

[COMMUNICATION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

**The Validity of the Ilkovic Equation in the Polarographic Analysis of Alkali Metals and the Characteristics of the Alkali Waves in Various Media**

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The alkali metals are deposited at the dropping mercury cathode at very negative potentials, at which the surface tension of mercury is relatively low. It was of interest to investigate under what conditions the experimentally determined diffusion currents  $i_d$  agree with those calculated from the Ilkovič equation<sup>1</sup>

$$i_d = 605nD^{1/2}Cm^{2/3}t^{1/3} \quad (1)$$

In this equation  $n$ ,  $D$  and  $C$  are, respectively, the valence, the diffusion coefficient, and the concentration of the reducible ion,  $m$  is the weight of mercury flowing from the capillary per second, and  $t$  is the drop time.

We have also analyzed the polarographic waves of alkali metals in order to test the validity of the wave equation, first given by Heyrovsky and Ilkovič.<sup>2</sup>

Moreover we have verified that the half-wave potentials of both potassium and sodium in a medium of water, 25, 50 and 80% ethanol as well as those of lithium in the latter two media are independent of the ion concentration and of the drop time.

**Experimental**

The Heyrovsky polarograph was used in all of the experiments. The electrolyses were carried out in a thermostat at 25°. The materials and electrolytic cells used in this work have been described in a previous paper.<sup>3</sup>

The reported values of the half-wave potentials refer to the saturated calomel electrode (S. C. E.) and are corrected for the  $iR$  drop. A similar correction was applied to the values of the cathode potential in the analysis of the polarographic waves.

The resistance across the cell with a mercury pool anode was found in two ways. It was calculated with the aid of an equation, derived by Ilkovič<sup>4</sup>

$$R_{av} = 4/3R_{min} = 4Kd/3\sqrt{q_1q_2} \quad (2)$$

in which  $R_{av}$  is the mean resistance during the formation of a drop,  $R_{min}$  is the minimum value at

(1) D. Ilkovič, *Coll. Czech. Chem. Comm.*, **6**, 498 (1934).(2) J. Heyrovsky and D. Ilkovič, *ibid.*, **7**, 198 (1935).(3) Ignace Zlotowski and I. M. Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, **14**, in press (1942).(4) D. Ilkovič, *ibid.*, **8**, 13 (1936).

the moment when the drop falls,  $K$  is the specific resistance of the solution,  $d$  is the distance between the two electrodes, and  $q_1$  and  $q_2$  are their respective surfaces. The surface of the dropping mercury cathode can be calculated from the experimentally determined values of  $m$  and  $t$ .

The resistance was also estimated from the slope of the straight line deposition branch of the current-voltage curve of the supporting electrolyte. The slope of this line ( $dE/di$ ) is approximately numerically equal to the resistance at potentials where the supporting electrolyte is discharged. This method, if carried out at potentials close to those where the alkali waves occur, is simpler than the classical method with the Wheatstone bridge. With the latter, the minimum was so poorly defined that the resistances could not be determined with a precision greater than 20%.

That the values of  $R_{av}$ , calculated by means of Eq. (2), agree satisfactorily with those derived from the slope of the deposition line of the supporting electrolyte, is evident from the data in Table I.

**Results**

**Equation of the Alkali Metal Waves.**—In a previous paper 50% ethanol was recommended as the most suitable medium for the determination of potassium and sodium. Several of the polarographic waves obtained in this medium, using tetraalkylammonium hydroxides as supporting electrolytes, have been analyzed by plotting  $\log i/(i_d - i)$  vs. the cathode potential, the latter being corrected for the  $iR$  drop. An example of such an analysis is given in Fig. 1, in which both the wave and the plot of  $\log i/(i_d - i)$  against the cathode potential are given. The log plot yields a straight line with a slope of 0.061 in excellent agreement with the Heyrovsky and Ilkovič equation<sup>2</sup>

$$\pi = \pi^{1/2} - (RT/F) \ln (i/i_d - i)$$

corresponding to a reversible reduction of an univalent metal ion under conditions of equilibrium at the dropping mercury cathode.<sup>5</sup> According

(5) Cf. I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 142.

