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Velocity of Sound and Molecular Association in Liquids

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Two new, empirical criteria for determining molecular association in liquids are pointed out. One is the quantity P_CR/T_C in which R is a function of the velocity of sound; the other is the ratio of the velocity of sound in a liquid to the velocity of sound in the gas of the same compound. In both cases low numerical values of the ratios are qualitative indicators of association.

ALTHOUGH a great many physical properties have been used as evidence for molecular association in liquids, the velocity of sound does not appear to have been studied in this connection. It is perhaps of interest then to point out two quantities involving the velocity of sound which seem to afford a qualitative test for association. These are empirical in nature, and, as is the case with other properties, association is ascribed to those substances which behave abnormally.

The first function proposed is

$$P_CR/T_C=K, \tag{1}$$

where P_C is the critical pressure, T_C the critical temperature, and K a quantity varying from liquid to liquid, but remainly roughly constant. The quantity R, analogous to the molecular refraction and the parachor, is quite constant for any one liquid under changing conditions. Its constancy was first pointed out by Rao[1] who defined it as

$$R=MV^{\frac{1}{4}}/d,$$

where V is the velocity of sound in the liquid. For the calculation of K, values of the critical temperature and pressure were secured from the *International Critical Tables*. Most of the values of R were obtained from Rao.[1,2] R for water was calculated from the data of Bergmann,[3] and R for acetic acid was calculated from the data of Smith and Ewing.[4]

Table I gives values of K calculated by Eq. (1) for several substances. It is seen that K is roughly constant for most of the normal liquids examined. However, it appears to assume decreased values for those substances which are commonly believed to be associated. Unfortunately data on fused metals and salts and other associating compounds are not available to test this observation further. Although K contains the value of the molecular weight, and it is possible to calculate the degree of association, it does not seem worth while to do so here.

Another apparent indicator of association in the liquid state is the ratio of the velocity of sound in a liquid to the velocity of sound in the gas of the same compound. For the determination of this ratio data were taken from the literature. Because of the marked changes in velocity of sound with temperature in both liquids and gases, it was decided to reduce all the gas velocities to their values at corresponding temperatures of 0.700 of the critical temperatures, and use velocities in liquids measured at about 23°C. To bring the measured velocities in gases to those at corresponding temperatures use was made of the correction formula

$$V_1/V_2=(T_1/T_2)^{\frac{1}{4}}, \tag{2}$$

TABLE I. Calculated values of P_CR/T_C.

Compound	T_C (°K)	P_C (Atmos.)	R	P_CR/T_C
Acetic acid	594.7	57.2	629	61
Methyl alcohol	513.1	78.7	421	65
Water	647	217.7	207	69
Acetone	508.1	47	781	72
n-propyl acetate	549.3	32.9	1211	73
n-propyl alcohol	536.8	49.9	806	75
Ethyl alcohol	516.2	63.1	624	76
n-butyl alcohol	560	48.4	1004	87
Ethyl ether	466.9	35.5	1040	79
Chlorobenzene	632	44.6	1106	78
Aniline	699	52.4	1078	81
Carbon tetrachloride	556.2	45.0	944	76
n-pentane	470.3	33.0	1160	81
n-hexane	507.9	29.5	1356	79
n-heptane	539.9	26.8	1545	76
n-octane	569	24.6	1746	75
Chloroform	536.0	53.8	803	81
Benzene	561.6	47.7	979	83
Toluene	593.7	41.6	1170	82
Methyl acetate	506.8	46.3	851	78
Ethyl acetate	523.2	37.8	1037	75

[1] M. Rama Rao, J. Chem. Phys. **9**, 682 (1941).
[2] M. Rama Rao, Ind. J. Phys. **14**, 109 (1940).
[3] L. Bergmann, *Ultrasonics* (G. Bell and Sons, London, 1938).
[4] A. W. Smith and L. M. Ewing, J. Chem. Phys. **7**, 632 (1939).

