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Changes of Volume on Mixing Electrolytic Solutions with Water*

(Received December 2, 1958)

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Abstract

A method of calculation has been devised by the present writer, by which we may evaluate from the density table changes of volume on diluting electrolytic solutions. Values of the volume change which occurs on mixing each of 1-1 electrolytic solutions of various concentrations with an equi-volume of water at 20°C have been calculated. We have, on the other hand, derived from Masson's linear relationship an expression which predicts the proportionality of a volume change fraction on diluting the solutions at an equi-voluminal ratio to 3/2 power of the initial concentration in moles per liter, and have checked the calculated data. It has been found that the relationship derived by the present writer holds over a remarkably wide range of concentration with all the seven electrolytes studied. Furthermore the deviations from this relationship have been explained.

I. Introduction

It was noticed in an early period that there is a volume change, which is generally a contraction, on diluting electrolytic solutions, but there are only a few data[1] and no investigation has as yet been made to quantitatively correlate the change of volume with concentration. With seven 1-1 electrolytes, we have, in the present paper, evaluated a great number of changes of volume on mixing their solutions of various concentrations with an equi-volume of water at 20°C, and have noticed that these data obey a simple law derived from the following relationship which was discovered by Masson:[2] the apparent molal volumes of most electrolytes appear to be a linear function of the square root of the volume concentration.

In calculating the volume change, we have evaluated the densities of diluted solutions from the density table. The weight per cent concentrations of diluted solutions

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(1) J. D'Ans and E. Lax, "Taschenbuch für Chemiker und Physiker," 2nd Ed., Springer-Verlag, Berlin, p. 821 (1949)
J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. 2, 1st Ed., Longmans, Green and Co., London. p. 33 (1951)

(2) D. O. Masson, Phil. Mag., 8, 218 (1929)

can be evaluated from the initial concentrations, so the densities of these solutions may be obtained by interpolation from the density table. Densities have been fully known at intervals of one or two per cent concentration, so they are not seriously influenced by interpolation as dealt with later.

II. Calculations

Dilutions by Unequal Volume.— If Vml. of a C moles/liter electrolytic solution, of which the deasity is denoted by d, is mixed with V'ml. of water at constant temperature, the volume change observed can be calculated as follows.

The weight per cent concentration of the mixture is represented by the equation

$$a=\frac{MCV}{10\,(dV+d_wV')} \tag{1}$$

where d_w is the deasity of water, and M is the molecular weight of the solute. If the density of this solution is denoted by d^*, the apparent molal volume of the solute in a C moles/liter solution by Φ_c and that of the solute in the diluted solution by Φ^*, the apparent molal volumes are defined by the equations, respectively.

$$\Phi_c=\left(1000-\frac{1000d-CM}{d_w}\right)\frac{1}{C} \tag{2}$$

$$\Phi^*=\frac{M}{a}\left(\frac{100}{d^*}-\frac{100-a}{d_w}\right) \tag{3}$$

Assuming that the volume change on dilution is only due to the change in the apparent molal volume of the solute, the volume change in ml. is given by

$$\Delta V=(\Phi^*-\Phi_c)\frac{CV}{1000} \tag{4}$$

where ΔV is negative when the volume decreases.

Therefore, the change of volume can be calculated even if any solution should be mixed with water in any ratio. On the other hand ΔV may be directly represented by means of the equation.

$$\Delta V=\left(\frac{dV+d_wV'}{d^*}\right)-(V+V') \tag{5}$$

We may choose between Eq. (4) and Eq. (5) to evaluate ΔV, because substitution of Eqs. (1), (2) and (3) into Eq. (4) gives Eq. (5).

Dilutions by Equal Volume.— If a C moles/liter solution which occupies a volume V ml. is mixed with an equi-volume of water, the weight per cent concentration of the mixture is shown as the following equation from Eq. (1).

$$a_i=\frac{MC}{10\,(d+d_w)} \tag{6}$$

If the density of this solution is designated by d_i^* and the apparent molal volume of the solute in this solution by Φ_i^*, the volume change in ml. on mixing a C moles/liter solution which occupies a volume V ml. with an equi-volume of water is given by (using Eq. 4)

$$\Delta V_i=(\Phi_i^*-\Phi_c)\frac{CV}{1000} \tag{7}$$

or by an alternative formula (using Eq. 5)

$$\Delta V_i=\left(\frac{d+d_w}{d_i^*}-2\right)V \tag{8}$$

Then substituting Ψ for $(\Delta V_i/2V)\times 10^3$ in Eqs. (7) and (8) gives the equations.

$$\Psi=(\Phi_i^*-\Phi_c)\frac{C}{2} \tag{9}$$

$$\Psi=\left(\frac{d+d_w}{2d_i^*}-1\right)\times 10^3 \tag{10}$$

Now we will for convenience' sake call Ψ, which represents the rate of change of the volume on mixing the solution which an equi-volume of water, "*Volume Change Fraction*". The numerical value of Ψ represents the difference between the sum of the volume of the solution before mixing plus that of water, which are equally 500 ml., and the total volume in ml. of the resulting solution. When the volume decreases, Ψ is negative.

