Adiabatic Compressibility of Aqueous Solution. II. Amino Acids, Amides and related Compounds*

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by

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The ultrasonic investigation of aqueous solution of amino acids, amides and related compounds will be presented in this paper, in continuation of the previous study of organic acids.[1] As has been reported previously, the adiabatic compressibility of aqueous solution, obtained by measuring ultrasonic velocity, gives much informations about the interactions between solute molecules and those of water.

In addition to a number of investigations in this field carried out in Japan, which were referred to in the previous paper, several studies have been reported in foreign literatures. The first application of ultrasonics to

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1) Y. Miyahara, This Bulletin, **25**, 326 (1952).

the study of solvation was reported by Passynsky.[2] He estimated the amount of hydrated water of strong electrolytes,[2] non-electrolytes[3] and colloids[4] in his series of investigations. He assumed that the volume of the incompressible part of the solution, obtained from the ratio of compressibilities of solution and solvent, corresponds to the solvation volume. However, since this volume included that of the solute molecule, as is shown by the comparison of his equation with ours, which has been reported in the previous paper, the stated assumption could not fully be accepted.

More recently, Jacobson[5] has studied the liquid mixtures, aqueous solution of non-electrolytes, amino acids and proteins. His treatment was based on the same picture as that adopted by us, and he introduced a correction term in his equation of compressibility of solution, representing the effects of electrostriction and of breaking of hydrogen bond of surrounding water by inserted solute molecules.

On the other hand, Gucker and co-workers[6] treated this problem from an entirely different viewpoint in their study on amino acids solutions. Their investigation was based on Kirkwood's theories of mutual interaction and solvation of zwitter ion. This may also be another important way to attack this problem.

Experimental

The velocity of ultrasonic waves in solution was measured with an ultrasonic interferometer and has been briefly described in the previous paper. The details shall be presented herein. The sectional diagram of the interferometer is shown in Fig. 1. The reading scale on which the reflector is carried was part of a commercial sliding type traveling micrometer (Shimazu Scientific Co.). This scale was furnished with a vernier, graduated to 1/100 mm. The essential part of the cell was made of brass, coated with silicone resin, NS NO. 150. The crystal was cemented with the same resin. As has been shown in the wiring diagram in the previous paper, the single-tube oscillator was used to drive the crystal of the interferometer. Hence, the frequency of ultrasonic waves varied markedly in the vicinity of the points at which standing waves occured. In order to obtain the wave length at a definite frequency, the reading was made at a moment when the current flowing in the microammeter was at a minimum and the beat frequency

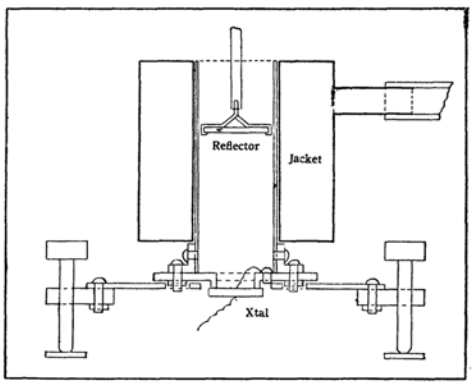
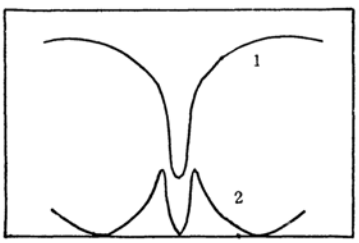


Fig. 1.



Position of Reflector

Fig. 2.

1.....Current
2.....Beat frequency

became zero. This condition was secured by a manual adjustment for each measurement run. The relations between beat frequency, current dips and position of reflector thus adjusted are shown in Fig. 2. By these methods the frequency of ultrasonics when standing waves were set up, could be adjusted to the standard. The frequency of a commercial radio station, JOAR, 1090KC. was used as a standard, and beats were detected with a superheterodyne radio receiver. The resonance frequency of the X-cut crystal used was 1270 KC. The temperature of the cell was held constant by circulating water from a thermostat through a jacket around the interferometer. The velocity measurements were made at 30.0°C.

