THE RELATION BETWEEN THE IONIZING POWER AND THE DIELECTRIC CONSTANTS OF SOLVENTS.

By Herbert N. McCoy.

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In a recent paper, Walden[1] gives an account of his newer studies on the conductivities of solutions of salts in numerous organic solvents. Among other conclusions, Walden has pointed out a very simple quantitative relationship between the ionizing power of a solvent and its dielectric constant. Nernst[2] had observed earlier, that liquids with high dielectric constants are good ionizing solvents, and gives a theoretical explanation. Walden finds that in case solutions of one and the same electrolyte in various solvents have the same degree of ionization, then the product of the dielectric constant and the cube-root of the dilution for all such solutions, has practically a constant value. Thus if $\alpha = \alpha_1$, then $\varepsilon\sqrt[3]{V} = \varepsilon_1\sqrt[3]{V_1}$; where α = the degree of ionization, ε = the dielectric constant, and V = the dilution. The nature of Walden's results is illustrated by the figures in Table I, for the salt tetraethyl ammonium iodide, dissolved in various solvents.

Table I. ($\alpha = 0.47$).

Solvent.	ϵ.	V.	$\epsilon\sqrt[3]{V}$.
Methyl alcohol	32.5	8	65
Ethyl alcohol	21.7	50	80
Acetyl bromide	16.2	100	75
Benzaldehyde	16.9	64	78
Acetonitrile	35.8	10	77

This relation, involving $\sqrt[3]{V}$ suggests that found by Kohlrausch[3] between the equivalent conductivity of an aqueous salt solution and its concentration, *viz*: $\Lambda = \Lambda_\infty - k\sqrt[3]{C}$; where Λ is the equivalent conductivity at the concentration C, Λ_∞ is the conductivity at infinite dilution, and k is a constant. Instead of following the procedure of Kohlrausch, by testing the applicability of this equation graphically, in the case of any specific electrolyte, one may by a simple algebraic expedient proceed arithmetically and obtain at the same time the value of Λ_∞. In practice, the values of C are usually multiples, by a power of 2, of the smallest concentration. Suppose $C_1 = 8C_2$; then $\sqrt[3]{C_1} = 2\sqrt[3]{C_2}$: $\Lambda_1 = \Lambda_\infty - k\sqrt[3]{C_1}$ and $\Lambda_2 = \Lambda_\infty - k\sqrt[3]{C_2}$. Therefore, $\Lambda_\infty = 2\Lambda_2 - \Lambda_1$. If Λ_∞, as calculated for several pairs of concentrations, is constant, then the Kohlrausch equation applies to the case. Thus, for an aqueous solution of common salt, at 25°, $2\Lambda_{256} - \Lambda_{32} = 130\ 6$; $2\Lambda_{512} - \Lambda_{64} = 131.5$; $2\Lambda_{1024} - \Lambda_{128} = 131.4$. Therefore, the Kohlrausch law holds for the case, and $\Lambda_\infty = 131.2$.

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[1] *Z. physik. Chem.*, **54**, 133 (1906).

[2] *Ibid.*, **3**, 531 (1894).

[3] *Wied. Ann.*, 26, 200 (1885).

The Kohlrausch equation may be written $\Lambda/\Lambda_\infty = 1 - k/\Lambda_\infty \sqrt[3]{C}$; or $\alpha = 1 - K\sqrt[3]{C_1}$ (1) where the degree of ionization, $\alpha = \Lambda/\Lambda_\infty$ and $k/\Lambda_\infty = K$, a constant. Transformation of equation (1) gives

$$K = (1 - \alpha)\sqrt[3]{V}. \qquad (2)$$

Table II gives complete data and results for sodium chloride. The values of α, column 5, are calculated by equation (1). Column 6 contains the differences between the observed and calculated values of α; these differences are of the same order as the probable experimental errors.

TABLE II.

V.	Λ.	α.	K.	α Calc.	$\Delta\alpha$.
32	114.6	0.874	0.400	0.872	0.002
64	117.9	0.899	0.404	0.899	0.000
128	120.4	0.918	0.413	0.920	0.002
256	122.6	0.935	0.413	0.936	0.001
512	124.7	0.950	0.400	0.949	0.001
1024	125.9	0.960	0.403	0.960	0.000
∞	131.2		——		——
		Mean,	0.405	Mean,	0.001

In order to find how well equations (1) and (2) represent the behavior of common electrolytes, I have made calculations like those of Table II for about 30 salts. The data are from measurements by Ostwald, Walden, Bredig and Francke.[1] As Table III shows, the mean difference, $\Delta\alpha$, between α as calculated and as observed is 0.2 per cent., which difference may easily be ascribed to experimental error.

Calculation shows that equation (1) applies also, with fair accuracy, to many solutions in non-aqueous solvents. Suppose the same salt dissolves in two different solvents; then

$$\alpha_1 = 1 - K_1\sqrt[3]{C_1} \text{ and } \alpha_2 = 1 - K_2\sqrt[3]{C_2}$$

will represent the existing relationships in the two cases. Now, suppose $\alpha_1 = \alpha_2$; then

$$K_1\sqrt[3]{C_1} = K_2\sqrt[3]{C_2} \text{ or } K_1\sqrt[3]{V_2} = K_2\sqrt[3]{V_1}. \qquad (3)$$

But Walden has shown, as already stated, that if $\alpha_1 = \alpha_2$, $\varepsilon_1\sqrt[3]{V_1} = \varepsilon_2\sqrt[3]{V_2}$. Therefore,

$$K_1\varepsilon_1 = K_1\varepsilon_2 = \text{a constant}. \qquad (4).$$

But since both K and ε are independent of α, equation (4) should hold for all values of α. Table IV gives the values of $K = (1 - \alpha)\sqrt[3]{V}$, ε and $K\varepsilon$ for the salt $(C_2H_5)_4NI$ in various solvents, as calculated from Walden's data. While the mean deviation from the mean value of $K\varepsilon$ is ±10 per cent., nevertheless, it seems certain that a fundamental connection exists between K and ε; but that it is modified by unknown causes.