TABLE I  
 EVALUATION OF THE CELL RESISTANCE

Supporting electrolyte	$K$ , ohm cm.	$d$ , cm.	Surface of the anode $q_1$ , sq. cm.	$\pi_{d.e.}$ (vs. S. C. E.)	$m$ , mg. sec. <sup>-1</sup>	$t_{\pi}$ , sec.	Surface of the cathode $q_2$ , sq. cm.	Calcd. from the Ilkovič eq.		$R_{av}$ calcd. from slope
								$R_{min}$	$R_{av}$	
0.1 $N$ $(C_2H_5)_4NOH$	54.6	1.2	3.15	2.25	1.790	2.03	0.005	546	730	800
0.1 $N$ $LiOH$	56.0	0.9	3.15	2.41	1.866	1.53	0.004	445	593	620

to this equation the theoretical value of the slope is 0.059 at 25°.

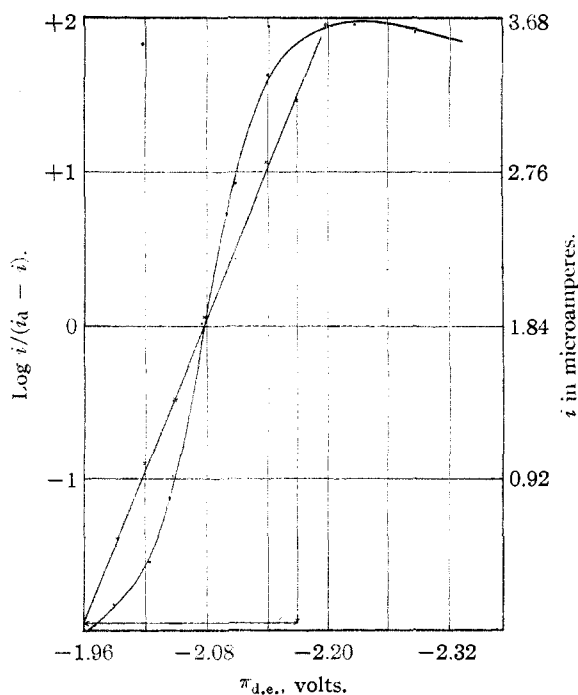


Fig. 1.—Test of the Heyrovsky-Ilkovic wave equation in the discharge of 0.0012  $N$  potassium chloride from 50% ethanol with 0.16  $N$  tetraethylammonium hydroxide as supporting electrolyte:  $S = 0.21/3.44 = 0.061$ .

Moreover, we found the wave equation fulfilled by showing that within the experimental error ( $\pm 10$  millivolts) the cathode potential at which  $\log (i/i_d - i)$  is zero, agreed with the half-wave potential of the reducible ion.

**Half-Wave Potentials of Potassium, Sodium and Lithium.**—Table II shows that the half-wave potentials of potassium in a given medium are practically constant within the concentration range investigated. Constant values at different concentrations were also obtained for sodium in all four media as well as for lithium in 50% and 80% ethanol. From the data presented it is also evident that the half-wave potentials do not vary with the drop time of the capillary. The half-wave potentials of potassium and sodium in water are in reasonably good agreement with those reported by Heyrovsky and Ilkovič.<sup>2</sup> These authors using tetramethylammonium hydroxide as a supporting electrolyte found for  $\pi_{1/2}(K^+) - 2.17$  v. and for  $\pi_{1/2}(Na^+) - 2.15$  v. It is to be noted that with this supporting electrolyte we found the same average half-wave potential values as with tetraethylammonium hydroxide.