III. Results and Discussion

The volume change on mixing a solution with water which occupy an equal volume 500 ml., i. e. the volume change fraction defined above, may be calculated by the method mentioned in the above section.

The final concentration is given by Eq. (6), so the density of this solution is obtained by interpolation from the density data of the "International Critical Tables."[3]

Therefore, values of Ψ are calculated by Eq. (10). In Table I are shown volume change fractions of seven 1-1 electrolytes at 20°C; as well as apparent molal volumes[4] from which the slope S_v in eq. (13) and hence the coefficient K in Eq. (19) can be obtained.

The Degree of Uncertainty in Ψ.— Whether the values of Ψ in Table I are nearly the same as those obtained by a strict experiment or not depends upon the extent to which an error is made in evaluating the density by interpolation. Therefore we will attempt to estimate the error in density caused by interpolation.

If the density of a x% solution is denoted by d_x and that of a y% solution by d_y,

(3) "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., P. 79 (1928)

(4) The Degree of Uncertainty in Φ_c · - Differentiating of Eq. (2) at constant C shows that

$$\delta\Phi_c=-\frac{1000}{C}\frac{\delta d}{d_w}$$

so that an error of 0.001 per cent in density would cause an uncertainty of 0.01ml. in Φ_c when $C=1$. Consequently Φ_c is very sensitive to uncertainties in the density at high dilution.

the density of a $(x+y)/2\%$ solution obtained by interpolation is given by $d_c=(d_x+d_y)/2$. Then if the observed density of a $(x+y)/2\%$ solution is denoted by d_o, the error in density which would be caused by interpolation with this solution may be defined by $100(d_c-d_o)/d_o$ per cent. In the cases of the electrolytic solutions here studied, errors in density caused by applying the interpolation at intervals of four per cent concentration, i. e. $x\sim y=4$, have been calculated from the "International Critical Tables" density data and summarized in Table II.

Table I. Volume Change Fractiom at 20°C.

(I-1) Nacl. aq.

Initial concs.	The Apparent Molal Volume of the Solute in this Soln.	Final Concs.	Density ofthe Diluted Soln.	Vol. Change Fraction, Ψ.
C (moles/liter)	Φ_c (ml.)	a_i %	d_i*	$-\Psi$
0.1720	17.13	0.502		
0.3464	17.42	1.007	1.00539	0.04
0.7026	17.83	2.028	1.01266	0.14
1.0688	18.24	3.063	1.02008	0.32
1.4451	18.59	4.112	1.02761	0.54
1.8317	18.94	5.175	1.03530	0.82
2.2288	19.29	6.252	1.04311	1.11
2.6397	19.58	7.342	1.05108	1.47
3.0553	19.87	8.446	1.05919	1.86
3.4855	20.17	9.565	1.06756	2.23
3.9272	20.40	10.697	1.07590	2.69
4.3808	20.63	11.843	1.08448	3.13
4.8465	20.93	13.003	1.09328	3.62
5.3251	21.16	14.178	1.10222	4.10

(I-2) NaBr. aq.

C	Φ_c	a_i %	d_i*	$-\Psi$
0.0978	23.57	0.502		
0.1971	23.67	1.008	1.00605	0.02
0.4003	23.98	2.031	1.01410	0.06
0.6100	24.29	3.070	1.02240	0.17
0.8264	24.49	4.126	1.03087	0.23
1.0497	24.74	5.197	1.03965	0.36
1.2804	24.96	6.286	1.04864	0.46
1.5187	25.16	7.391	1.05793	0.59
1.7649	25.32	8.514	1.06749	0.73
2.0194	25.52	9.654	1.07734	0.88
2.2825	25.73	10.811	1.08754	1.09
2.5547	25.93	11.987	1.09798	1.22
2.8365	26.09	13.182	1.10890	1.49
3.1281	26.24	14.395	1.12009	1.69
3.4303	26.45	15.627	1.13168	1.92
3.7433	26.55	16.879	1.14370	2.20
4.5783	29.96	20.098	1.17550	2.82
5.4951	27.37	23.446	1.21039	3.59

(I-3) NaI. aq.

