{\mathrm{HCl}}}$ to zero concentration of the acid, gave the E^0 value. This is in accordance with relation (10) above. Table I and the curves of Figs. 1 and 2 give the data and E^0 values for the three dioxane: water ratios chosen.

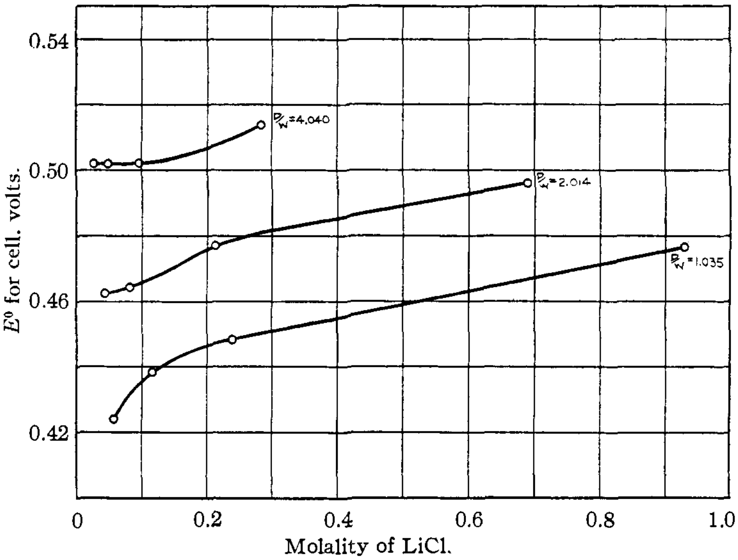

Fig. 2.—Variation of E^0 for cell with LiCl concentration.

Table I

E^0 Values at 25° for Cells

A. Solvent medium: Dioxane: water ratio = 1.035

Molality LiCl	E^0, v.
0.9274	0.4768
.2379	.4485
.1212	.4385
.05924	.4240

B. Solvent medium: Dioxane: water ratio = 2.014

Molality LiCl	E^0, v.
0.6895	0.4962
.2121	.4773
.08177	.4644
.04422	.4627

C. Solvent medium: Dioxane: water ratio = 4.040

Molality LiCl	E^0, v.
0.2827	0.5140
.09607	.5026
.04888	.5021
.02643	.5022

The titration data for the four acids are exemplified in the curves of Fig. 3. Drifting potentials resulted when the end-point was overreached to any extent.[23]

The linear character of the data obtained by plotting e. m. f. against log $(1 - X)/X$ are shown in Fig. 4. The average slope for the curves is 0.058 ± 0.002. This is in satisfactory agreement with the theoretical slope 0.059.

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(23) La Mer and Downes, *J. Biol. Chem.*, **57**, 622 (1923).

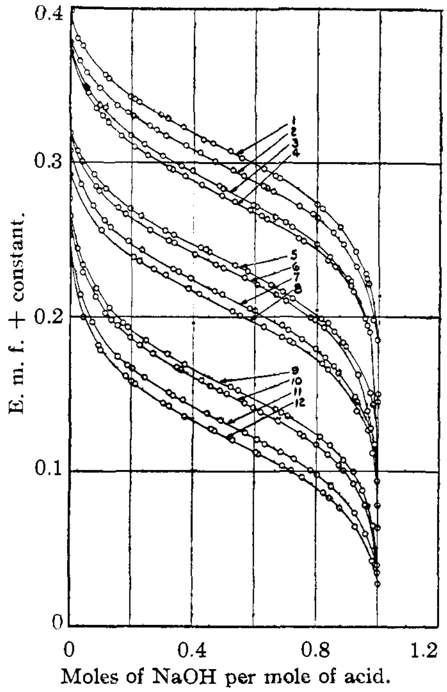

Fig. 3.—Titration curves for the acids.