The materials investigated were as follows;

2) A. Passynsky, *Acta Physicochim.* U.R.S.S., **11**, 606(1938).
3) A. Passynsky, *Acta Physicochim.* U.R.S.S., **22**,137(1947).
4) A. Passynsky, Acta Physicochim. U. R. S. S., **22**, 263 (1947).
5) B. Jacobson, *Arkiv För Kemi*, **2**, 177 (1950).
6) F. T. Gucker, F. W. Lamb, G. A. Marsh and R. M. Haag, *J. Am. Chem. Soc.*, **72**, 310 (1950).

Material	Source	Original Purity	Times of Recrystallization
Urea		c.p.	3
Thiourea		c.p.	3
Urethan		c.p.	3
Urotropine	Takeda	c.p.	1
Creatinine	Fisher	c.p.	0
Glycine	E. Merk	g.p.	0
α-Alanine	Ishizu	g.p.	1
L-Leucine	Takeda	c.p.	1
DL-Valine	Matheson	c.p.	1
DL-Methionine	Takeda	c.p.	1
L-Proline	Takeda	c.p.	1

Results and Discussion

The experimental results of ultrasonic velocity and other related values are given in Tables 1-11. The notations used are as follows;

c .....ultrasonic velocity in solution,
c_0.....ultrasonic velocity in water,
V_0 ...apparent volume of water in solution defined as

$$V_0=(D_s-x)/D_w$$

x .....concentration of solute in gram per cc. solution,
D_s.....density of solution at 30°C.,
D_w ...density of water at 30°C.,
K.....defined as

$$K=V_0-\kappa/\kappa_0$$

κ .....adiabatic compressibility of solution,
κ_0 ...adiabatic compressibility of water.

The physical meanings were explained in the previous paper.

Table 1
Urea

No.	x	c/c_0	κ/κ_0	V_0	K
1	0.0303	1.0082	0.9759	0.9778	0.0019
2	0.0312	1.0083	0.9758	0.9769	0.0011
3	0.0333	1.0090	0.9738	0.9754	0.0016
4	0.0386	1.0102	0.9701	0.9715	0.0014
5	0.0426	1.0111	0.9674	0.9684	0.0010

Table 2
Thiourea

No.	x	c/c_0	κ/κ_0	V_0	K
1	0.0330	1.0070	0.9776	0.9758	−0.0016
2	0.0294	1.0065	0.9793	0.9785	−0.0008
3	0.0354	1.0082	0.9747	0.9740	−0.0007
4	0.0355	1.0077	0.9755	0.9740	−0.0015
5	0.0342	1.0072	0.9769	0.9750	−0.0019
6	0.0300	1.0064	0.9795	0.9780	−0.0015

Table 3
Urethan

No.	x	c/c_0	κ/κ_0	V_0	K
1	0.0294	1.0076	0.9818	0.9739	−0.0079
2	0.0350	1.0091	0.9781	0.9691	−0.0090
3	0.0324	1.0086	0.9794	0.9713	−0.0081
4	0.0339	1.0090	0.9785	0.9699	−0.0086
5	0.0332	1.0089	0.9790	0.9704	−0.0086

Table 4
Urotropine

No.	x	c/c_0	κ/κ_0	V_0	K
1	0.0195	1.0046	0.9871	0.9844	−0.0027
2	0.0180	1.0042	0.9881	0.9857	−0.0024
3	0.0180	1.0044	0.9877	0.9857	−0.0020
4	0.0202	1.0044	0.9871	0.9840	−0.0031

Table 5
Creatinine

No.	x	c/c_0	κ/κ_0	V_0	K
1	0.0192	1.0059	0.9836	0.9857	0.0021
2	0.0213	1.0066	0.9816	0.9841	0.0025

Table 6
Glycine

No.	x	c/c_0	κ/κ_0	V_0	K
1	0.0301	1.0131	0.9622	0.9824	0.0202
2	0.0116	1.0052	0.9850	0.9932	0.0082
3	0.0155	1.0069	0.9801	0.9910	0.0109
4	0.0192	1.0088	0.9746	0.9891	0.0145