C	Φ_c	a_i %	d_i*	$-\Psi$
0.0671	34.78	0.502		
0.1352	34.86	1.008	1.00602	0.01
0.2747	35.05	2.031	1.01405	0.03
0.4187	35.21	3.071	1.02237	0.11
0.5674	35.37	4.126	1.03085	0.10
0.7209	35.51	5.198	1.03968	0.19
0.8795	35.66	6.288	1.04873	0.21
1.0434	35.79	7.394	1.05812	0.30
1.2130	35.93	8.518	1.06779	0.36
1.3884	36.06	9.661	1.07779	0.44
1.5700	36.18	10.821	1.08815	0.53
1.7582	36.29	12.001	1.09879	0.56
1.9532	36.40	13.200	1.10994	0.71
2.1553	36.52	14.419	1.12140	0.80
2.3650	36.63	15.657	1.13329	0.90
2.5827	36.76	16.916	1.14566	1.06
3.1647	37.06	20.157	1.17857	1.40
3.8076	37.35	23.537	1.21499	1.91
4.5210	37.63	27.064	1.25530	2.46
5.3168	37.90	30.747	1.30037	3.20
6.2098	38.16	34.597	1.35039	3.65
2.6868	38.40	38.625	1.40745	4.59

(I-4) KCl. aq.

C	Φ_c	a_i%	d_i*	$-\Psi$
0.1347	27.06	0.501		
0.2712	27.44	1.006	1.00467	0.04
0.5494	27.88	2.025	1.01119	0.12
0.8345	28.26	3.057	1.01784	0.27
1.1267	28.63	4.101	1.02457	0.43
1.4262	29.00	5.157	1.03142	0.63
1.7332	29.30	6.227	1.03839	0.85
2.0478	29.60	7.309	1.04549	1.09
2.3716	29.82	8.403	1.05271	1.35
2.7004	30.12	9.511	1.06007	1.64
3.0389	30.35	10.631	1.06757	1.92
3.3859	30.57	11.765	1.07521	2.22
3.7417	30.79	12.911	1.08302	2.56

(I-5) KBr. aq.

C	Φ_c	a_i %	d_i*	$-\Psi$
0.0845	33.92	0.502		
0.1702	34.16	1.007	1.00547	0.01
0.3453	34.40	2.029	1.01289	0.04
0.5256	34.63	3.065	1.02056	0.14
0.7112	34.88	4.117	1.02836	0.19
0.9023	35.12	5.183	1.03643	0.31
1.0993	35.35	6.265	1.04466	0.38
1.3021	35.54	7.362	1.05317	0.53
1.5113	35.73	8.475	1.06188	0.62
1.7269	35.91	9.604	1.07085	0.75
1.9494	36.07	10.750	1.08010	0.89
2.1789	36.23	11.913	1.09941	0.99
2.4157	36.38	13.092	1.08957	1.16
2.6605	36.54	14.288	1.10949	1.31
2.9131	36.69	15.503	1.11993	1.51
3.1741	36.85	16.735	1.13069	1.71
3.8661	37.24	19.895	1.15910	2.28
4.6196	37.62	23.173	1.19006	3.08

(I-6) KI. aq.

C	Φ_c	a_i %	d_i*	$-\Psi$
0.0606	45.32	0.502		
0.1220	65.32	1.007	1.00559	0.01
0.2477	45.49	2.030	1.01320	0.03
0.3772	45.62	3.067	1.02105	0.10
0.5106	45.80	4.119	1.02904	0.09
0.6482	45.95	5.188	1.03735	0.18
0.7900	46.12	6.272	1.04584	0.20
0.9364	46.27	7.372	1.05464	0.29
1.0875	46.42	8.490	1.06369	0.36
1.2435	46.55	9.642	1.07301	0.43
1.4047	46.68	10.775	1.08299	0.52
1.5713	46.81	11.944	1.09255	0.55
1.7434	46.93	13.131	1.10287	0.68
1.9217	47.05	14.337	1.11346	0.76
2.1060	47.16	15.561	1.12445	0.87
2.2972	47.28	16.804	1.13583	0.99
2.8056	47.56	19.999	1.16596	1.23
3.3632	47.86	23.322	1.19910	1.69
3.9771	48.18	26.780	1.23547	2.22
4.6556	48.49	30.381	1.27572	2.91
5.4093	48.81	34.132	1.32047	3.77

(I-7) NaOH. aq.