Dioxane-water ratios		1.035	2.014	4.040
Curves and acids	Benzoic	1	5	9
	Acetic	2	6	10
	Propionic	3	7	11
	Butyric	4	8	12

In our preliminary work, we frequently encountered slopes of 0.08 and even as high as 0.11. We attribute our failure to obtain the theoretical slope at that time to a combination of several disturbing factors, which deserve mention. The preliminary methods were entirely volumetric and the necessarily larger quantities of aqueous titrating solution produced significant dilutions of the medium which resulted in a progressive increase in the dielectric constant and a decrease in the total salt concentration during the progress of titration. Potassium chloride, which was being used at that time, is not as soluble as lithium chloride in dioxane–water mixtures, and hence is less suited for maintaining a constant ionic environment. Figure 4 shows that with the final technique described no difficulty was encountered in reproducing the theoretical slope.

From the titration data the values of the dissociation constants for the acids have been calculated by use of eq. (1), from the point at which one-fourth of the acid was neutralized, to minimize the effect of dilution produced by the addition of the titrating base. The results are given in Table II and are represented graphically in Fig. 5. The dielectric constants were interpolated from the data of Åkerlöf and Short.[16]

TABLE II

VALUES OF THE ACID CONSTANTS AT 25°

Dioxane–water ratio	Dielectric constant	M	$-\log K_{HA}$ for acids Acetic	Propionic	Butyric	Benzoic
1.035	34.3	0.9274	5.593	5.845	5.928	5.411
		.2379	5.812	6.051	6.116	5.640
		.1212	5.975	6.213	6.285	5.793
		.05924	6.066	6.303	6.366	5.883
2.014	21.0	.6895	6.197	6.500	6.611	6.119
		.2121	6.496	6.777	6.863	6.337
		.08177	6.750	7.036	7.113	6.594
		.04422	7.015	7.286	7.337	6.855
4.040	11.7	.2827	6.979	7.298	7.411	6.883
		.09607	7.373	7.660	7.767	7.228
		.04888	7.678	7.975	8.094	7.513
		.02643	7.983	8.269	8.353	7.801

Extrapolations of the curves of Fig. 5 give roughly the values of the constants at zero lithium chloride concentration. The low acid concentrations employed permit the assumption that these constants approach the thermodynamic dissociation constants defined with respect to

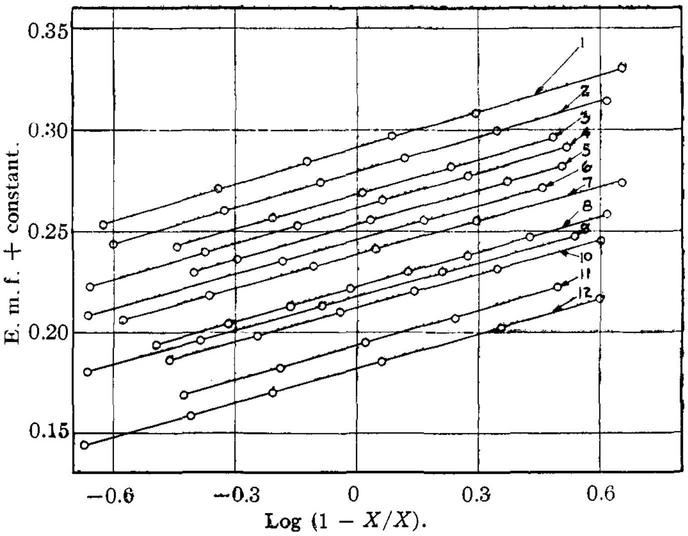

Fig. 4.—Obedience of titration curves to Nernst relation.

Dioxane-water ratios		1.035	2.014	4.040
Curves and acids	Benzoic	1	5	9
	Acetic	2	6	10
	Propionic	3	7	11
	Butyric	4	8	12

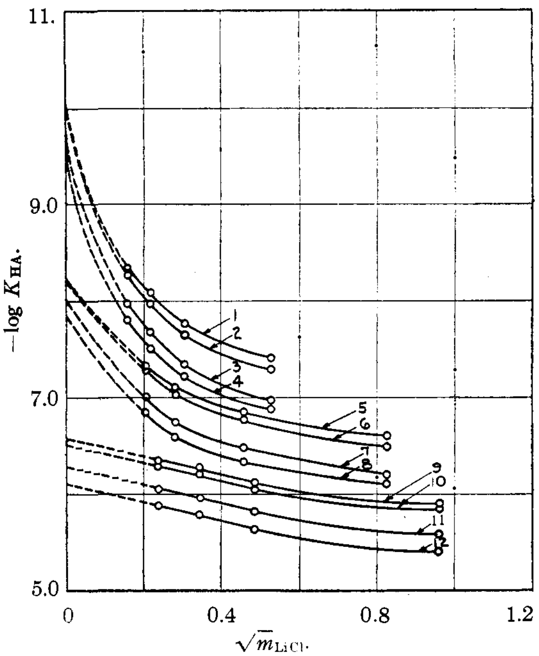

Fig. 5.—Extrapolation of $-\log K_{HA}$ values to zero LiCl concentration.

