ADIABATIC COMPRESSIBILITY OF AQUEOUS SOLUTION OF INORGANIC ACID*

BY

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1. Introduction

The author recently investigated the ultrasonic sound velocity and the adiabatic compressibility of aqueous solution of H_2SO_4 (1, 2). This time the ultrasonic velocities of the aqueous solutions of HCl and HNO_3 were measured and the adiabatic compessibilities were computed from them. We report here the procedure to derive an empirical formula for adiabatic compressibility of inorganic acid by the use of Gucker-Bachem's theory (3, 4).

2. Outline of Gucker-Bachem's theory

We define *the apparent molal volume* by the following equation:

$$\phi(V_2) = \frac{V - V_1}{n_2}, \qquad (1)$$

where V_1 [cm³] is the volume of pure water and V the volume of the solution when n_2 mole of a solute is dissolved in V_1. If c is the molal concentration of the solution, we have

$$V = \frac{n_2}{c} \times 1000. \qquad (2)$$

If d and d_1 are the density of the solution and that of the water respectively and M_2 is the molecular weight of the solute, we get, by the relation between masses,

$$V_1 d_1 = Vd - n_2 M_2. \qquad (3)$$

Substituting V and V_1 as obtained from (2) and (3) in Eq. (1), we get

$$\phi(V_2) = \frac{1000}{c}\left(1 - \frac{d}{d_1}\right) + \frac{M_2}{d_1}. \qquad (4)$$

The right-hand side of this equation consists of measurable quantities.

Next, we define *the apparent molal compressibility* by

$$\phi(K_2) = \frac{\left(-\dfrac{\partial V}{\partial p}\right) - \left(-\dfrac{\partial V_1}{\partial p}\right)}{n_2}, \tag{5}$$

where p denotes pressure. If β and β_1 are the adiabatic compressibilities of the solution and the water respectively, they are defined as:

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right), \quad \beta_1 = -\frac{1}{V_1}\left(\frac{\partial V_1}{\partial p}\right).$$

So, Eq. (5) can be converted into the form:

$$\phi(K_2) = \frac{\beta V - \beta_1 V_1}{n_2}.$$

By the use of Eqs. (2) and (3), we obtain

$$\phi(K_2) = \beta\frac{1000}{c} - \frac{\beta_1}{d_1}\left(\frac{1000\,d}{c} - M_2\right). \tag{6}$$

The right-hand side of this equation consists also of measurable quantities.

By Gucker, Bachem and others, the following formulae were empirically established for aqueous solutions of strong electrolytes:

$$\phi(V_2) = \phi^0(V_2) + S_v c^{1/2}, \tag{7}$$

$$\phi(K_2) = \phi^0(K_2) + S_k c^{1/2}. \tag{8}$$

Here, $\phi^0(V_2)$, $\phi^0(K_2)$, S_v and S_k are constants.

From Eqs. (4), (6), (7) and (8), we can get the expression for the adiabatic compressibility as:

$$\beta = \beta_1 + Ac + Bc^{3/2}, \tag{9}$$

with

$$\left.\begin{aligned}
10^3 A &= \phi^0(K_2) - \beta_1 \phi^0(V_2), \\
10^3 B &= S_k - \beta_1 S_v.
\end{aligned}\right\} \tag{10}$$

Our problem is to ascertain whether Eqs. (7) and (8) hold for aqueous solutions of inorganic acids and, if so, to obtain an experimental formula for β by calculating the constants A and B.

3. Treatment of experimental data

The ultrasonic velocities V and the densities d of $(HCl)_{aq}$, $(HNO_3)_{aq}$, and $(H_2SO_4)_{aq}$ at 30°C were measured at several concentrations, and the adiabatic compressibilities were calculated by $1/dV^2$. The results are tabulated in Appendix.

