pentanols and hexanols. If details are desired, reference should be made to the article on pentanols. The results seem reliable to better than 0.1 weight per cent. and the authors feel that the validity of the results will approach this limit.

Summary

Aqueous solubilities of eight isomeric heptanols have been determined for 20, 25 and 30° and one for 40°. The seven tertiary isomers are more soluble than the two most compact secondary isomers. Maximum solubility is obtained by having the hydroxyl group as close as possible to the center of a compact tertiary molecule. Solubility of the isomers decreases as the temperature increases from 20 to 30°.

GREENSBORO, N. C. RECEIVED JUNE 27, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Densities of Aqueous Solutions of Urea at 25 and 30° and the Apparent Molal Volume of Urea[1]

BY FRANK T. GUCKER, JR., FRED W. GAGE AND CHARLES E. MOSER

Introduction

In 1929 Masson[2] showed that the apparent molal volume of an electrolyte is a linear function of the square root of the concentration, while that of a weak electrolyte or a non-electrolyte is a linear function of a higher power of the concentration. The relationship for electrolytes has been confirmed by numerous investigators. In reviewing this and other properties of electrolytic solutions, one of us[3] pointed out that the data of Perman and Urry[4] for the apparent molal volumes and compressibilities of sucrose and of urea also might be represented as linear functions of the square root of the concentration. Redlich and Klinger[5] subsequently proved from more accurate density data that the change of the apparent molal volume of sucrose was much more nearly linear with the first power than with the square root of the concentration. We then found that the data of Perman and Urry could be represented equally well by either plot, within the limit of 0.1% to which their data were tabulated. The present work was undertaken to determine the apparent molal volumes of urea in aqueous solutions with high enough precision to determine whether it was also a linear function of the concentration—like sucrose.

Experimental Methods.—In order to attain an accuracy of a few parts per million (p. p. m.) the densities were measured differentially, using three pycnometers of about 60-ml. capacity. Two of them were filled with solution and the third with water. After all three had come to equilibrium in a thermostat and the volumes were adjusted in the capillaries, the pycnometers containing solution were weighed successively against the water-filled tare. Such a differential arrangement minimizes errors due to changes in the temperature of the thermostat, and also decreases the errors due to adsorption of moisture on the surface of the pycnometers and the correction required in reducing the weights to the vacuum standard.

In adjusting the pycnometers, they were placed in a thermostat holding 36 liters of water. The bottom and sides of the thermostat were protected by a 5-cm. layer of magnesia insulation and the top was covered with a wooden lid, in the center of which was a glass panel, through which the capillaries of the pycnometers were read.

The thermostat was equipped with an adequate stirrer and heated by means of three coils of bare nichrome wire connected to the lighting circuit through a thyratron relay. During the first series of measurements (made by F. W. G.) the relay was actuated by a large ether-filled regulator with mercury contact, which kept the temperature constant to ±0.002° under most conditions and to ±0.005° at all times. The temperature throughout the bath was found to be uniform to 0.001°. These temperatures were measured with a calibrated Beckmann thermometer. During the second series of measurements (made by C. E. M.) the regulator consisted of a pair of 100-ohm nickel resistance thermometers, connected in opposite arms of a Wheatstone bridge, equipped with a sensitive galvanometer. The light from the galvanometer mirror actuated a photoelectric cell which controlled the relay. This system gave more rapid response and kept the temperature constant to ±0.0004°, as measured by a platinum resistance thermometer. This regulator has the added advantage of great flexibility and instant response at any desired temperature.

The pycnometers were constructed of Pyrex glass, which has the advantage of chemical inertness but the disadvantage of changing volume appreciably with time. The body of each pycnometer was made from 2-cm. tubing bent into a U which was 6 cm. in total width and about 13 cm. high.

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(1) Part of this paper was presented before the Symposium on "The Electrochemistry of Solutions" held by the Division of Physical and Analytical Chemistry at the Kansas City meeting of The American Chemical Society, April, 1936.

(2) Masson, *Phil. Mag.*, [7] **8**, 218 (1929).

(3) Gucker, *Chem. Rev.*, **13**, 111 (1933).

