Stoichiometric Investigations of the Liquid State. I. The Relation between the Sound Velocity and the Chemical Structure. (1). The Physical Meaning of the Molar Sound Velocity of the Unassociated Liquid

By Kiyoshi TYUZYO[1]

(Received April 17, 1954)

Introduction

Thermodynamic quantities such as adiabatic compressibility ($\beta_{ad}=1/\rho u^2$, where ρ is density, u is ultrasonic velocity in the liquid) and ratio of specific heat ($\gamma=\beta_{iso}/\beta_{ad}$ where β_{iso} is isothermal compressibility of liquid) can easily be evaluated from the ultrasonic velocity in the liquid. Therefore, the measurement of the ultrasonic velocity in the liquid is important to clarify the intermolecular force in the liquid[2].

On the other hand, in 1940, Rao found that K, expressed in the following equation, is a characteristic constant of each liquid and is independent of temperature[3].

$$K=u^{1/3}V \qquad (1)$$

where V is molar volume of the liquid.

Moreover, in 1941, Rao found that K in Eq. 1 can be given as the sum of increments of the constitutive elements[4]. That is, K, as well as parachor and molar refraction, is independent of temperature and has the additive property.

K is now designated as molar or molecular sound velocity. It is now possible from this investigation to treat quantitatively the relation between sound velocity and the chemical structure of liquid. Thereafter, investigations of this field were remarkably developed and were dealt with very strictly by Lagemann[5], Weissler[6], Schaafs[7], etc. But the theoretical investigation of molar sound velocity has scarcely ever been performed[7a].

The present author can satisfactorily interpret the physical meaning of molar sound velocity (K), its temperature-invariance, and its additive property on the basis of the simple theory of liquid state, which will be reported in the following series of papers.

The Physical Meaning of Molar Sound Velocity, $\mathbf{K}$

According to Kincaid and Eyring[8], the sound velocity in a liquid (u) is expressed by the following equation,

$$u=u_{gas}\left(\frac{v}{v_f}\right)^{1/3}=\left(\frac{v}{v_f}\right)^{1/3}\left(\frac{RT\gamma}{M}\right)^{1/2} \qquad (2)$$

where u_{gas} is sound velocity in a gas, v is molecular volume, and v_f is free volume of a liquid.

v_f is approximately given by the following equation[8],

$$v_f=\left(\frac{CRT\ V^{1/3}}{N^{1/3}E_{vap}}\right)^3, \qquad (3)$$

where E_{vap} is the energy of vaporization and

---

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

[2] L. Bergmann, "Der Ultraschall" (1949).

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

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

[5] R. T. Lagemann and W. S. Dunbar, *J. Phys. Chem.*, **49**, 428 (1945), etc.

[6] A. Weissler, J. W. Fitzgerald and I. Resnick. *J. Appl. Phys.*, **18**, 434 (1974), etc.

[7] W. Schaafs, *Z. phys. Chem.*, **A 194**, 28 (1944), etc.

[7a] Recently, some theoretical explanation of the Rao's relation has been given by O. Nomoto and T. Kishimoto on the basis of the Lennard-Jones, Devonshires' model: *J. Phys. Soc. Japan*, **9**, 59, 66, 73 (1954).

[8] J. F. Kincaid and H. Eyring, *J. Chem. Phys.*, **6**, 620 (1938).

C is the packing number of liquid. (This is equal to 2 for cubic packing.)

Then, u is expressed by Eq. 4, making use of Eq. 2 and 3.

$$u=\frac{E_{\text{vap}}\,\gamma^{1/2}}{C(MRT)^{1/2}} \tag{4}$$

Therefore,

$$u^{1/3}\,V=\left[\frac{E_{\text{vap}}\,\gamma^{1/2}}{C(MRT)^{1/2}}\right]^{1/3}V \tag{5}$$

In comparison of Eq. 5 and Rao's Eq. 1, the molar sound velocity is expressed as follows,

$$K=\left[\frac{E_{\text{vap}}\,\gamma^{1/2}}{C(MRT)^{1/2}}\right]^{1/3}V \tag{6}$$

Namely, Rao's characteristic constant, K, as is shown in Eq. 6, contains several factors such as geometrical configuration of the liquid state (C, V), thermodynamic property of the gaseous state (γ), and property of equilibrium state between liquid and gas (E_{vap}). Therefore, it is rather questionable to conclude simply the additivity of K as was done by Rao[3] and Lagemann[9]. The author will discuss this conclusion in the second paper of this series.

