Adiabatic Compressibility of Aqueous Solution. I. Dicarboxylic and Oxycarboxylic Acid*

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In a series of investigations, carried out in this laboratory(1)(2) and elsewhere,(3)(4)(5)(6) concerning the ultrasonic velocity measurement of aqueous solution, it has been shown that the adiabatic compressibility of solution is intimately related to the hydration of solute. The present study concerns the results obtained with dicarboxylic and oxycarboxylic acid solution.

Experimental

The ultrasonic velocity was measured by an ultrasonic interferometer. The wiring diagram is shown in Fig. 1. The frequency of ultrasonics was 1090 KC. The constant frequency applied during each measurement was obtained by adjusting it to the same frequency of commercial radio (JOAR) by heterodyne method. The diameter and resonance frequency of X-cut crystal used were 20 mm. and 1270 KC respectively. The precision of each measurement of sound velocity was ±0.02 percent.

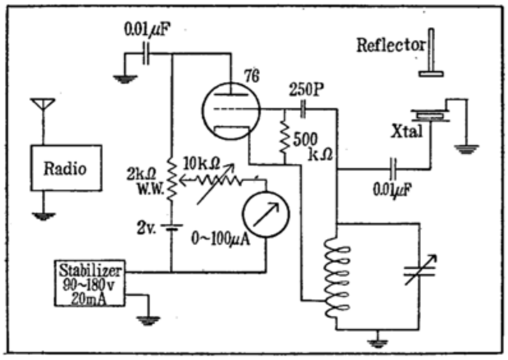

Fig. 1.

The materials used were recrystalized from G. P. or E. P. grade chemicals in trade.

Results and Discussion

As has been well known, adiabatic compressibility is related to sound velocity in the following formula;

$$\kappa=\frac{1}{Dc^2} \qquad (1)$$

where D and c are density and velocity of sound respectively. And as reported in the previous paper (see appendix), we have the following relations between compressibility and hydration;

$$K\equiv V_0-\frac{\kappa}{\kappa_0}=v_h\left(\frac{D_h}{D_0}-\frac{\kappa_h}{\kappa_0}\right) \qquad (2)$$

$$V_0=\frac{D_s-x}{D_0} \qquad (3)$$

where we set up the following notations;

κ ····adiabatic compressibility of solution,
κ_h ····adiabatic compressibility of hydrated water,
κ_0 ····adiabatic comressibility of water,
v_h ····volume of hydrated water in 1 cc. of solution,
D_h ····density of hydrated water,
D_0 ····density of water,
D_s ····density of solution,
x ····concentration of solute in gram per 1 cc. solution.

For a mole of solute, we have

$$K_m=\frac{KM}{x}=v_h'\left(\frac{D_h}{D_0}-\frac{\kappa_h}{\kappa_0}\right) \qquad (4)$$

where M is molecular weight, v_h' the volume of hydrated water per mole of solute.

The obtained values of c/c_0 (where c_0 is sound velocity in water), κ/κ_0, V_0 and K at 20°C. are given in Table 1~8.

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(3) Y. Wada, G. Shinpo, M. Oda and J. Nagumo, Oyo butsuri (*J. Applied Phys. Japan*), **17** 257 (1948).

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(5) T. Yasunaga and T. Sasaki, *J. Chem. Soc, Japan*, **72**, 366 (1951).

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Table 1
Malonic Acid

No.	x g./cc.	c/c_0	κ/κ_0	V_0	K
1	0.0351	1.0047	0.9782	0.9776	−0.0006
2	0.0462	1.0062	0.9715	0.9705	−0.0010

Table 2
Succinc Acid

No.	x g./cc.	c/c_0	κ/κ_0	V_0	K
1	0.0274	1.0050	0.9822	0.9806	−0.0016
2	0.0384	1.0066	0.9756	0.9732	−0.0024
3	0.0302	1.0054	0.9803	0.9790	−0.0013

Table 3
Glutaric Acid

No.	x g./cc.	c/c_0	κ/κ_0	V_0	K
1	0.0347	1.0076	0.9766	0.9739	−0.0027
2	0.0254	1.0053	0.9834	0.9809	−0.0025

Table 4
Oxalic Acid

No.	x g./cc.	c/c_0	κ/κ_0	V_0	K
1	0.0392	1.0030	0.9761	0.9793	0.0032
2	0.0260	1.0020	0.9838	0.9864	0.0026
3	0.0361	1.0028	0.9780	0.9806	0.0026
4	0.0265	1.0021	0.9832	0.9863	0.0031
5	0.0288	1.0022	0.9822	0.9849	0.0027