(4) Perman and Urry, *Proc. Roy. Soc.* (London), **A126**, **44** (1929).

(5) Redlich and Klinger, *Sitzb. Akad. Wiss. Wien*, Abt. IIb, **143**, 489 (1934); *Monatsh.*, **65**, 137 (1934).

Heavy capillary tubes of 0.4-mm. bore, sealed to the tops of the U, extended vertically for 2 cm. and then were bent at right angles. Each horizontal section was 6 cm. in length and its end was covered with a ground glass cap to minimize evaporation. The end of one was drawn down to a bore of about 0.1 mm., while the central portion of the other was graduated with 20 clearly-etched lines about 1 mm. apart. This allowed a latitude of about 0.002 ml. in setting the pycnometer. If a single mark were used, the volume would have to be set to 0.00006 ml. in order to give a sensitivity of 1 p. p. m.

Before the graduated capillaries were sealed into place, each was tested by measuring the length of a short mercury thread in different positions. When it was found to be uniform,[6] it was calibrated by measuring the length of a mercury thread which nearly filled the graduated section and then weighing the mercury. The volume per graduation was 0.00012 ml. in pycnometers 1 and 3, and 0.00013 ml. in number 2. An error of 0.5 mm. in reading the capillary therefore would only make an error of 1 p. p. m.

The volume of each pycnometer was determined by filling it with distilled water to some point on the graduated capillary and weighing the water it contained. The volume from the constricted end to the *first* mark on the graduated arm was then found by subtracting the volume of water in the graduated arm. The pycnometers were standardized at 25° and then at 30° in the summer of 1936. Two standardizations were carried out at each temperature, agreeing on the average to 12 p. p. m. No regular change in volume was observed during the few weeks in which the work was done. However, when the second series of measurements were made, starting in December, 1937, a decrease of 0.114% was found in the volume of pycnometer 2 and a decrease of 0.115% in 1 and 3. This evidently was due to the contracting of the pycnometers on aging, although they were annealed when they were made.

The weights used in this investigation were standardized to 0.01 mg. by the well-known method of Richards[7] as modified by Weatherill to employ transposition. They were checked from time to time and found consistent to a few hundredths of a milligram. The weighings in the first series of experiments were made on a good analytical balance of the required sensitivity. Those in the second series were made on a semi-micro balance with a notched beam graduated in hundredths of a milligram and with magnetic damping which decreased the time required to determine the balance point. In the second series, all weighings were made by transposition, to eliminate the effect of a difference of about 0.01% in the length of the balance arms.

Throughout this work, all weighings were reduced to the vacuum standard. The density of the brass weights was taken as 8.4, the figure given by the manufacturer. Calculations showed that an error of 10% in this value would not affect the results by 1 p. p. m. The density of 2.25 for Pyrex, given in the "International Critical Tables,"[8] was used in calculating the vacuum corrections for the pycnometers in the first series of experiments. Later, direct weighings in air and in water gave the value 2.234 which was used in the second series. The density of solid urea was taken as 1.335[9] at 20°. At the end of this work we found the value 1.329 at 25° as described in a later paragraph. Both these differences are negligible in calculating vacuum corrections. The atmospheric pressure was read on a mercurial barometer, corrected for temperature and the local value of the gravitational acceleration. The relative humidity was read on a hair hygrometer. The density of the air was calculated from these values, the room temperature and corresponding aqueous tension, by the formula given in the "International Critical Tables."[10]

Materials and Solutions.—The urea used in this work was prepared by crystallizing the commercial C. P. product twice from water, draining the crystals centrifugally and drying the product *in vacuo* at 50–60°, as described in a previous paper.[11] After use in the pycnometers, the solution was evaporated at 50° until crystallization began, then poured into an equal volume of redistilled ethanol held in an ice-bath at 0°. The urea precipitated in this way was collected on a sintered glass crucible and dried as before. Since urea is fairly soluble in 50% alcohol the filtrate was evaporated further and a second batch of crystals was reclaimed.

The water used in this work was redistilled from alkaline permanganate and had a specific conductance of about 1.5×10^{-6} mhos. It was always deaerated immediately before use by means of a water aspirator.