Temperature-invariance of K

In Eq. 6, $E_{\text{vap}}^{1/6}$, $\gamma^{1/6}$, $C^{1/3}$ and V are dependent on temperature. But, among them, temperature-variance of $\gamma^{1/6}$ is negligible and $C^{1/3}$ can be regarded as temperature-invariable in the range of ordinary temperature (ca. 0° to 100°C). C must be equal to 2 for the cubic packing. For normal unassociated liquids, this value was computed from the vapor pressure data by Eyring and others and is approximately equal to 2. The present author has examined the temperature-variance of C by calculating it from Eq. 5, using the observed value of u, and found that its temperature-variance does not exceed several percent in the range of 50°C for normal liquids. Examples are shown in Table I. Table II shows the comparison of C values obtained from sound velocity and from vapor pressure. The coincidence of the values from two different methods is satisfactory and both methods give $C=2$ on the average, but in general, the value from sound velocity is somewhat smaller than that from vapor pressure.

As no satisfactory theoretical equation for the temperature-variance of E_{vap} and V can be found, so their values at each temperature were obtained from International Critical Table and other tables.

TABLE I

THE TEMPERATURE-INVARIANCE OF PACKING NUMBER, C

Temperature (°C)	C
Benzene	
10	1.80
20	1.80
30	1.80
40	1.80
50	1.81
60	1.81
Chloroform	
0	1.82
10	1.82
20	1.81
30	1.81
40	1.81
50	1.81
60	1.81

TABLE II

PACKING NUMBER, C, OF NORMAL LIQUIDS

Substance	C from Sound Velocity	C from Vapor Pressure[10]
n-Heptane	—	1.60
n-Octane	1.61	—
Ethyl ether	1.89	1.92
Benzene	1.80	2.12
Acetone	2.09	1.76
Carbon disulfide	1.76	2.05
Ethyl bromide	1.89	—
Ethylene chloride	1.81	—
Chloroform	1.81	2.44
Carbon tetrachloride	1.77	2.08

γ is the value from the Taschenbuch[11], but in the case of the compound of which γ is unknown, its value is approximately obtained from the following method. As the first approximation, γ-values are determined by the number of atoms constructing the molecule, then the relation between known values of γ and numbers of atoms constructing the molecule is drawn in Fig. 1. As is

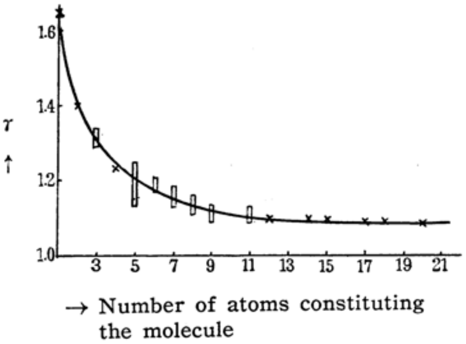

Fig. 1. The relation between the ratio of specific heats (γ) and the number of atoms constituting the molecule in the gaseous state.

---

[9] R. T. Lagemann, J. S. Evans, and D. R. McMillan, Jr, *J. Amer. Chem. Soc.*, **70**, 2696 (1948).

[10] H. Eyring and J. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937).

[11] J. D'Ans and E. Lax, "Taschenbuch für Chemiker und Physiker" (1949).

shown in the figure, γ varies in the considerably broad range in the molecules which are made of small numbers of atoms, but the values become fixed dependent only upon the numbers of atoms constructing the molecule when the molecules are made of many numbers of atoms. If the experimental values are connected with a smooth curve as in the figure, γ can be determined from this curve when the number of atoms constructing the molecule is known. (As γ appears in Eq. 6 with 1/6-power, this degree of approximation is quite satisfactory.)

With these treatments, E_{vap}, γ, C and V-values are known, and so K-values can be calculated by Eq. 6 at several temperatures.

Results are shown in Table III for several normal liquids. As is clear from the table, K is almost independent of temperature and this result is consistent with that of Rao and others.

