AN OBJECTIVE STUDY OF DILUTE AQUEOUS SOLUTIONS OF UNI-UNIVALENT ELECTROLYTES[1]

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Graphical methods of smoothing data are influenced by the personal judgment and the personal prejudices of the operator, who may emphasize either the agreement with some theory or the deviations from it. The difficulties are increased in extrapolation to zero concentration, because the measurements generally become less accurate as the concentration decreases, and because most of us draw curves which approach a linear asymptote too rapidly. An objective method, which reduces all matters of judgment to forms which can be definitely stated and systematized, is that of least squares. The results may or may not be better than those from more subjective methods, but they are always more definite.

A good body of data for the application of such a method consists of the measurements made in our laboratory of the freezing point depressions for twenty-five uni-univalent salts. All measurements below 0.1 M are treated; included in the tables are the three other series for uni-univalent electrolytes with a sufficient number of accurate measurements in this range. The measurements are so weighted that a deviation below 0.01 M of two-hundred thousandths of a degree (0.00002°C.) is equivalent to a deviation above 0.01 M of five hundredths of 1 per cent (0.05 per cent); that is, the function j of Lewis and Randall is given unit weight for depressions greater than 0.04°C., and weighted proportionally to the square of the ratio of the depression to 0.04°C.

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for smaller depressions. Our own measurements for all the salts except the slightly soluble potassium perchlorate have approximately the same distribution. For them a systematic error of one-tenth of 1 per cent in the concentration or in the temperature would give a deviation in the A coefficient of about 2.5 per cent for equation 2 and of about 4.5 per cent for equation 3. Such an error might arise for any one salt from an error in the analysis or from impurities. An error in the temperature scale would cause the same deviation for all the salts. In a recent calibration of our thermocouples the standard deviation for forty-three measurements was 0.08 per cent, and considerable confidence is placed in the result. Coefficients have been calculated for the equations:

$$j = Am^{1/2} \tag{1}$$
$$j = Am^{1/2} + Bm \tag{2}$$
$$j = Am^{1/2} + Bm + Cm^{3/2} \tag{3}$$
$$j = Am^{1/2} + Bm + Cm^{3/2} + Dm^2 \tag{4}$$
$$j = 0.3738\,m^{1/2} + Bm \tag{5}$$
$$j = 0.3738\,m^{1/2} + Bm + Cm^{3/2} \tag{6}$$
$$j = 0.3738\,m^{1/2} + Bm + Cm^{3/2} + Dm^2 \tag{7}$$

Equation 1 need not be considered because the agreement with the data is poor, and equation 4 is eliminated because the agreement is only slightly better than for equation 3 while the coefficients become very large.

Table 1 shows the percentage deviation of the A coefficients from the theoretical value 0.3738 for equations 2 and 3. The difference between these deviations for the two equations is a measure of the reliability of either value. The average deviations for twenty-one alkali salts are -9 per cent for equation 2 and -3 per cent for equation 3, and half the individual deviations are less than 10 per cent. The measurements on the acids and on thallium chloride agree, probably within their accuracy. These results indicate that the limiting slope is probably not more than 10 per cent different than that calculated from the Debye theory.

To determine whether the measurements demand a slope slightly smaller than that given by the theory, the standard deviations (root-mean-square deviations) in per cent from equations

TABLE 1

Least square treatment of freezing point measurements

SALT	REFER-ENCE	DEVIATION OF A IN PER CENT		STANDARD DEVIATIONS IN PER CENT				
		Equa-tion 2	Equa-tion 3	Equa-tion 2	Equa-tion 3	Equa-tion 5	Equa-tion 6	Equa-tion 7
LiCl..................	(14)	−1	+18	0.14	0.09	0.14	0.13	0.11
LiBr:.................	(14)	−13	−4	0.08	0.06	0.23	0.07	0.07
LiNO₃...............	(11)	−10	−1	0.11	0.09	0.18	0.09	0.09
LiClO₃...............	(14)	−8	+7	0.11	0.09	0.15	0.10	0.10
LiClO₄...............	(14)	−15	−10	0.09	0.09	0.23	0.09	0.09
LiO₂CH.............	(14)	−7	−3	0.21	0.21	0.25	0.21	0.21
LiO₂C₂H₃.............	(14)	−8	−3	0.14	0.14	0.20	0.14	0.14
NaCl.................	(14)	−11	−9	0.13	0.13	0.22	0.14	0.14
NaBr.................	(14)	−24	−17	0.09	0.08	0.40	0.12	0.07
NaNO₃...............	(11)	−12	−6	0.07	0.06	0.20	0.07	0.06
NaClO₃..............	(14)	−8	−5	0.08	0.08	0.14	0.08	0.08
NaClO₄..............	(14)	−6	−7	0.08	0.08	0.13	0.09	0.08
NaO₂CH.............	(14)	−12	−12	0.13	0.13	0.25	0.15	0.14
NaO₂C₂H₃.............	(14)	−7	+10	0.13	0.11	0.20	0.11	0.11
KCl..................	(14)	−7	+5	0.21	0.19	0.24	0.20	0.19
KBr..................	(14)	−11	−10	0.07	0.07	0.19	0.09	0.07
KNO₃................	(11)	−4	−21	0.10	0.08	0.11	0.10	0.06
KClO₃...............	(14)	−16	−36	0.11	0.11	0.30	0.16	0.11
KClO₄*...............	(14)	+7	+44	0.26	0.24	0.27	0.27	0.24
KO₂CH..............	(14)	−15	−10	0.18	0.18	0.33	0.19	0.18
KO₂C₂H₃.	(14)	−6	+21	0.28	0.23	0.29	0.26	0.23
Average..............		−9	−3	0.13	0.12	0.22	0.14	0.12
NH₄Cl.	(12)	+16	+45	0.21	0.08	0.34	0.29	0.17
NH₄Br.	(12)	+21	+54	0.24	0.08	0.43	0.35	0.20
NH₄I.................	(12)	+6	+22	0.16	0.13	0.19	0.18	0.15
NH₄NO₃..............	(12)	+14	+35	0.17	0.11	0.27	0.23	0.16
HCl..................	(7)	−3	−3	0.09	0.09	0.09	0.09	0.08
HNO₃................	(1)	−18	−50	0.33	0.31	0.38	0.34	0.32
TlClt†.................	(7)	−18	−1	0.15	0.14	0.22	0.15	—

