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Intermolecular Free Lengths in the Liquid State. I. Adiabatic and Isothermal Compressibilities

BERTIL JACOBSON

Biochemical Department, Karolinska Institutet, Stockholm, Sweden

It was pointed out in a preliminary communication that certain properties of the liquid state can be studied to advantage as a function of the free length between the molecules (Jacobson [1])*. These properties include compressibility, surface tension, viscosity and diffusion constants *i.e.*, those that are mainly dependent on the forces between the molecules.

The reason for choosing the intermolecular free length for these studies instead of the distances between centres such as are usually employed are as follows. The intermolecular forces, which in one way or another determine the said properties of liquids, consist of attractive forces and repulsive forces. These forces have opposite directions but are numerically equal under given external conditions. The attractive forces are dependent on the distance between what are called the centres of attraction of the molecules, whereas the repulsive forces are dependent on the distance between the surfaces of the molecules. The distance between centres of attraction is a property extremely difficult of definition, one reason being that this centre does not coincide with the geometrical centre of the molecules of the liquid (Hildebrand [2], Hudleston [3]). The distances between the surfaces of the molecules, on the other hand, have a clear physical significance, and thus lend themselves more easily to clear definition. For these reasons, we may anticipate the most simple relations if the intermolecular free length is used.

In some subsequent works surface tension, viscosity, thermal expansion and molecular association will be related to the intermolecular free length. The present work will deal with the adiabatic and isothermal compressibilities for liquids and liquid mixtures.

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* Owing to an unfortunate printer's error equation (1) was wrongly given. It should read:

$$j = kL^p$$

DEFINITIONS

The intermolecular free length in a liquid can be obtained if there is taken as basis a molecular model similar to that employed by Eyring [4] in his theory of the liquid state (*Cf.* also Brinkman [5]).

At absolute zero a liquid has the molar volume $V_0 = M/\varrho_0$, where M is the molecular weight and ϱ_0 is the density at $0°$K. The molecules have then their closest packing possible, which is shown in Figure 1. The total surface of all the molecules in one mole is designated by Y and will here be called the internal surface of the liquid. If the temperature is raised to $T°$K the liquid is expanded as a whole through molecular oscillations, though the molecules themselves are not expanded. If the molar volume is designated by V_T the increase in volume will be equal to the available volume $V_a = V_T - V_0$ (Kittel [6]). The free length L between the surfaces of the molecules, hereafter designated the free length, can be obtained when the surface Y is unaltered after a rise in temperature

$$L = \frac{2\,V_a}{Y} \tag{1}$$

This equation involves an approximation and gives values for the free length that are too large. Nevertheless, equation (1) will be regarded as a definition of the free length at temperatures considerably lower than the critical temperature, for the following reasons.

Any exact computation of the free length has to be based on a given type of packing and a given form of the molecules of the liquid. For hexagonal packing of spherical molecules, the length according to the Eyring theory is $L_{hex} = (2^{\frac{1}{2}}/N)^{\frac{1}{3}}\,(V_T^{\frac{1}{3}} - V_0^{\frac{1}{3}})$ where N is Avogadro's number. For organic liquids of various types at room temperature, L according to (1) is app. 20% greater than L_{hex}. For practical purposes, it is of lesser importance that one should regularly get too great a numerical value of the free length. It is more essential that L according to (1) should have a clear physical significance which always makes possible a simple computation from V_T and V_0, even in those cases where an exact treatment may be impossible, *i.e.*, in liquid mixtures and with molecular association. With rising temperature the error in L according to (1) increases and therefore the normal boiling point of the liquid concerned should be put as the upper temperature limit for the range of applicability of the definition.