TABLE III

TEMPERATURE-INVARIANCE OF THE CAICULATED K-VALUES FOR NORMAL LIQUIDS

Temperature (°C)	E_{vap} (cal/mol)	ρ(g./cc.)	K_{calc} (c.g.s.)
n-Octane, $M=114.2$, $\gamma=1.05$			
0	7660	0.719	7410
20	7620	0.702	7470
40	7580	0.686	7540
Benzene, $M=78.2$, $\gamma=1.10$			
10	7640	0.890	4370
20	7500	0.879	4360
30	7360	0.868	4360
40	7220	0.858	4370
50	7070	0.847	4370
60	6920	0.836	4370
Ethyl bromide, $M=109.0$, $\gamma=1.19$			
0	6240	1.501	3260
10	6150	1.480	3270
20	6070	1.461	3250
30	6010	1.440	3290
Ethylene chloride, $M=99.0$, $\gamma=1.37$			
0	7870	1.281	3780
10	7780	1.267	3780
20	7670	1.251	3780
30	7550	1.238	3790
40	7430	1.223	3790
50	7300	1.209	3800
Chloroform, $M=119.4$, $\gamma=1.15$			
0	7170	1.525	3620
10	7040	1.506	3620
20	6900	1.487	3610
30	6780	1.467	3620
40	6640	1.449	3620
50	6500	1.429	3620
60	6370	1.409	3630
Carbon tetrachloride, $M=153.9$, $\gamma=1.13$			
0	7740	1.633	4270
10	7460	1.613	4240
20	7210	1.594	4220
30	7080	1.575	4210
40	7000	1.556	4230
50	6930	1.536	4240
Acetone, $M=58.05$, $\gamma=1.1$			
0	7260	0.813	3690
10	7170	0.801	3710
20	7050	0.791	3710
30	6920	0.779	3720
40	6790	0.767	3740
50	6640	0.755	3750
Ether, $M=74.1$, $\gamma=1.08$			
0	6290	0.736	4750
10	6090	0.725	4750
20	5880	0.714	4750
30	5700	0.702	4750
Methyl acetate, $M=74.1$, $\gamma=1.14$			
10	7570	0.946	3950
20	7300	0.932	3930
30	7070	0.918	3930

Comparison of the Calculated and Observed K-values

It was found in the previous paragraph that K calculated from Eq. 6 is independent of temperature and is the characteristic constant of the substance. Next, the K-values calculated from Eq. 6 and observed (Eq. 1) are compared. Results are shown in Table IV[12]. It is clear from the table,

$$K_{\mathrm{calc}}/K_{\mathrm{obs}}=1$$

(Accuracy is about ±5%.)

TABLE IV

THE CALCULATED AND OBSERVED MOLAR SOUND VELOCITIES, K

Substance	K_{calc}	K_{obs}	$K_{\mathrm{calc}}/K_{\mathrm{obs}}$
n-Hexane	6070	6260	0.969
n-Octane	7470	7990	0.936
Benzene	4360	4530	0.962
Carbon disulfide	2810	2940	0.957
Ethyl bromide	3250	3340	0.973
Ethylene chloride	3780	3910	0.967
Chloroform	3610	3730	0.968
Carbon tetrachloride	4220	4390	0.962
Ether	4750	4830	0.983
Acetone	3710	3610	1.027
Methyl acetate	3930	3890	1.010
Ethyl acetate	4770	4810	0.992
Ethyl formate	3260	3730	0.874
Ethyl iodide	3480	3570	0.974
Toluene	6040	6240	0.969
Cyclohexane	5100	5430	0.939

Summary

(1) The physical meaning of Rao's molar sound velocity (K) is given.

(2) It is found that K-values calculated from the theory are independent of temperature in the case of normal liquids.

(3) It is found that the calculated K-values are satisfactorily coincident with the observed ones for normal liquids (aliphatic and aromatic hydrocarbons, ether, acetone, esters, alkyl halides).

---

[12] As the sound velocity, u is ordinarily expressed in the unit of m./sec., so K_{obs} must be converted in the c. g. s. unit. Namely, ordinary K must be multiplied by $(100)^{1/3}=4.62$.

The author expresses his hearty thanks to Prof. Dr. N. Sata of the Osaka University for his valuable encouragement throughout this task. The author also expresses his sincere thanks to Mr. M. Okuyama of the Osaka University for his valuable discussions and Dr. O. Nomoto of the Kobayashi Institute of Physical Research for his kind suggestions, although his opinion is not always consistent with the author's own.

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