It is seen that the half-wave potentials shift to more positive values with increasing alcohol concentration, which is to be expected. However,

 TABLE II  
 HALF-WAVE POTENTIALS (vs. S. C. E.) OF POTASSIUM WITH TETRAETHYLAMMONIUM HYDROXIDE AS SUPPORTING ELECTROLYTE

Medium	Concn. of KCl $N \times 10^3$	Half-wave pot. of potassium		Average values of $\pi_{1/2}$ (vs. S. C. E.)		
		Initial drop time $t_0 = 4.75$ sec.	Initial drop time $t_0 = 1.8$ sec.	$K^+$	$Na^+$	$Li^+$
80% Ethanol	0.77	-2.049	-2.055	-2.05	-2.035	-2.26
	1.41	-2.051	-2.042			
	1.96	-2.056	-2.050			
	2.43	-2.051	.....			
50% Ethanol	1.41	-2.092	-2.099	-2.095	-2.07	-2.31
	2.43	-2.097	.....			
	3.19	-2.097	-2.090			
	4.25	-2.100	.....			
25% Ethanol	0.77	-2.119	.....	-2.12	-2.10	....
	1.25	-2.117	-2.111			
	2.43	-2.112	-2.114			
Water	1.25	-2.140	-2.143	-2.14	-2.12	....
	2.43	-2.132	-2.140			
	3.39	-2.140	-2.130			

TABLE III  
CONSTANCY OF THE  $i_d/m^{2/3}t^{1/3}$  RATIO

Medium	Reduced ion	Initial drop time, $t$ sec.	$\pi_d$ , e.	$t_\pi$	$m$ , mg. sec. <sup>-1</sup>	$m^{2/3}t^{1/3}$	$i_d$ milliamp. per millimole per liter	$i_d/m^{2/3}t^{1/3}$
50% Ethanol	K <sup>+</sup>	4.85		2.03	1.801	1.67	2.80	1.67
		3.10	-2.25	1.36	2.719	2.05	3.54	1.72
		1.80		0.78	4.618	2.66	5.21	1.95
50% Ethanol	Na <sup>+</sup>	4.78		1.97	1.818	1.67	2.33	1.39
		3.10	-2.25	1.29	2.705	2.03	2.86	1.41
		1.88		0.75	4.660	2.63	4.30	1.63
50% Ethanol	Li <sup>+</sup>	4.65		1.63	1.835	1.63	1.90	1.18
		3.10	-2.37	1.14	2.709	1.98	2.24	1.14
		1.82		0.71	4.644	2.62	3.27	1.25
80% Ethanol	Li <sup>+</sup>	4.48		1.55	1.876	1.63	1.78	1.10
		3.12	-2.41	1.08	2.691	1.96	2.22	1.13

it should be mentioned that the exact values in the alcoholic media are somewhat uncertain due to the unknown liquid junction potentials in the measurements against the aqueous saturated calomel electrode.

**The Relation between the Diffusion Current and the Drop Time.**—According to the Ilkovič Eq. (1) the ratio  $i_d/m^{2/3}t^{1/3}$  should be constant in a given solution. By working with the same capillary but by varying the pressure on the mercury we have determined  $i_d$  of potassium, sodium and lithium at different values of  $m^{2/3}t^{1/3}$ . All values of  $i_d$  were corrected for the residual current of the supporting electrolyte.

From the data presented in Table III, it is seen that the ratio  $i_d/m^{2/3}t^{1/3}$  is constant within three per cent. when the initial drop time of the capillary is greater than three seconds. In the table,  $t_\pi$  denotes the drop time at the potential at which the diffusion current was measured. With faster dropping the value is no longer constant but increases with decreasing drop time.

It is surprising that the relation holds so well when the initial drop time is of the order of three seconds. It is seen from the table that this drop time was reduced to 1.36 seconds at the cathode potential at which the diffusion current was measured.

Another capillary was used, the initial drop time of which was varied between eight and fifteen seconds. In this range the  $i_d/m^{2/3}t^{1/3}$  ratio was found to be constant within 2%.

From the practical viewpoint it may be concluded that in the polarographic analysis of alkali metal ions, the relation between the diffusion current  $i_d$  and the  $m^{2/3}t^{1/3}$  product satisfies the

Ilkovič equation if the initial drop time is greater than three seconds.

