[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BAVARIAN ACADEMY OF SCIENCES, DIVISION OF PHYSICAL CHEMISTRY]

THE HEATS OF DILUTION OF POTASSIUM CHLORIDE IN SUCROSE AND UREA SOLUTIONS AS SOLVENTS BELOW 0.1 *M* AT 25°[1]

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RECEIVED JULY 8, 1930 PUBLISHED NOVEMBER 5, 1930

Introduction

With the use of a sensitive differential calorimeter,[2] the integral heats of dilution of a number of strong electrolytes in water in the concentration range 10^{-1}–10^{-5} *M* have been measured in this Laboratory.[3] The thermodynamic usefulness of such quantities is illustrated, for example, in Latimer's treatment of the problem of aqueous ionic entropies.[4] For an exact comparison of the measurements with theoretical heats of dilution[5] calculated in accordance with the Gronwall, La Mer and Sandved[6] development of the fundamental theory of activity coefficients of Debye and Hückel,[7] an exact knowledge of dD/dT for the solvent is necessary. Unfortunately, the measurements at hand, even for water, show such discrepancies among the different series of results that such a comparison is at present somewhat uncertain.[8] The experimental results obtained with a number of 1–1 type salts may be summarized as follows: (a) the integral heat of dilution (V_c) is positive and is proportional to the square root of the concentration (expressed in moles of salt per liter of solution) from the most extreme dilution up to a concentration of about 0.01 *M* on the average; (b) the different salts have individual slopes in this concentration range ($V_c = A\sqrt{c}$), the individuality persisting down to the lowest measured concentration; (c) the values of the initial slopes *A* range from 280 to 430, which values correspond to '*a*' values (apparent ionic diameters) of a reasonable order of magnitude, although, as mentioned, the uncertainty in the dD/dT value does not permit a more definite evaluation of these parameters.

It was thought of interest to extend these measurements to non-aqueous

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[1] Twenty-eighth Communication on Thermochemical Researches. A list of the previous papers in this series of thermochemical investigations by E. Lange and coworkers is given in *Z. physik. Chem.*, **148A**, 97 (1930).

[2] A detailed description of the calorimeter is given in Lange and Monheim, *ibid.*, **149A**, 51 (1930). A description of the calorimeter and a summary of the work on the heats of dilution of strong electrolytes will appear shortly in *Chemical Reviews*.

[3] Lange, Robinson, Monheim and Streeck, *Z. Elektrochem.*, **36**, 772 (1930).

[4] Latimer and Buffington, THIS JOURNAL, **48**, 2297 (1926).

[5] Lange and Meixner, *Physik. Z.*, **30**, 670 (1929).

[6] Gronwall, La Mer and Sandved, *ibid.*, **29**, 358 (1928).

[7] Debye and Hückel, *ibid.*, **24**, 185 (1923).

[8] Lange and Robinson, THIS JOURNAL, **52**, 2811 (1930).

solvents where from all theoretical considerations the dielectric constant and d*D*/d*T* for the solvent in question should be the influencing factors in determining the values of the integral heats of dilution. The experimental difficulties are not much greater than in the case of aqueous solutions and it is intended to carry out such measurements in the near future. There is also the possibility of using as solvents aqueous solutions of nonconducting substances which alter the dielectric constant and d*D*/d*T* of water. In comparing the results obtained with aqueous solutions with the demands of the theory, the *D* and d*D*/d*T* values for pure water have been used; a justification for this usage has been shown by Debye and Pauling.[9] By the use of solvents such as those used in these measurements, it was hoped to bring further evidence to test whether the dielectric properties of the medium are the constants to be used for dilute salt solutions. In this paper are reported measurements of the integral heats of dilution of potassium chloride in a 15 weight per cent. aqueous solution of sucrose and a 5 weight per cent. aqueous solution of urea; for these two solvents there are dielectric constant and d*D*/d*T* measurements by Kockel.[10]

Experimental Results

Materials.—The potassium chloride was a de Haen guaranteed pure preparation which after drying was used without further purification. Previous experience with this salt had shown that traces of impurities did not influence the measured heats of dilution beyond the calorimetric error of ±2%. A fresh solution was prepared for each new concentration measurement.