One particular advantage of equation (1) is that it does not necessarily require spherical molecules. For spherical molecules the internal surface is $Y = (36\,\pi N V_0^2)^{\frac{1}{3}}$. For a molecule of another form the internal surface will be

$$Y = \mathrm{f}(36\pi N V_0^2)^{\frac{1}{3}} \tag{2}$$

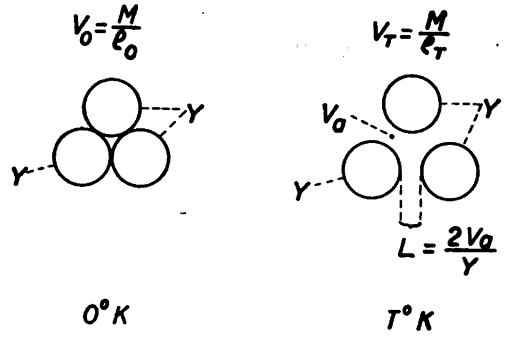

Fig. 1. The intermolecular free length (L) can be obtained from the available volume ($V_a = V_T - V_0$) and the internal surface (Y) of the liquid.

where f is a form factor giving the ratio between the surface of the molecule and the imagined spherical surface which encloses the same volume as the volume of the molecule. By the introduction of the form factor f it is possible to compute L for any form of the molecules. For all low molecular weight substances one may with good approximation put $f = 1$, and this has been done in all cases in the present work. For high molecular weight substances with highly asymmetrical molecules f is considerably greater than 1. The form factor has been introduced to make (1) applicable to solutions of such high molecular weight substances.

Equation (1) includes the zero volumes V_0. This can be obtained in two ways. V_0 can be theoretically computed according to Sugden [7] for any chemical compound of known composition and structure by the addition of atomic and structural constants. Greater accuracy of V_0 is obtained, however, if the critical temperature T_c is known and Sugden's formula can be used, which gives the variation of molar volume with the temperature

$$V_0 = V_T \left(1 - \frac{T}{T_c}\right)^{0.3} \tag{3}$$

ADIABATIC COMPRESSIBILITY OF NORMAL LIQUIDS AT 20° C

The adiabatic compressibility β_{ad} is easy to compute with great accuracy from measured values of the density ϱ of the liquids and the sound velocity u according to the formula $\beta_{ad} = 1/\varrho u^2$. Detailed information is furnished by the literature regarding the compressibility of organic liquids (Bergmann [8]; Lagemann *et al.*[9]; Weissler [10]; Schaaffs [14]). All non-associated organic liquids for which it has been possible to find accurate values for critical temperature and adiabatic compressibility have been tabulated in Table 1. The critical

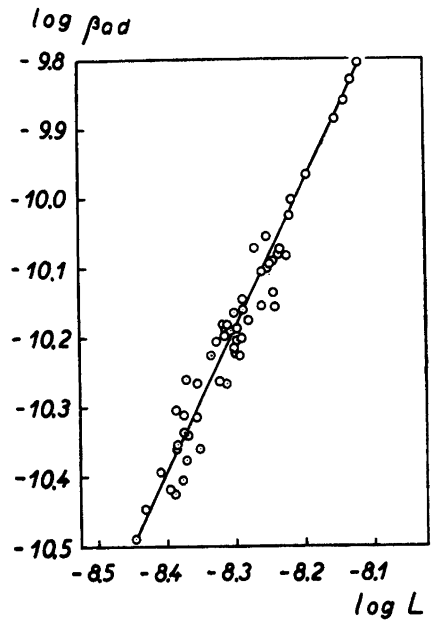

Fig. 2. Adiabatic compressibilities as a function of intermolecular free lengths in 54 organic non-associated liquids at 20° C.

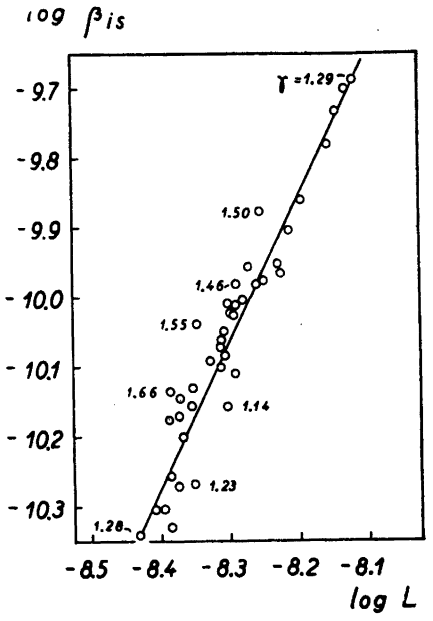

Fig. 3. Isothermal compressibilities as a function of intermolecular free lengths in 40 organic non-associated liquids at 20° C.

temperatures, taken from Landolt-Börnstein Physikalisch-Chemische Tabellen and International Critical Tables, are required for computation of the values for V_0 given in the table. The free length L has been computed according to (1) from molar volumes V_0 and V_T. In Figure 2 the adiabatic compressibilities for these 54 non-associated liquids have been plotted as a function of the free length both in logaritmic scale. As will be seen from the figure all points lie around a straight line corresponding to a relation of the type

$$\beta_{ad} = k \cdot L^p \tag{4}$$

where $p = 2.082$ and $\log k = 7.097$ for c.g.s. units at 20° C.