As the pressure on the dropping mercury affects the  $m^{2/3}t^{1/3}$  value according to the hydrodynamic equation of Poiseuille,<sup>6</sup> the above result implies that the ratio of the diffusion current to the square root of the pressure on the mercury should be constant at a given cathode potential. Experimentally we found that to be true within 3%.

**Relation between the Diffusion Current and the Diffusion Coefficients of the Alkali Metal Ions.**—According to the Ilkovič equation the diffusion current is proportional to the square root of the diffusion coefficient of the reduced substance. Since the diffusion coefficients ( $D_i$ ) of the alkali metal ions in the alcohol-water mixtures are not given in the literature, the corresponding values have been calculated by means of the Nernst formula,<sup>5</sup>  $D_i = RT\lambda_i^0/nF^2$ , where  $\lambda_i^0$  is the equivalent conductance of the ion at infinite dilution,  $n$  is its valence, and  $R$ ,  $T$  and  $F$  have their usual significance.

Fergusson and Vogel<sup>7</sup> give the following values for the mobilities (in sq. cm./ohm equiv.) of the alkali metal ions in water at 25°:  $\lambda_{K^+}^0 = 75.63$ ,  $\lambda_{Na^+}^0 = 51.42$ ,  $\lambda_{Li^+}^0 = 39.6$ .

In mixtures of water and ethanol no mobilities of sodium, potassium and lithium are reported in the literature. Accepting the values of the equivalent conductance of potassium iodide reported by Jones and co-workers, in water<sup>8</sup> (142.6) and in 50% ethanol<sup>9</sup> (52.8), and assuming

(6) Cf. I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

(7) A. Fergusson and I. Vogel, *Phil. Mag.*, **4**, 240 (1927).

(8) H. C. Jones and C. G. Carroll, *Am. Chem. J.*, **32**, 521 (1904).

(9) H. C. Jones and C. F. Lindsay, *ibid.*, **26**, 329 (1902).

TABLE IV

EQUIVALENT CONDUCTANCES AT INFINITE DILUTION AND DIFFUSION COEFFICIENTS OF ALKALI METAL IONS AT 25°

Medium	K <sup>+</sup>		Na <sup>+</sup>		Li <sup>+</sup>	
	$\lambda^0$ $\frac{\text{sq. cm.}}{\text{ohm. equiv.}}$	$D \times 10^6$ $\frac{\text{sq. cm.}}{\text{sec.}}$	$\lambda^0$ $\frac{\text{sq. cm.}}{\text{ohm. equiv.}}$	$D \times 10^6$ $\frac{\text{sq. cm.}}{\text{sec.}}$	$\lambda^0$ $\frac{\text{sq. cm.}}{\text{ohm. equiv.}}$	$D \times 10^6$ $\frac{\text{sq. cm.}}{\text{sec.}}$
Water	75.63	20.2	51.42	13.7	38.7	10.4
50% Ethanol	28.00	7.48	19.0	5.07	14.3	3.82
80% Ethanol	22.10	5.90	15.9	4.22	12.6	3.36

TABLE V

EXPERIMENTAL TEST OF ILKOVIČ EQUATION IN THE ELECTROLYSIS OF ALKALI METAL IONS

Medium	Salt	Initial drop time, $t_0$ sec.	$\pi_{d,e}$	$t_{\pi}$ sec.	$m^{2/3}t^{1/6}$ $\text{mg.}^{2/3}\text{sec.}^{-1/2}$	$i_d$ microamps. per millimole per liter		$\Delta\% = \frac{a-b}{a} 100$
						Calcd. (a)	Measured (b)	
Water	NaCl	3.70	-2.25	1.52	1.62	3.64	3.69	- 1.4
	KCl	4.75	-2.25	2.03	1.67	2.76	2.79	- 1.1
	KCl	3.10	-2.25	1.36	2.05	3.38	3.44	- 1.8
	KCl	1.80	-2.25	0.78	2.66	4.39	5.21	-18.7
50% Ethanol	NaCl	4.78	-2.25	1.97	1.67	2.27	2.38	- 4.8
	NaCl	3.10	-2.25	1.29	2.03	2.76	2.92	- 5.8
	NaCl	1.88	-2.25	0.75	2.63	3.58	4.30	-20.1
	LiCl	4.65	-2.37	1.63	1.63	1.92	1.86	+ 3.1
	LiCl	3.10	-2.37	1.14	1.98	2.34	2.29	+ 2.1
80% Ethanol	LiCl	4.48	-2.42	1.55	1.63	1.81	1.78	+ 1.6
	LiCl	3.12	-2.42	1.08	1.96	2.17	2.22	- 2.3