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[1] Landolt, Börnstein, Meyerhoffer, Tabellen (1905).

TABLE III.

	Λ_∞.	*K*.	$\Delta\alpha$.	Observer.
LiCl	122.0	0.493	0.003	W.
LiI	120.1	0.431	0.003	O.
$LiClO_3$	106.7	0.465	0.002	O.
$LiClO_4$	118.6	0.462	0.001	O.
$LiMnO_4$	107.4	0.617	0.005	F.
$LiNO_3$	114.8	0.478	0.003	O.
NaF	109.3	0.479	0.001	W.
NaCl	131.2	0.405	0.001	W.
NaBr	134.1	0.460	0.002	O.
NaI	134.0	0.537	0.004	O.
$NaClO_3$	118.1	0.460	0.002	O.
$NaClO_4$	130.9	0.442	0.005	W.
$NaIO_3$	94.5	0.406	0.003	W.
$NaNO_3$	126.4	0.464	0.002	O.
$NaMnO_4$	118.9	0.512	0.002	F.
KF	131.3	0.401	0.000	W.
KCl	154.6	0.381	0.001	[1]
KBr	158.1	0.426	0.003	O.
KI	156.9	0.412	0.002	O.
$KClO_3$	141.8	0.307	0.001	W.
$KClO_4$	154.4	0.470	0.003	O.
$KBrO_3$	131.7	0.414	0.001	W.
KIO_3	118.4	0.474	0.001	W.
KNO_3	150.0	0.472	0.003	O.
$KMnO_4$	137.5	0.355	0.002	B.
RbCl	157.2	0.387	0.001	B.
CsCl	158.4	0.413	0.001	B.
NH_4Cl	153.3	0.372	0.001	B.
$TlNO_3$	149.8	0.433	0.003	F.

TABLE IV.

$(C_2H_5)_4NI$.

Solvent.	*K*.	ϵ.	$K\epsilon$.
Water	0.48	80.0	38.4
Methyl alcohol	1.30	32.5	42.2
Ethyl alcohol	2.08	21.7	45.1
Glycol	0.97	34.5	33.5
Benzaldehyde	1.01	16.0	32.3
Furfural	0.96	39.4	37.7
Acetic anhydride	1.90	17.9	34.0
Citraconic anhydride	0.84	39.5	33.2
Acetyl bromide	2.46	16.2	39.8
Cyanacetic methyl ester	1.48	28.8	41.7
Cyanacetic ethyl ester	1.67	26.2	43.7
Nitromethane	1.05	40.0	42.0
Nitrobenzene	1.44	33.4	48.1
		Mean,	39.3

[1] The conductivity values for KCl are the mean results of several observers.

TABLE V.

Solvent.	K.	ϵ.	$K\epsilon$.	Observer.
		KI.		
Water	0.412	80.0	33.0	Ostwald
Ethyl alcohol	1.67	21.7	36.2	Walden
Acetonitrile	1.45	35.8	51.9	Walden
		$LiNO_3$.		
Water	0.478	80.0	38.2	Ostwald
Methyl alcohol	1.174	32.5	38.2	Jones and Lindsay[1]
50 per cent. methyl alcohol	0.632	57.4[2]	36.3	Jones and Lindsay

Table V gives a few results for two inorganic salts. In the case of potassium iodide, $K\varepsilon$ has nearly the same value for water and ethyl alcohol, but for acetonitrile as solvent, the value of $K\varepsilon$ is abnormally large. For lithium nitrate the product $K\varepsilon$ is the same for both water and methyl alcohol. In 50 per cent. methyl alcohol, one might, at first thought, expect K to be the mean of the values for water and methyl alcohol separately. This mean is 0.826 for lithium nitrate. If, however, the product $K\varepsilon$ has the same value for the mixed solvents as for each separately, ε being the mean of the separate values,[3] then K should be 0.679; the actual value is 0.632.

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THE VISCOSITY OF NON-AQUEOUS SOLUTIONS OF POTASSIUM IODIDE.

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The study of aqueous solutions of certain electrolytes exhibiting negative viscosity has led to the view that the cations are the effective agents in lowering the viscosity of the solvent while the anions and the undissociated molecules invariably tend to increase it.[4]

It seemed desirable to test this theory by working with non-aqueous solutions in which the degree of ionization is known to be less than in water. Fortunately, potassium iodide, which exhibits negative viscosity to a marked degree in dilute aqueous solutions, is quite soluble in a number of organic solvents of relatively low dissociating power.

The solvents employed in this investigation were methyl alcohol, ethyl alcohol, ethylene glycol, glycerol, furfural, acetone and pyridine. These were obtained either from Kahlbaum or Merck, special precautions being taken to insure their purity and the absence of moisture.

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[1] *Amer. Chem. J.*, **28**, 329.

[2] Drude, *Z. physik. Chem.*, **23**, 300.

[3] Drude, *Loc. cit.*

[4] Getman, *Jour. chim. phys.*, **5**, 344 (1907); Getman, THIS JOURNAL, **30**, 721 (1908).