THE THERMODYNAMIC IONIZATION CONSTANT OF ACETIC ACID IN WATER-METHANOL SOLUTIONS

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Introduction

In a solution of any electrolyte MA there should be an equilibrium between free ions and undissociated molecules

$$MA \rightleftharpoons M^+ + A^- \qquad (a)$$

If α represents the degree of dissociation and c the total concentration, then α c represents the concentration of dissociated M^+ and A^- and $(1 - \alpha)c$ the concentration of undissociated MA. On application of the mass law the so-called dilution law, first derived by Ostwald[1] is obtained as

$$K' = \frac{\alpha^2}{1 - \alpha} c \qquad (b)$$

in which it is implied that K' is constant. The failure of highly conducting solutions to follow the mass law and the general inadequate picture of the phenomena occuring in solutions of electrolytes can be shown to lie in the calculation of α by the classical theory of Arrhenius[2] in which the degree of dissociation, α, of any electrolyte at a concentration, c, is found by means of the simple formula

$$\alpha = \frac{\Lambda}{\Lambda_0} \qquad (c)$$

in which Λ is the equivalent conductance at the concentration in question, and Λ_0 is the limiting or "infinite dilution" value of that conductance. If u and v are the velocities of the ions at the concentration c and u_0 and v_0 are the values at infinite dilution, then[3]

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[1] Ostwald, Z. Physik. Chem., 2, 36, 270 (1888) by way of: MacInnes, Principles of Electrochemistry, 56, Reinhold (1939).

[2] Arrhenius, Ibid., 631 (1887).

[3] Glasstone, Textbook of Physical Chemistry, 2nd ed., 902 D. Van Nostrand (1946).

$$\frac{\Lambda}{\Lambda_o} = \frac{\alpha k(u+v)}{k(u_o+v_o)} \qquad \text{(d)}$$

$$\alpha = \frac{\Lambda k(u_o+v_o)}{\Lambda_o k(u+v)} \qquad \text{(e)}$$

Thus, the fundamental error in the Arrhenius theory (equation c) is the assumption that ionic velocities do not change with concentration. Because of the mutual interaction of the ions at appreciable concentrations the velocities would be expected to decrease and α values as computed by equation (c) would be too low. Thus we can account for the unmistakeable drift of the ionization "constant" K' as expressed by the Ostwald dilution law[4].

Equation (e) may be put in the form

$$\alpha = \frac{\Lambda}{\Lambda e} \qquad \text{(f)}$$

in which $\Lambda e = k\ (u - v)$, i.e. Λe is the sum of the conductances of the two ions in solution at the same <u>ionic concentration</u> as the solution under consideration. Thus, values for the "classical" ionization constant (K') may be calculated from values of α as given by equation (f) from conductance measurements.

The Kohlrausch law of independent ionic migration has been shown to hold accurately[5] for aqueous solutions and for methyl alcohol solutions[6] and, therefore, should hold for water-methanol mixtures.

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[4] MacInnes, <u>Principles of Electro-Chemistry</u>, 57, Reinhold (1939).

[5] MacInnes, Ibid., 340.

[6] MacInnes, Ibid., 359.

Thus, if completely dissociated acetic acid were capable of existence, the value of its equivalent conductance Λe would be

$$\Lambda e(HAc) = \Lambda_{HCl} + \Lambda_{NaAc} - \Lambda_{NaCl} \qquad (g)$$

Following Kohlrausch's early suggestion[7] equations for Λ_{HCl} , Λ_{NaAc} , and Λ_{NaCl} may be found from conductance measurements by simply plotting values of Λ as a function of the square root of the concentration and extending to the zero axis. The extrapolation may, of course, be carried out using the method of least squares. A difficulty with this method is, however, that the greatest weight is given to the data on very dilute solutions where the experimental errors are the greatest. This method was unsuccessful in this research and the results are included in the Miscellaneous Observations.

Another method is based on the assumption that the Onsager equation[8]

$$\Lambda = \Lambda_o - (\theta \Lambda_o + \sigma)\sqrt{C} \qquad (h)$$

is the true limiting equation in which θ and σ are constants (see section E, Experimental Results), and the quantity $(\theta \Lambda_o + \sigma) = A$ is the limiting slope. Solving (h) for Λ_o one obtains

$$\Lambda_o = \frac{\Lambda + \sigma \sqrt{C}}{1 - \theta \sqrt{C}} \qquad (i)$$

Shedlovsky[9] has found that the values of Λ_o as calculated from equation (i) are not constant over any appreciable concentration range showing that the data do not follow the limiting Onsager equation. However,

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[7] MacInnes, Ibid., 337.

[8] Shedlovsky, J. Am. Chem. Soc., 54, 1407 (1932).

[9] Shedlovsky, Ibid., 54, 1407 (1932).

Shedlovsky found that these computed values of Λ_o, which will be designated by Λ'_o, plotted against the first power of the concentration gave straight lines up to about 0.1 normal. On this basis the correct Λ_o value for each electrolyte is the intercept of the Λ'_o vs. c line at c = 0. If the slope of these lines is represented by B, we have the following conductance equation[10]

$$\Lambda'_o = \frac{\Lambda + \sigma \sqrt{C}}{1 - \theta \sqrt{C}} - BC \qquad (j)$$

In short, this second "Shedlovsky" method is more convenient to use because one does not have to work in a very dilute range, but, rather, in the range from approximately 0.01 to 0.1 normal. Furthermore, the resistances encountered in this "concentrated" range are not so high as in a very dilute range and are thereby more easily measured.

The computation of α with the aid of equations (f) and (g) requires a short series of approximations[11], since the value of Λ_e must be that corresponding to the ion concentration αC. A first approximation may be made using $\Lambda_o = \Lambda_e$ in equation (f) and with this preliminary value of α an estimate of Λ_e from equation (g) may be obtained which in turn may be substituted in equation (f). This procedure is continued until repetition fails to change the resulting value for α. (See Miscellaneous Observations).

The true or thermodynamic ionization constant K which may be

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[10] Shedlovsky, Ibid., <u>54</u>, 1407 (1932).

[11] MacInnes and Shedlovsky, Ibid., <u>54</u>, 1430 (1932).

expressed by

$$K = \frac{a_{cation} \cdot a_{anion}}{a_{undissociated}} = \frac{C_{M^+} \cdot C_{A^-}}{C_{MA}} \times \frac{f_{M^+} \cdot f_{A^-}}{f_{MA}} \qquad (k)$$

is a true constant. From equation (k) we see a simple relation between the thermodynamic ionization constant and the "classical" ionization constant (equation b) which is

$$K = K' \times \frac{f_{M^+} \cdot f_{A^-}}{f_{MA}} \qquad (l)$$

in which f stands for the activity coefficient. The activity coefficient of undissociated MA may be taken as unity in sufficiently dilute solutions.[12] If we take the logarithm of equation (l) and apply the familiar Debye-Hückel relation (which holds only in very dilute solutions)[13]

$$-\log f_i = A z_i^2 \sqrt{\alpha C} \qquad (m)$$

to our particular case acetic acid (HAc), we obtain the Debye-Hückel Limiting Law (D.H.L.L.) which is

$$\log K = \log K' - 2A\sqrt{\alpha C} \qquad (n)$$

$$\log K' = \log K + 2A\sqrt{\alpha C} \qquad (o)$$

Therefore, if we plot K' vs. $\sqrt{\alpha C}$ we should get a straight line of positive slope (2A) and y-intercept log K from which we may evaluate K. MacInnes and Shedlovsky[14] have shown that acetic acid in aqueous solutions follows the D.H.L.L. at concentrations up to about 0.03 normal, and then the curve bends and assumes a negative slope showing a pronounced

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[12] MacInnes, Principles of Electro-Chemistry, 57, Reinhold (1939).

[13] Glasstone, Textbook of Physical Chemistry, 2nd. ed., 959, D. Van Nostrand (1946).

[14] MacInnes and Shedlovsky, Ibid., 54, 1435 (1932).

divergence from the D.H.L.L. This is not unusual since as the concentration of acetic acid is increased the solvent progressively changes from pure water to a mixture of undissociated acetic acid. The properties of undissociated acetic acid are quite different from those of water. For example, the acid has a dielectric constant less than 10% that of water, and its presence in aqueous solutions should be expected to influence the mobilities as well as the activities of the ions. Careful studies of the conductances of weak acids in methanol have been made by Goldschmidt and associates [15] and the D.H.L.L. was followed in a rather rough manner. Since the function of the methanol is to further "slow down" the ions, it is to be expected that if acetic acid is to follow the D.H.L.L. it will do so at lower concentrations than in pure water, the curve will show greater deviations from the "limiting" slope A, and the negative or deviating part of the curve will show up sooner, i.e. at lower concentrations than in pure water.

We have seen that as the concentration becomes greater, the medium progressively changes and exerts a pronounced effect on the behavior of an electrolyte. This behavior or "medium effect" has been partially accounted for by an equation developed by Saxton, Langer and Meier[16]. The expression for $\alpha \left(\frac{\Lambda}{\Lambda e}\right)$ is very nearly correct, but it is not exact, especially at higher concentrations where the "medium effect" begins to have a pronounced influence. If C_u is the concentration of undissociated acetic acid then $C_u = C - C_i$ moles per liter of acetic

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[15] Goldschmidt, Z. Physik. Chem., 91, 45 (1916) by way of: MacInnes, Principles of Electrochemistry, 362.

[16] Saxton and Langer, J. Am. Chem. Soc., 55, 3638 (1933). Saxton and Meier, Ibid., 56, 1918 (1934).

acid and $C_i = \alpha C$. Harned and Owen[17] show a plot of this equation (7-6-12)

$$\log K' - 2A\sqrt{\alpha c} = \log K - \beta C_u \qquad (p)$$

in which $\log K' - 2A\sqrt{\alpha c}$ is plotted against C_u and a straight line of negative slope whose y-intercept is log K is obtained. It is to be observed that the D.H.L.L. is usually reliable up to concentrations of about 0.003 normal while the "Harned and Owen" method (H. & O. method) is used above 0.005 normal. Thus, the H. & O. method can be used at concentrations above which the D.H.L.L. may not hold. Unquestionably the D.H.L.L. is the more difficult method while the H. & O. method is more convenient. In short, the H. & O. method is an extension of the D.H.L.L. to higher concentrations.

In this research, the Shedlovsky limiting conductance method(Λ_0') was used. The values of Λ_0 so obtained were used in the Onsager limiting law and the equations so obtained, which are of the old Kohlrousch form ($\Lambda = \Lambda_0 - A\sqrt{C}$), were used to evaluate Λ_e (equation g). The acetic acid itself was measured in concentrations approximately from 0.001 to 0.04 normal. It should be pointed out again that under the heading of Miscellaneous Observations are included, for purely "historical" interest, values obtained by using the Kohlrousch method for the conductance equations which has already been outlined. Also included is an Λ_e value for acetic acid in which it was attempted, for reasons already made obvious, to work in very dilute solutions.

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[17] Harned and Owen, Physical Chemistry of Electrolytic Solutions, 209, Reinhold (1943).

At this point it is profitable to point out that this research problem arose from the work of Giuliano and Hill[18] in which the ionization constants for acetic acid in water-methanol solutions were determined by the application of the D.H.L.L. in concentrations where the D.H.L.L. would most certainly not be expected to hold. Moreover, the extrapolated curves have a very pronounced negative slope which is in direct opposition to the predicted, mathematical slope (equation o), and the plot of log K vs. the reciprocal of the dielectric constant does not give a curve which is in reasonable agreement with the E.M.F. data of Harned and Embree[19].

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[18] Giuliano and Hill, J. Am. Chem. Soc., 68, 2359 (1946).

[19] Harned and Embree, J. Am. Chem. Soc., 57, 1669 (1935).