that the transference numbers of the ions are the same in both media, we find that  $\lambda_{K^+}^0$  (50% ethanol) =  $(52.8/142.6) \times 75.63 = 28.0$ .

In a similar way, by interpolation of the data of Jones and Lindsay, we find for the mobility of potassium ( $\lambda_{K^+}^0$ ) in 80% ethanol a value of 22.5. This is in fairly good agreement with the value calculated from the conductance data of potassium iodide in water and in 50% ethanol given by Cohen.<sup>10</sup> From his results  $\lambda_{K^+}^0$  in 80% ethanol is calculated to be 21.7. We have adopted an average value of  $\lambda_{K^+}^0$  (80% ethanol) = 22.1.

Using Cohen's ratio data for sodium chloride in water and in various alcohol-water mixtures, we calculated the following values for the equivalent ionic conductances of sodium:  $\lambda_{Na^+}^0$  (50% ethanol) = 19.0 and  $\lambda_{Na^+}^0$  (80% ethanol) = 15.9.

No conductance data of lithium salts in 50% ethanol are available. Since the ratio of the ionic mobilities in water to those in 50% ethanol was found to be the same within a few per cent. for both potassium and sodium, we assumed that the same ratio would hold for lithium. With the mean ratio value of 0.36 we find  $\lambda_{Li^+}^0$  (50% ethanol) =  $39.6 \times 0.36 = 14.3$ .

Finally from conductance data of lithium chloride in 80% ethanol<sup>11</sup> and in water<sup>12</sup> we find  $\lambda_{Li^+}^0$  (80% ethanol) =  $39.6 \times (36.6/115.25) = 12.6$ .

(10) E. Cohen, *Z. physik. Chem.*, **25**, 1 (1898).(11) H. Goldschmidt, *ibid.*, **89**, 129 (1925).(12) R. T. Lattey, *Phil. Mag.*, **6**, 258 (1928).

The calculated values of the alkali ion mobilities and the corresponding diffusion coefficients are summarized in Table IV.

We are now in a position to test the validity of the entire Ilkovič equation. Some results are presented in Table V. From the differences between the calculated and experimentally determined diffusion currents, reported in the last column, it may be concluded that the Ilkovič equation holds in the electrolysis of alkali metal ions at the dropping mercury cathode, provided the initial drop time of the capillary is equal to or greater than three seconds.

With decreasing drop time the calculated diffusion currents become increasingly less as compared to the experimental values.

Peracchio and Meloche<sup>13</sup> found that the wave height of the alkali metals decreases in the presence of various alcohols. The ratios of the diffusion currents of equimolecular solutions of potassium and sodium in water, 50%, and 80% ethanol as well as those of potassium and lithium in the last two media should be equal to the ratios of the square roots of the diffusion coefficients of those ions in the corresponding solvents, provided that the  $i_d$  values are compared at the same value of the  $m^{2/3}t^{1/6}$  product. A comparison of the experimentally determined and the calculated ratios is given in Table VI, in which are also pre-

(13) E. A. Peracchio and V. W. Meloche, *THIS JOURNAL*, **60**, 1770 (1938).