I. Case of HCl

The apparent molal volume $\phi(V_2)$ and the apparent molal compressibility $\phi(K_2)$

were calculated by Eqs. (4) and (6), and are plotted against $\sqrt{c}$ in Fig. 1 (a) and (b). Although the points in the figure are somewhat scattered, we can obtain respective straight lines by the method of least squares. Namely,

$$\phi(V_2) = 18.06 + 1.062\, c^{1/2}, \tag{11}$$

and
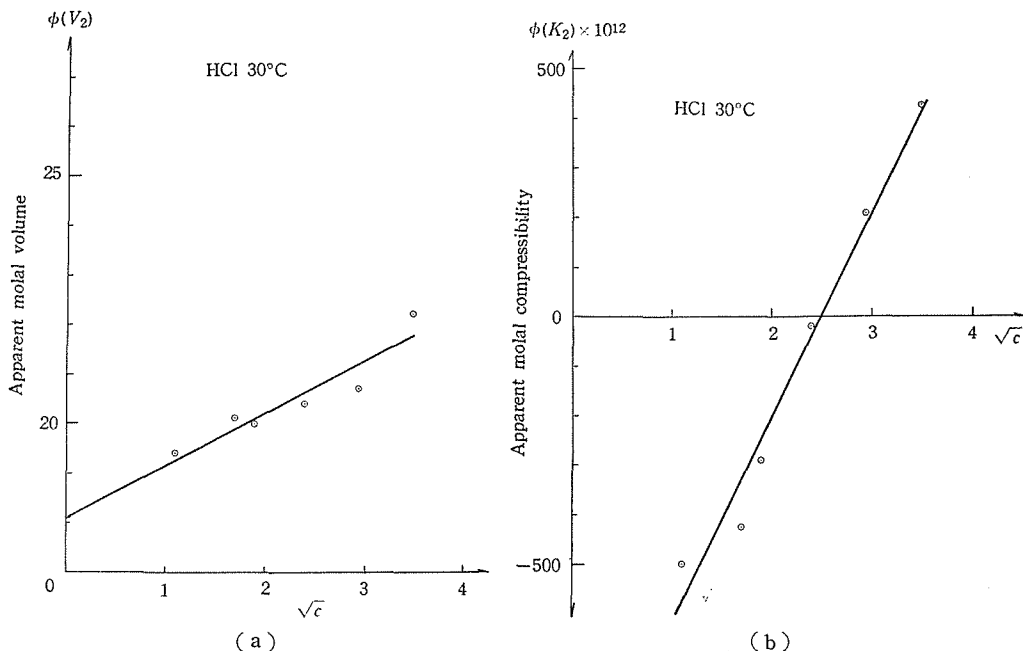$$10^{12}\phi(K_2) = -1028 + 409.7\, c^{1/2}. \tag{12}$$

Fig. 1. Apparent molal volume and apparent molal compressibility *versus* square root of concentration in the case of $(HCl)_{aq}$.

Calculating the constants A and B by (10) using four coefficients in Eqs. (11) and (12), we obtain

$$10^{12}\beta = 44.11 - 1.825\, c + 0.3629\, c^{3/2}. \tag{13}$$

In Fig. 2 the compressibility-curve is drawn by the use of this formula. The measured values of β (as calculated from $1/dV^2$) are also shown and it will be seen that they coincide well with the calculated curve, the mean deviation being 0.5%. The velocity-curve is also drawn in the same figure. It has a maximum at about 4 mole.