Ordinary lump sugar was found to give results indistinguishable from a Kahlbaum preparation for thermochemical determinations and was, therefore, used for most of the sugar solution measurements.

The urea used was partly a pure preparation from Kahlbaum, and for a portion of the measurements a doubly purified preparation from de Haen. The two gave entirely concordant results.

Measurements.—For details of procedure in carrying out the measurements we refer the reader to previous publications.[11] The metal pipets containing the solution to be diluted had, respectively, volumes of 24.6 ± 0.1 cc. in the left half (l) of the calorimeter and 24.9 ± 0.1 cc. in the right half (r). The calorimeter halves were filled with 800 cc. (l) and 810 cc. (r) of solvent. After the solutions in both halves had been diluted, the pipets were pumped out and refilled with the same solution, so that so-called "second dilutions" could be carried out. As the concentrations in Tables I and II show, the end concentration after a "second dilution" was, with sufficient exactness, the same as the end concentration after a "first dilution" with a solution of double initial concentration, so that all measurements could be plotted on a common curve, practically without interpolation. Column 4 in the same tables shows the heat given to the opposite half—since all dilutions produced an evolution of heat—as compensation by electrical heating during the dilution, so that the temperature difference between the two calorimeter halves could be kept as small as possible. Column 6 gives the uncertainties in the

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[9] Debye and Pauling, This Journal, **47**, 2129 (1925).

[10] Kockel, *Ann. Physik*, **77**, 430 (1926).

[11] In particular Lange and Monheim, *Z. physik. Chem.*, **149A**, 51 (1930).

individual measurements due to the uncertainty in the extrapolation of the galvanometer readings before and after the dilution and does not take into account any systematic

Table I

Heats of Dilution[a] of Potassium Chloride in 15% Aqueous Sucrose Solution at 25°

Concentration mole/liter		Calorimeter	cal. compensation	cal. measured	cal. uncertainty	Heat of dilution cal./mole salt	
c_{initial}	c_{end}	Half				$V_{c_{\text{in.}}\, c_{\text{end}}}$	Mean
0.1	0.00308	(r)	0.1814	0.1838	0.0004	73.8	74.3 ± 0.5
.1	.00308	(l)	.1818	.1839	.0004	74.7	
.1	.00605	(r)	.3266	.3191	.0007	65.1	64.9 ± 0.2
.1	.00605	(l)	.2909	.3133	.0008	64.7	
.05	.00154	(r)	.0723	.0762	.0002	61.2	62.0 ± 0.6
.05	.00154	(l)	.0727	.0769	.0002	62.5	
.05	.00154	(r)	.0725	.0776	.0004	62.3	
.05	.00302	(r)	.1205	.1332	.0006	54.4	55.6 ± 0.8
.05	.00302	(l)	.1212	.1357	.0009	56.1	
.05	.00302	(r)	.1208	.1388	.0010	56.2	
.025	.000770	(r)	.0241	.0283	.0003	45.4	47.0 ± 0.8
.025	.000770	(l)	.0242	.0289	.0002	47.0	
.025	.000770	(r)	.0241	.0290	.0003	46.6	
.025	.000770	(l)	.0242	.0296	.0003	48.2	
.025	.000770	(r)	.0241	.0297	.0005	47.7	
.025	.001515	(r)	.0481	.0519	.0005	42.3	42.7 ± 0.6
.025	.001515	(l)	.0483	.0531	.0006	43.9	
.025	.001515	(r)	.0482	.0508	.0008	41.5	
.025	.001515	(l)	.0484	.0521	.0005	43.1	
.025	.001515	(r)	.0482	.0525	.0010	42.8	
.0125	.000385	(r)	...	.0102	.0005	36.0	34.4 ± 1.4
.0125	.000385	(l)	...	.0098	.0006	32.0	
.0125	.000385	(r)	...	.0109	.0006	35.1	
.0125	.000385	(l)	...	.0106	.0004	34.5	
.0125	.000754	(r)	...	.0191	.0010	31.3	31.7 ± 0.4
.0125	.000754	(l)	...	.0194	.0009	32.1	
.0125	.000754	(r)	...	.0189	.0010	30.9	
.0125	.000754	(l)	...	.0197	.0008	32.5	

[a] In the notation of Lewis and Randall, "Thermodynamics," pp. 88, $V_{c_{\text{in.}}\, c_{\text{end}}} = \bar{L}_{2\text{in.}} - \bar{L}_{2\text{end}} = \bar{H}_{2\text{in.}} - \bar{H}_{2\text{end}}$ and $V_c = \bar{H}_2 - \bar{H}_2^0 = \bar{L}_2$.