Experimental

A. Bridge Circuit (Figure No. 1)

A conventional Wheatstone Bridge was used. A General Radio type 510F resistance of 100,000 ohms in 10,000 ohm steps was used in conjunction with a 10,000 to 1 ohm Leeds and Northrup type 4745 A-C resistance box in the "balancing arm". The slide was a Kohlrausch slide wire type 4258 made by Leeds and Northrup. The drum type of slide, although not recommended by some observers due to mutual self-induction effects,[20] was used. The error introduced by the drum is of the order of ±0.05% which is insignificant in this research. The capacitors used were a General Radio No. 1686 variable condenser (45-1019 $\mu\mu$f) and a standard radio variable condenser (20-3600 $\mu\mu$f). The capacitors were only found of use when measuring solutions of the order of 0.002 normal in the case of NaCl, HCl, and NaAc, and in the case of HAc when the solutions were about 0.001 to 0.04 normal. Values for the capacitances were not recorded, however, they varied and did not show any regular trends. The resistance coils of A-C Leeds and Northrup resistors have been tested and are supposedly very accurate (0.001%) according to Dike[21]. The decade used was compared to another L. and N. decade of exactly the same type inserted in place of the conductance cell. When the two decades were interchanged they read to within 0.1% of each other at resistances of the order of 25,000 ohms, and gave exactly the same readings (±0.001%) when the resistance of one was of the order of 5,000

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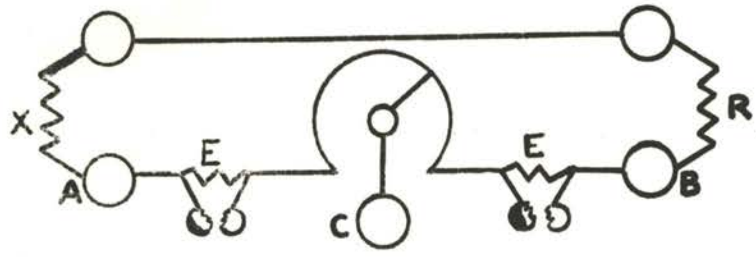
[20] Grindley and Davies, Trans. Faraday Soc., 25, 133 (1929).

[21] Dike, Review of Sci. Inst., 2, 379 (1931).

SCHEMATIC DIAGRAM

Instrument No. 70139



E = END COIL

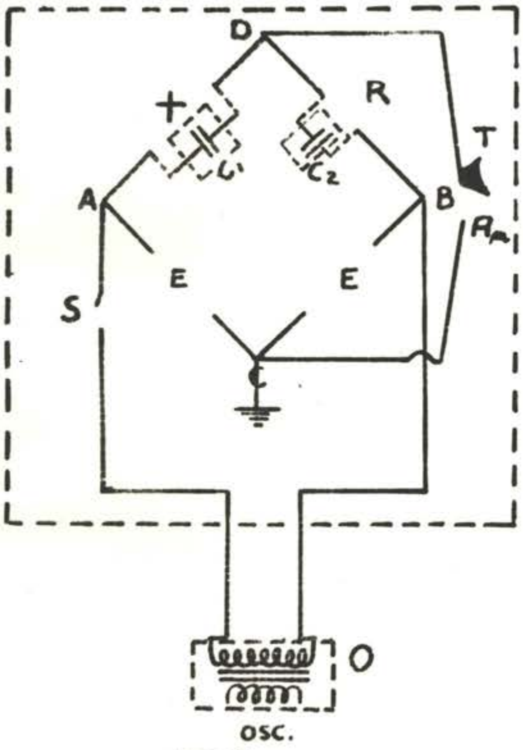
R = KNOWN RESISTANCE

X = UNKNOWN RESISTANCE

ith end coils in circuit the value of the unknown resistance "X" for any dewire setting "A" is given by the formula

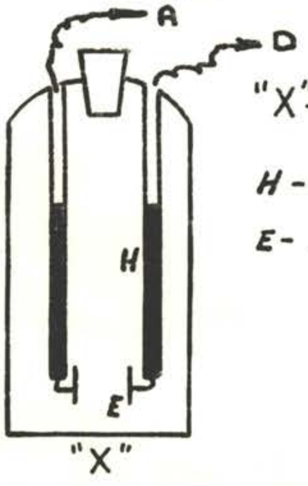
$$X = R\frac{4500 + A}{5500 - A}$$

A = Scale Reading
R = Known Resistance
X = Unknown Resistance



R - General Radio 510 F 100,000 Ω
LEEDS & NORTHRUP No. 727049 10,000 Ω
C_1 - General Radio Variable CONDENSER No. 1686 45-1019 uuf
C_2 - STUDENT Constructed Vaniable condenser 0-360 uuf
O - HEWLETT PACKARD Audio OSCILLATOR MODEL 200 A.
S - SINGLE Pole, Single throw Switch
T - Telephone headset
A_m - AMPLIFIER, LUDER, J.A.C.S. <u>62</u>, 91 (1940)

All connections made with low RESISTANCE BELL WIRE



"X" - FREAS TYPE CONDUCTIVITY CELL

H - Hg

E - Pt BLACK ELECTRODES

FIGURE No. 1

ohms. In the same manner, the 100,000 ohm resistor was found to be good (0.1%) up to 30,000 ohms. Many thanks are due to Mr. Alfred Christofferson and his co-workers of the Engineering Department of this institution who constructed the amplifier. The amplifier was designed by Professor C. F. Muckenhoupt of Northeastern University[22]. The oscillator used as a Hewlett-Packard model 200A which was moved about thirty feet away from the bridge proper[23]. A frequency of 1,000 cycles was used throughout since low frequencies tend to introduce local polarization effects, while high frequencies (5,000-10,000 cycles) tend to introduce the Debye-Falkenhagen effect[24]. For practical reasons, magnetic shielding was not attempted[25]. All connections were made with low resistance bell wire.

B. Conductivity Cells

Two platinized Freas type cells were used. The cells were rinsed at least six times with each solution to be measured. The data of Jones and Bradshaw[26] for KCl was taken as the standard in determining the cell constants. The cells were checked about every three weeks and no significant changes in cell constant were noted.

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[22] Luder, J. Am. Chem. Soc., 62, 91 (1940).

[23] Jones and Josephs, Ibid., 50, 1049 (1928).

[24] Falkenhagen, Electrolytes, 222, Oxford (1934).

[25] Shedlovsky, Physical Methods of Organic Chemistry, Weissberger (ed.) 1021, Interscience (1946).

[26] Jones and Bradshaw, J. Am. Chem. Soc., 55, 1780 (1933).

C. Temperature Control

Although Jones and Josephs[27] recommend that oil be used in the bath, a water bath was used for practical reasons. The temperature was regulated to within ±0.03°C. by a mercury thermoregulator connected through a Cenco-Gilson Electronic Relay (No. 99782) to an electric heater. An Aimer and Amend thermometer (No. 87266), which had been calibrated against a National Bureau of Standards (No. 90794) thermometer, was used to measure the temperature.

D. Preparation of Solutions

Solvent: The methanol used was Du Pont synthetic and no precautions were taken to distil it using magnesium to remove water since measurements were not made in anhydrous methanol. The amount of water which the methanol contained (0.1% per liter) was not critical for the measurements. Re-distilled distilled water was used in making all of the solvents. The densities of the 20.50, 40.26, and 59.47% of H_2O-MeOH mixtures were determined by the use of an Ostwald type pyknometer. No "solvent correction" was applied because the resistances of the solvents were too high (40,000 to 100,000 ohms) to have any significant effects on the calculated equivalent conductance values.

Solutes: Sodium chloride and Sodium Acetate. C. P. NaCl and NaAc were placed in an over at 120°C. for two hours or more and further dried in a desiccator. Pyrex glass 250c.c. flasks, which had previously been rinsed out with hot "cleaning solution" and distilled water, were

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[27] Jones and Josephs, Ibid., <u>50</u>, 1065 (1928).

steamed for at least twenty minutes each. The solvent (H_2O-MeOH) was weighed out by use of a calibrated Voland balance capable of an accuracy of ±0.005 g. The dry NaCl and NaAc (solutes) were weighed by difference from a weighing bottle by use of a calibrated Christian-Becker (No. 34815) chainomatic balance capable of an accuracy of ±0.0001 g. A "hydrolysis correction" was not noted in the sodium acetate readings, but, if it had, it could have been easily determined by taking readings at short intervals of time and extrapolating to zero time.

Hydrochloric Acid.

The solvent was weighed as in the previous cases. After many futile analysis, readings, etc., it was found that constant boiling HCl gave accurate results (see Miscellaneous Observations). The HCl (180.07 g. of solution contained 1 mole of HCl) was prepared by Professor H. M. Trimble of this institution. A concentrated "stock" solution was prepared by adding the required (calculated) amount of pure methanol. From this original (stock) solution, the more dilute solutions were prepared by use of a 30 ml. weight burette.

Acetic Acid.

C. P. synthetic acetic acid was purified by distilling the material from 2% by weight of potassium permanganate and the product was again distilled from a little chromic anhydride[28]. The first fractions were discarded. A stock solution was then prepared and from this the more dilute solutions were prepared by use of the weight burette.

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[28] MacInnes and Shedlovsky, Ibid., <u>54</u>, 1431 (1932).

E. Results

All experimental results are given in the form of tables and graphs. The Onsager equation (h) involves two constants θ and σ which depend respectively upon the dielectric constant and viscosity of the solvent. For univalent ions equation (h) is[29]

$$\Lambda = \Lambda_0 - \left[\frac{8.147 \times 10^5}{(DT)^{3/2}} + \frac{40.93}{(DT)^{1/2}\eta} \right] \sqrt{C} \qquad (q)$$

that is, $\theta = \frac{8.147 \times 10^5}{(DT)^{3/2}}$ and $\sigma = \frac{40.93}{(DT)^{1/2}\eta}$ where

D = the dielectric constant of the solvent and η = the viscosity of the solvent (poise). The dielectric constants of water-methanol solutions were obtained from a plot of the data of Albright and Josting[30], and viscosity values were obtained likewise from the data in I. C. T.[31] The quantity inside the brackets represents the slope A, and Λ_0 is the "infinite" or limiting conductance determined by the Shedlovsky method. The Debye-Hückel limiting slope A is given by[32]

$$A = \frac{N^2 \epsilon^2}{2.303 R^{3/2}} \left(\frac{2\pi}{1000} \right)^{1/2} \frac{1}{(DT)^{3/2}} \qquad (r)$$

where N = 6.023 x 10^{23}, ϵ = 4.802 x 10^{-10} e.s.u., and R = 8.314 x 10^7 ergs.

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[29] MacInnes, Principles of Electrochemistry, 327.

[30] Albright and Josting, J. Am. Chem. Soc., 68, 1063 (1946).

[31] International Critical Tables, 5, 22.

[32] Glasstone, Textbook of Physical Chemistry, 2nd ed., 959.

Table A

Summary of the Onsager constants θ and σ and the Debye-Hückel limiting slopes (A) for water-methanol solutions.

%MeOH	T	D	A	x 10^3 (poise)	θ	σ
20.50	298.2	69.70	0.6086	14.20	0.2719	39.98
40.26	308.2	56.90	0.7853	12.19	0.3365	49.92
59.47	308.2	49.00	0.9827	10.94	0.4390	60.89

Table I

HCl: at 25° C. in 20.50% Methanol

C (M./l.)	R(ohms)	$100\sqrt{C}$	Λ calc. (mhos)	Λ'_0 (mhos)
0.015351	107.0	12.3	249.90	263.63
0.025438	64.69	15.9	249.44	267.35
0.030595	54.19	17.4	247.58	267.17
0.042174	39.61	20.5	245.72	268.90
0.062996	26.98	25.0	241.51	269.84

Λ calc. $= \frac{1000}{C} \times \frac{k}{R}$ in which k ("cell constant") = 0.44345 and density (used to calculate C) = 0.9643.

