Stoichiometric Investigations of the Liquid State. III. The Relation between the Sound Velocity and the Chemical Structure. (3). Molar Sound Velocity and its Additivity for Associated Liquids

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Introduction

The author theoretically calculated the molar sound velocity of unassociated liquid and found its calculated value to be independent of temperature and to be satisfactorily consistent with the observed value[2]. Then, the author interpreted the additivity of the molar sound velocity and also showed that the calculated atomic or radical sound velocity was satisfactorily consistent with the observed one[3]. In this paper, results of the same analysis for associated liquids will be reported.

The Temperature Variation of the Molar Sound Velocity of Associated Liquids

According to the first paper, Rao's molar sound velocity, K, is expressed by the following equation.

$$K=\left[\frac{E_{\text{vap}}\gamma^{1/2}}{c(MRT)^{1/2}}\right]^{1/3} V \qquad (1)$$

The previous paper may be referred to about the meaning of notations in Eq. 1.

The temperature variation of K calculated from Eq. 1 is shown in Table I. There are few substances of which all values in Eq. 1 are complete. They are only water, methyl alcohol and ethyl alcohol. As the special case, the liquefied gas, oxygen and nitrogen, are also added in the table.

TABLE I

TEMPERATURE VARIANCE OF MOLAR SOUND VELOCITY OF ASSOCIATED LIQUID AND LIQUEFIED GAS

Temperature (°C)	E_{vap} (cal/mole)	ρ (g/cc)	K_{calc}
Water (M=18.0, γ=1.336)			
0	10170	1.000	1310
10	10050	1.000	1300
20	9920	0.998	1270
30	9800	0.996	1275
40	9700	0.992	1270
50	9570	0.988	1260
60	9460	0.983	1260
70	9340	0.978	1255
80	9210	0.972	1250
Methyl alcohol (M=32.04, γ=1.203)			
0	8540	0.810	2420
10	8450	0.801	2430
20	8350	0.791	2430
30	8220	0.782	2440
40	8080	0.772	2430
50	7950	0.763	2440
Ethyl alcohol (M=46.07 γ=1.13)			
0	9550	0.806	3380
10	9480	0.798	3390
20	9400	0.789	3395
30	9320	0.781	3405
40	9250	0.772	3410
50	9130	0.764	3420
Oxygen (M=32.00, γ=1.425)			
−210	306	1.272	978
−200	270.5	1.224	955
−190	234	1.176	926
−185	217	1.152	909
Nitrogen (M=28.02, γ=1.42)			
−203	192	0.843	1110
−201	184.5	0.834	1110
−199	177	0.824	1100
−197	170	0.815	1090

It is clear from the table that K of water, liquid oxygen and liquid nitrogen are considerably dependent on temperature, but K of alcohols are nearly independent of temperature like unassociated liquids. Weissler accurately measured the sound velocity in a number of alcohols and calculated the molar sound velocity on the bases of the definition, $K=u^{1/3}V$.[4] Then, he found that K of alcohols are independent of temperature, in contrast with water. This result is quite consistent with the above result of calculation.

In the calculation from Eq. 1, all values are observed ones except $C=2$. But whether $C=2$ or not is questionable. On trial, C was calculated from sound velocity by the following equation[2].

$$C=\frac{E_{\text{vap}}\gamma^{1/2}}{u(MRT)^{1/2}} \qquad (2)$$

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[2] K. Tyuzyo, This Bulletin, **27**, 300 (1954).

[3] K. Tyuzyo, This Bulletin, **27**, 303 (1954).

[4] A. Weissler, *J. Amer. Chem. Soc.*, **70**, 1634 (1948).

The calculated temperature variation of C is shown in Table II. It is clearer than in Table I that C of water, liquid oxygen, and liquid nitrogen are dependent on temperature but those of alcohols are almost constant.

TABLE II

TEMPERATURE VARIANCE OF PACKING NUMBER, C

temperature (°C)	C
water	
0	5.47
10	5.15
20	4.69
30	4.67
40	4.48
50	4.30
60	4.17
70	4.05
80	3.94
liquid oxygen	
−210	1.04
−200	0.93
−190	0.81
−185	0.76
liquid nitrogen	
−203	0.81
−201	0.79
−199	0.76
−197	0.73
methyl alcohol	
0	3.87
10	3.86
20	3.86
30	3.86
40	3.84
50	3.83
ethyl alcohol	
0	3.34
10	3.36
20	3.38
30	3.40
40	3.41
50	3.42

In Table III C-values at 20°C are shown for several associated liquids. The C-values in the third row are the calculated ones from vapor pressure by Eyring and others5). The values of C of water, ethylene glycol, and glycerol are much larger than 2, while on the contrary, C those of liquid oxygen and nitrogen, are much smaller than 2. However, in methyl and ethyl alcohol the value is much larger than 2, and the higher the alcohol, the smaller C becomes and its value converges to 2. For fatty acids C is generally 2 except formic and acetic acid. The above facts will be discussed later. Perhaps these are due to the difference in the associated state of the associated liquid.

