Stoichiometric Investigations of the Liquid State. II. The Relation between the Sound Velocity and the Chemical Structure. (2). The Additivity of the Molar Sound Velocity of Unassociated Liquids

By Kiyoshi TYUZYO[1]

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Introduction

According to the first paper of this series[2], Rao's molar sound velocity[3] ($K=u^{1/3}V$) is derived from the simple theory of the liquid state and the calculated molar sound velocity is independent of temperature. Furthermore, the calculated and observed molar sound velocities are coincident with each other with the accuracy of ±5%. The molar sound velocity, K, is expressed by the following equation from the theory,

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

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

Rao[4] found experimentally that K has the additive property. The additivity of K for normal unassociated liquids will be explained theoretically in this paper.

Calculation of "Atomic-" and Radical Sound Velocity"

If K has the additive property, it is reasonable to assume as follows on the basis of Eq. 1.

$$K=\Sigma K_{\mathrm{a}} \qquad (2)$$

$$K_{\mathrm{a}}=\frac{\gamma^{1/6}}{C^{1/3}(RT)^{1/6}}\left[\frac{\Delta E}{M_{\mathrm{a}}{}^{1/2}}\right]^{1/3}V_{\mathrm{a}} \qquad (3)$$

In Eq. 2 and 3, M_{a}, V_{a} mean the corresponding values for each constitutive atom or radical and ΔE is the energy of vaporization per each element. This value can be approximately substituted by the cohesive energy as shown below. K_{a} may be named as "atomic-" or "radical sound velocity". Lagemann and others[5] have already pointed out that the additivity of K does not completely hold but some constitutive effect is present. As K_{a} contains the packing number and energy factor (C, ΔE), so it is natural that some constitutive effect is present as long as C and ΔE-values are related with the intermolecular interaction. Here, the author does not enter into such a detailed discussion as the influence of intermolecular interaction but calculates only K-values as the first approximation.

Because the packing number and ratio of specific heats seem to be not so remarkably dependent on the species of molecules, and, moreover, because γ enters with the 1/6 power, C enters with the 1/3 power in Eq. 3, γ and C are put equal to 1.4 and 2 respectively. In the ordinary range of liquid (0～100°C), absolute temperature (T) is nearly 300～400° and furthermore, it enters in Eq. 3 with the 1/6 power, and so T is put equal to 300 approximately. Moreover, if ΔE and R are expressed in cal/mol, then Eq. 3 becomes the following.

$$K_{\mathrm{a}}=5.42\times\left[\frac{\Delta E}{M_{\mathrm{a}}{}^{1/2}}\right]^{1/3}V_{\mathrm{a}} \qquad (4)$$

where, of course, $M_{\mathrm{a}}=\sum_{i}M_{\mathrm{ai}}$. M_{ai} is the atomic weight that constitutes the atoms or radicals and V_{a} is the sum of the constituting atoms (V_{ai}) in the corresponding state.

V_{a} may be put equal to $\sum_{i}V_{\mathrm{ai}}$ approximately[6]. This approximation is quite satisfactory for the present case. (V_{ai} is the atomic volume in the liquid state.)

ΔE corresponds to the cohesive energy and M.

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[1] Present address: Research Laboratory, Dai-Nippon Celluloid Co. Ltd., Sakai City, Osaka.

[2] K. Tyuzyo, The first paper of this series.

[3] M. R. Rao, *Indian J. Phys.*, **14**, 109 (1940).

[4] M. R. Rao, *J. Chem. Phys.*, **9**, 682 (1941).

[5] R. T. Lagemann, J. S. Evans, and D. R. McMillan, Jr. *J. Amer. Chem. Soc.*, **70**, 2996 (1948).

[6] Even the proportionality does not hold between the so-called zero-point atomic volume in the solid state and the atomic volume in the liquid state. Therefore, the atomic volume in the liquid state must be adopted as the V_{ai}-value.

Dunkel has already found the approximate additivity for this quantity[7].

Now, we can calculate atomic or radical sound velocity (K_a) from Eq. 4. The calculated K_a-values from Eq. 4, the observed ones, and the $K_{a\text{calc}}/K_{a\text{obs}}$ are shown in Table I. It is clear from the table that the calculated K_a-values are approximately equal to the observed ones with the accuracy of about ±10%.

TABLE I

CALCULATED AND OBSERVED ATOMIC OR RADICAL SOUND VELOCITY (K_a)

Atom or radical	ΔE[8] (cal/mole)	M_a	V_a[9]	$K_{a\text{calc}}$	$K_{a\text{obs}}$[10]	$K_{a\text{calc}}/K_{a\text{obs}}$
$-CH_2-$	990	14.0	22.0	763	905	0.850
$-CH_3$	1780	15.0	27.5	1154	1330	0.868
$-O-$	1630	16.0	7.8	313	345	0.907
$-Cl$	3400	35.5	22.1	993	1055	0.941
$-Br$	4300	79.9	27.8	1179	1137	1.037
$-I$	5040	126.7	37.5	1550	1300	1.191
$>C=O$	4270	28.6	18.8	949	860	1.103
$=CH$	1780	14.0	(22.0)[10a]	(930)	1416	(0.795)

If several assumptions and approximations made for the above calculation are allowed for, this result seems to be quite satisfactory.