$\Lambda_0 = 265.12$ $\qquad$ $\Lambda = 265.12 - (0.2719 \times 265.12 - 39.98)\sqrt{C}$

$\Lambda = 265.12 - 112.07\sqrt{C}$

A = 112.07 = slope of Onsager limiting equation

B = 115.0 = slope of Shedlovsky equation

Λ_0 = 265.12 = limiting or infinite conductance

NaAc:

C (M./l.)	R(ohms)	$100\sqrt{C}$	Λ calc. (mhos)	Λ'_o (mhos)
0.01389	542.0	11.8	54.62	61.24
0.01853	402.48	13.6	54.36	62.09
0.02184	350.85	14.65	53.56	61.91
0.03865	205.7	19.5	51.63	62.81
0.11335	71.0	33.35	51.00	70.92

$$\Lambda_o = 60.80$$

$$\Lambda = 60.80 - 56.51\sqrt{C}$$

NaCl:

C (M./l.)	R(ohms)	100 C	calc. (mhos)	(mhos)
0.01006	568.00	10.03	71.83	77.96
0.01472	390.78	12.13	71.35	78.77
0.02430	242.00	15.60	69.51	79.03
0.03919	153.61	19.79	68.18	80.31
0.05580	113.00	23.58	65.09	79.60
0.06108	102.00	24.68	65.88	81.20
0.08012	77.15	28.26	66.40	84.16

$$\Lambda_o = 77.58$$

$$\Lambda = 77.58 - 61.06\sqrt{C}$$

$$\Lambda_e\,\mathrm{HAc} = 60.80 - 56.51\sqrt{C}$$

$$-77.58 - 61.06\sqrt{C}$$

$$+265.12 - 112.07\sqrt{C}$$

$$\Lambda_e\,\mathrm{HAc} = 248.34 - 107.52\sqrt{\alpha C}$$

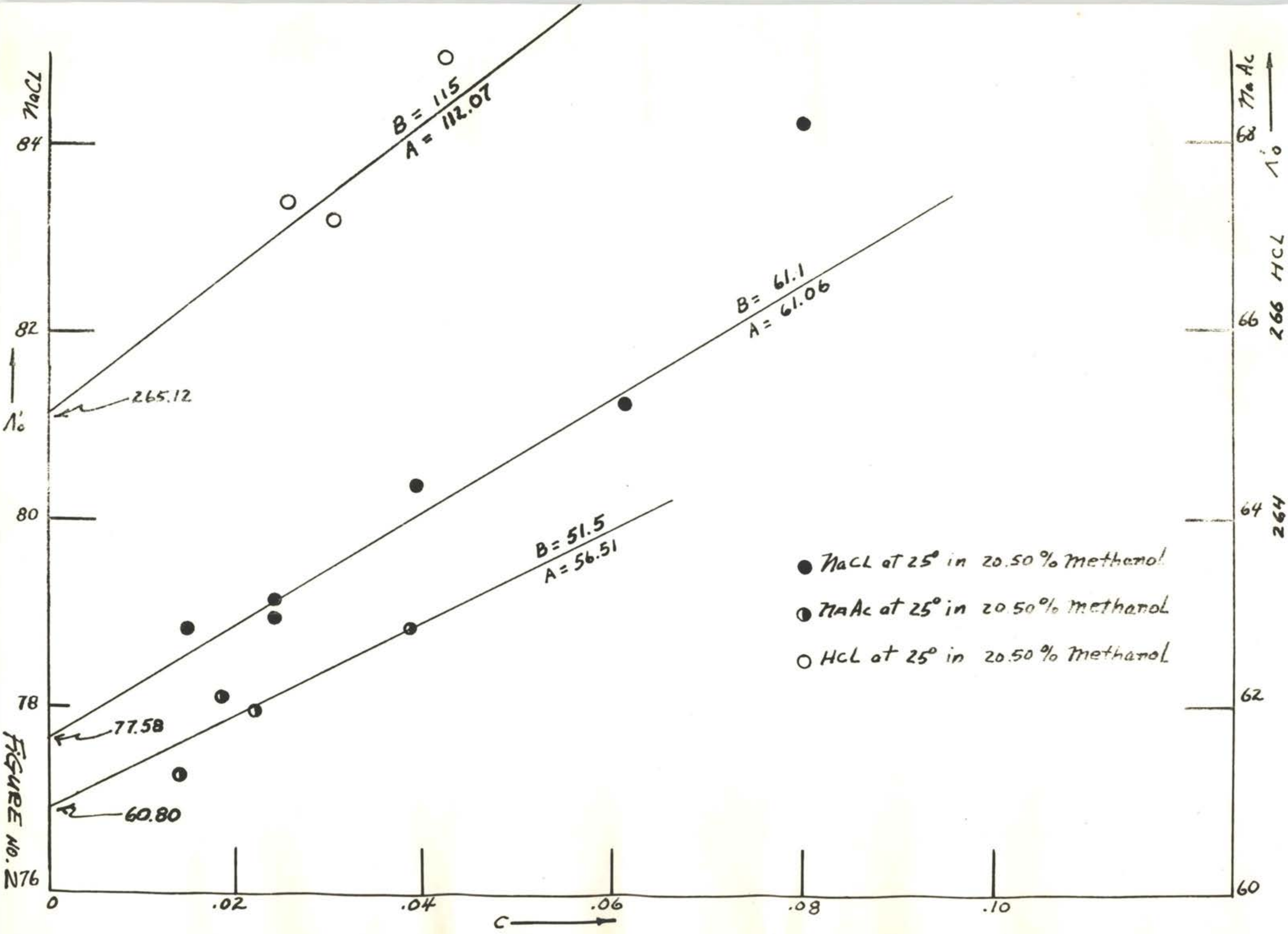
FIGURE NO. N76

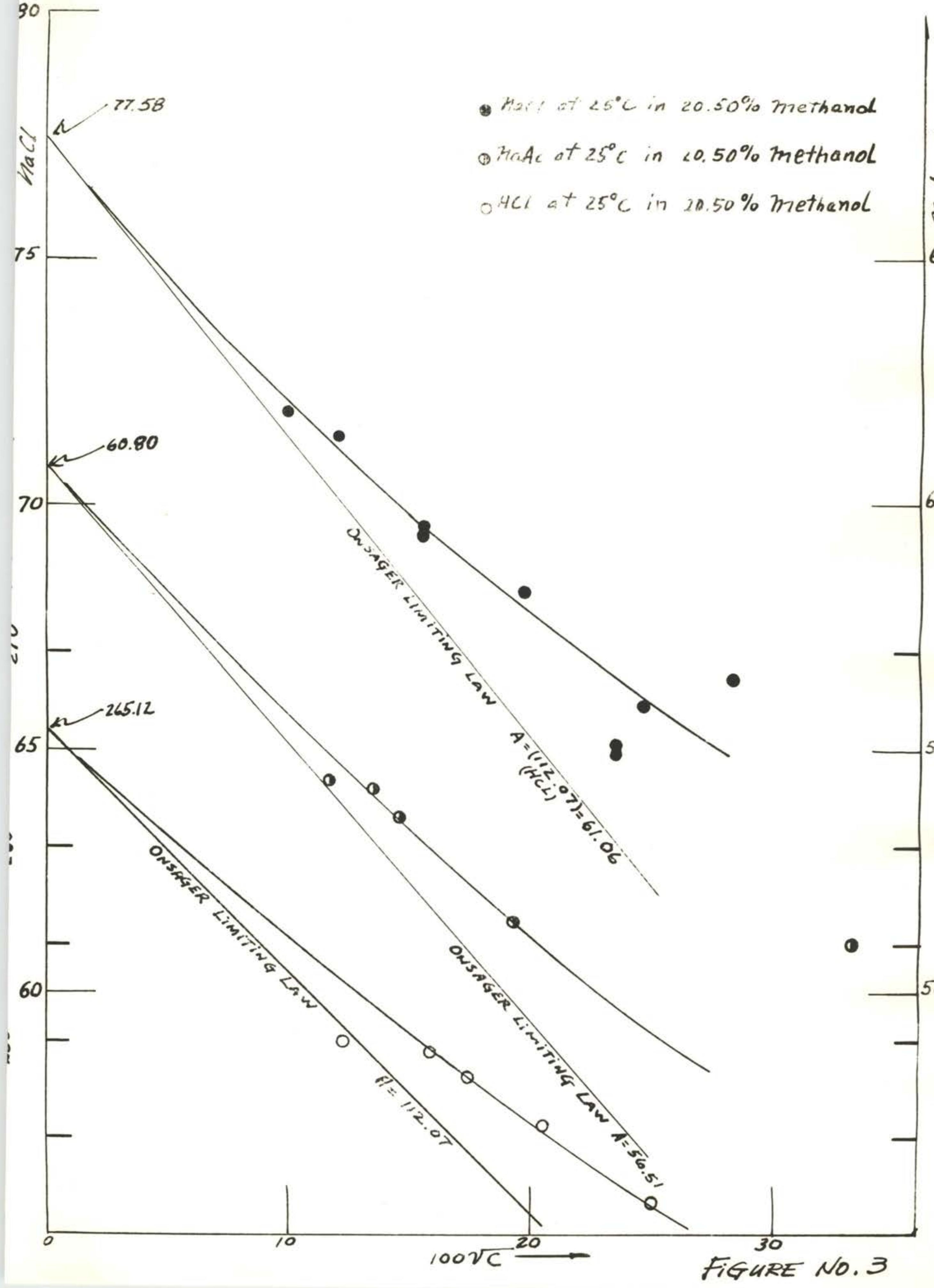
80
75
70
65
60
NaCl
77.58
60.80
265.12
65
60
55
50
NaAc Λ
● NaCl at 25°C in 20.50% methanol
◍ NaAc at 25°C in 20.50% methanol
○ HCl at 25°C in 20.50% methanol
ONSAGER LIMITING LAW A=(112.07)=61.06 (HCL)
ONSAGER LIMITING LAW A=56.51
ONSAGER LIMITING LAW A=112.07
0
10
20
30
100√C

FIGURE NO. 3

HAc:

C(M./l.)	100$\sqrt{C}$	R (ohms)	Λ exp. (mhos)	Λ Calc. (mhos)	α	100$\sqrt{\alpha C}$	K'x10^6	log K' + 6
0.00124	3.52	17,838	19.96	247.27	0.0803	1.00	8.693	0.9391
0.00174	4.17	15,260	16.70	247.18	0.06756	1.08	8.517	0.9303
0.00227	4.76	13,637	14.75	247.10	0.05969	1.16	8.601	0.9345
0.00282	5.30	10,909	13.34	247.02	0.0540	1.23	8.692	0.9391
0.00556	7.45	7,736.9	9.542	246.78	0.0386	1.46	8.616	0.9353
0.00779	8.81	6,469.2	8.145	246.64	0.03279	1.60	8.806	0.9447

Average K = (8.34 = 0.06) x 10^{-6} (best D.H.L.L. line through the points)

Using equation 7-6-12 of the Harned and Owen monograph:

C_i(M./l.)	$\sqrt{C_i}$	K'x10^6	log K' + 6	1.217$\sqrt{C_i}$	log K' + 6-1.217$\sqrt{C_i}$	C_u(M./l.)
0.995 x10^{-4}	0.996 x10^{-2}	8.697	0.9394	0.0121	0.9273	1.14 x10^{-2}
1.18	1.086	8.530	0.9310	0.0132	0.9178	1.62
1.355	1.161	8.620	0.9355	0.0141	0.9214	2.13
1.523	1.233	8.685	0.9388	0.0150	0.9238	2.67
2.146	1.461	8.609	0.9350	0.0178	0.9172	5.35
2.554	1.596	8.665	0.9378	0.0194	0.9184	7.53

log K = 0.9274^{-6}; K = 8.461 x 10^{-6}

Simple average of column 6 (8.64 = 0.05) x 10^{-6} (best line through points gives same value)

Harned and Embree data for K = 8.20 x 10^{-6} (33)

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(33) Harned and Embree, J. Am. Chem. Soc., 57, 1669 (1935).