C	Φ_c	a_i %	d_i*	$-\Psi$
0.2523	-4.68	0.503		
0.5103	-4.04	1.011	1.0096	0.14
0.7738	-3.39	1.525	1.0154	0.43
1.0427	-2.74	2.044	1.0212	0.73
1.3071	-2.18	2.568	1.0270	0.98
1.5970	-1.69	3.097	1.0329	1.40
1.8824	-1.20	3.631	1.0387	1.68
2.1735	-0.79	4.170	1.0447	2.07
2.4700	-0.35	4.714	1.0507	2.57
2.7719	0.08	5.263	1.0567	3.03
3.3923	0.90	6.374	1.0689	4.11
4.0350	1.65	7.504	1.0614	5.39
4.6998	2.38	8.651	1.0941	6.80
5.3867	3.07	9.816	1.1069	8.34
6.0947	3.77	10.996	1.1199	10.09
6.8252	4.43	12.193	1.1330	11.80
7.5765	5.08	13.405	1.1464	13.82
8.3502	5.70	14.632	1.1600	15.91
9.1437	6.31	15.872	1.1737	18.24
9.9580	6.91	17.126	1.1875	20.60
10.7907	7.51	18.391	1 2015	23.21
11.6401	8.12	19.667	1.2155	26.01
12.5084	8.70	20.953	1.2296	28.84
13.3943	9.27	22.250	1.2438	31.86
14.2982	9.83	23.557	1 2581	35.03
15.2168	10.37	24.875	1.2725	38.37
16.1515	10.91	26.195	1.2869	41.56
17.1018	11.43	27.526	1.3031	44.95
18.0757	11.91	28.871	1.3158	48.21
19.0639	12.38	30.222	1.3302	51.42

Table II[a]

The Error in Density caused by Interpolation.

Electrolyte	$100\ (d_c-d_o)\ /d_o$ (d_o is the observed density, and d_c is the density calculated by interpolation at intervals of 4 % conc.)		The Maximum of the Errors[b] (expected by interpolation at intervals of 2 % conc.)
	the range	the average	
NaCl	0.007∼0.010	0.009	2.5×10^{-3}
NaBr	0.019∼0.010	0.024	7.0×10^{-0}
NaI	0.023∼0.033	0.028	8.3×10^{-0}
KCl	0.006∼0.010	0.007	2.5×10^{-0}
KBr	0.017∼0.023	0.020	5.8×10^{-0}
KI	0.020∼0.030	0.025	7.5×10^{-0}

[a] In the case of sodium hydroxide, densities of its solution in the "International Critical Tables" density data have been known at intervals of one per cent concentration at low concentrations and at intervals of two per cent concentration at high concentrations and they have been obtained to four places of decimals.

Now the densities calculated from the density data of the "International Critical Tables" by interpolation at intervals of two or four per cent concentration are nearly in good agreement with the observed densities. In this case, therefore, when the densities of the diluted solutions are calculated down to four places of decimals by interpolation at intervals of one or two per cent concentration, we need not consider the error in density.

b) We have regarded it as the equal of the quotient when the maximum of the values of $100(d_c-d_o)/d_o$ obtained by interpolation at intervals of four per cent concentration was divided by four.

Now the error in density caused by interpolation at intervals of two per cent concentration is less than one fourth of that at intervals of four per cent concentration. Accordingly it would be rightly considered that the maximum of the errors which would be expected by interpolation at intervals of two per cent concentration is from three thousandth to eight thousandth per cent with each electrolyte, as illustrated in Table II. It is needless to say that this error is nearly negligible, if the density data are given at intervals of one per cent concentration.

Then we will discuss how such an error in density affects the value of the volume change fraction. If we denote the volume change fraction obtained from the observed density d_o by Ψ_o and that obtained from the calculated d_c by Ψ_c, we may readily derive the following equation by using Eq. (10).

$$\Psi_c-\Psi_o=-(\Psi_o+10^3)\left(\frac{\Delta d}{d_o}\right) \tag{11}$$

where $\Delta d=d_c-d_o$. However, the term Ψ_o within the brackets is negligible, as far at least as the discussion of the above-mentioned subject is concerned. So we obtain

$$\Psi_c-\Psi_o\doteqdot-10^3\left(\frac{\Delta d}{d_o}\right) \tag{12}$$

Therefore, an error of 0.001 per cent in density would cause an uncertainty of 0.01 in Ψ. In the case of sodium chloride, as an example, the error in density is from zero to three thousandth per cent as shown in Table II, so Ψ_c may be slightly less than Ψ_o,[5] but the difference between the two is not beyond 0.03. This is the same order with the uncertainty in Ψ which is caused by ordinary experimental error in density.