The solutions were made up determinate from the dry urea and this water. The urea was weighed into a 500-ml. flask to which the desired amount of water was added. After the solution was mixed thoroughly and brought up to room temperature, it was weighed and the amount of water found by difference. The solutions more concentrated than 4 molar required special treatment to prevent the appearance of small air bubbles which coalesced very slowly in the viscous medium. It was necessary to apply the full suction of the water aspirator, or the partial suction of a Hyvac pump, and to shake the flask at intervals for about a half hour in order to deaerate the solution completely. The final weighing was not made until this process was complete.

The pycnometers were cleaned with sulfuric acid and dichromate solution, rinsed with distilled water and dried with a current of filtered air. One of the capillary tubes was then connected, by means of a piece of gum-rubber tubing, to a glass tube extending through a rubber stopper into the suction flask containing the solution. The solution was forced into the pycnometer by air pressure from a rubber aspirator bulb connected to the side-arm of the flask. In some of the most concentrated solutions, a small amount of insoluble matter was removed by connecting a platinum sponge filter to the end of the glass tube through which the solution was forced.

After the pycnometers had come to equilibrium in the water-bath, the liquid menisci were adjusted as usual with a thin V-shaped piece of filter paper. When the meniscus remained stationary for five minutes, its position was read

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(6) These fine, uniform tubes were supplied to us by the Corning Glass Works, through the courtesy of Dr. Ralph K. Day.

(7) T. W. Richards, THIS JOURNAL, **22**, 144 (1900); Weatherill, *ibid.*, **52**, 1938 (1930).

(8) "I. C. T.," Vol. II, p. 93.

(9) "I. C. T.," Vol. I, p. 177.

(10) "I. C. T.," Vol. I, p. 71.

(11) Gucker and Ayres, THIS JOURNAL, **59**, 2152 (1937).

TABLE I[a]

DENSITIES OF AQUEOUS SOLUTIONS OF UREA AT 30° AND CORRESPONDING APPARENT AND PARTIAL MOLAL VOLUMES

Expt.	c	d	Δd (in p. p. m.)	ΦV_2 (obsd.)	ΦV_2 (calcd.)	$\overline{V}_2$ (calcd.)	$\overline{V}_1$ (calcd.)
	0.00000	0.995673			44.546	44.546	18.0945
6a	.08056	.996976	39	44.1	44.55	44.56	18.0945
b		.996926	−11	44.7			
10a	.15060	.998069	33	44.34	44.56	44.58	18.0945
b		.998017	−19	44.69			
3	.19976	.998785	−21	44.67	44.57	44.59	18.0944
4a	.39455	1.001898	45	44.47	44.59	44.63	18.0941
b		1.001842	−11	44.61			
8a	.49616	1.003471	32	44.53	44.60	44.65	18.0940
b		1.003407	−32	44.66			
7a	.66822	1.006159	40	44.56	44.62	44.69	18.0936
b		1.006104	−15	44.64			
9a	.82859	1.008651	39	44.59	44.64	44.72	18.0931
b		1.008596	−16	44.65			
1a	1.15522	1.013644	−27	44.695	44.672	44.791	18.0919
b		1.013631	−40	44.706			
2a	1.92868	1.025517	−43	44.778	44.756	44.948	18.0872
b		1.025506	−54	44.784			
5	2.95029	1.041061	− 5	44.868	44.867	45.145	18.0774
11a	4.39481	1.062650	46	45.013	45.024	45.406	18.0566
b		1.062601	− 3	45.024			

[a] In this table and the next, c is the concentration of solute in moles per liter; d, the density of the solution in g. per ml.; and Δd, the observed density minus that calculated from the equation. The density of pure water is taken from the "I. C. T.," Vol. III, p. 25.

and recorded. All three pycnometers were then removed from the water-bath, rinsed with distilled water, wiped with a lintless towel and hung in the balance room. After a period of thirty or forty-five minutes, the weighings were made.