Conductivities of HAc in 20.50% Methanol at 25°C.

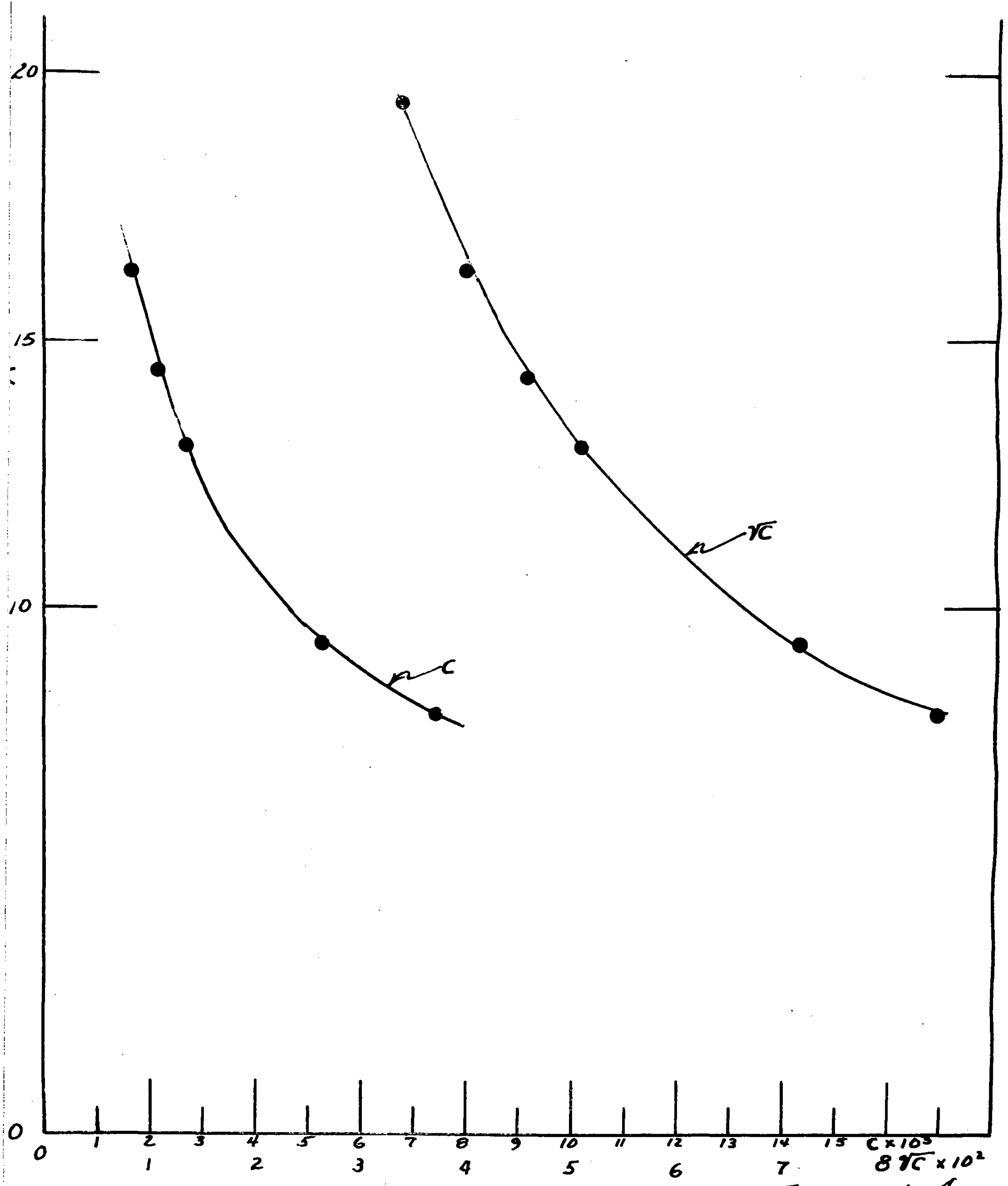
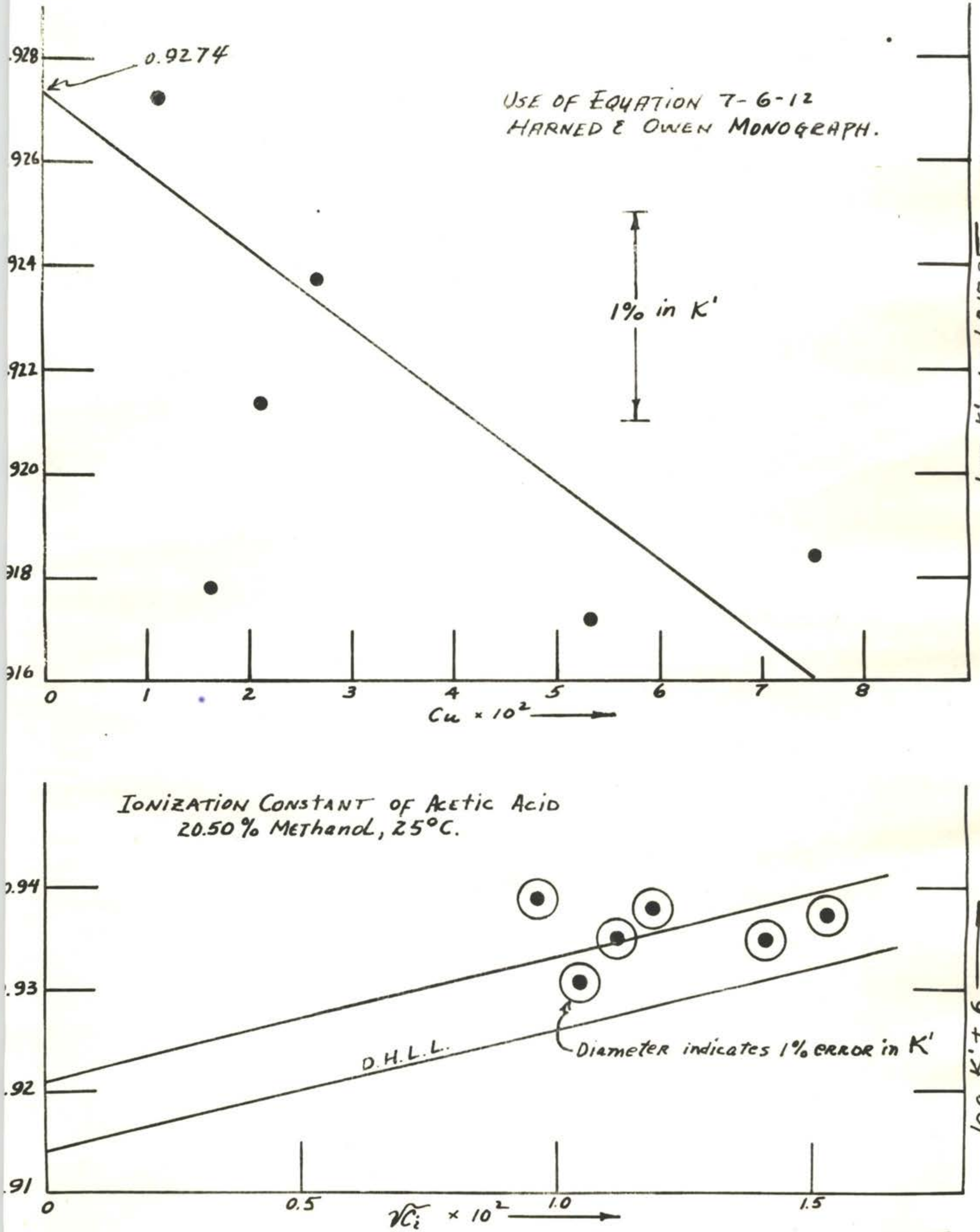


FIGURE NO. 4



.928
.926
.924
.922
.920
.918
.916
0.9274
USE OF EQUATION 7-6-12
HARNED & OWEN MONOGRAPH.
1% in K'
Log K' + 6 - 1.217 $\sqrt{C_i}$ →
0
1
2
3
4
5
6
7
8
Cu × 10^2 →
IONIZATION CONSTANT OF ACETIC ACID
20.50 % METHANOL, 25°C.
.94
.93
.92
.91
D.H.L.L.
Diameter indicates 1% ERROR in K'
log K' + 6 →
0
0.5
1.0
1.5
$\sqrt{C_i}$ × 10^2 →

FIGURE NO. 5

Table II

HCl: at 35°C. in 40.26% Methanol; K = 0.4333 and density of solvent = 0.9252

C(M./l.)	R(ohms)	$100\sqrt{C}$	Λ calc. (mhos)	Λ_0' (mhos)
0.014166	149.7	11.9	204.32	219.02
0.023328	92.7	15.2	200.36	219.15
0.024553	87.38	15.6	201.96	221.36
0.031025	71.19	17.6	196.18	217.86
0.032127	68.28	17.9	197.52	219.68
0.032531	66.65	18.0	199.84	222.28

$$\Lambda_0 = 217.5$$

$$\Lambda = 217.5 - 123.10\sqrt{C}$$

NaAc:

0.02055	404.4	14.3	52.13	62.26
0.02770	301.6	16.6	51.86	63.70
0.03300	257.2	18.1	51.65	64.54
0.04660	195.2	22.3	48.26	65.29
0.06442	128.7	25.3	52.26	70.09

$$\Lambda_0 = 58.55$$

$$\Lambda = 58.55 - 69.62\sqrt{C}$$

NaCl:

0.02465	231.7	15.7	75.86	88.80
0.04501	140.2	21.2	68.66	85.32
0.05920	109.08	24.3	67.05	86.23
0.06079	105.0	24.6	67.88	87.39
0.1155	59.0	33.9	63.58	90.86
0.1491	46.9	38.6	62.00	93.39