In conclusion, the values of Ψ shown in Table I leave more or less room for doubt at 2 places of decimals. For this reason, some of the values of Ψ obtained at low concentrations, especially in sodium and potassium iodides, appear to be in considerable doubt. In the cases of sodium and potassium chlorides, however, the values of Ψ (at appreciably lower concentrations) published in Landolt, Börnstein Tables[6] show a good agreement with our data. (cf. Tables I and III) And this agreement has been found more satisfactory in Figs. (2) and (5).

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(5) In general Ψ is negative, so $|\Psi_c|\geqq|\Psi_o|$.

(6) Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th Ed., Vol. I, Springer-Verlag, Berlin, P. 427 (1923)

Table III[a)]
Volume Change Fractions of Sodium and Potassium Chlorides
at 20° C Published in Landolt, Börnstein Tables.

Electrolyte	Initial concs. C (moles/liter)	Final concs. C^* (moles/liter)	Volume Change Fractions Ψ
NaCl	0.1920	0.096	−0.016
	0.4300	0.215	−0.071
	0.7978	0.399	−0.214
	0.9997	0.500	−0.316
KCl	0.1900	0.095	−0.023
	0.4260	0.213	−0.077
	0.6119	0.306	−0.144
	0.7439	0.372	−0.197
	0.9997	0.500	−0.317

The values of C were calculated from the values of C^* and Ψ given in the tables of Landolt-Börnstein.

IV. Volume Change Fraction—Concentration Relationships

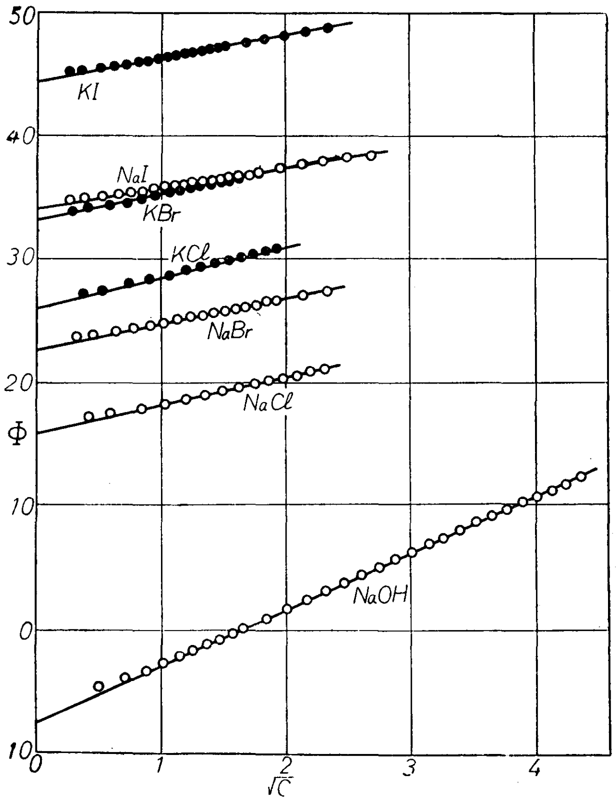

Fig. 1. Apparent molal volume of seven 1-1 electrolytes in water at 20°C plotted against $\sqrt{C}$; C=the number of moles of solute in 1 liter of solution.

Derivations of Relationships. — It has been well known that the apparent molal volumes of most electrolytes are expressed as a linear function of the square root of the volume concentration. That is, the following Masson's linear relationship holds over a wide range of concentration.

$$\Phi_c=\Phi^o+S_v\sqrt{C} \tag{13}$$

where C is the concentration in moles/liter, and Φ^o and S_v are constants. For each electrolyte the volues of Φ_c shown in Table I have been plotted against $C^{1/2}$ and found to lie along a straight line over the striking wide range of concentration, except at high dilution, as shown in Fig. (1). The parameters of Eq. (13) at 20°C obtained by graphical estimation of the $\Phi_c-\sqrt{C}$ curves are recorded in Table IV.

Table IV[a]
Values of the Parameters of Eq. (13) for Aqueous Solutions at 20°C.

Electrolyte	Φ^0 [b]	S_v [c]
NaCl	15.82	2.32
NaBr	22.63	2.04
NaI	34.12	1.64
KCl	26.04	2.47
KBr	33.15	2.08
KI	44.50	1.84
NaOH	-7.45	4.55

a) The values of Φ^o and S_v given in this table were not evaluated from data at high dilution. Therefore such values should not be used for estimating Φ_c at high dilution.

b) This is not the most accurate value of the physical quantity, Φ^o.

c) This value has been used in the estimation of some derived quantities which appear later in Table V.

Then with the aid of this function, we will correlate the volume change fraction of electrolytic solutions with the concentration. Over the whole range of concentration in which Eq. (13) holds, the volume change fraction is represented by (using Eq. 9)

$$\Psi=(\sqrt{C^*}-\sqrt{C})\frac{S_vC}{2} \tag{14}$$

where C^* is the concentration in moles/liter of the solution after diluting a C moles /liter solution at an equi-voluminal ratio.