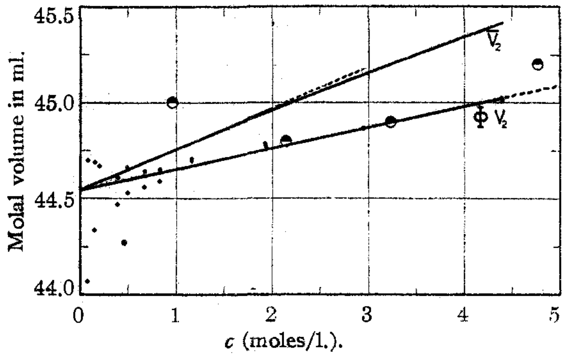

Fig. 1.—Apparent and partial molal volumes of urea at 30°: ●, this investigation; ◓, Perman and Urry.

Experimental Results.—We originally planned a series of experiments over the whole concentration range at 25°. After the first six of these were made (by F. W. G.), hot weather necessitated a change to 30°. The series at 25° was completed later (by C. E. M.). The experimental results, numbered chronologically, are collected in Tables I and II, which include all the experiments except those affected by some known error. Duplicate experiments were always made, but in seven cases minor accidents prevented the completion of one of the pair. From the densities, the apparent molal volumes were calculated by the equation

$$\Phi V_2 = \frac{1000}{c}\left(\frac{d_1 - d}{d_1}\right) + \frac{M_2}{d_1} \qquad (1)$$

where c is the concentration in moles per liter, d_1 and d the densities of water and of solution, and M_2 the molecular weight of urea (60.058). A plot of the apparent molal volume at 30° (Fig. 1) showed that within experimental error it is a linear function of c up to the highest concentration studied. The best straight line representing the experimental values was found by the method of least squares, weighting each point according to its probable accuracy, measured by $(d - d_1)$. It was found to be

$$\Phi V_2 = 44.546 + 0.1087c$$

Substituting this value in equation (1) gives for the density the equation

$$d = 0.995673 + 0.015705c - 1.082 \times 10^{-4}\,c^2$$

Values calculated from this equation were compared with the experimental results and the differences, as shown in Table I, average ±29 p. p. m.

TABLE II

DENSITIES OF AQUEOUS SOLUTIONS OF UREA AT 25° AND CORRESPONDING APPARENT AND PARTIAL MOLAL VOLUMES

Expt.	c	d	Δd (in p. p. m.)	ΦV_2 (obsd.)	ΦV_2 (calcd.)	$\overline{V}_2$ (calcd.)	$\overline{V}_1$ (calcd.)
	0.00000	0.997074			44.218	44.218	18.0691
4a	.11394	.998896	5	44.20	44.23	44.25	18.0691
b		.998888	− 3	44.26			
2	.15077	.999475	− 4	44.26	44.24	44.26	18.0690
7a	.35215	1.002682	2	44.26	44.27	44.32	18.0688
b		1.002683	3	44.26			
1a	.41500	1.003676	− 1	44.28	44.28	44.34	18.0687
b		1.003674	− 3	44.28			
3	.62386	1.006983	0	44.30	44.30	44.38	18.0681
5a	1.00812	1.013039	6	44.351	44.356	44.486	18.0666
b		1.013038	5	44.352			
8a	1.36866	1.018667	− 9	44.411	44.405	44.576	18.0646
b		1.018670	− 6	44.409			
6a	1.88532	1.026703	2	44.472	44,473	44.698	18.0607
b		1.026694	− 7	44.477			
13a	2.42107	1.034945	− 9	44.546	44.542	44.817	18.0556
b		1.034936	−18	44.550			
12a	3.33355	1.048842	− 9	44.659	44.656	45.004	18.0445
b		1.048833	−18	44.662			
10a	3.98193	1.058615	4	44.734	44.734	45.123	18.0350
b		1.058608	− 3	44.735			
9	5.05362	1.074560	17	44.856	44.859	45.302	18.0168
11a	5.92297	1.087291	− 7	44.958	44.956	45.428	18.0002
b		1.087287	−11	44.958			
14	7.28543	1.106989	−17	45.103	45.100	45.597	17.9717
15a	8.20269	1.120038	−60	45.199	45.191	45.690	17.9516
b		1.120039	−59	45.199			
16a	9.52555	1.138980	220	45.293	45.315	45.801	17.9220
b	9.52469	1.138878	130	45.302	45.315	45.801	17.9220
17a	9.53161	1.138911	67	45.310	45.316	45.802	17.9219
b		1.138909	65	45.310			