$$\Lambda_0 = 81.77$$

$$\Lambda = 81.77 - 77.43\sqrt{C}$$

$$\Lambda_e \text{ HAc} = 194.28 - 115.29\sqrt{\alpha C}$$

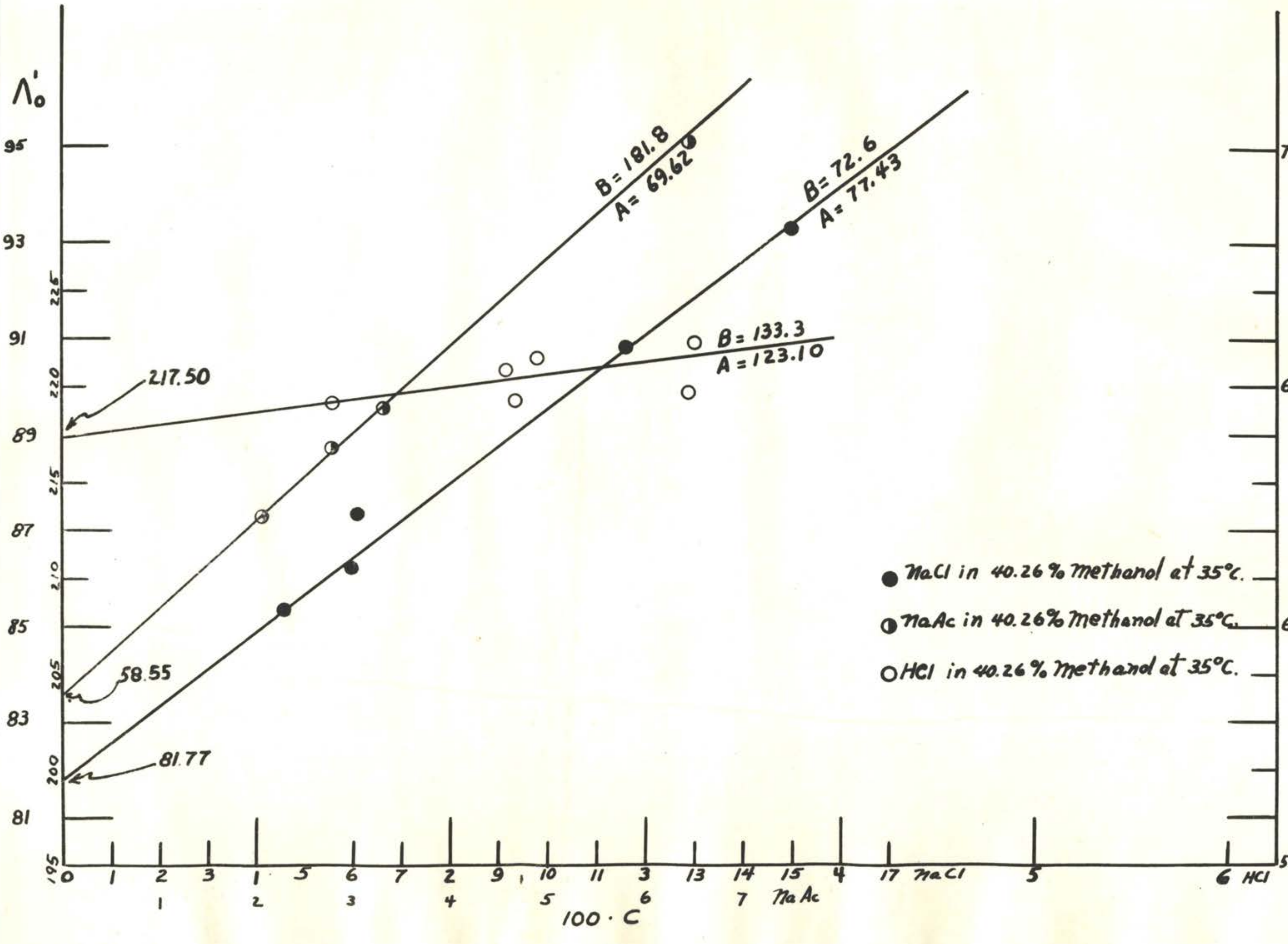

Λ'_0
95
93
91
89
87
85
83
81
195
200
205
210
215
220
225
Λ'_0
70
65
60
55
B = 181.8
A = 69.62
B = 72.6
A = 77.43
B = 133.3
A = 123.10
217.50
58.55
81.77
● NaCl in 40.26% methanol at 35°C.
◐ NaAc in 40.26% methanol at 35°C.
○ HCl in 40.26% methanol at 35°C.
0 1 2 3 1 5 6 7 2 9 10 11 3 13 14 15 4 17 NaCl
5
6 HCl
1 2 3 4 5 6 7 NaAc
100 · C

FIGURE No. 6

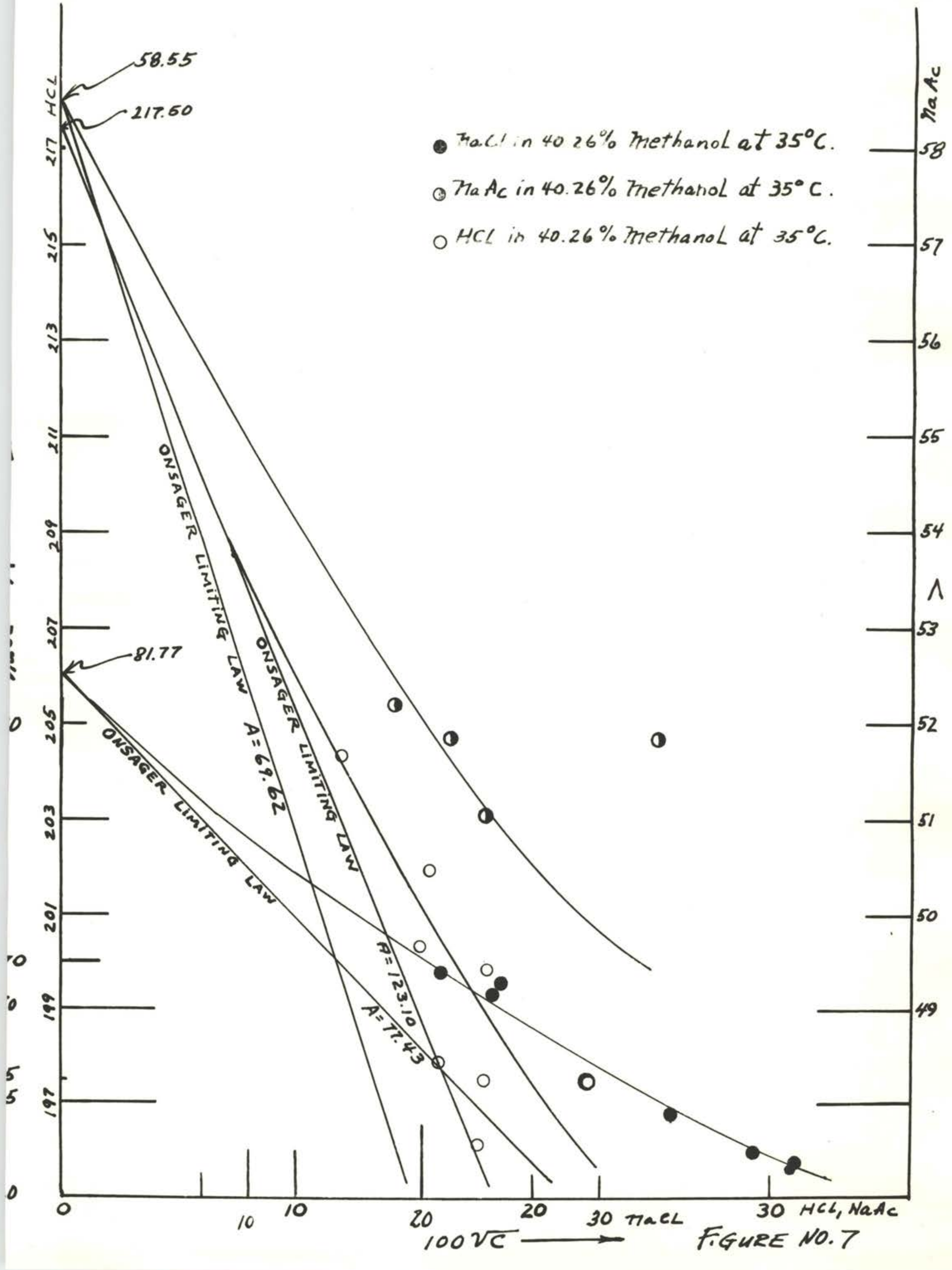

58.55
HCL
217.50
217
215
213
211
209
207
205
203
201
199
197
81.77
● NaCl in 40.26% methanol at 35°C.
◐ NaAc in 40.26% methanol at 35°C.
○ HCL in 40.26% methanol at 35°C.
NaAc
58
57
56
55
54
Λ
53
52
51
50
49
ONSAGER LIMITING LAW
A=69.62
ONSAGER LIMITING LAW
A=123.10
ONSAGER LIMITING LAW
A=77.43
0
10
10
20
20
30 NaCL
30 HCL, NaAc
100√C →

FIGURE NO. 7

HAc:

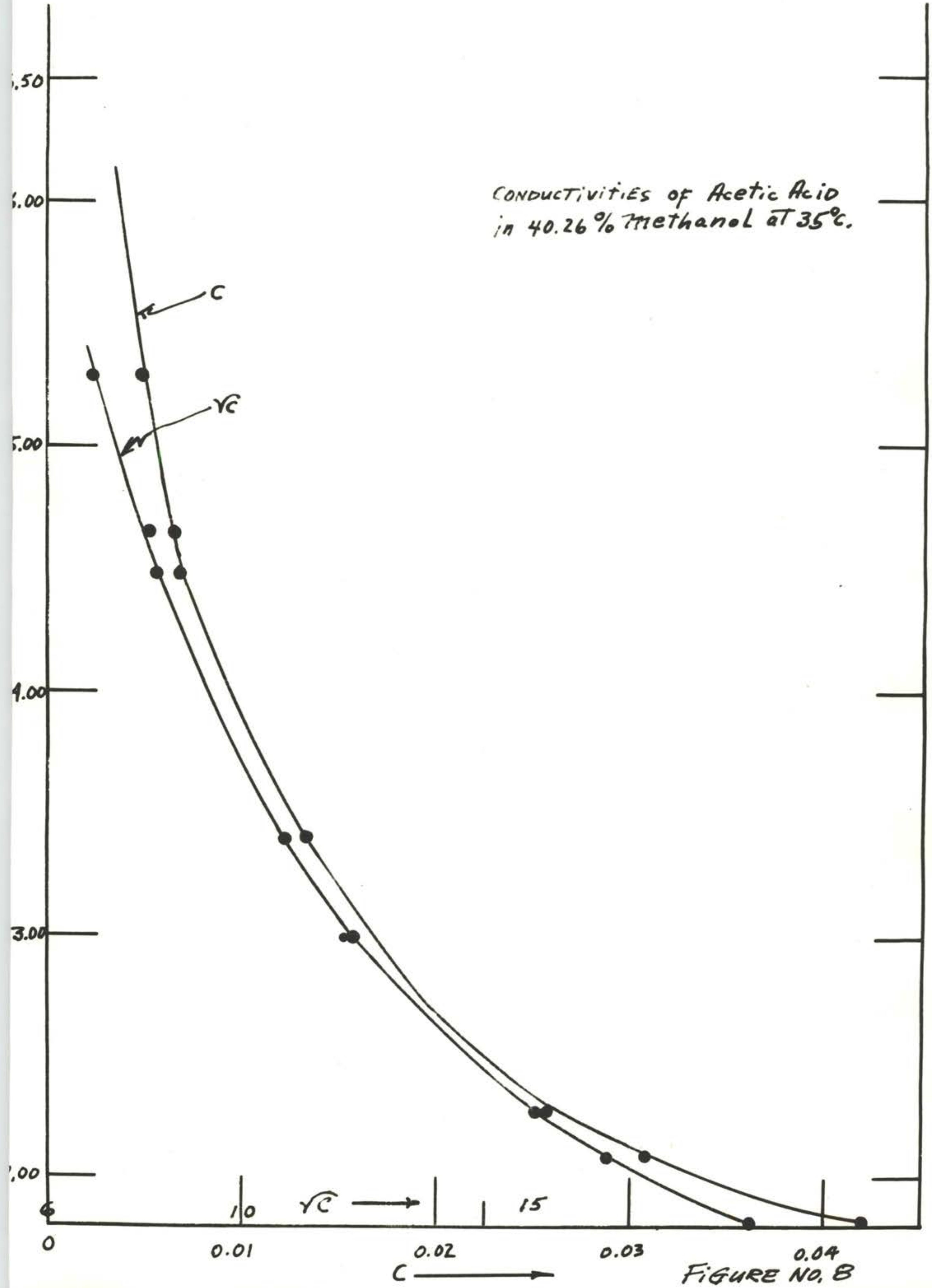
C(M./l.)	$100\sqrt{C}$	R (ohms)	Λ exp. (mhos)	Λ calc. (mhos)	$\alpha \times 10^2$	$100\sqrt{\alpha C}$	$K' \times 10^6$	$\log K' + 6$
0.00366	6.05	19,260	6.146	193.05	3.183	1.07	3.830	0.58320
0.00482	6.94	17,020	5.281	192.97	2.736	1.14	3.709	0.56926
0.00652	8.07	14,284	4.652	192.64	2.414	1.25	3.893	0.59028
0.00679	8.23	14,252	4.477	192.84	2.321	1.25	3.744	0.57334
0.01208	10.96	10,734	3.341	192.62	1.734	1.44	3.696	0.56773
0.01518	12.32	9,560	2.985	192.52	1.550	1.53	3.704	0.56867
0.02581	16.08	7,362.9	2.280	192.28	1.085	1.74	3.667	0.56431
0.03085	17.58	6,730.0	2.086	192.19	1.085	1.82	3.671	0.56478
0.04201	20.50	5,705.7	1.805	192.01	0.940	1.98	3.751	0.57415

Figure No. 9 shows D.H.L.L. not really applicable in this range of concentrations. Nevertheless

Average $K = (3.54 = 0.08) \times 10^{-6}$ (best D.H.L.L. line through the points)

Using equation 7-6-12 of the Harned and Owen monograph a plot of $\log K' + 6 - 1.57\sqrt{C_i}$ vs. C_u gives an intercept at about 0.5545 or $K = 3.59 \times 10^{-6}$; values used were:

C_i(M./l.)	$\sqrt{C_i}$	$\log K' + 6$	$1.57\sqrt{C_i}$	$\log K' + 6 - 1.57\sqrt{C_i}$	C_u(M./l.)
1.165×10^{-4}	1.078×10^{-2}	0.58327	0.0169	0.5664	0.003543
1.319	1.252	0.56935	0.0180	0.5514	0.004688
1.576	1.254	0.57346	0.0197	0.5538	0.006632
2.095	1.446	0.56779	0.0227	0.5451	0.01187
2.353	1.532	0.56885	0.0241	0.5448	0.01494
2.854	1.688	0.56414	0.0265	0.5376	0.02552
3.347	1.827	0.56480	0.0287	0.5361	0.03052
3.954	1.988	0.57428	0.0312	0.5431	0.04166



CONDUCTIVITIES OF Acetic Acid in 40.26% Methanol at 35°C.