Table 7
α-Alanine

No.	x	c/c_0	κ/κ_0	V_0	K
1	0.0289	1.0135	0.9646	0.9803	0.0157
2	0.0324	1.0152	0.9605	0.9777	0.0172

Table 8
L-Leucine

No.	x	c/c_0	κ/κ_0	V_0	K
1	0.0144	1.0075	0.9826	0.9882	0.0056
2	0.0153	1.0083	0.9809	0.9875	0.0069
3	0.0110	1.0059	0.9863	0.9911	0.0048

Table 9
DL-Valine

No.	x	c/c_0	κ/κ_0	V_0	K
1	0.0201	1.0103	0.9754	0.9844	0.0090
2	0.0132	1.0070	0.9832	0.9898	0.0066
3	0.0202	1.0109	0.9741	0.9844	0.0103

Table 10
DL-Methionine

No.	x	c/c_0	κ/κ_0	V_0	K
1	0.0101	1.0040	0.9892	0.9929	0.0037
2	0.0101	1.0040	0.9891	0.9930	0.0039
3	0.0191	1.0076	0.9794	0.9865	0.0071
4	0.0163	1.0062	0.9832	0.9883	0.0051

Table 11
L-Proline

No.	x	c/c_0	κ/κ_0	V_0	K
1	0.0160	1.0068	0.9820	0.9886	0.0066
2	0.0190	1.0073	0.9802	0.9865	0.0063

The molar value, K_m of the respective substances, which is calculated by the method of least squares assuming that it is independent of concentration, is also listed in Table 12 and Table 13, as well as those calculated from the data of Passynsky, Jacobson and Gucker. K_m is defined as

$$K_m = MK/x$$

where M is the molecular weight; it is related to the commonly used apparent compressibility by the following equation:

$$K_m = -\Phi/\kappa_0$$

where Φ is defined as

$$\Phi = (1000/c)\kappa - (1000D_s/c - M)\kappa_0/D_w$$*

(1) Amides and Related Compounds—The influences of the radicals which directly interact with the surrounding water molecules upon the values of K_m were studied quantitatively in the previous paper, and it was shown that the values of K_m could be expressed as the sum of $K_{m,r}$ assigned to the individual radicals for a series of homologous molecules.

This additive law does not hold strictly in the present case which includes various types of molecules. However, the qualitative tendency may still remain; negative values for those of hydrophobic radicals, such as methylene and thioketone could also be assigned. The effects of radicals such as acid amides and non-ionic amines are relatively small, in marked contrast to those of amino radicals in amino acids.

(2) Amino Acids—In spite of the fact that the various amino acids investigated had alkyl chains of different lengths, which would reduce K_m to negative values, it was found that K_m was almost constant for the various compounds.

This may be interpreted as follows: the magnitude of the effect of metheylene radicals on K_m is very small as compared with that of ionized groups. Therefore it may not

Table 12
K_m

	30°C*	25°[6]	20°[5]	20°[3]
Urea	2.3			2.0
Thiourea	−3.1			
Urethan	−23			
Urotropine	−19			
Creatinine	13			
Glycolamide		−6.0	2.0	
Lactamide		−9.5	−5.4	

Table 13
K_m

	30°*	25°[6]	20°[5]	20°[3]
Glycine	52	60	60	58
α-Alanine	48	59	58	60
β-Alanine		61	60	
L-Leucine	56			
DL-Valine	56			
DL-Methionine	53			
L-Proline	42			

be illogical to suspect that when a molecule has hydrophobic radicals such as methylene radicals together with ionic groups, the effect of the former on K_m is entirely masked by the strong electrical force of the latter, since the weak interaction between such hydrophobic radicals and the surrounding water molecules are non-electrical in nature.

Assuming that the water in the nearest vicinity of the zwitter ion becomes incompressible by the strong electrostatic force, as in the case of strong electrolytes, the amount of hydrated water is found to be about 54 g./mol., or three molecules per on pair of zwitter ion. This values may be some measure of hydration of zwitter ion in comparison with that of strong electrolytes.

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* c . . . mole per 1000 cc. solution

* Present data