The partial molal volumes of solvent ($\overline{V}_1$) and solute ($\overline{V}_2$) are defined as

$$\overline{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{n_2,\,T} \text{ etc.}$$

where V is the volume occupied by n_1 moles of solvent and n_2 of solute. These values were calculated from the apparent molal volume of the solute by the equations[12]

$$\overline{V}_1 = \frac{1000\,\overline{V}_1^{\circ}}{1000 + c^2\dfrac{\partial \Phi V_2}{\partial c}} \tag{2}$$

$$\overline{V}_2 = \Phi V_2 + \left[\frac{1000 - c\Phi V_2}{1000 + c^2\dfrac{\partial \Phi V_2}{\partial c}}\right] c\,\frac{\partial \Phi V_2}{\partial c} \tag{3}$$

These values are also collected in Table I and $\overline{V}_2$ is plotted in Fig. 1. It starts with twice the slope of the ΦV_2 curve and is practically linear to 1 molar, above which it increases somewhat less rapidly, as shown.

In Table II are given the results of the more complete series at 25°, which extends nearly to the saturated solution. Here also the apparent molal volume of urea may be represented as a linear function of c to a concentration of 3 molar by the equation

$$\Phi V_2 = 44.224 + 0.1319c$$

which was fitted to these data by the method of least squares. The corresponding equation for the density

$$d = 0.997074 + 0.015964c - 1.315 \times 10^{-4}c^2$$

reproduces the experimental values with an average deviation of ±5 p. p. m.

In more concentrated solutions, the increase is less rapid, as shown in Fig. 2. The whole series

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[12] The first is analogous to that derived by Gibson, *J. Phys. Chem.*, **38**, 320 (1934), and listed as equation (6). The second was derived by Geffcken, *Z. physik. Chem.*, **A155**, 1 (1931), and used by Gucker, *J. Phys. Chem.*, **38**, 311 (1934).

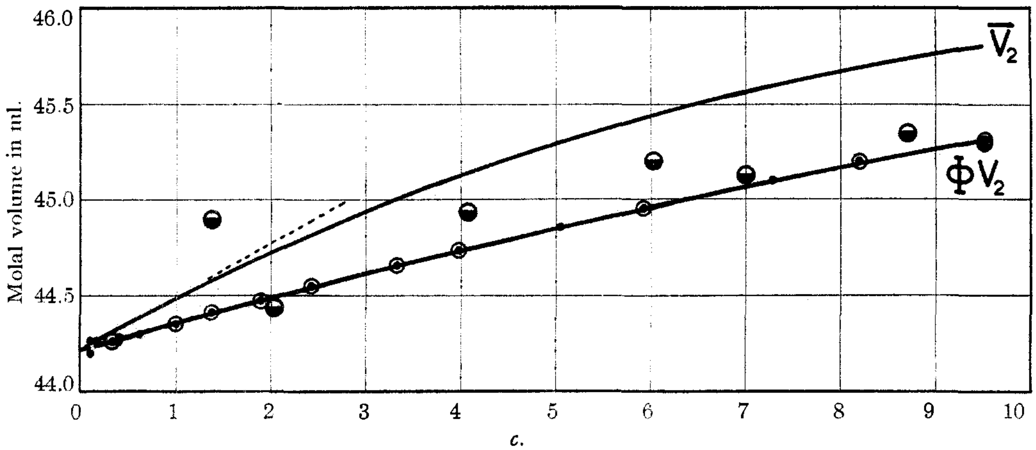

Fig. 2.—Apparent and partial molal volumes of urea at 25°: ● and ○, our data; ◒, Dunstan and Mussell.

lies along a smooth curve which is represented very satisfactorily by the second order equation

$$\Phi V_2 = 44.218 + 0.13999c - 0.002601c^2$$

The corresponding expression for the density is

$$d = 0.997074 + 0.0159686c - 1.3958 \times 10^{-4}c^2 + 2.593 \times 10^{-6}c^3$$

The experimental results agree with the values calculated from this equation with an average deviation of only ±7 p. p. m. up to 7 molar and ±26 p. p. m. over the whole range. The values of $\overline{V}_1$ and $\overline{V}_2$ were calculated as before and are included in Table II.