II. Case of HNO_3

The $\phi(V_2)-\sqrt{c}$ curve and the $\phi(K_2)-\sqrt{c}$ curve of $(HNO_3)_{aq}$ are shown in Fig. 3 (a) and (b). $\phi(V_2)$ is constant when $\sqrt{c} < 2.2$ and varies linearly with $\sqrt{c}$ when $\sqrt{c} > 2.2$. Namely,
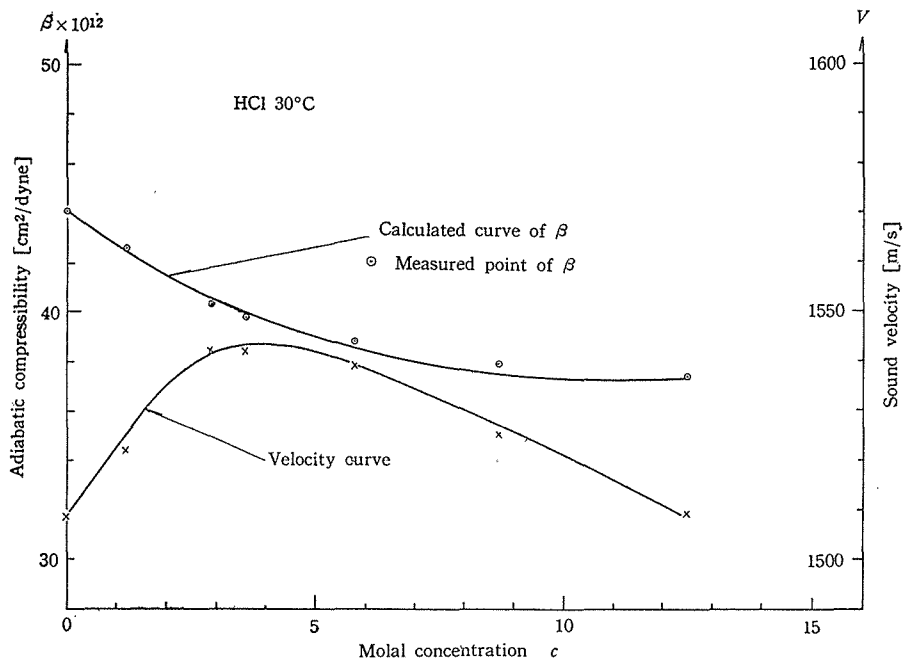
Fig. 2. Adiabatic compressibility and ultrasonic sound velocity *versus* concentration
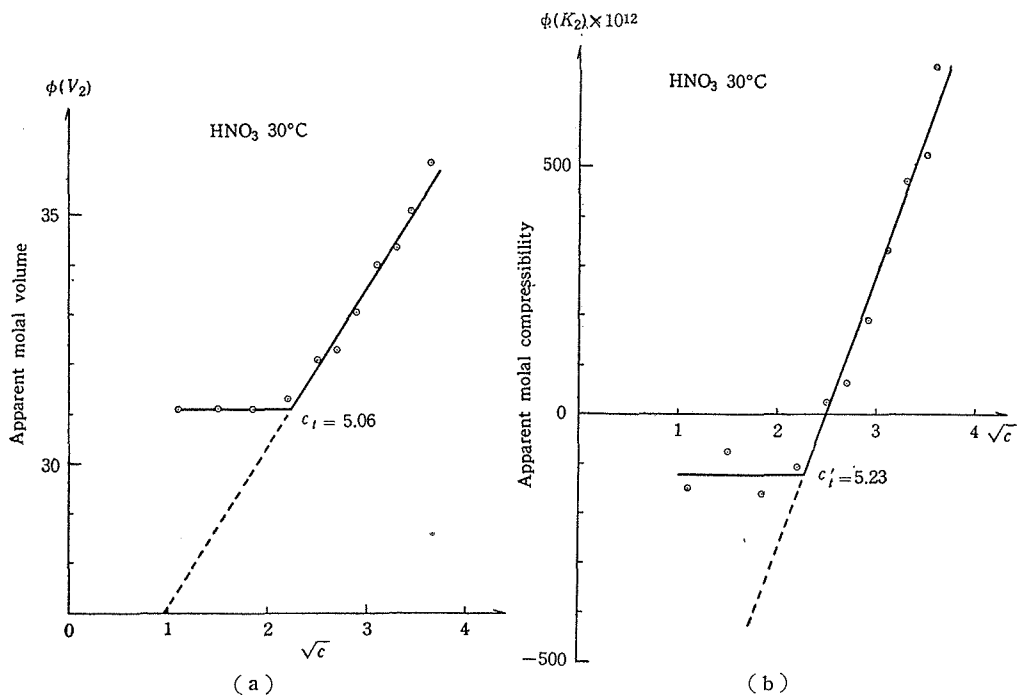in the case of $(HCl)_{aq}$.

Fig. 3. Apparent molal volume and apparent molal compressibility *versus* square root of
concentration in the case of $(HNO_3)_{aq}$.

$$\phi(V_2) = 33.10 \qquad \text{when } \sqrt{c} < 2.2, \qquad (14a)$$

and
$$\phi(V_2) = 23.87 + 3.223 \, c^{1/2} \qquad \text{when } \sqrt{c} > 2.2. \qquad (14b)$$

The concentration c_t at the transition point has been calculated to be 5.06 mole by equating (14a) and (14b).