TABLE II

THE CALCULATED AND OBSERVED MOLAR SOUND VELOCITY

Substance	Chemical Formula	$K_{\text{obs}}=u^{1/3}V$	$K_{\text{calc}}=\Sigma K_{a\text{calc}}$	$K_{\text{calc}}/K_{\text{obs}}$	Literature
n-Pentane	C_5H_{12}	5390	4610	0.855	(11)
n-Hexane	C_6H_{14}	6260	5380	0.859	〃
n-Heptane	C_7H_{16}	7130	6150	0.863	〃
n-Octane	C_8H_{18}	7990	6910	0.865	〃
n-Nonane	C_9H_{20}	8650	7680	0.888	〃
Ethyl bromide	C_2H_5Br	3335	3100	0.929	(12)
Ethyl iodide	C_2H_5I	3570	3470	0.972	〃
n-Propyl chloride	C_3H_7Cl	4210	3680	0.874	(5)
n-Propyl bromide	C_3H_7Br	4200	3870	0.922	〃
n-Butyl chloride	C_4H_9Cl	5070	4450	0.878	〃
n-Butyl bromide	C_4H_9Br	5020	4640	0.925	〃
n-Butyl iodide	C_4H_9I	5230	5010	0.958	(12)
Methylene chloride	CH_2Cl_2	3040	2760	0.909	(5)
Methylene bromide	CH_2Br_2	3210	3130	0.975	〃
Methylene iodide	CH_2I_2	3690	3870	1.048	(12)
Ethylene chloride	$C_2H_4Cl_2$	3910	3520	0.901	(5)
Ethylene bromide	$C_2H_4Br_2$	4010	3890	0.970	〃
Propylene chloride	$CH_2ClCH_2CH_2Cl$	4760	4290	0.901	〃
Propylene bromide	$CH_2BrCH_2CH_2Br$	4820	4160	0.863	〃
Ethyl ether	$C_2H_5OC_2H_5$	4820	4160	0.863	(2)
Acetone	CH_3COCH_3	3620	3260	0.900	〃
Methyl acetate	CH_3COOCH_3	3890	3570	0.917	(13)
Ethyl acetate	$CH_3COOC_2H_5$	4660	4330	0.929	〃

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7) M. Dunkel, *Z. phys. Chem.*, A**138**, 42 (1928).

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

9) S. Glsstone, " Textbook of Physical Chemistry," p. 525 (1946).

10) R. T. Lagemann, and W. S. Dunbar, *J. Phys. Chem.*, **49**, 425 (1945).

10a) As the correction for the atomic volume for the double bond is not made, the $K_{a\text{calc}}$ of (CH=) is somewhat inaccurate.

11) L. Bergmann, "Der Ultraschali," (1949).

12) R. T. Lagemann, D. R. McMillan, Jr., and W. E. Woolf, *J. Chem. Phys.*, **17**, 369 (1949).

13) R. T. Lagemann. E. G. McLeroy, and O. Milner, *J. Amer. Chem. Soc.*, **73**, 5891 (1951).

Comparison of the Observed Molar Sound Velocities and the Calculated Ones from the Atomic and Radical Sound Velocities.

As an application of the above result, the calculated K from $K_{a\text{calc}}$-values in Table I and the observed ones for unassociated liquids are shown in Table II. The consistency of K_{calc} and K_{obs} is quite satisfactory, and so the above method of calculation is fully reasonable as the first approximation.

Discussion

If the quantities which may be regarded as constant in Eq. 1 are written A, then

$$K=A\left(\frac{E_{\text{vap}}}{M^{1/2}}\right)^{1/3}V \qquad (5)$$

From the assumption of Eq.2 and 3, Eq. 5 is

$$K=\Sigma K_a=A\Sigma\left[\left(\frac{\Delta E}{M_a^{1/2}}\right)^{1/3}V_a\right] \qquad (6)$$

On the other hand, from the assumptions,

$$\left.\begin{aligned} M&=\Sigma M_a,\\ E_{\text{vap}}&=\Sigma\Delta E,\\ V&=\Sigma V_a. \end{aligned}\right\} \qquad (7)$$

Therefore, from Eq. 5 and 7,

$$K=A\left[\frac{\Sigma(\Delta E)}{(\Sigma M_a)^{1/2}}\right]^{1/3}(\Sigma V_a) \qquad (8)$$

In general, Eq. 6 is not consistent with Eq. 8, and Eq. 8 contains many more cross terms than Eq. 5. Therefore, it is not clear at present whether the discrepancy (about 10%) between the calculated and observed values in Table II is due to the existence of these cross terms or the constitutional effect of ΔE and V coming from the intermolecular interaction. But, considering the fact that the calculated and observed K_a (Table I) has already about 10% difference, the influence of the constitutive effect of ΔE and V seems to be larger than that of the cross terms. (If the influence of cross terms is large, the deviation of the calculated K-value must be larger than that of the calculated K_a-value.) Of course, more detailed investigation is necessary for this point.

Next, as a useful application of Eq. 4, molar cohesion, ΔE, can be reversely calculated if K_a, M_a, V_a are known. ΔE, is derived from the temperature-variance of vapor pressure until now and that method is considerably difficult, but from Eq. 4, its value is very simply calculated.

Summary

(1) The additivity of molar sound velocity has theoretically been derived and the calculated and observed "atomic-" and "radical sound velocity" were shown to coincide with each other with the accuracy of about ±10%.

(2) The molar sound velocity derived from the calculated atomic and radical sound velocity was shown to coincide with the observed value with about 10 % deviation for unassociated liquids. (e. g., paraffins, alkyl halides, ethers, ketones, esters)

(3) The cause of deviation of the calculated and observed values and the application of this theory are briefly discussed.

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Department of Chemistry, Faculty of
Science, Osaka University,
Nakanoshima, Osaka