One other interesting experimental value was the density of solid urea, from which its molal volume in the solid state could be calculated. The value of 1.335 for the density at 20° which is tabulated in the "International Critical Tables"[9] apparently was determined by Mez.[13] It is frequently quoted in the literature. We were surprised to find, however, that another volume of the same Tables[14] listed, among "values reliable to four decimals or values over a temperature range," the figures of 1.3190 and 1.3617 determined by Dewar[15] at 17 and −188°, respectively. Assuming linear expansion, this would give the value 1.3184 at 20°, which is 1.2% lower than the value of Mez. Further search also disclosed the values of 1.333 and 1.323 found by Schröder[16] by the displacement of benzene and olive oil, respectively. No statement of the temperature was found, but it was probably 18 or 20°. Because of the diversity of these results, we measured the density at 25° in a specific gravity bottle with a ground plug. As the displacing liquid we used *n*-heptane, in which urea was found to be insoluble. The urea was powdered and dried as before and the liquid level was adjusted in the same thermostat. Five experiments were made. One of these was discarded because, for an unknown reason, the weight of the bottle increased upon standing on the balance pan. The other results were 1.3308, 1.3286, 1.3284 and 1.3279. We therefore took as a reliable average of our results the value 1.329 g./ml. at 25°. Correcting the other values to 25° we find that our results are half-way between those of Schröder and Mez, and about 1% higher than those of Dewar, as the following comparison shows:

Dewar (corr.)	1.317
Schröder (corr.)	1.327
This investigation	1.329
Mez (corr.)	1.334

Discussion

These measurements show conclusively that the apparent molal volume of urea is a linear function of the first power of the volume concentration from 0.1 to about 3 molar. This is demonstrated in Fig. 3, where the results for 25° are plotted against c along the upper line and against $c^{1/2}$ in the lower curve. The same conclusion follows from the results at 30°, although the experimental uncertainty is somewhat greater. Our results at 25° show a maximum difference from those of Dunstan and Mussell[17] of −0.6% and an average of −0.2%. Since their results are only given to 0.1%, this agreement is quite satisfactory. Our results at 30° agree with those of Perman and

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(13) Mez, *Z. Krist.*, **35**, 247, quoted in Beilstein, "Handbuch" 4th Edition, Vol. III, p. 45.

(14) "I. C. T.," Vol. III, p. 45.

(15) Dewar, *Chem. News*, **91**, 216 (1905).

(16) Schröder, *Ber.*, **12**, 562 (1879).

(17) Dunstan and Mussell, *J. Chem. Soc.*, **97**, 1935 (1910).

Urry[4] within the accuracy of 0.1% with which they were tabulated. Four of their values, covering the range of our results, are plotted in Fig. 1, and six of the eight data of Dunstan and Mussell in Fig. 2. One of the others fell above and the second below the range of our figure. The large scattering emphasizes the difficulty of determining the true function of the concentration from them. Taking our value of the density of the solid, we find that its molal volume is 45.19 ml. at 25°. This differs very little from the volume in solution. In fact, it is the same as the apparent molal volume in a 6.5 molar solution or the partial molal volume in a 3.5 molar solution. Urea therefore is very nearly a perfect solute and does not cause the large electrostriction typical of electrolytes and of polar non-electrolytes,[18] nor does its apparent molal volume change so much with concentration. The increase from 0 to 1 molar solution is only about 4% of that of a typical 1-1 electrolyte.