$\phi(K_2)$ is considered to be constant when $\sqrt{c} < 2.3$ and varies linearly with $\sqrt{c}$ when $\sqrt{c} > 2.3$. That is,

$$10^{12}\phi(K_2) = -121.7, \qquad (15a)$$

and
$$10^{12}\phi(K_2) = -1401 + 559.2 \, c^{1/2}. \qquad (15b)$$

And the concentration c_t' at the transition point has been obtained as 5.23 mole.

Calculating A, B by using coefficients in Eqs. (14b) and (15b), we get

$$10^{12}\beta = 44.11 - 2.454 \, c + 0.4170 \, c^{3/2}. \qquad (16)$$

Since $\phi(V_2)$ and $\phi(K_2)$ are constant when $c < 5.06$, we get $S_k = S_v = 0$. Accordingly B becomes zero and we get a linear relation:

$$10^{12}\beta = 44.11 - 1.495 \, c. \qquad (17)$$

The concentration c_T at the transition point between (16) and (17) has been found to be 5.29 mole by equating both equations. In Fig. 4 the compressibility-curve is drawn
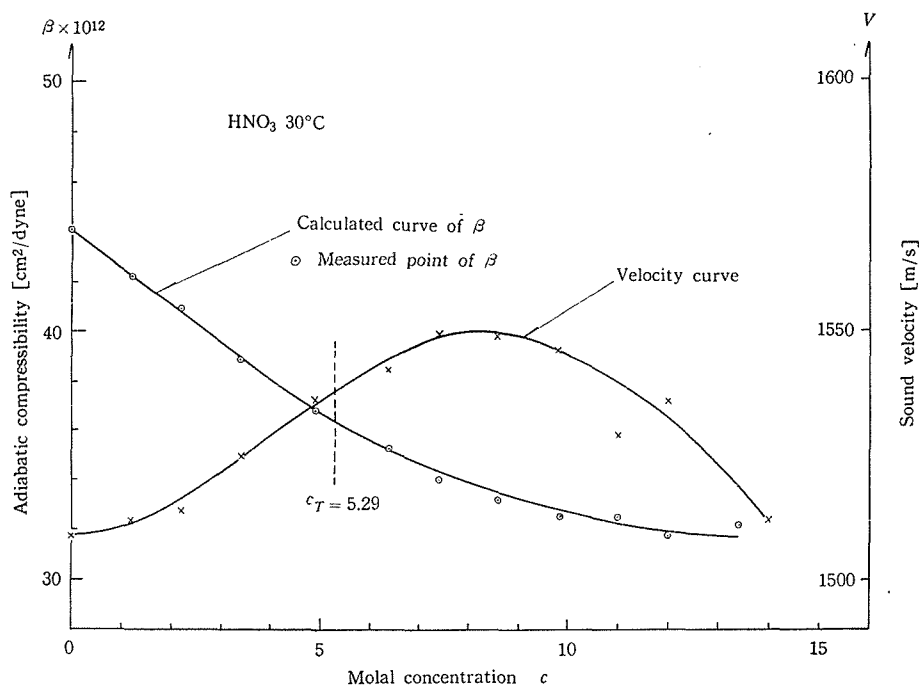

Fig. 4. Adiabatic compressibility and ultrasonic sound velocity *versus* concentration in the case of $(HNO_3)_{aq}$.

by the use of the formula (16) when $c > 5.29$ and of the formula (17) when $c < 5.29$. The measured values are also plotted and it is found that they coincide well with the calculated curve, the mean deviation being 0.4%. The velocity-curve is also drawn in the same figure. It has a maximum at about 8 mole.