TABLE VI

COMPARISON OF RATIOS OF DIFFUSION CURRENTS AND OF THE SQUARE ROOTS OF DIFFUSION COEFFICIENTS OF ALKALI METAL IONS IN VARIOUS MEDIA

Medium	$\pi_{d.e.}$ , volts	$m^2/s^2$ , mg. <sup>2</sup> /3 sec. <sup>-1/2</sup>	$i_d(\text{K}^+)/i_d(\text{Na}^+)$		$(D_{\text{K}^+}/D_{\text{Na}^+})^{1/2}$	$i_d(\text{K}^+)/i_d(\text{Li}^+)$		$(D_{\text{K}^+}/D_{\text{Li}^+})^{1/2}$
			Z. and K. <sup>a</sup>	P. and M. <sup>b</sup>		Z. and K. <sup>a</sup>	P. and M. <sup>b</sup>	
Water	-2.25	1.62	1.24		1.22	..	..	..
	-2.40	1.57	1.20	1.19		..	..	..
50% Ethanol	-2.25	1.67	1.18		1.20			
	-2.25	2.05	1.21					
	-2.26	2.66	1.20	1.00			1.48	
	-2.37	1.63	1.18				1.52	1.40
	-2.37	1.98	1.21					
80% Ethanol	-2.41	1.63	1.16			1.35		
	-2.41	1.96	1.18	1.09	1.14	1.36	1.43	1.33
	-2.55	1.45	1.19			1.33		

<sup>a</sup> Zlotowski and Kolthoff. <sup>b</sup> Peracchio and Meloche.

sented the ratios calculated from the experimental data of Peracchio and Meloche.<sup>14</sup>

In general the experimental diffusion current ratios are in good agreement with the ratios of the square roots of the diffusion coefficients. The largest deviation of about 7% is found for the  $i_d(\text{K}^+)/i_d(\text{Li}^+)$  ratio in 50% ethanol. The polarographic method seems suitable for rapid determination of diffusion coefficients of the alkali ions as well as of their mobilities at infinite dilution in water-ethanol mixtures.

**Acknowledgment.**—This work was started with the aid of a grant from the Carnegie Cor-

(14) It is to be noted that the diffusion wave heights given by these authors<sup>13</sup> under the heading "Sodium Chloride" apparently are for potassium chloride and those under "Potassium Chloride" for the sodium salt. The data given in their Table I probably represent but approximate values. As a matter of fact Peracchio and Meloche found the wave heights of potassium and sodium unchanged when the ethanol concentration was changed from 50 to 70%, while in 80% ethanol (compare Figs. 3 and 7 in their paper) the diffusion currents were from 10 to 15% smaller.

poration of New York City and was concluded with the aid of a grant received by one of us (I. Z.) from the Rockefeller Foundation.

### Summary

1. A satisfactory agreement is found between the experimentally determined diffusion currents of the alkali metals and the values calculated by means of the Ilkovič equation, provided that the initial drop time of the capillary be equal to or greater than three seconds.

2. The equation of the alkali metal waves corresponds to the reversible reduction of a univalent ion.

3. Half-wave potentials of potassium, sodium, and lithium in water and in water-ethanol mixtures were determined and found to be constant within the concentration range investigated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

## The System $\text{Ca}(\text{NO}_3)_2\text{-Sr}(\text{NO}_3)_2\text{-H}_2\text{O}$ at 25 and 60°

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The chief use of strontium nitrate is in pyrotechnics, where the specifications of the technical salt call for substantial freedom from calcium nitrate, as this compound is extremely hygroscopic. Fractional crystallization has been considered as a means of producing strontium nitrate from the impure celestite-strontianite deposits in the State of Washington and elsewhere. Information as to the ternary system,  $\text{Ca}(\text{NO}_3)_2\text{-Sr}(\text{NO}_3)_2\text{-H}_2\text{O}$

necessary for an effective execution of this process, is not available in the literature, although both binary systems,  $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$  and  $\text{Sr}(\text{NO}_3)_2\text{-H}_2\text{O}$ , have been mapped out completely.

### Experimental

**Materials.**—The calcium nitrate used in this work was Merck Reagent Grade chemical; the strontium nitrate Baker c. p. Grade. The analyses on the labels showed them to be essentially free from impurities. Qualitative tests substantially confirmed these claims.

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