Dioxane–water ratios		4.040	2.014	1.035
Curves and acids	Butyric	1	5	9
	Propionic	2	6	10
	Acetic	3	7	11
	Benzoic	4	8	12

infinite dilution in *each* dioxane–water mixture as the standard state of reference. Table III lists the extrapolated values from the curves.

TABLE III

DISSOCIATION CONSTANTS FOR THE ACIDS AT 25°. EXTRAPOLATED VALUES TO THE ZERO SALT CONCENTRATION

Acid	Dielectric constant	K^0_{HA}	$-\log K^0_{HA}$
Acetic	34.3	5.01×10^{-7}	6.250
	21.0	8.75×10^{-9}	8.058
	11.7	1.08×10^{-10}	9.967
Propionic	34.3	3.47×10^{-7}	6.460
	21.0	5.30×10^{-9}	8.273
	11.7	6.92×10^{-11}	10.16
Butyric	34.3	2.88×10^{-7}	6.540
	21.0	5.97×10^{-9}	8.224
	11.7	7.58×10^{-11}	10.12
Benzoic	34.3	7.67×10^{-7}	6.115
	21.0	1.33×10^{-8}	7.875
	11.7	2.68×10^{-10}	9.572

As typical examples of the application of such a medium for titrating difficultly soluble weak organic acids, samples of purified abietic acid and U. S. P. stearic acid were titrated volumetrically with 0.33 N sodium hydroxide in the solvent of dioxane : water ratio 4.040 with lithium chloride concentration 0.1550 M. The titration curves are shown in Figs. 6 and 7. From the titration, the abietic acid was found to be 100.2 ± 0.5% pure, and the dissociation constant $K = 4.5 \times 10^{-9}$ for this medium; the stearic acid titration showed a purity of 105.2 ± 0.5%, and a dissociation constant $K = 7.8 \times 10^{-9}$. The sodium salt in the case of stearic acid soon reached saturation and then continuously precipitated from the solution during titration. Adsorption of the titrating base by the sodium stearate would account for the high value obtained for the purity of the acid.

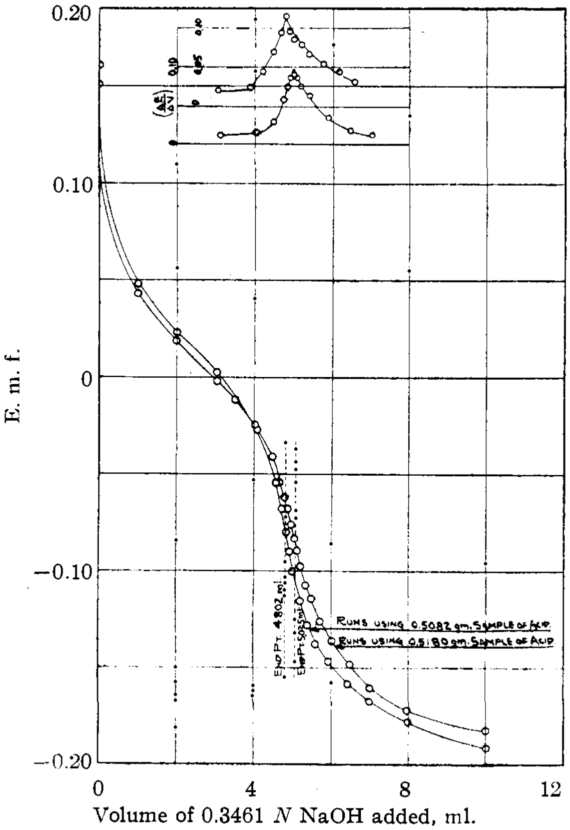

Fig. 6.—Titration curves for abietic acid in dioxane: water 4.040.