III.   Case of H_2SO_4

The $\phi(V_2) - \sqrt{c}$ curve and the $\phi(K_2) - \sqrt{c}$ curve of $(H_2SO_4)_{aq}$ are shown in Fig. 5 (a) and (b). $\phi(V_2)$ varies linearly with $\sqrt{c}$ up to $\sqrt{c} = 3.8$, and deviates upward
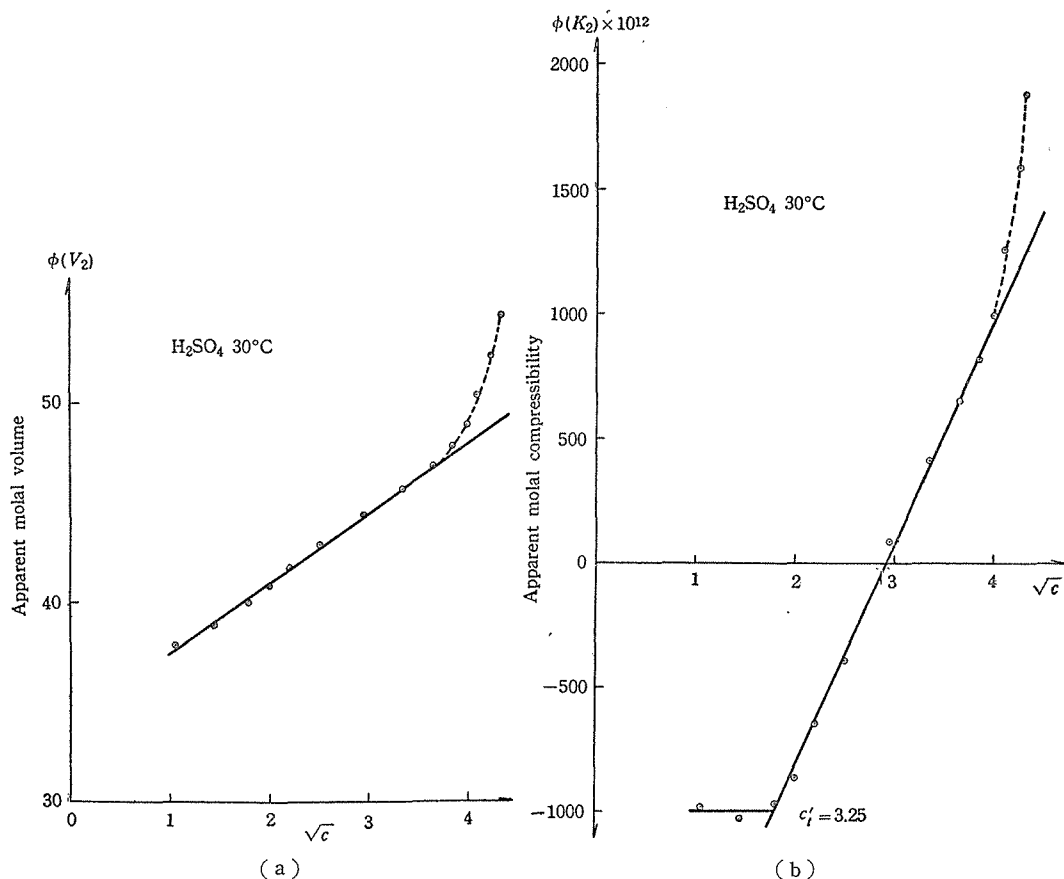
Fig. 5.   Apparent molal volume and apparent molal compressibility *versus* square root of concentration in the case of $(H_2SO_4)_{aq}$.

rapidly from the straight line when $\sqrt{c} > 3.8$. In the region of the straight line, we get

$$\phi(V_2) = 33.89 + 3.511\ c^{1/2}.\qquad\qquad (18)$$

$\phi(K_2)$ is constant when $\sqrt{c} < 1.8$ and varies linearly with $\sqrt{c}$ in the region $1.8 < \sqrt{c} < 4$ and deviates upward from the straight line when $\sqrt{c} > 4$. And we get

$$10^{12}\phi(K_2) = -994.3 \qquad\qquad \text{when } \sqrt{c} < 1.8, \qquad (19a)$$

$$10^{12}\phi(K_2) = -2609 + 895.6\ c^{1/2} \qquad \text{when } 1.8 < \sqrt{c} < 4. \quad (19b)$$

The concentration c_t', at the transition point, is 3.25 mole. In the region $1.8 < \sqrt{c} < 3.8$, we get from (18) and (19b):

$$10^{12}\beta = 44.11 - 4.104\ c + 0.7407\ c^{3/2}. \qquad (20)$$

Since S_k becomes zero when $\sqrt{c} < 1.8$, we obtain:

$$10^{12}\beta = 44.11 - 2.489\ c - 0.1548\ c^{3/2}. \qquad (21)$$

It should be noted that the coefficient of $c^{3/2}$ is negative in (21). When $\sqrt{c} > 3.8$, β cannot be expressed by any formula of this form.