TABLE III

PACKING NUMBER, C, OF ASSOCIATED LIQUIDS (20°C)

Substance	C	C from vapor pressure
water	4.69	—
ethylene glycol	3.17	—
glycerol	2.74	—
oxygen	0.93 (−200°C)	—
nitrogen	0.79 (−201°C)	—
mercury	—	0.21
methyl alcohol	3.86	0.43
ethyl alcohol	3.38	—
n-propyl alcohol	2.57	—
n-butyl alcohol	2.36	—
n-amyl alcohol	2.26	—
n-hexyl alcohol	2.16	—
n-heptyl alcohol	2.10	—
n-octyl alcohol	2.03	—
formic acid	1.46	—
acetic acid	1.51	—
n-propionic acid	1.72	—
n-butylic acid	2.17	—
n-valeric acid	2.04	—
n-caproic acid	1.94	—
n-heptylic acid	1.86	—
n-caprylic acid	1.82	—

The Calculated Values of Molar Sound Velocity

Table IV shows the calculated (C is put equal to 2) and observed molar sound velocity, K. K_{calc} of water, ethylene glycol, glycerol, oxygen, nitrogen, methyl alcohol, ethyl alcohol, formic acid, and acetic acid are considerably different from K_{obs}, but others are consistent with K_{calc}. (about 5% deviation).

TABLE IV

CALCULATED AND OBSERVED VALUES OF MOLAR SOUND VELOCITY, K

Substance	K_{calc}	K_{obs}	$K_{\mathrm{calc}}/K_{\mathrm{obs}}$
water	1070	955	1.198
ethylene glycol	3520	3020	1.167
glycerol	4700	4220	1.114
oxygen	955	1234	0.774
nitrogen	1110	1490	0.747
methyl alcohol	2430	1955	1.242
ethyl alcohol	3400	2860	1.188
n-propyl alcohol	3920	3720	1.053
n-butyl alcohol	4620	4625	0.999

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4) H. Eyring and J. Hirshfelder, *J. Phys. Chem.*, **41**, 249 (1937).

n-amyl alcohol	5300	5440	0.973
n-hexyl alcohol	6120	6380	0.958
n-heptyl alcohol	6950	7200	0.965
n-octyl alcohol	7630	8080	0.944
formic acid	1630	1905	0.857
acetic acid	2360	2780	0.850
n-propionic acid	3240	3650	0.888
n-butylic acid	4410	4530	0.974
n-valeric acid	5110	5430	0.942
n-caproic acid	5830	6300	0.927
n-heptylic acid	6550	7210	0.908
n-caprylic acid	7260	8090	0.899

Additivity of Molar Sound Velocity

According to the second paper of this series[3)], the molar sound velocity, K, is expressed as the sum of atomic or radical sound velocities, K_a. Namely,

$$K=\sum K_a \qquad (3)$$

$$K_a=5.42\times\left[\frac{\Delta E}{M_a^{1/2}}\right]^{1/3} V_a \qquad (4)$$

The previous paper may be referred to about the meaning of notations in Eq. 4.

Table V shows the radical sound velocities of hydrogen-bonding radicals calculated from Eq. 4. Generally, the calculated value is larger than the observed, but the deviation is not much larger than that of the normal radicals except amine-radical.

Table VI shows the calculated K using the valve of Table V and the observed one of associated liquids. The consistency is generally satisfactory. Perhaps, the fact that the deviations of $-CH_2-$ and $-OH$ radical compensate each other is the cause of this fact.

TABLE V

RADICAL SOUND VELOCITY OF HYDROGEN-BONDING RADICALS

radical	ΔE(cal/mole)[(6)]	M_a	V_a[(7)]	K_{acalc}	K_{aobs}	K_{acalc}/K_{aobs}
—OH	7250	17.0	13.3	869	773	1.124
—COOH	8970	45.0	32.1	1910	1633	1.170
—SH	4250	33.1	28.1	1308	—	—
—NH_2	3530	16.0	21.5	1116	842	1.325

TABLE VI

CALCULATED K AS THE SUM OF ATOMIC OR RADICAL SOUND VELOCITY AND OBSERVED ONES FOR ASSOCIATED LIQUIDS

substance	K_{obs}	K_{calc}	K_{calc}/K_{obs}	literature of K_{obs}
water	955	—	—	(8)
ethylene glycol	3020	3272	1.083	〃
glycerol	4220	—	—	〃
methyl alcohol	1955	2023	1.033	(4)
ethyl alcohol	2860	2790	1.011	〃
n-propyl alcohol	3720	3557	0.956	〃
n-butyl alcohol	4625	4324	0.935	〃
n-amyl alcohol	5440	5091	0.937	〃
formic acid	1905	—	—	(8)
acetic acid	2780	3064	1.101	〃
n-propionic acid	3650	3831	1.049	〃
n-butylic acid	4530	4600	1.014	〃
n-valeric acid	5430	5365	0.988	〃

Discussion

Summarizing the results of the previous sections.