TABLE II. Ratio of sound velocity in liquids to sound velocity in gases.

Compound	Temperature (°C)	Liquid Velocity of sound (m/sec.)	Reference	Temperature (°C)	Gas Velocity of sound (m/sec.)	Reference	V_{liquid}/V_{gas}
Water	24	1494	*B*	179.8	519.6	*C*	2.88
Methyl alcohol	23.8	1130	*B*	86.1	350.5	*D*	3.22
Ethyl alcohol	23.5	1207	*B*	88.2	274.2	*D*	4.40
n-butyl alcohol	23	1315	*B*	119.0	235.9	*D*	5.57
Acetic acid	25	1140	*E*	143.2	210.9	*C*	5.41
Carbon disulphide	23	1149	*B*	109.1	216.4	*A*	5.31
n-pentane	18	1052	*B*	56.1	195.5	*C*	5.38
Ethyl acetate	23.5	1187	*B*	93.1	213.1	*D*	5.57
Acetone	22.5	1203	*B*	82.6	213.5	*C*	5.64
Methylene chloride	23.5	1064	*B*	89.6	188.4	*C*	5.65
Chloroform	23.5	1001	*B*	102.1	171.5	*D*	5.84
Carbon tetrachloride	23	929	*B*	116.2	158.2	*D*	5.87
Benzene	23	1310	*B*	120.0	219.4	*D*	5.97
n-hexane	23	1113	*B*	82.4	184.9	*C*	6.02

[A] *International Critical Tables.*
[B] Bergmann, *Ultrasonics* (G. Bell and Sons, London, 1938).
[C] I.C.T. and correction by Eq. (2).
[D] Bergmann and correction by Eq. (2).
[E] A. W. Smith and L. M. Ewing, J. Chem. Phys. **7**, 632 (1939).

where temperatures are in degrees Kelvin. That this would correct the data with adequate precision was determined by testing it on data for several gases found in the I.C.T. Irons[5] has also shown that it applies to several gases over a wide range of temperature.

Table II gives the velocity of sound in several gases corrected to 0.700 of the critical temperatures. In column 3 are recorded velocities in liquids measured at the temperatures given in column 2. The last column gives the ratio of the velocity of sound in the liquid to that in the gas of the same compound. It may be seen that for those compounds commonly accepted as being associated the ratio is smaller than for the normal liquids. The relatively high value for acetic acid may be caused by the fact that it is more associated in the gaseous state than are the other compounds listed. According to Laplace's equation, the increased molecular weight would lower the velocity in the gas below its value for the monomer and raise the ratio above its expected value. This explanation is supported by the case of oxygen where it has been found that the presence of ozone decreased the velocity of sound in the gas.

COMPARISON WITH OTHER METHODS

It is difficult to compare these results with previous methods for determining association because the earlier methods do not agree even as to the relative order in which to place various substances. Furthermore, the two proposed schemes do not possess high correlation.

It should be pointed out that the foregoing functions of sound velocity cannot be used to predict correctly changes in the association of a liquid with changes in temperature. In fact, the ratio of the liquid to the gas velocity for any substance except water (where velocity in the liquid increases with increase in temperature) indicates an increase in association with increase in temperature, in direct contradiction to accepted belief. Therefore, these two quantities are considered to be only qualitative criteria for association.

It is usually found that increase in the parachor with increase in temperature is indicative of association. The same does not appear to be true for the analogous function R. From the work of Rao[2] R may be seen to increase slightly with increase in temperature in certain non-associated as well as certain associated liquids.

An advantage of the sound velocity criteria for association over some other properties is that the former are independent of measurements connected with the liquid surface where unusual conditions exist. On the other hand, the well-known use of ultrasonics both as a dispersive and as a coagulating agent may change the degree of association even as the velocities are being measured. As more data become available it would be of interest to test the above considerations on other substances, particularly some of the lower aldehydes and nitriles.

[5] E. J. Irons, Phil. Mag. **3**, 1274 (1927).