* Maximum concentration = 0.05 M.
† Maximum concentration = 0.006 M.

2, 3, 5, 6, and 7 are given in the next columns of table 1.   Except for equation 5 the standard deviations are essentially the same;

that is, if more than one constant is determined from the data, it makes little difference whether there are two or three such constants and whether one of them is proportional to the square root of the concentration or the square-root term is determined from the theory and all adjustable constants attributed to higher terms. The measurements give no indication that the limiting law is different from the theoretical limiting slope.

The results for the ammonium salts, however, differ markedly from the others. The slope obtained is much larger than the theoretical, but the difference between the deviations for the two equations may be taken as evidence that the form of the equations is not adapted to these data, and that the measurements on ammonium salts furnish no evidence either for or against the theory.

The difficulty of obtaining the initial deviation from the limiting law may be seen from the first three columns of table 2, which are the values of $-B$ from equation 5 determined from our smoothed curve at 1.0 M, 0.1 M, and 0.01 M, respectively. The last place given corresponds to 0.01, 0.001, and 0.0001 in j. Throughout this range the variation left to personal judgment is less than 0.001, so that the 1.0 M results are precise as given, the 0.1 M ones uncertain to about one unit in the second place, and the 0.01 M results uncertain to one unit in the first place. At 1.0 M, however, the spread in the individual results is small and the concentration much too great for a simple interpretation. The fact that the value of B changes so much with the concentration shows that the problem of obtaining the initial value is a difficult one, and indicates the reason for the large deviations from equation 5 in the least square treatment.

The last two columns of table 2 show the values of $-B$ from equations 6 and 7 by the least square method. The difference between these two also gives an indication of the reliability of either. If they disagree, it requires a very careful analysis to tell which is to be preferred. We cannot say that either is better than the value from the smoothed curve at 0.01 M, except that the values from least squares are entirely objective.

In the majority of cases the three do not differ greatly except

for lithium chloride and the ammonium salts, for which the measurements indicate much curvature in very dilute solutions.

TABLE 2

$-B$ *coefficients*

SALT	EQUATION 5 AT CONCENTRATION			LEAST SQUARES	
	$1.0\,M$	$0.1\,M$	$0.01\,M$	Equation 6	Equation 7
LiCl	0.40	0.61	0.46	0.70	0.35
LiBr	0.43	0.70	0.97	1.01	1.09
LiNO$_3$	0.38	0.63	0.81	0.90	0.97
LiClO$_3$	0.40	0.66	0.90	0.92	0.78
LiClO$_4$	0.45	0.73	1.09	1.17	1.40
LiO$_2$CH	0.30	0.52	0.70	0.68	0.72
LiO$_2$C$_2$H$_3$	0.36	0.58	0.73	0.77	0.82
NaCl	0.28	0.52	0.77	0.76	0.87
NaBr	0.31	0.60	1.15	1.17	1.62
NaNO$_3$	0.18	0.38	0.63	0.68	0.87
NaClO$_3$	0.21	0.42	0.59	0.62	0.74
NaClO$_4$	0.23	0.46	0.57	0.62	0.86
NaO$_2$CH	0.30	0.55	0.79	0.81	1.05
NaO$_2$C$_2$H$_3$	0.38	0.66	0.86	0.85	0.62
KCl	0.25	0.45	0.59	0.64	0.60
KBr	0.25	0.47	0.65	0.72	0.94
KNO$_3$	0.06	0.15	0.26	0.24	1.05
KClO$_3$	—	0.22	0.66	0.73	1.49
KClO$_4$	—	—	−0.05	−0.21	−1.20
KO$_2$CH	0.31	0.56	0.88	0.87	1.04
KO$_2$C$_2$H$_3$	0.40	0.67	0.85	0.88	0.33
NH$_4$Cl	0.26	0.40	−0.37	0.18	−0.78
NH$_4$Br	0.26	0.40	−0.57	0.11	−0.96
NH$_4$I	0.27	0.46	0.07	0.40	−0.10
NH$_4$NO$_3$	0.16	0.27	−0.24	0.08	−0.70
HCl	—	—	0.76	0.76	0.68
HNO$_3$	0.34	0.58	0.62	1.01	2.38