Discussion

The results obtained demonstrate that the general theory of titration, well established in aqueous and other polar solvents, applies satisfactorily in a mixed solvent composed of a polar and a non-polar component of low dielectric constant. The extrapolation to zero lithium chloride concentration is satisfactory in dioxane: water ratio of 1.035, but in the higher ratios extrapolation was difficult even when an analytical relation for the curve was employed. These results, therefore, must be taken only within the large limits of error involved. To observe how great a variation may have arisen in the extrapolation of log K_{HA}, the values for zero lithium chloride concentration were plotted against the reciprocal of the dielectric constant in Fig. 8. The values for the acids in water were taken from the "International Critical Tables." In all cases except that of benzoic acid straight lines resulted, departing from linearity only in the region of lowest dielectric constant. Harned and Kazanjian[24] have determined the dissociation constants for acetic acid from cell measurements in dioxane–water mixtures, employing the hydrogen electrode in conjunction with a silver–silver chloride electrode. Their results, represented by the concentric circles, agree reasonably well with our own.

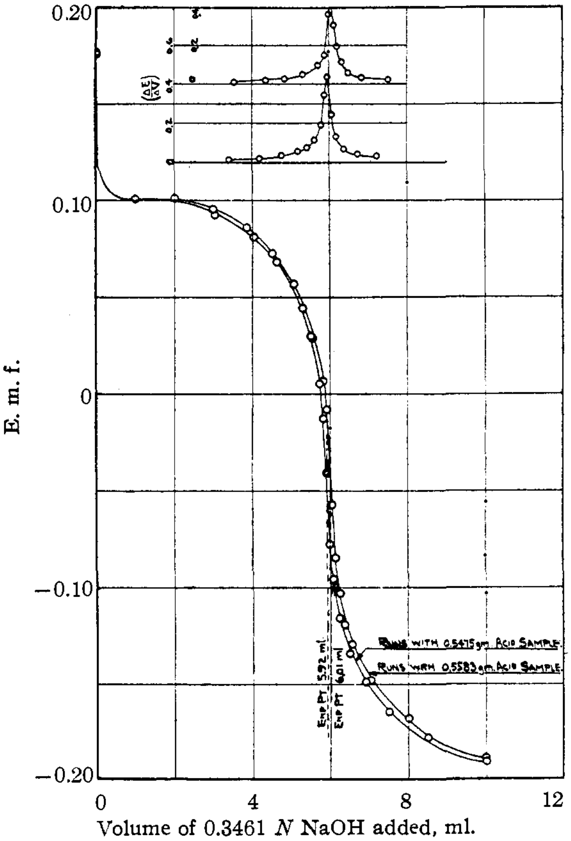

Fig. 7.—Titration of stearic acid in dioxane: water 4.040.

The linear dependence of log K upon $1/D$ follows from Coulomb's law for the electric potential, $\varphi = z^2e^2/Da$, of two spheres of charge ze at their minimum distance of approach $r = a =$ the average diameter.

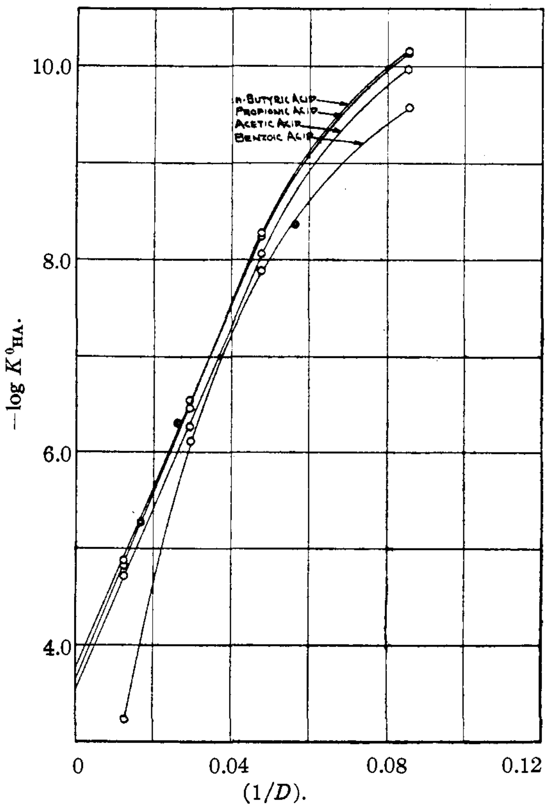

Fig. 8.—◉, (HAC) values of Harned and Kazanjian.