FIGURE NO. 8

Analysis of Acetic Acid DATA
in 40.26% Methanol at 35°C

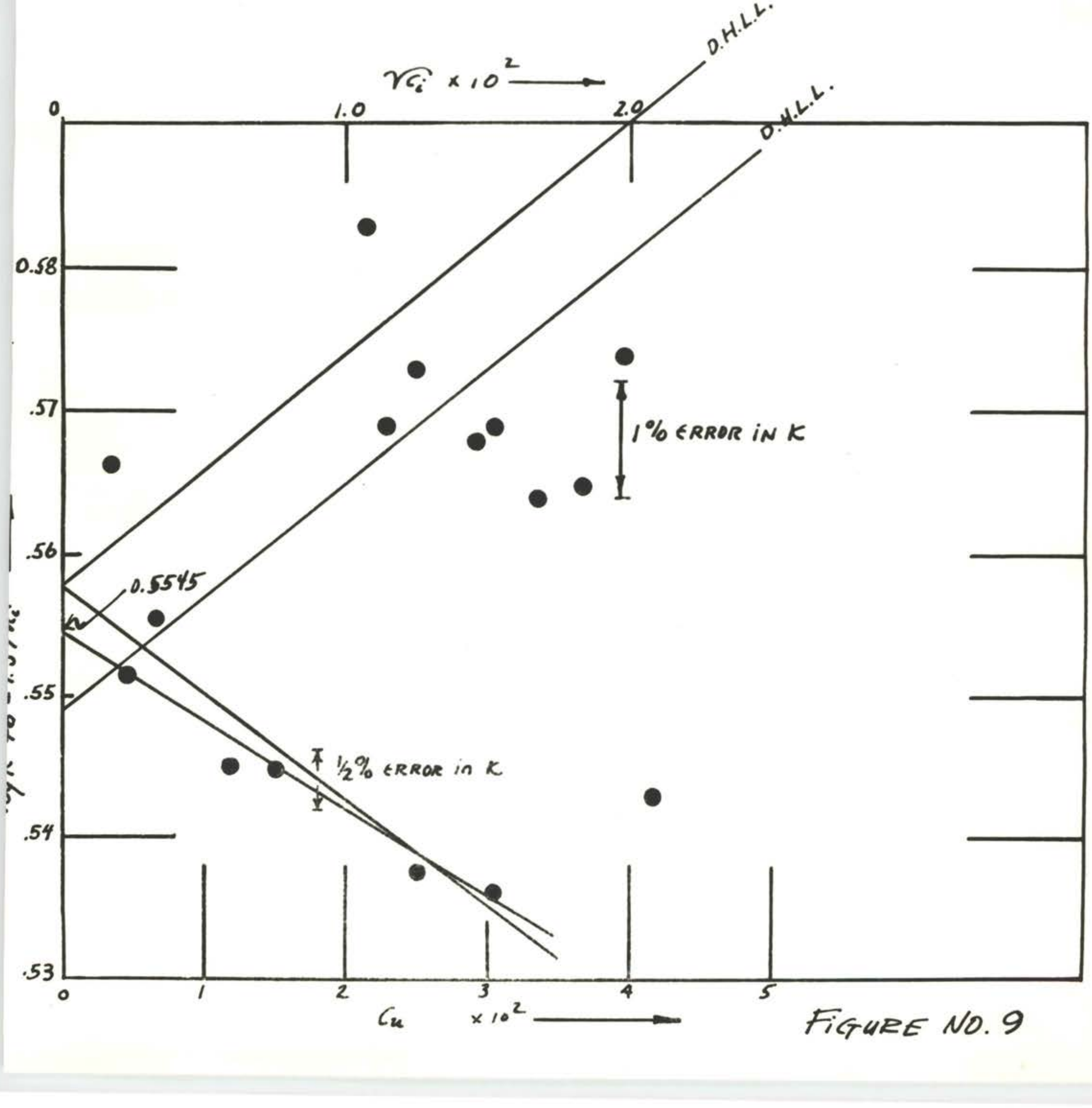


FIGURE NO. 9

Table III

HCl: at 36°C. in 59.47% methanol; k = 0.4333 and density of solvent = 0.8843.

C(M./l.)	R(ohms)	$100\sqrt{C}$	Λcalc. (mhos)	Λ_0' (mhos)
0.01680	186.44	12.9	138.33	154.95
0.02415	131.89	15.5	136.03	156.08
0.02600	122.81	16.1	135.70	156.56
0.02785	115.10	16.6	135.17	156.69
0.02835	112.96	16.8	135.30	157.11

$$\Lambda_0 = 152.47$$

$$\Lambda = 152.47 - 127.824\sqrt{C}$$

NaAc:

C(M./l.)	R(ohms)	$100\sqrt{C}$	Λcalc. (mhos)	Λ_0' (mhos)
0.03809	239.47	19.5	47.50	64.93
0.04427	209.87	21.3	46.63	65.74
0.04791	198.23	21.8	45.62	65.12
0.06099	157.96	24.6	44.97	67.20
0.10182	102.48	31.9	41.52	70.86
0.13441	82.19	36.6	39.22	73.27

$$\Lambda_0 = 61.62$$

$$\Lambda = 61.62 - 87.94\sqrt{C}$$

NaCl:

C(M./l.)	R(ohms)	$100\sqrt{C}$	Λcalc. (mhos)	Λ_0' (mhos)
0.05705	123.46	23.8	61.51	84.86
0.05977	118.35	24.4	61.25	85.23
0.07252	99.43	26.9	60.10	86.71
0.08925	82.14	29.8	59.10	88.87
0.11987	62.72	34.6	57.63	92.79
0.12087	62.84	34.7	57.04	92.21
0.12748	61.57	35.7	55.20	91.23

$$\Lambda_0 = 77.90$$

$$\Lambda = 77.90 - 95.088\sqrt{C}$$

$$\Lambda_{e\ \mathrm{HAc}} = 136.19 - 120.676\sqrt{\alpha C}$$

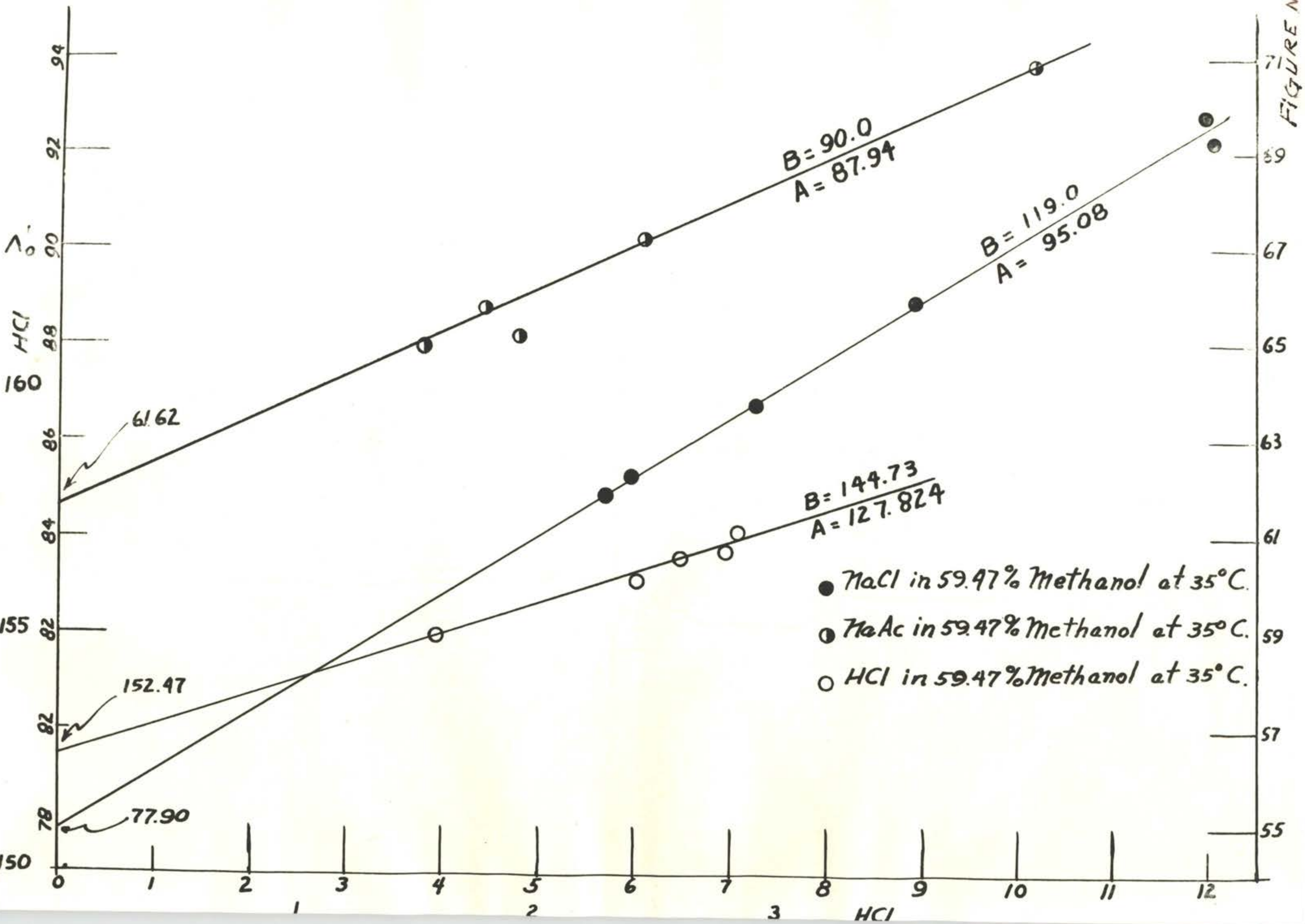

94
92
90
88
86
84
82
82
78
160
155
150
Λ_o'
HCl
61.62
152.47
77.90
B = 90.0
A = 87.94
B = 119.0
A = 95.08
B = 144.73
A = 127.824
● NaCl in 59.47% Methanol at 35°C.
◐ NaAc in 59.47% Methanol at 35°C.
○ HCl in 59.47% Methanol at 35°C.
71
69
67
65
63
61
59
57
55
0
1
2
3
4
5
6
7
8
9
10
11
12
1
2
3
HCl