Since the apparent molal compressibility[19] is the pressure derivative of the apparent molal volume

$$\Phi K_2 = -\left(\frac{\partial \Phi V_2}{\partial P}\right)_T$$

we would expect it to be the same function of the concentration as the apparent molal volume. A review of the literature did not disclose enough accurate data to prove this point, but we may reasonably assume that accurate compressibility measurements would show that the apparent molal compressibility of urea is also a linear function of c rather than $c^{1/2}$ as we first thought.[3]

In the case of electrolytes, the apparent molal heat capacity was found to parallel the volume properties.[3] The same is true of sucrose,[20] but the case of urea is different, since the apparent molal heat capacity[11] does not change in a simple manner with either c or $c^{1/2}$.

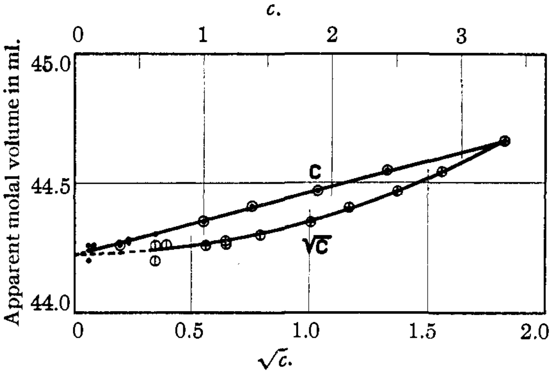

Fig. 3.—Comparison of abscissas for urea at 25°.

Added in Proof.—Recently we have found an article by Skarre, Demidenko and Brodskiĭ,[21] on the densities and apparent molal volumes of urea at 25° from 0.003 to 1.3 molar. They employed the differential flask method which Washburn[22] and his collaborators used to determine the density of heavy water, and consider their results accurate to 1 p. p. m. Their ten results from 0.003 to 0.09 molar differ on the average by only ±1.3 p. p. m. from the densities calculated from our equation, using the 1936 value of the molecular weight (60.047) which they apparently employed. Their results at the four higher concentrations show increasingly negative deviations of 16, 26, 66 and 102 p. p. m. for which we have no explanation.

They plotted their results against $c^{1/2}$ and found a nearly linear relationship from 1.3 down to 0.05 molar. At greater dilution, their results fell *below* the line, and they hesitated to extrapolate to infinite dilution. However, their values of the apparent molal volume, tabulated to 0.001 ml., are accurate only to 0.1 ml. at 0.1 molar and 1 ml. at 0.004 molar. The average deviation in density is only 1 p. p. m., which seems to us to be within their probable experimental error. Their range of concentrations was not great enough to allow a satisfactory comparison of the $c^{1/2}$ and c plot, although they state that unpublished work by Dikowa in their laboratory indicates an upward concavity in the $c^{1/2}$ plot such as we have found.

Acknowledgments.—It is a pleasure to acknowledge our indebtedness to Dr. Ralph K. Day of the Corning Glass Works for supplying us with the capillary tubing used in our pycnometers; to Paul Kleppisch who, working on an N. Y. A. grant, purified the urea for these measurements; and to Nicholas Boukidis, also an N. Y. A. assistant, who helped in the construction of the thermostat.

Summary

Using a differential pycnometer method, we have measured the densities of aqueous solutions of urea from 0.1 to 4 molar at 30° and from 0.1 to 9.5 molar at 25°.

The apparent molal volume of urea is a linear

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(18) Cohn, McMeekin, Edsall and Blanchard, THIS JOURNAL, **56**, 784 (1934).

(19) Gucker, *ibid.*, **55**, 2709 (1933), see also reference (3).

(20) Gucker and Ayres, *ibid.*, **59**, 447 (1937).

(21) Skarre, Demidenko and Brodskiĭ, *J. Phys. Chem.* (U. S. S. R.), **9**, 152 (1937); *Acta Physicochim., U. R. S. S.*, **6**, 297 (1937).

(22) Washburn, Smith and Frandsen, *Bur. Standards J. Research*, **11**, 457 (1933); **12**, 306 (1934).

function of the volume concentration, *c*, over the whole range at 30° and up to 3 molar at 25°. Urea therefore behaves like sucrose and not like typical electrolytes, the apparent molal volumes of which increase linearly with $c^{1/2}$. The experimental results and the partial molal volumes of urea and water are tabulated. Equations giving the apparent molal volume and density as functions of concentration are also included.