In a standard medium of dielectric constant D_0 the standard free energy change $\Delta F^0_{D_0} = -RT \ln K_{D_0}$ for the process HA $\rightleftarrows$ $H^+ + A^-$. If in passing to a medium of dielectric constant D, the *only significant* factor involved is the electric work of transferring the H^+ and A^- ions from one medium to the other, then

$$\mathrm{d} \log K = \frac{-z^2e^2}{2.3\,RT}\cdot\frac{1}{a}\cdot d\left(\frac{1}{D}\right)$$

and

$$\frac{\mathrm{d} \log K}{\mathrm{d}\left(\frac{1}{D}\right)} = \frac{-243}{10^8 a}$$

From the slopes of the curves we obtain the following values of 10^8a at the various dielectric constant values.

Acid	D	10^8a
Acetic, propionic and butyric	78–21.0	2.6
	11.7	9.4
Benzoic	78	1.3
	34.3	1.9
	21.0	3.2
	11.7	9.4

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(24) Harned and Kazanjian, THIS JOURNAL, 58, 1912 (1936).

The value of 2.6Å., valid for the three fatty acids over a wide range of dielectric constant, is an entirely reasonable value, and is evidence that the primary electric forces are the principal factors in determining the dissociation with change of medium. The deviation from linearity between $D = 21$ to 11.7 can arise, of course, from the uncertainty of the extrapolation to zero lithium chloride concentration. An exact agreement between the a values from crystal structure and the Born equation must not be expected since other forces (van der Waals and the like) exist between molecules.

Titrations of abietic acid indicate a successful, practical application of such a mixed solvent as a titrating medium. Many acids soluble in dioxane–water mixtures may be titrated similarly. The limitations are set by the magnitude of the dissociation constant and the solubility of the sodium salt in the solvent. This latter point is well illustrated by the titration curves of stearic acid (Fig. 7). The initial drop in e. m. f. is due to the increasing concentration of sodium stearate which soon reaches saturation, indicated by the flat portion of the curve. The course of the remainder of the curve is due to the reduction of the stearic acid concentration, the concentration of sodium stearate remaining constant.

Summary

1. Potentiometric titrations of acetic, propionic, butyric and benzoic acids have been performed in dioxane–water mixtures ranging from 50 to 80% dioxane corresponding to the dielectric constants 34.3, 21.0, and 11.7, with a quinhydrone–calomel electrode chain without liquid junction. The addition of lithium chloride was found necessary for adequate conductivity, for the maintenance of a constant ionic environment during the progress of the titration, and for the elimination of liquid junction potentials.

2. Auerbach and Smolcyzk's treatment of acid–base titration has been extended to include the influence of ion-association of salts in low dielectric media. An equation showing the influence of ion-association of the salts upon the dissociation of the acids is given.

3. The standards of reference of hydrogen ion activity (E^0 values) for each medium and for each lithium chloride concentration have been determined by measuring cells with decreasing hydrochloric acid concentration and extrapolating to zero concentration of acid.

4. The dissociation constants of the four acids have been determined from the titration curves at progressively decreasing concentrations of lithium chloride, whereby an extrapolation to zero concentration of lithium chloride could be made to evaluate the dissociation constants of the acids in the mixed solvents in the absence of added neutral salt. The logs of these extrapolated constants except for benzoic acid are linear functions of the reciprocal of the dielectric constant from $D = 78$ to $D = 21$.

5. With abietic and stearic acids as examples it has been shown that weak acids which are insoluble in water may be titrated directly in an 80% dioxane medium ($D = 11.7$) containing 0.1550 M lithium chloride and their dissociation constants determined for comparison with those of other acids. In this medium K for acetic acid $= 6.9 \times 10^{-8}$, for abietic acid $K = 4.5 \times 10^{-9}$, for stearic acid $K = 7.8 \times 10^{-9}$.

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NEW YORK, N. Y.

RECEIVED MARCH 14, 1938