FIGURE NO. 10

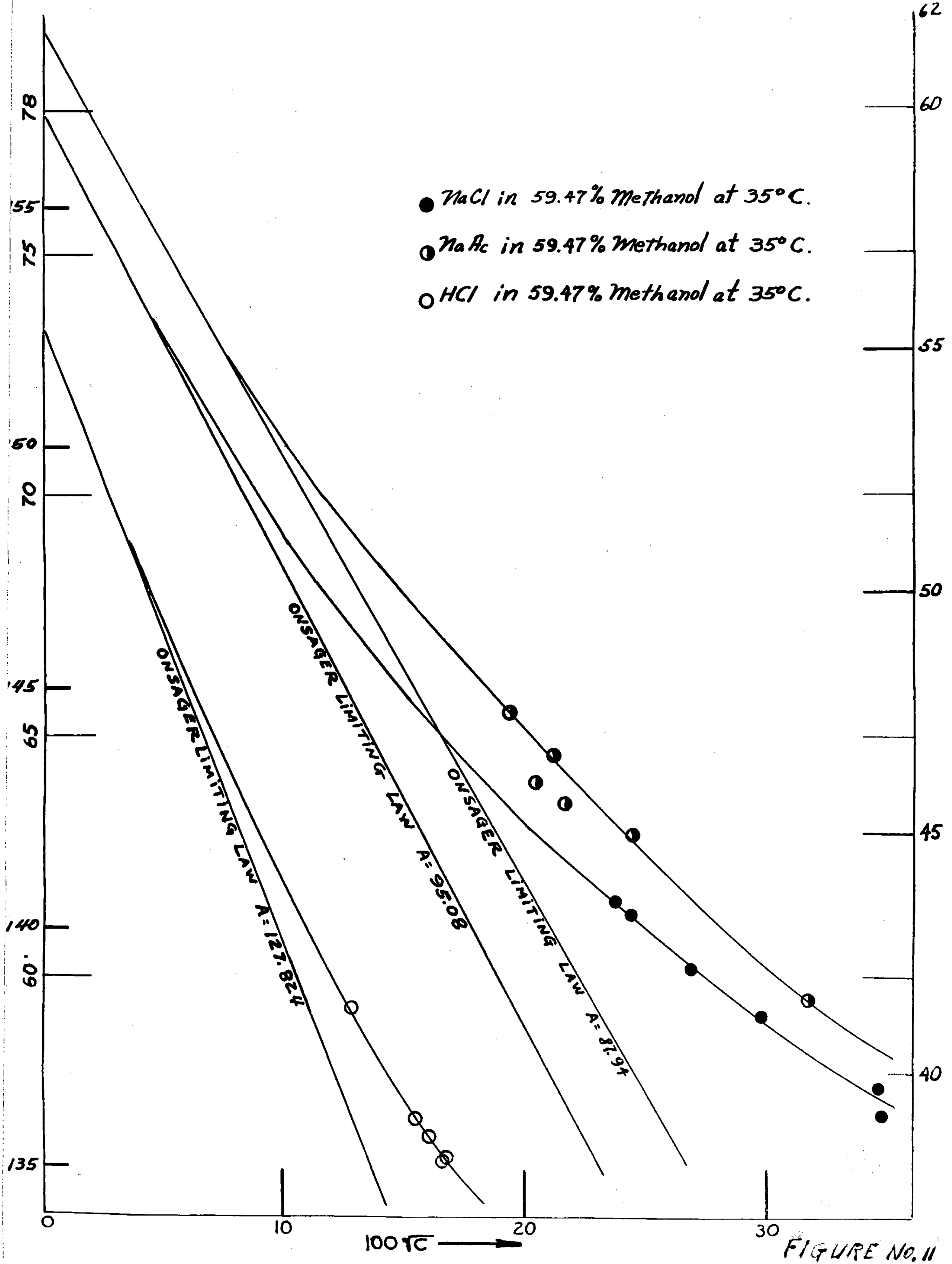

● NaCl in 59.47% Methanol at 35°C.
◐ NaAc in 59.47% Methanol at 35°C.
○ HCl in 59.47% Methanol at 35°C.
ONSAGER LIMITING LAW A= 127.824
ONSAGER LIMITING LAW A= 95.08
ONSAGER LIMITING LAW A= 87.94
78
155
75
150
70
145
65
140
60
135
62
60
55
50
45
40
0
10
20
30
100√C →

FIGURE NO. 11

HAc:

C(M./l.)	R(ohms)	Λ exp. (mhos)	α	Λ calc. (mhos)	$100\sqrt{KC}$	$K' \times 10^6$	log $K' + 6$
0.00713	31,110	1.9534	0.01447	134.98	1.01	1.514	0.1801
0.01660	20,900	1.2489	0.00927	134.71	1.24	0.439	0.1580
0.01741	20,487	1.2147	0.009017	134.70	1.25	0.428	0.1547
0.029821	18,620	1.1176	0.00830	134.64	1.31	0.446	0.1661
0.025082	17,587	0.98227	0.007298	134.58	1.35	0.346	0.1290
0.03084	15,275	0.01975	0.00684	134.45	1.45	0.345	0.1287
0.03759	14,101	0.81745	0.00608	134.37	1.51	0.398	0.1455

Data indicate definitely not in D.H.L.L. range. Graph of log $K' - 1.96\sqrt{C_i}$ vs. C_u gives $K = 1.48 \times 10^{-6}$ (from the intercept of the best line through points). Values used were:

C_i(M./l.)	C_u(M./l.)	$1.965\sqrt{C_i}$	log $K' + 6$	log $K' + 6 - 1.965\sqrt{C_i}$
1.0×10^{-4}	0.00703	0.0199	0.1801	0.1602
1.5	0.01645	0.0244	0.1581	0.1337
1.6	0.01725	0.0246	0.1547	0.1301
1.7	0.02065	0.0257	0.1661	0.1404
1.8	0.02490	0.0265	0.1291	0.1026
2.1	0.03063	0.0285	0.1287	0.1002
2.3	0.03736	0.0296	0.1455	0.1159

Analysis of Acetic Acid Data
in 59.47% Methanol at 35°C.

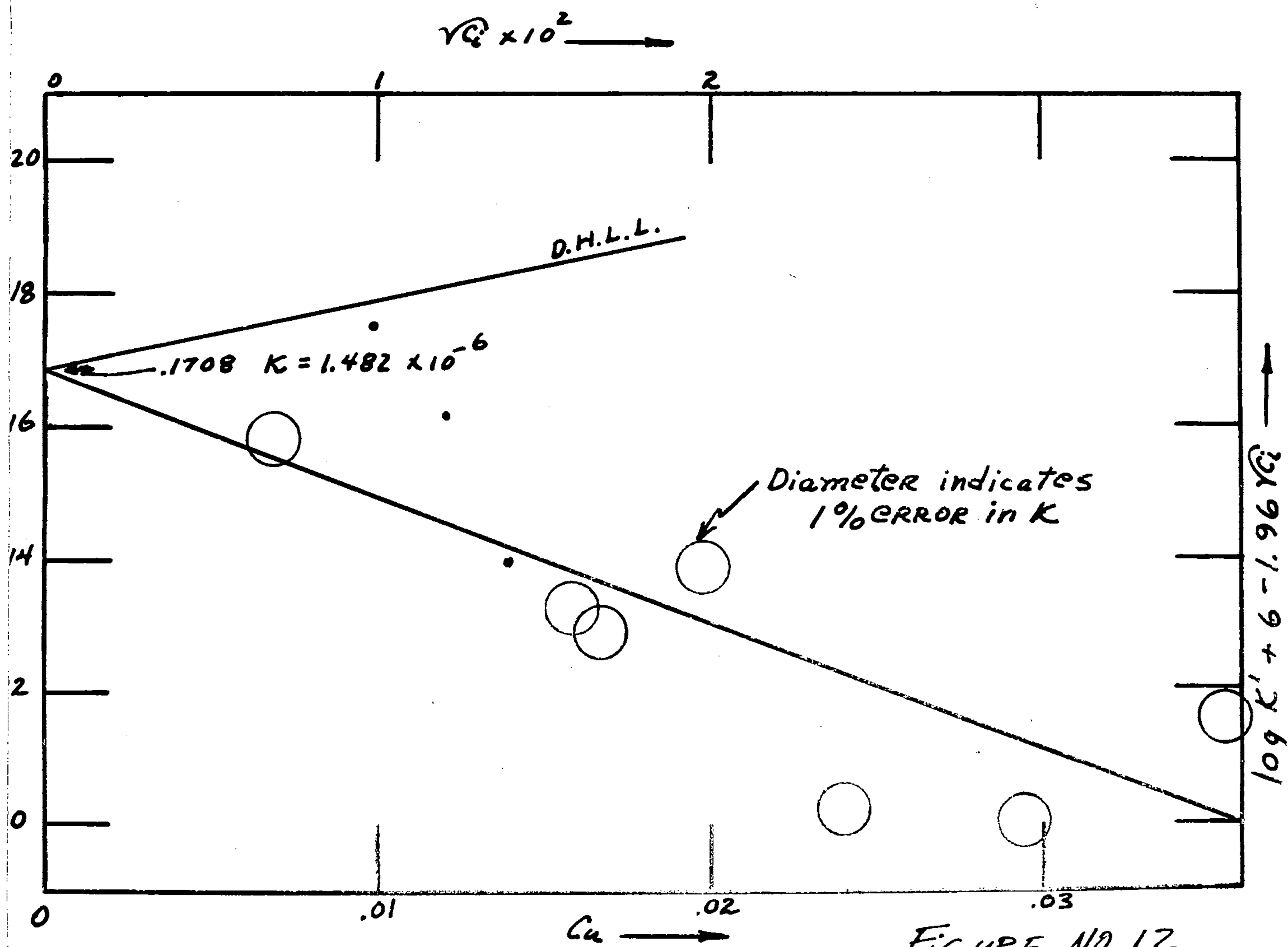
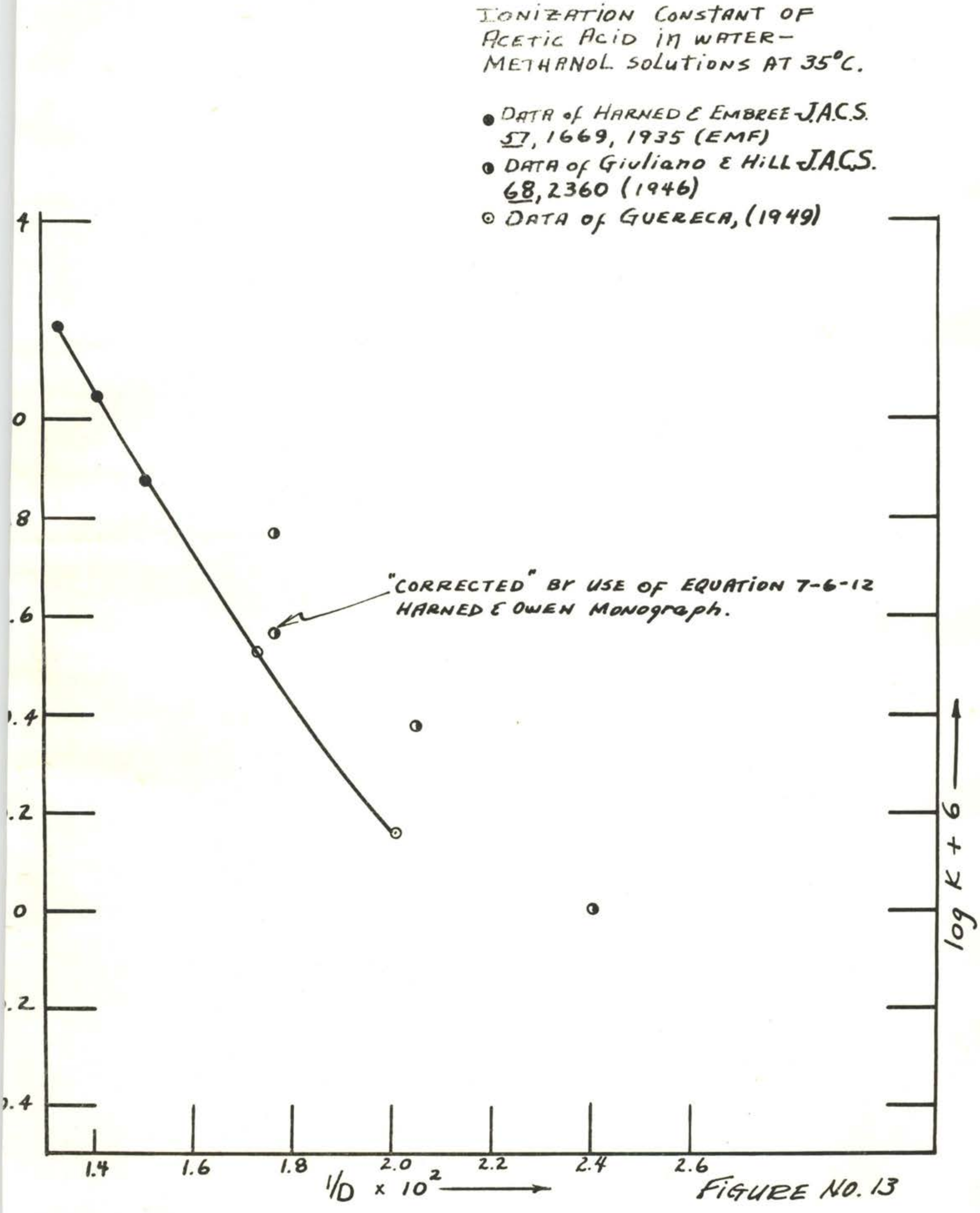


FIGURE NO. 12



IONIZATION CONSTANT OF ACETIC ACID IN WATER-METHANOL SOLUTIONS AT 35°C.