Table II

Heats of Dilution of Potassium Chloride in 5% Aqueous Urea Solution at 25°

Concentration mole/liter		Calorimeter	cal. compensation	cal. measured	cal. uncertainty	Heat of dilution cal./mole salt	
c_{initial}	c_{end}	Half				$V_{c_{\text{in.}}\, c_{\text{end}}}$	Mean
0.1	0.00308	(r)	0.1446	0.1432	0.0005	58.2	57.7 ± 0.4
.1	.00308	(l)	.1444	.1403	.0003	57.1	
.1	.00308	(r)	.1445	.1438	.0003	57.7	
.1	.00605	(r)	.2530	.2435	.0009	50.4	50.0 ± 0.3
.1	.00605	(l)	.2526	.2415	.0006	49.9	
.1	.00605	(r)	.2528	.2441	.0007	49.8	

TABLE II (*Concluded*)

Concentration mole/liter c_{initial}	Concentration mole/liter c_{end}	Calorimeter Half	cal. compensation	cal. measured	cal. uncertainty	Heat of dilution cal./mole salt $V_{c_{\text{in.}}, c_{\text{end}}}$	Heat of dilution cal./mole salt Mean
0.05	0.00154	(r)	0.0483	0.0600	0.0004	48.2	49.0 ± 0.8
.05	.00154	(l)	.0673	.0619	.0004	50.4	
.05	.00154	(r)	.0669	.0603	.0005	48.4	
.05	.00302	(r)	.0966	.1044	.0009	42.6	43.4 ± 0.6
.05	.00302	(l)	.1076	.1072	.0008	44.3	
.05	.00302	(r)	.1072	.1062	.0010	43.4	
.025	.000770	(r)	.0268	.0243	.0003	39.5	37.9 ± 0.8
.025	.000770	(l)	.0269	.0228	.0005	37.0	
.025	.000770	(r)	.0268	.0237	.0003	38.1	
.025	.000770	(l)	.0269	.0228	.0003	37.0	
.025	.001515	(r)	.0402	.0424	.0006	35.0	34.3 ± 0.4
.025	.001515	(l)	.0403	.0416	.0010	33.7	
.025	.001515	(r)	.0402	.0411	.0007	34.0	
.025	.001515	(l)	.0403	.0422	.0006	34.4	

TABLE III

INTEGRAL HEATS OF DILUTION (INTERPOLATED) AT 25°

Initial concentration in mole/liter $\sqrt{c}$	Initial concentration in mole/liter c	V_c in cal./mole of salt KCl in 15% sucrose	V_c in cal./mole of salt KCl in 5% urea	Initial concentration in mole/liter $\sqrt{c}$	Initial concentration in mole/liter c	V_c in cal./mole of salt KCl in 15% sucrose	V_c in cal./mole of salt KCl in 5% urea
0.01	0.0001	4.0	3.4	0.19	0.0361	67.4	55.3
.03	.0009	11.7	9.9	.21	.0441	73.3	59.9
.05	.0025	19.3	16.6	.23	.0529	78.6	64.1
.07	.0049	27.2	23.1	.25	.0625	83.5	67.8
.09	.0081	34.8	29.2	.27	.0729	87.8	71.0
.11	.0121	41.6	35.1	.29	.0841	91.5	73.8
.13	.0169	48.7	40.7	.31	.0961	94.7	75.8
.15	.0225	55.4	45.6	.33	.1089	97.1	77.8
.17	.0289	61.5	50.4				

errors which may have been present. The latter may take the form of absorption heats, but from various considerations[12] we believe that such disturbing factors were not present. Moreover, the inner walls of the Dewar vessel were covered with a thin layer of pure vaseline. Controls in the form of blank runs repeatedly gave a zero galvanometer deflection when both pipets (filled with solvent or with the same solution that was contained in the calorimeter) were opened simultaneously. The sensitivity of the galvanometer was 0.0007 cal. per mm. of deflection or about 8×10^{-7}° per mm.; a greater sensitivity was not required for these measurements. The average reproducibility of the individual measurements was ±0.0004 cal., corresponding to about 4.5×10^{-7}°.