If a C moles/liter solution, which occupies a volume V ml., is mixed with an equi-volume of water and the resulting solution occupies a volume $(2V+\Delta V_i)$ ml., where ΔV_i is negative when the volume decreases, C^* is shown by

$$C^*=\frac{C}{2\left(1+\frac{\Delta V_i}{2V}\right)} \tag{15}$$

Substituting Eq. (15) in Eq. (14) and then putting the latter in order by the binomial formula, we find the following equation,

$$\Psi=\frac{\sqrt{2}-2}{4}S_vC^{\frac{3}{2}}\left\{1-(\sqrt{2}+1)\sum_{r=1}^{\infty}\binom{-\frac{1}{2}}{r}\left(\frac{\Delta V_i}{2V}\right)^r\right\} \tag{16}$$

In this equation, the terms $\sum_{r=2}^{\infty}\binom{-\frac{1}{2}}{r}\left(\frac{\Delta V_i}{2V}\right)^r$ are negligible,[7] so that we may write

$$\Psi=\frac{\sqrt{2}-2}{4}S_vC^{\frac{3}{2}}\left\{1+\frac{\sqrt{2}+1}{2}\left(\frac{\Delta V_i}{2V}\right)\right\} \tag{17}$$

Replacing $(\Delta V_i/2V)$ by $10^{-3}\ \Psi$ and then solving it with respect to Ψ, we may derive the following function of Ψ.

$$\Psi=KC^{\frac{3}{2}}+K'C^3 \tag{18}$$

where

$$K=\frac{\sqrt{2}-2}{4}S_v$$

$$K'=\frac{\sqrt{2}-1}{1.6\times10^4}S_v^2$$

In Table V are summarized values of the coefficients K and K' at 20°C which have been calculated from the values of S_v shown in Table IV. With the electrolytic solution of which the volume decreases on dilution, K is negative and K' is positive, because S_v is positive.

Table V[a]

Values of the Parameters of Eq. (18) for Aqueous Solutions at 20°C.

Electrolyte	K	$K'\times10^4$	$K'\times(C_{max.})^3$ [b]
NaCl	−0.339 (−0.34)	1.4	0.02
NaBr	−0.298 (−0.31)	1.1	0.02
NaI	−0.241 (−0.25)	0.7	0.03
KCl	−0.361 (−0.36)	1.6	0.01
KBr	−0.304 (−0.31)	1.1	0.01
KI	−0.269 (−0.29)	0.9	0.01
NaOH	−0.659 (−0.66)	5.4	3.74

[a] The values of K were calculated from equation $K=\frac{\sqrt{2}-2}{4}S_v$, and K' from equation $K'=\frac{\sqrt{2}-1}{1.6\times10^4}S_v^2$.
Again the values in parentheses were obtained by graphical estimation of the $\log(-\Psi)-\log C$ curves in Figs. (2)∼(8).

[b] This value shows the maximum value of the second term in Eq. (18).

(7) The maximum of the values of the term shown by

$$-\frac{\sqrt{2}-2}{4}S_vC^{3/2}(\sqrt{2}+1)\binom{-\frac{1}{2}}{2}\left(\frac{\Delta V_i}{2V}\right)^2$$

is of the order of magnitude of 10^{-5} for each electrolyte, except in the case of sodium hydroxide. Even in this single exception, the contribution of this term to the value of Ψ does not exceed 0.3 per cent.

As illustrated in Table V, K' is far less than the numerical value of K. Therefore it is considered that the value of Ψ mainly depends on the first term in Eq. (18). In fact the maximum value of the second term in Eq. (18) is only of the order of magnitude of the experimental error, except in the case of sodium hydroxide. (cf. Table V)

Accordingly with most 1-1 electrolytes up to a concentration of several molal, Eq. (18) is approximately represented by means of the equation,

$$\Psi = KC^{\frac{3}{2}} \tag{19}$$

After all, it has necessarily been followed that the volume change fraction, with most electrolytes, is proportional to 3/2 power of the initial concentration in moles/liter. Then the coefficient K in this equation shows the volume change fraction of a one mole/liter solution and is specific for each electrolyte. With the electrolyte of which the value of K has been known, the values of Ψ, and hence the volume changes ΔV_t, at various concentrations are readily evaluated. In general, K is negative for the electrolytic solution of which the volume decreases on dilution, and this contraction of volume is great with the electrolyte of a large numerical value of K.