In Fig. 6 the compressibility-curve is drawn by the formula (21) when $c < 3.25$ and by the formula (20) when $c > 3.25$. The measured values are also plotted and it is found that they coincide well with the calculated curve when $c <$ about 14 mole, the mean deviation being 0.4%, but they disagree with it beyond the concentration of 14 mole. Since the transition seems to occur at the minimum point of $\beta - c$ curve, the concentration c_T at the transition point can be calculated to be 13.63 mole by solving the equation $d\beta/dc = 0$ obtained from (20). Beyond the concentration of 13.63
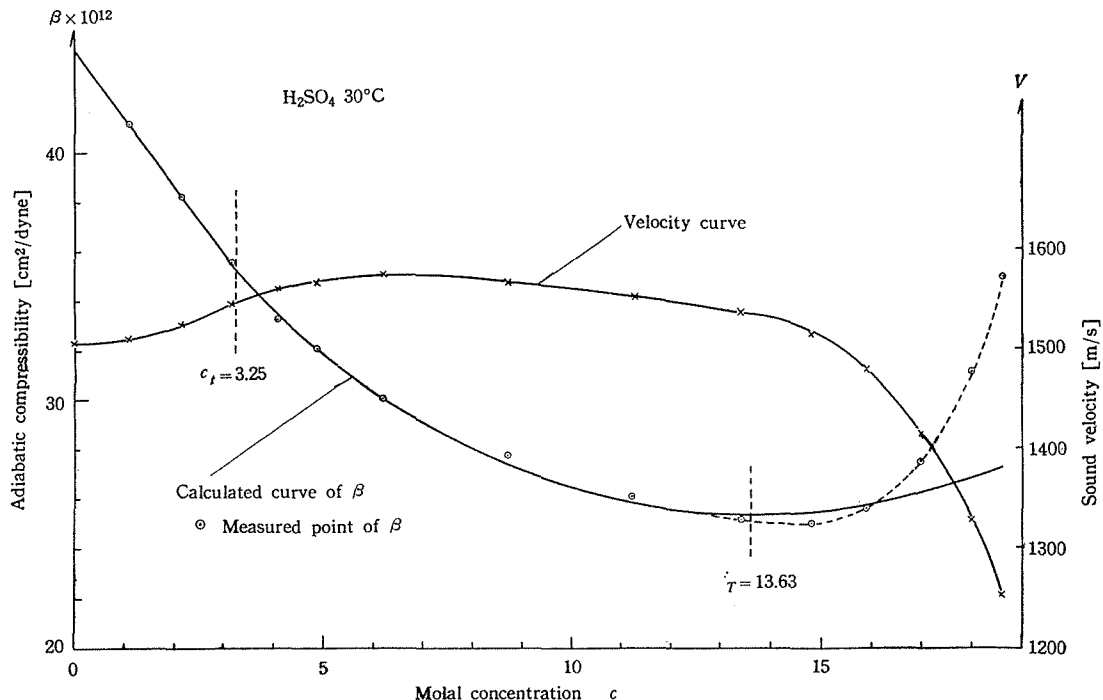

Fig. 6. Adiabatic compressibility and ultrasonic sound velocity *versus* concentration in the case of $(H_2SO_4)_{aq}$.

mole, the form of β has not yet been found. Consequently the form of β of $(H_2SO_4)_{aq}$ is divided into three parts. The velocity-curve is also drawn in the same figure and has a flat maximum which covers a wide range of concentration.

4. Summary and discussion

In Table I the coefficients of the experimental formulae which were obtained in the preceding section are summarized and compared with those given by Bhimasenachar and Subrahmanyam (5).

<p align="center">Table I. Coefficients of experimental formulae.</p>

	Present author (30°C)			Bhimasenachar-Subrahmanyam (27°C)		
	Range of concentration [mol]	$A \times 10^{12}$ [C.G.S.]	$B \times 10^{12}$ [C.G.S.]	Range of concentration [mol]	$A \times 10^{12}$ [C.G.S.]	$B \times 10^{12}$ [C.G.S.]
HCl	$0 < c < 12.5$	-1.825	$+0.3629$	$0 < c < 4.5$	-1.692	$+0.226$
HNO$_3$	$0 < c < 5.29$	-1.495	0.0000	$0 < c < 6.0$	-1.8097	$+0.1855$
	$5.29 < c < 13.4$	-2.454	$+0.4170$			
H$_2$SO$_4$	$0 < c < 3.25$	-2.489	-0.1548	$0 < c < 3.4$	-3.402	$+0.123$
	$3.24 < c < 13.6$	-4.104	$+0.7407$	$3.4 < c < 9.0$	-4.695	$+0.957$
	$13.6 < c$	undetermined				