From the experimental data curves were plotted which showed, below 0.008 *M*, a proportionality with $\sqrt{c}$ within the limit of experimental error, and which were therefore extrapolated linearly to $c = 0$. The A values obtained by extrapolation are 386 ± 3% for the 15% sugar solution as solvent and 332 ± 3% for the 5% urea solution as solvent, as compared with 376 ± 3% for potassium chloride in pure water.[13] From the smooth curves the values for the integral heats of dilution given in Table III were ob-

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[12] Lange and Messner, *Z. Elektrochem.*, **33**, 439 (1927).

[13] Lange and Leighton, *ibid.*, **34**, 566 (1928).

tained. These values we believe to be exact to within $\pm 2\%$ plus an additive uncertainty of 0.5 cal. introduced by the extrapolation.

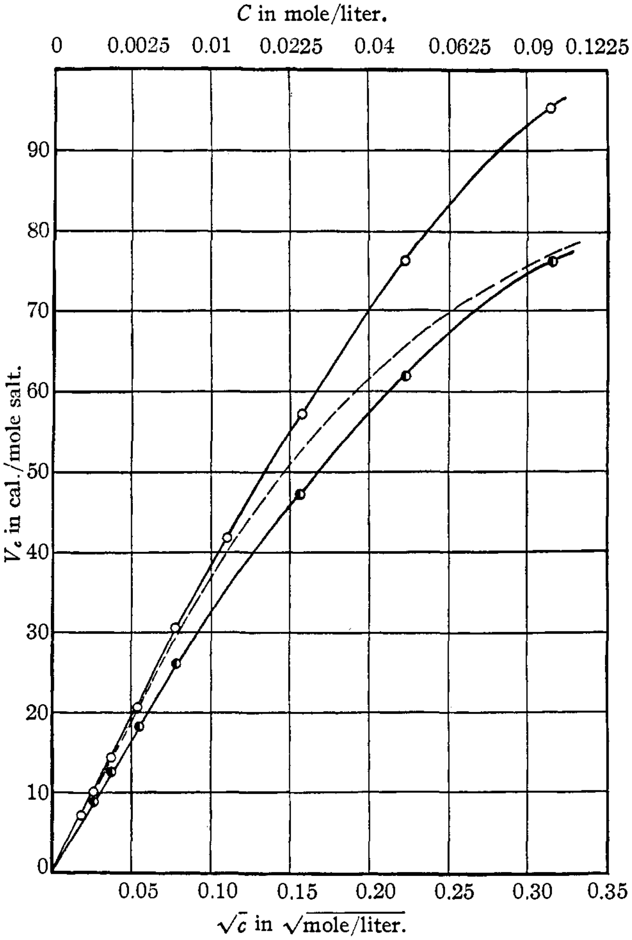

Fig. 1.—○, 15% sucrose; ◐, 5% urea; — — — —, water.

Discussion of Results

At first glance it is seen that the two measured dilution curves are entirely similar in their general nature to the previously obtained curves for potassium chloride and other 1–1 type salts in water; there is the same initial linearity with $\sqrt{c}$ and the initial slopes correspond well with the values mentioned above. However, the differences between the curves for the sugar and urea solutions as solvents and that for pure water, partly at low concentrations and partly at higher concentrations, are real and entirely outside of the experimental error. In the case of the sugar solution there is considerable evidence[14] to indicate that the sucrose molecules are hydrated, probably with approximately six water molecules, and the higher heats of dilution of the potassium chloride in this solvent might be explained as being caused by an increase in the potassium chloride concentration due to the removal of (6 × moles of sucrose) moles of water. A simple calculation shows that this explanation is inadequate, accounting at the most at a potassium chloride concentration of 0.1 *M* for but 10% of the observed difference. From the classical point of view another possible explanation is that the dielectric constant of this solution is, according to Kockel's measurements, about 5% lower than that of pure water and that if in these dilute solutions undissociated potassium chloride molecules are present, a larger number of such molecules might be expected in the solvent of lower dielectric power, accounting for the more positive values of V_c. But this explanation demands a positive dissociation heat for potassium chloride, which does not agree with the case for potassium chloride in pure water, where the effect of the hypothetical association at higher concentrations is to produce more negative heats of dilution.