Discussion of Eq. (19).—To verify the relationship derived above, values of $\log(-\Psi)$ are plotted against $\log C$ in Figs. (2)~(8).

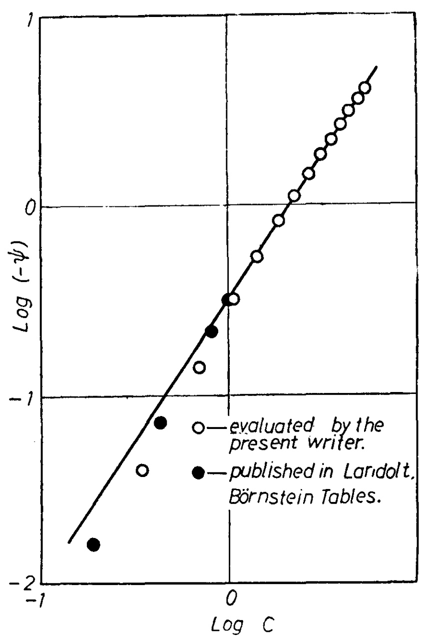

Fig. 2. Volume change fraction of sodium chloride at 20°C; C=moles per liter.

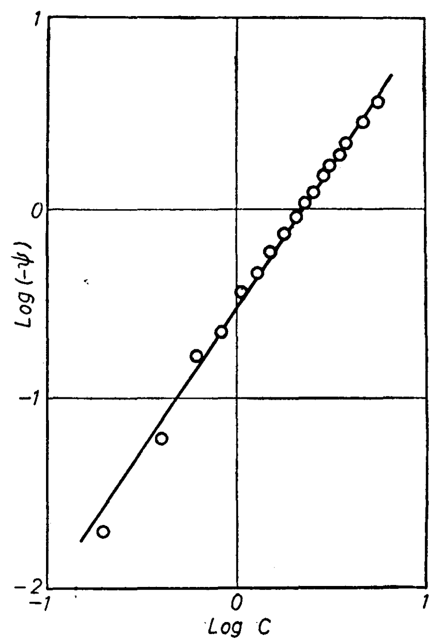

Fig. 3. Volume change fraction of sodium bromide at 20°C.

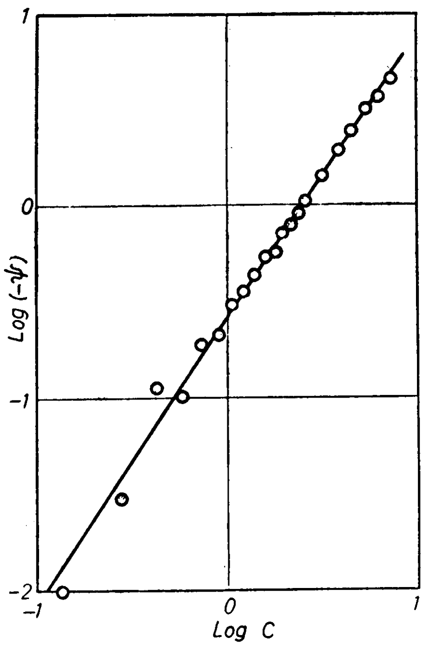

Fig. 4. Volume change fraction of sodium iodide at 20°.

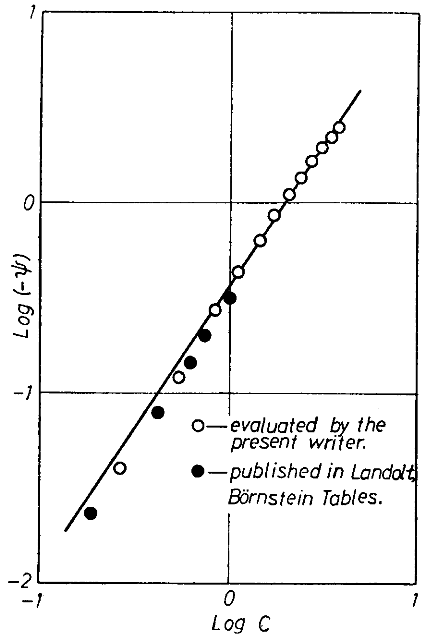

Fig. 5. Volume change fraction of potassium chloride at 20°.