Any one shows that the effect is far too complicated to be explained by a single parameter such as the mean collision diameter. The three methods together give twenty-one comparisons of the

order of arrangement of the alkali salts of the seven anions studied. In order of increasing magnitude they are: K–Na–Li, 7; K–Li–Na, 4; Li–Na–K, 4; Li–K–Na, 3; Na–K–Li, 2; Na–Li–K, 1. The seven averages of the three methods for each anion give five of the six possibilities. The choice of material studied is too arbitrary to draw many conclusions other than the proof that the problem of the specific characteristics of the ions is a very complex one.

TABLE 3

Electromotive force of hydrochloric acid cells in millivolts

OBSERVER	HIGHEST CONCENTRATION	$E_0 - 222.00$				A		B		STANDARD DEVIATION			
		Equation 8	Equation 9	Equation 10	Equation 11	Equation 8	Equation 9	Equation 10	Equation 11	Equation 8	Equation 9	Equation 10	Equation 11
	M												
Carmody (2).....	0.01	0.43	0.28	*0.21*	0.22	−17	−5	*86*	89	0.08	0.07	0.08	0.08
Linhart (5)......	0.01	0.71	0.56	*0.52*	0.53	−19	−3	*105*	120	0.11	0.09	0.09	0.09
Nonhebel (6)....	0.01	0.82	0.98	*0.52*	0.65	−26	−41	*151*	403	0.14	0.12	0.16	0.14
Roberts (8)......	0.01	0.89	0.32	*0.45*	0.41	−22	7	*93*	66	0.08	0.07	0.07	0.07
Roberts (8)......	0.1		0.55		*0.37*		−7		88		0.09		0.09
Harned (3)......	0.1		0.67		*0.44*		−8		89				

The opportunity to compare the measurements of several observers with the same material is offered on the electromotive force of the cell
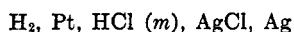
$$H_2, Pt, HCl\ (m), AgCl, Ag$$

Table 3 contains the data for the treatment of these results with the equations

$$E_0' = E_0 - Am^{1/2} \tag{8}$$
$$E_0' = E_0 - Am^{1/2} + Bm \tag{9}$$
$$E_0' = E_0 - 59.62\ m^{1/2} + Bm \tag{10}$$
$$E_0' = E_0 - 59.62\ m^{1/2} + Bm + Cm^{3/2} \tag{11}$$

The values are expressed in millivolts. The concentration range is from the greatest dilution to 0.01 *M* or to 0.1 *M*, both ranges being used when the distribution of measurements warrants it, and the measurements are each given unit weight.

These measurements give the same indication as the freezing points regarding the limiting law. Equation 8 leads to a slope about 20 per cent less than the theory up to 0.01, and about 40 per cent too small up to 0.1 M, but equation 9 gives a slope within a few per cent of the theoretical; equation 10 with the theoretical slope agrees practically as well as equation 9 with adjustable slope. It should be noted that these results are all carried to one place further than the experimental data of Linhart and of Carmody.

If the theoretical slope is assumed, equation 10 gives the best values of the constants in the range to 0.01 M, and equation 11 to 0.1 M. The respective values of E_0 and of B are italicized. The values of B for Carmody's, Roberts' (two ranges), and Harned and Ehlers' measurements agree very closely. Linhart's measurements lead to a slightly higher value, and Nonhebel's are seriously different. In the E_0 values Roberts and Harned and Ehlers agree closely, Carmody yields a value 0.2 millivolt lower, and Linhart and Nonhebel 0.1 millivolt higher. Probably Nonhebel's results should be given little weight on account of the large deviations; and all of Linhart's measurements except those with the second and third most dilute solutions fit very closely the curve for Roberts' measurements. There remains the discrepancy of 0.2 millivolt between the measurements of Carmody and those of other observers, which appears to be almost independent of the concentration. It is possible that it should be attributed to differences in the silver–silver chloride electrodes, but further experiments would be required to show this. Again it is not claimed that the least square results have any advantage other than that of complete objectivity over intelligent extrapolation by other methods. The E_0 obtained from Linhart's measurements lies between the values obtained by Scatchard (222.6) (9) and by Hitchcock (222.4) (4) from graphic extrapolation of the earlier measurements; that from Carmody's measurements agrees well with the value obtained by Spencer (222.2) (13); and the results from the Yale laboratory's measurements agree very well with the values (222.40 and 222.39) obtained by the observers (8, 3), and lies midway between the two results (222.35 and 222.45) obtained by Scatchard (10) from Linhart's measurements

at 0.01 M and his own results for higher concentrations.   In all these cases the agreement depends largely upon the acceptance of the theoretical limiting law.

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