There is also the possibility to consider of compound formation between the ions and the sugar or urea molecules, similar to the more or less stable binding of water molecules by the ions. In terms of the interionic theory this could be interpreted as a change—very likely an increase—in the '*a*' value for potassium chloride. A further discussion of this possibility does not seem possible in view of the lack of experimental facts.

Assuming that such effects are not present, an explanation for the experimental curves, not explainable by hydration of the sucrose molecules or an increased association of the potassium chloride, may be sought in a consideration of the dielectric properties of the solvents.

The relation of the initial slope *A* to the dielectric properties of the medium (limiting Debye–Hückel case) is shown by the equation

$$V_c = -1.66116 \times 10^7 \times 1/D \times 1/\sqrt{DT}(1 + T/D\ \mathrm{d}D/\mathrm{d}T)\sqrt{c} = A\sqrt{c}\ \text{cal./mole of salt}$$

Plotting Kockel's data, we have obtained the following values at 25°: for a 15% sugar solution $D = 74.25$ and $\mathrm{d}D/\mathrm{d}T\ -0.38$, for a 5% urea solution $D = 82.8$ and $\mathrm{d}D/\mathrm{d}T = -0.20$. The calculation of *A* gives +532 for the sugar solution and −228 for the urea solution as compared with +661 for pure water (again using Kockel's measurements for the sake of comparison). The great sensitivity of the factor $(1 + T/D \times \mathrm{d}D/\mathrm{d}T)$ to small changes or uncertainties in $\mathrm{d}D/\mathrm{d}T$ makes impossible any certain decision in the case of the sugar solution, and water curves but, if Kockel's values for the urea solution are even only approximately correct, we should get a curve with a negative instead of a positive slope. The evident contradiction in this case could be avoided by using the *D* value for water, and

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[14] McBain and Kistler, *J. Phys. Chem.*, **33**, 1806 (1929).

not the D for the urea solution. On the other hand, there has been no doubt as yet in investigations of the activity coefficients of strong electrolytes in non-aqueous solvents that the D value of the particular solvent should be used.[15] Accordingly we should use the dielectric constants of these two solutions in question and in view of the unexplainable discrepancy in the case of the urea solution we might conclude that there is an error in the measured dD/dT value, although Kockel reported reproducible measurements in the temperature range 5–35°. The question seems to be interesting enough to warrant further accurate measurements of dD/dT for aqueous solutions of non-conducting substances, at least relative to the value for water, since the corresponding heat of dilution measurements can be made accurately and without great difficulty.

We thank the Notgemeinschaft der Deutschen Wissenschaft and the Kaiser Wilhelm Institut für Physik for their support in this work through the furnishing of necessary apparatus. One of us (A. L. R.) was on leave of absence from the University of Pittsburgh during the course of this work.

Summary

The integral heats of dilution of potassium chloride in a 15% sucrose solution and a 5% urea solution as solvents have been measured in the concentration range 10^{-1}–10^{-4} M at 25° with an exactness of ±2% plus an added uncertainty of 0.5 cal. introduced by the extrapolation to infinite dilution.

The curves are of the same general nature as those obtained for a number of 1–1 type salts (including potassium chloride) in water, but the deviations from the curve obtained for potassium chloride in pure water throughout the entire measured concentration range are outside of the limit of error.

It does not seem possible to explain these deviations in terms of concentration or association effects (if the formation of compounds between potassium chloride and sucrose or urea molecules is excluded). The differences are possibly due to the different dielectric properties of the solvents used, although uncertainties in the values of these constants make an exact comparison impossible.

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[15] La Mer, *Trans. Am. Electrochem. Soc.*, **51**, 507 (1927).