The density of solid urea is found to be 1.329 g./ml. at 25° and its molal volume 45.19 ml.

EVANSTON, ILLINOIS RECEIVED AUGUST 1, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Kinetics of Neutralization of Pseudo Acids in H_2O and D_2O

BY SAMUEL H. MARON[1] AND VICTOR K. LA MER

In this paper are reported kinetic measurements by a conductance method on the neutralization at 0 and 5° of nitromethane, nitroethane, and nitroisopropane by hydroxyl and deuteroxyl ions.

The familiar protolytic processes of ionization and neutralization of acids are in most cases not amenable to kinetic study for they proceed, if not instantaneously, at least with velocities too high to measure. In the class of substances designated as pseudo acids, however, ionization and neutralization proceed at a much slower rate, and in certain cases can be followed kinetically.

This difference in rates of protolytic transfer has been employed by Hantzsch[2] to define a pseudo acid as a substance whose salt formation is a function of time, as against the acid whose neutralization is essentially instantaneous. He states, further, that "if the salt formation is a function of the time, then it is evidence that the molecule undergoes a change in the salt formation process; it is also evidence for the fact that the undissociated substance and its ions are constitutionally different."

As a class, the primary and secondary nitroparaffins have long been recognized as pseudo acids. Ley and Hantzsch[3] have postulated that the primary and rate determining step in the neutralization of a nitroparaffin by a base is the isomerization of the nitro to the aci form, with subsequent rapid neutralization of the latter, *i. e.*

$$RCH_2NO_2 + B \xrightarrow[k_1]{} RCH{=}NOOH + B \xrightarrow[k_2]{} RCH{=}NOO^- + BH^+ \quad (1)$$

and $k_1 << k_2$. In this mechanism the sequence of transformations is nitroparaffin → undissociated aci acid → aci ion. However, Pedersen[4] has shown that this view is inconsistent with present ideas of acid–base catalysis as outlined by Brönsted.[5] The isomerization of a nitroparaffin must be considered a prototropic process, and as such it cannot take place spontaneously, but must involve the intermediary of an acid or basic catalyst. In conformity with this view he actually found the isomerization of nitromethane to the aci form to be a reaction subject to general base catalysis.[4] He consequently postulated as the mechanism of neutralization

$$RCH_2NO_2 + B \xrightarrow[k']{} RCH^-{\cdot}NO_2 + BH^+ \xrightarrow[k']{} RCH{=}NO_2^- + BH^+ \quad (2)$$

i. e., the nitro form donates a proton to the base, and the residue is converted rapidly by an electron shift to the ion. Thus $k_1' << k_2'$, and is rate determining. The aci ion may associate under the proper conditions, to form the aci acid. In this scheme the sequence is nitroparaffin → aci ion → aci acid.

Pedersen's formulation of the mechanism of isomerization of the nitroparaffins has been accepted by Junell,[6] Wynne-Jones,[7] and Reitz,[8] and will be employed to explain the results of this paper.

Following Hantzsch and Veit's[9] orienting semi-quantitative conductivity measurements, Junell[6] studied in H_2O at 0° the neutralization by sodium hydroxide of nitromethane, nitroethane, nitropropane, and nitroisopropane by a modification of

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[2] Hantzsch, *Ber.*, **32**, 575–600 (1899).

[3] Ley and Hantzsch, *ibid.*, **39**, 3149 (1906).

[4] Pedersen, *Det. Kgl. Vidensk. Selskab., Math.-fys. Medd.*, **12**, 1–16 (1932) (in English).

[5] Brönsted, *Chem. Rev.*, **5**, 231 (1928).

[6] Junell, (a) *Arkiv Kemi*, **11B**, No. 34 (1934); (b) *Svensk Kem. Tid.*, **46**, 125–136 (1934); (c) Dissertation, Uppsala, 1935.

[7] Wynne-Jones, *J. Chem. Phys.*, **2**, 381–385 (1934).

[8] Reitz, *Z. physik. Chem.*, **A176**, 363–387 (1936).

[9] Hantzsch and Veit, *Ber.*, **32**, 607–627 (1899).