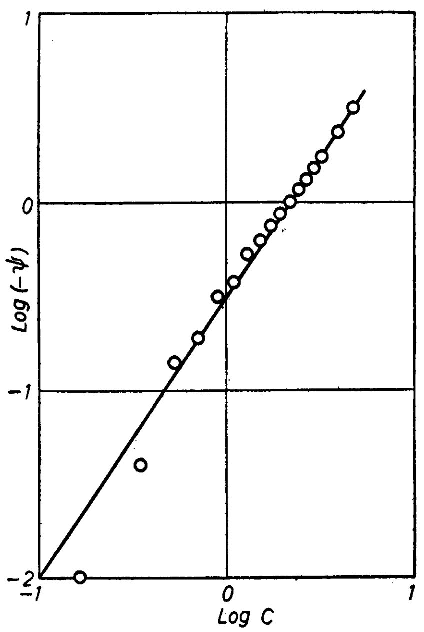

Fig. 6. Volume change fraction of potassium bromide at 20°.

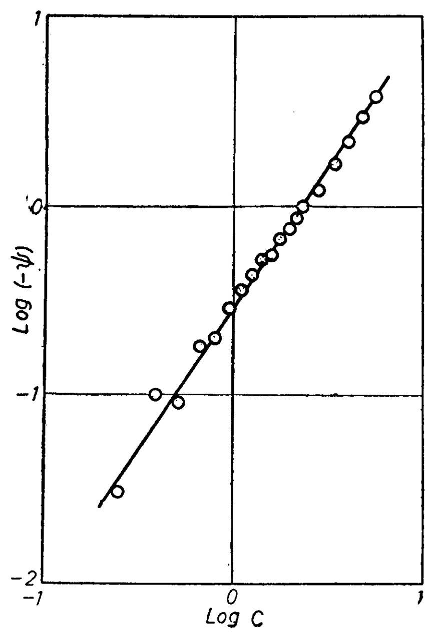

Fig. 7. Volume change fraction of potassium iodide at 20°.

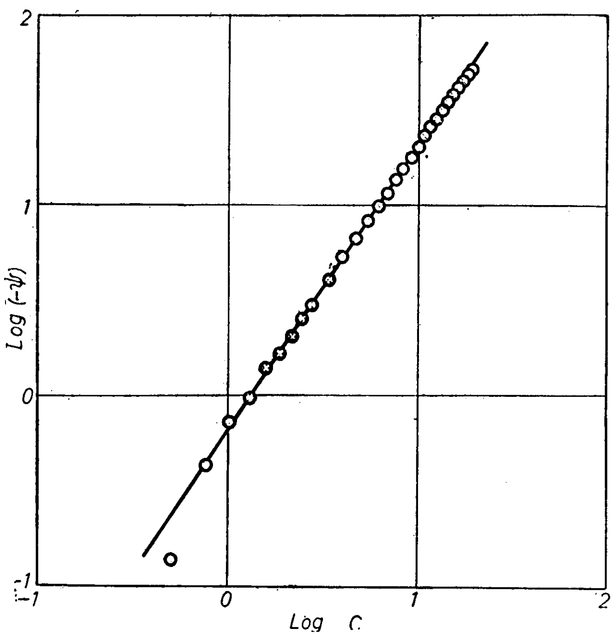

Fig. 8. Volume change fraction of sodium hydroxide at 20°.

It is seen that all seven electrolytes show excellent linearity over a remarkably wide range of concentration, and all the slopes of the $\log(-\Psi)-\log C$ lines are 3/2. On the other hand, the values of K obtained by graphical estimation of the $\log(-\Psi)-\log C$ curves are in good agreement with those which were calculated from S_v, as shown in Table V.

Therefore, it has been confirmed for all the seven electrotytes here studied that the volume change fraction obeys the simgle relationship, which has been derived by the present writer, from appreciably dilute solutions to those several molal or even more concentrated. Then discrepancy at extreme dilutions would be understood by examining the range of concentration in which eq. (13) holds (cf. Fig. 1), and reexamining the derivation of Eq. (14). As shown in Eig. (1), plots of Φ_c against $\sqrt{C}$ have been curved at high dilution, that is, the slopes of the $\Phi_c-\sqrt{C}$ lines at high dilution are different from those at higher concentrations, as has already been noted by Geffcken and Price.[8] It is therefore considered that the value of the volume contraction observed in a dilute solution would be slightly smaller than its numerical value calculated by Eq. (19). A study of Figs. (2) ~(8) will show a good agreement of the results with this consideration.

On the other hand in the case of sodium hydroxide, the deviations at high concentrations, which are shown in Fig. (8), are explained as due to the extremely higher saturated concentration rather than to the larger S_v, as has been pointed out in the derivation of Eq. (19). In this case the value of Ψ calculated by Eq. (19) differs from the observed value by nearly 7.3 per cent in the 19.06 moles/liter solution. Thus it is desirable for sodium hydroxide to evaluate the values of Ψ at high conceetrations by Eq. (18).

[8] W. Geffcken and D. Price, Z. physik. Chem., B26, 81 (1934)