● DATA of HARNED & EMBREE - J.A.C.S. 57, 1669, 1935 (EMF)

◐ DATA of Giuliano & Hill - J.A.C.S. 68, 2360 (1946)

⊙ DATA of GUERECA, (1949)

"CORRECTED" BY USE OF EQUATION 7-6-12 HARNED & OWEN Monograph.

FIGURE NO. 13

Miscellaneous Observations

Using the method which Kohlrousch suggested, it was attempted to work in very dilute solutions (0.0005 to 0.005 normal). Conductance equations were obtained in which the method of least squares was used to extrapolate to zero concentration. For example, for a 19.23% methanol solution at 25°C., the following equations were obtained:

$$\begin{array}{lllll}
\text{(A)} & \text{HCl} & \Lambda = & 365.42 - 50.085 \times 100\sqrt{C} & \\
 & \text{NaAc} & \Lambda = & 60.82 - 2.972 \times 100\sqrt{C} & \\
 & \text{-NaCl -} & \Lambda = & -97.96 - 2.286 \times 100\sqrt{C} & \\
\cline{2-4}
 & \text{HAc} & \Lambda_e = & 328.28 - 50.771 \times 100\sqrt{C} & (C = \alpha C = C_i)
\end{array}$$

Data obtained using the Shedlovsky method for a 20.50% methanol solution at 25°C. were:

$$\begin{array}{lllll}
\text{(B)} & \text{HCl} & \Lambda = & 265.12 - 112.07\sqrt{C} & \text{(constant boiling HCl)} \\
 & \text{NaAc} & \Lambda = & 60.80 - 56.51\sqrt{C} & \\
 & \text{-NaCl-} & \Lambda = & -77.58 - 61.06\sqrt{C} & \\
\cline{2-4}
 & \text{HAc} & \Lambda_e = & 284.34 - 107.52\sqrt{C} & (C = \alpha C = C_i)
\end{array}$$

It will be noted that the HCl data (A) was of critical importance. A modified "Kipp" generator with sulfuric acid dropping on hydrochloric acid was used to generate "pure", anhydrous, gaseous HCl. The resulting solution was analyzed for the method of Talbot[34] for soluble chlorides. Eight separate analysis were taken before the normality results were reproducible to an accuracy of ± 0.07%. Nevertheless, an outrageous value for the slope of the HCl line was obtained (A = 5,008.5). The other slopes (A) are also too high from a comparison of values for

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[34] Hamilton and Simpson, Talbot's Quantitative Chemical Analysis, 8th ed., 201, MacMillan (1937).

NaCl, HCl, and NaAc obtained by other workers in pure water and pure methanol[35]. Tables showing the acetic acid data are not included because the results were very inconclusive although the values log K' were of the same order as those obtained for HAc at 25°C. in a 20.50 % methanol solution. Since the method is the same, a sample computation for α is shown below from the discarded data, i.e. α values remained constant after only two or sometimes three approximations for the sulutions measured (α values for HAc in Tables I, II, and III)

$$C = 0.000612 \text{ M./l.} \quad \Lambda \text{exp.} = 31.0 \text{ mhos}$$

$$\Lambda_o = 328.28 \text{ mhos}$$

$$\alpha' = \frac{\Lambda}{\Lambda_o} = \frac{31.0}{328.28} = 0.09443$$

$$\Lambda' = \Lambda_o - M\sqrt{\alpha' C} \; ; \alpha' C = (0.09443)(0.000612) = 0.00005779$$

$$\Lambda' = 328.28 - 5077.1\sqrt{\alpha' C} = 328.28 - 38.58 = 289.7$$

$$\alpha'' = \frac{31.0}{289.7} = 0.1070$$

$$\alpha'' C = (0.1070)(0.000612) = 0.00006548$$

$$\Lambda'' = 328.28 - 5077.1\sqrt{\alpha'' \cdot C} = 287.21$$

$$\alpha''' = \frac{31.0}{287.21} = 0.1079$$

$$\alpha''' C = (0.1079)(0.000612) = 0.00006603$$

$$\Lambda''' = 328.28 - 5077.1\sqrt{\alpha''' C} = 287.06$$

$$\alpha'''' = \frac{31.0}{287.06} = 0.1079$$

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[35] Shedlovsky, J. Am. Chem. Soc., 54, 1405, 1411 (1932).
MacInnes and Shedlovsky, Ibid., 54, 1429 (1932).
Unmack, Murray-Rust, and Hartley, Proc. Roy. Soc., A127,228 (1928).
MacInnes, Principles of Electrochemistry, 357.

Discussion of Results

When it is assumed that the resistance was reproducible to ±0.05%, and an error of ± 0.1% in the concentration on C, errors of ± 0.12% for Λ, ± 0.25% for α, ± 0.21% for Λ_o, and ± 0.5% in K result. That is, mathematically it appears that the data should be accurate to about ±1/2% provided that the temperature is regulated to within ± 0.03°C. The acetic acid data for the 20.50% methanol scatters too much for accurate extrapolation to zero ionic strength. Correction to $\sqrt{u} = 0$ assuming the D.H.L.L. applicable (A = 0.6086) gives an average K of $(8.34 \pm 0.06) \times 10^{-6}$. This compares favorably with 8.20×10^{-6} from the data of Harned and Embree[36] obtained using the E.M.F. method. It is possible that this agreement is satisfactory. The deviation of the data from the D.H.L.L. line is less than 1%. The HAc data for the 40.26% methanol shows that the D.H.L.L. range has been exceeded and a plot of the data using the H. & O. method gives a reasonable intercept at about 0.5545 or $K = 3.59 \times 10^{-6}$. Average of K values, i.e. using the D.H.L.L. is $(3.54 \pm 0.08) \times 10^{-6}$. The HAc data for the 59.47% methanol indicates that the concentration is not to the left of the expected "hump". The graph of $\log K' - 1.96 \sqrt{C_i}$ vs. C_u is fair, i.e. points deviate from 1-3 times the experimental error from a straight line. The intercept gives $K = 1.48 \times 10^{-6}$.

Harned and Embree[37] found that plots of log K vs. 1/D (where D = dielectric constant of the solvent) might be linearly extrapolated

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[36] Harned and Embree, J. Am. Chem. Soc., 57, 1669 (1935).

[37] Harned and Embree, Ibid., 57, 1669 (1935).

to "perhaps" 30% methanol with some degree of safety. Harned[38] has shown conclusively that such a plot gives curves of definite curvature, instead of straight lines. Such a plot of the data obtained in this study (Figure No. 13) has been included. The graph clearly shows a decided curvature and the points are in good agreement with the E.M.F. data. The Giuliano and Hill data[39] are also included and it is apparent that their values are too high. Furthermore, the 39.4% data of Giuliano and Hill has been recalculated according to the H. & O. method, and although still high, show better agreement with the values obtained in this research.

From a critical point of view, the data for the conductance curves are considered good. The values of the thermodynamic ionization constant K are not as good as it was hoped for, although the data strongly indicate the expected ideas outlined in the introduction. In order to work at concentrations in which the D.H.L.L. applies, the following suggestions would possibly help. A Shedlovsky type cell[40] to which weighed increments are added would help in getting more accurate values for concentrations which are critical in dilute solutions. A better method of temperature control would also help since the relay used in this thesis was rather "lazy", i.e. the solenoid remained magnitized for a short time after the circuit was open. Shielded cables could be

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[38] Harned, J. Phys. Chem., 43, 275 (1939).

[39] Giuliano and Hill, J. Am. Chem. Soc., 68, 2360 (1946).

[40] Shedlovsky, Ibid., 54, 1415 (1932).

used in the bridge proper to cut down on mutual inductance effects between the branches of the bridge proper. Of course, a highly accurate 10,000 ohm resistor could be placed in parallel with the cell to measure very dilute solutions[41]. I am rather skeptical about the cylindrical drum at high resistances because the "inductance" effect should not be neglected since the movement of the drum itself was the critical balancing factor and this was especially true in the acetic acid measurements in which very high resistances were encountered.

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[41] Shedlovsky, Ibid., 54, 1412 (1932).

Summary

Conductance measurements were made at 25°C. for NaCl, NaAc, HCl, and HAc in 20.50% methanol, and at 35°C. for the same electrolytes in 40.26% and 59.47% methanol respectively. Conductance equations were obtained for HAc and the degree of dissociation determined by a method involving successive approximations. Values for the thermodynamic ionization constant (K) of acetic acid were calculated using the Debye-Hückel limiting law (D.H.L.L.) and the Harned and Owen (H. & O.) method.

The acetic acid data strongly indicate that the D.H.L.L. was followed in the 20.50% methanol, and, that in the 40.26% and 59.47% methanol, the D.H.L.L. was not followed in the concentration ranges studied. A plot of the data for all three series of solutions using the H. & O. method confirmed this.

The values of log K when plotted against 1/D show that the determined values of K are reasonable. The ionization constants as determined by Giuliano and Hill are too high and confirm a wrong application of the D.H.L.L. The log K values of Giuliano and Hill at 35°C. do not give a "straight" line or even a reasonable curve when plotted against 1/D in direct opposition to their statement in the literature[42].

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[42] Giuliano and Hill, Ibid., 68, 2360 (1946).

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Harned, J. Phys. Chem., **43**, 275 (1939).

Harned and Embree, J. Am. Chem. Soc., **57**, 1669 (1935).

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Biography

Ross Antonio Guereca was born on June 13, 1923 at El Paso, Texas. He attended Cathedral High School of El Paso where he belonged to the Debating Team, Select Scholars, and was selected to the all-state basketball team. After graduation in May 1940, he worked for one year saving money to help pay for a college education. At Texas College of Mines and Metallurgy he participated in basketball, track and baseball. His college education was interrupted by his volunteering for the Army in 1943. After Infantry basic, he was sent to the University of Oklahoma to study Electrical Engineering where he completed term five. After serving with the Signal Corps in France, Belgium, and Germany, he received his honorable discharge early in 1946.

On May 27, 1947 he was married to Margaret Alvidrez of Anthony, New Mexico, and they are now parents of a son, Mark Anthony. After completing his B. S. in chemistry in January 1948, he worked for the El Paso Public School System before coming to Stillwater on a graduate fellowship in September 1948.

Typed by:

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