Table 5
Tartaric Acid

No.	x g./cc.	c/c_0	κ/κ_0	V_0	K
1	0.0481	1.0095	0.9608	0.9732	0.0124
2	0.0290	1.0053	0.9770	0.9838	0.0068
3	0.0286	1.0054	0.9772	0.9838	0.0066
4	0.0397	1.0076	0.9682	0.9777	0.0095

Table 6
Citric Acid

No.	x g./cc.	c/c_0	κ/κ_0	V_0	K
1	0.0336	1.0053	0.9764	0.9798	0.0034
2	0.0475	1.0079	0.9657	0.9719	0.0062
3	0.0308	1.0048	0.9784	0.9816	0.0032
4	0.0357	1.0057	0.9749	0.9785	0.0036

Table 7
Malic Acid

No.	x g./cc.	c/c_0	κ/κ_0	V_0	K
1	0.0081	1.0014	0.9942	0.9949	0.0007
2	0.0336	1.0058	0.9763	0.9789	0.0026
3	0.0264	1.0045	0.9815	0.9834	0.0019

Table 8
Maleic Anhydride

No.	x g./cc.	c/c_0	κ/κ_0	V_0	K
1	0.0397	1.0054	0.9763	0.9736	−0.0027
2	0.0420	1.0056	0.9752	0.9721	−0.0031
3	0.0488	1.0069	0.9704	0.9677	−0.0027

When a molecule has several radicals which interact with surrounding water molecules, K_m may be represented by the sum of each component of individual radical;

$$K_m=\sum_{r} K_{m,r} \qquad (5)$$

To testify this we would chose the values of $K_{m,r}$ for each radical rather arbitrarily as are shown in Table 9. In Table 10, the calculated values of K_m using these $K_{m,r}$ values are given. The coincidence between the experimental and calculated values are fairly good except in the case of citric acid.

Table 9

Radical	$K_{m,r}$
$-OH$	9.5
$-CH_2-$	−7.5
$-COOH$	4.0

Table 10

Acid	OH	CH_2	COOH	K_m cal.	K_m obs.
Malonic	0	1	2	0.5	−2.0
Succinic	0	2	2	−7.0	−6.6
Glutaric	0	3	2	−14.5	−11.2
Oxalic	0	0	2	8.0	8.0
Malic	1	1	2	10.0	10.1
Tartaric	2	0	2	27.0	37
Citric	1	2	3	6.5	21
Maleic anh.	—	—	—	—	−6.3
Glucose	5	1	0	>40.0	44(1)

It is interesting that the value of $K_{m,r}$ of methylene radical is shown as negative. It means rather formally from (4) that;

$$\frac{D_h}{D_0}<\frac{\kappa_h}{\kappa_0} \qquad \text{for } -\mathrm{CH_2}- \qquad (6)$$

However, it is not intended here to discuss the physical meaning of each term in (4) quantitatively. To state qualitatively, it is certain that the negativity of $K_{m,r}$ may be attributed to the hydrophobic nature of methylene radical.

Appendix

Compressibility of diluted aqueous solution.(1)(3)

The volume of solution V, containing x_g solute, may be represented by the sum of volume of solute in the solution v_m, of hydrated water v_h and of non-affected water V_0';

$$V=V_0'+v_m+v_h \qquad (1a)$$

If we assume that compressibility of such solution is represented by the sum of that of each component in their volume ratio, we have;

$$\kappa = \frac{V_0'}{V}\kappa_0 + \frac{v_m}{V}\kappa_m + \frac{v_h}{V}\kappa_h \qquad (2a)$$

where κ_m is compressibility of solute molecule.

For one cc. of solution (2a) becomes

$$\frac{\kappa}{\kappa_0} = V_0' + v_m\frac{\kappa_m}{\kappa_0} + v_h\frac{\kappa_h}{\kappa_0} \qquad (3a)$$

and

$$V_0' = 1 - v_m - v_h \qquad (4a)$$

In terms of density, (4a) takes the form

$$D_0V_0' = D_s - D_mv_m - D_hv_h \qquad (5a)$$

and as

$$v_mD_m = x \qquad (6a)$$

(3a) becomes

$$\frac{D_s - x}{D_0} - \frac{\kappa}{\kappa_0} = v_h\left(\frac{D_h}{D_0} - \frac{\kappa_h}{\kappa_0}\right) - v_m\frac{\kappa_m}{\kappa_0} \qquad (7a)$$

For a molecular solution, the compressibility of the molecule can be assumed to be zero, and we obtain (2).

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