(1) The calculated K of alcohols are almost independent of temperature, but that of water is remarkably dependent on temperature. This fact is clearer from the packing number, C. These results are censistent with the experimental results of Weissler. Below, for convenience, the associated liquids such as alcohols and fatty acids series are named as "the associated liquids of the first kind" and water, ethylene glycole, glycerol, etc. are named as" the associated liquids of the second kind."

(2) Packing number is much larger than 2 (normal value) for the associated liquids of the second kind, but is almost 2 for the asoociated liquids of the first kind except

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6) H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems," p. 144 (1950).

7) S. Glasstone, "Textbook of Physical Chemistry," p. 525 (1946).

8) L. Bergmann, "Der Ultraschall," p. 263 (1949).

the initial two members of the homologous series.

(3) The consistency of the calculated and observed K is unsatisfactory for the associated liquids of the second kind, but is satisfactory in those of the first kind except the initial two members of the homologous series.

(4) The calculated radical sound velocity is consistent with the observed value with the deviation of about 15% and the calculated molar sound velocity based on the additivity principle is satisfactorily consistent with the observed value in the associated liquids of the first kind. (Data for the associated liquids of the second kind are lacking, but the calculated value of K of ethylene glycol is consistent with the observed one).

Until now, methods of inferring the state of association of associated liquids from sound velocity were those of Lagemann[9] and van Itterbeek[10], but these are both unsatisfactory even qualitatively, as well as quantitatively. The results obtained in this paper are also not so striking, but it seems to be reasonable to divide the associated liquids into the first and the second kind. The author already showed that the associated liquids must be distinguished in the first and second kind by the analysis of the viscous flow[11]. It is a very interesting fact that this is also reasonable in the case of molar sound velocity. According to the author's opinion, it is probable that in the associated liquids of the second kind, there exist no clearly distinguishable associated units and they have a network structure as a whole, and their structures are remarkably deformable and also destroyed with the increase of temperature. In this case it is natural that molar sound velocity shows the several abnormalities as are shown above. On the other hand, in the associated liquids of the first kind, there exist clearly distinguishable associated units, and hydrogen bond connecting this unit is almost strong enough not to be influenced by temperature. Then, except the fact that the unit is large, the molecules of the associated liquids of the first kind are the same as the molecules of the normal liquids. Moreover, $E_{\mathrm{vap.}}$ V of Eq. 1 and ΔE, V_a of Eq. 4 contain already the factors of the associated state and so molar sound velocity has no abnormalities. Abnormalities of formic acid and acetic acid probably depend on the special type of association in the liquid state[11,12]. Abnormalities of methyl and ethyl alcohol can not be explained at present.

Lastly, among the methods of determining the state of association of the associated liquids, those methods are quite unsatisfactory which contain the energy of vaporization as an important factor; for example, surface tension, parachor[13] and sound velocity. In the energy of vaporization of the associated liquids, dissociation energy of associated units is contained in addition to the normal cohesive energy. Therefore, it seems to be very difficult to obtain any knowledge about the state of association from the vaporization phenomenon[14]. Those methods which use the properties of the liquids themselves such as viscosity are more effective than those which depend on the quantity of the equilibrium state of liquids and gases such as energy of vaporization for studying the state of association[11,12].

Summary

(1) Associated liquids are analysed with a method similar to that of the previous papers, and the temperature variation of molar sound velocity, comparison with experiment, calculation of the radical sound velocity, additivity, etc. are developed.

(2) It seems to be reasonable to distinguish the associated liquids to the first and second kind. This is consistent with the results of the author's investigation of the viscous flow.

(3) Something about the structure of the associated liquids of the first and second kind, and methods of investigating the state of association are discussed.

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[9] R. T. Lagemann, *J. Chem. Phys.*, **12**, 464 (1948).

[10] A. van Itterbeek and A. De Bock, *Nature*, **162**, 611 (1948).

[11] K. Tyuzyo, *Kolloid-Z.*, **131**, 40 (1953).

[12] K. Tyuzyo, The fourth and fifth paper of this series, to be published elsewhere.

[13] S. Sugden, "Parachor and Valency", Chap. VIII(1930).

[14] K. Tyuzyo, The sixth paper of this series, to be published elsewhere.