Both groups of values almost coincide with each other to the first order. We want to point out that the measurement of Bhimasenachar and Subrahmanyam was done in a comparatively narrow range of concentration. They determined also the coefficients A and B by direct application of the method of least squares to the compressibility-curve, on the assumption that the formula (9) would fit the curve. For the purpose of finding the coefficients A and B, their method is appropriate, but our method is more fundamental and orthodox. Moreover, the following instance may confirm the superiority of our method. As the value of B of H_2SO_4 at lower concentration, the author obtained the value of -0.1548, while they gave a quite different value of $+0.123$. When we calculate the value of B by direct application of the method of least squares to $\beta - c$ curve, it occurs that B becomes negative when calculated from the first three data $(0 < c < 3.2)$ and positive when calculated from the first four data $(0 < c < 4.7)$. And there is no definite criterion to determine whether we should take the first three or the first four. But in the author's method, there is a definite reason why B should be negative, namely, that the $\phi(K_2)$ is constant when $c < 3.25$.

APPENDIX

I. HCl (30°C)

Conc. [mol]	Density [g/cm³]	Velocity [m/s]	Measured* $\beta_m \times 10^{12}$	Calculated** $\beta_c \times 10^{12}$	Deviation $\beta_m - \beta_c$
1.190	1.0161	1522	42.49	42.41	+0.08
2.905	1.0435	1542	40.30	40.60	−0.30
3.602	1.0552	1542	39.85	40.02	−0.17
5.798	1.0892	1539	38.75	38.59	+0.16
8.680	1.1331	1525	37.93	37.55	+0.38
12.48	1.1746	1509	37.38	37.33	+0.05

* β_m computed by the formula $1/dV^2$.
** β_c calculated by the experimental formula (13).

II. HNO₃ (30°C)

Conc. [mol]	Density [g/cm³]	Velocity [m/s]	Measured $\beta_m \times 10^{12}$	Calculated* $\beta_c \times 10^{12}$	Deviation $\beta_m - \beta_c$
1.245	1.0357	1512	42.23	42.25	−0.02
2.185	1.0658	1514	40.95	40.84	+0.11
3.416	1.1053	1525	38.89	39.00	−0.11
4.917	1.1522	1536	36.79	36.76	+0.03
6.362	1.1932	1542	35.24	35.19	+0.05
7.400	1.2243	1549	34.04	34.34	−0.30
8.614	1.2551	1549	33.21	33.51	−0.30
9.847	1.2831	1546	32.60	32.84	−0.24
11.06	1.3147	1529	32.54	32.30	+0.24
11.97	1.3322	1536	31.81	32.01	−0.20
13.39	1.3589	1512	32.19	31.68	+0.51

* β_c calculated by the experimental formulae (16) and (17).

III. H₂SO₄ (30°C)

Conc. [mol]	Density [g/cm³]	Velocity [m/s]	Measured $\beta_m \times 10^{12}$	Calculated* $\beta_c \times 10^{12}$	Deviation $\beta_m - \beta_c$
1.104	1.0623	1512	41.18	41.18	0.00
2.138	1.1228	1526	38.24	38.30	−0.06
3.163	1.1799	1546	35.46	35.37	+0.09
4.068	1.2296	1563	33.28	33.49	−0.21
4.860	1.2711	1567	32.04	32.10	−0.06
6.185	1.3395	1577	30.02	30.12	−0.10
8.710	1.4658	1567	27.78	27.40	+0.38
11.24	1.5871	1553	26.12	25.89	+0.23
13.37	1.6844	1536	25.17	25.46	−0.29
14.79	1.7429	1515	25.00	25.54	−0.54
15.93	1.7826	1480	25.61	25.82	−0.21
17.04	1.8113	1416	27.53	26.28	+1.25
18.04	1.8256	1327	31.10	26.82	+4.28
18.63	1.8231	1253	34.94	27.21	+7.73

* β_c calculated by the experimental formulae (20) and (21).

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