In order to test the utility of equation (4) for computation of the intermolecular free length L from compressibility data such a computation has been made and the result is given in Table 1. It will be seen that the agreement is good between L computed from molar volumes according to the definition (1) and L computed from compressibilities according to (4). The percentage of deviation in the values thus computed for L is on the average 3.3 %. This deviation is mainly due to the difficulty in determining V_0 exactly, and therefore

Table 1. Intermolecular free lengths of organic liquids calculated from adiabatic compressibilities (eq. (4)) and from molar volumes (eq. (1)).

Substance	Formula	Molar volume at absolute zero, V_0	Molar volume 20°C, V_T	Compressibility at 20°C, β_{ad} 10^{-12} cm²/dyne	Intermolecular free length, L 10^{-8} cm	
					Calc. from V_0 and V_T	Calc. from β_{ad}
2-Methylbutane	C_5H_{12}	86.1	116.4	156.2	0.76	0.760
Pentane	C_5H_{12}	86.7	116.2	147.7	0.74	0.740
Benzene	C_6H_6	71.3	89.0	64.9	0.50	0.499
Cyclohexane	C_6H_{12}	86.2	108.0	78.2	0.55	0.545
Hexane	C_6H_{14}	100.8	131.8	130	0.70	0.696
Toluene	C_7H_8	86.7	106.4	65.5	0.49	0.501
Methylcyclohexan	C_7H_{14}	102.6	128.5	84.2	0.58	0.565
Heptane	C_7H_{16}	115.7	146.5	108	0.64	0.637
o-Xylene	C_8H_{10}	101.1	121.9	62.1	0.47	0.488
m-Xylene	C_8H_{10}	101.5	123.0	64.5	0.49	0.497
p-Xylene	C_8H_{10}	101.8	123.4	65.8	0.49	0.502
Ethylbenzene	C_8H_{10}	100.4	122.3	64.4	0.49	0.497
Octane	C_8H_{18}	130.8	162.5	99.3	0.60	0.612
Pseudocumene	C_9H_{12}	113.4	137.2	61.0	0.50	0.484
Cumene	C_9H_{12}	114.9	138.3	63.3	0.49	0.492
Mesitylene	C_9H_{12}	115.0	139.3	62.5	0.50	0.489
Ethylbromide	C_2H_5Br	57.7	74.6	84.5	0.56	0.566
Amylbromide	$C_5H_{11}Br$	100.0	123.5	85	0.53	0.568
Bromobenzene	C_6H_5Br	88.3	104.9	49.5	0.41	0.438
Octylbromide	$C_8H_{17}Br$	144.7	172.7	61.4	0.50	0.485
Carbontetrachloride	CCl_4	77.4	96.5	71.4	0.51	0.522
Chloroform	$CHCl_3$	63.3	80.3	66.5	0.52	0.504
Methylenechloride	CH_2Cl_2	49.5	63.6	62.8	0.51	0.491
Acetylenetetrachloride	$C_2H_2Cl_4$	87.7	104.9	45.6	0.43	0.421
Ethylenedichloride	$C_2H_4Cl_2$	63.3	79.1	54.0	0.49	0.456
Propylchloride	C_3H_7Cl	67.9	88.3	94.4	0.60	0.597
Chlorobenzene	C_6H_5Cl	84.4	101.7	54.1	0.44	0.457
p-Chlorotoluene	C_7H_7Cl	100.1	118.7	54.8	0.42	0.460
n-Octylchloride	$C_8H_{17}Cl$	140.4	170.5	70.0	0.55	0.517
Methyleneiodide	CH_2I_2	68.4	80.6	32.4	0.36	0.357
Methyliodide	CH_3I	48.9	62.3	63.3	0.49	0.493
Ethyliodide	C_2H_5I	64.3	80.6	68.2	0.50	0.511
Iodobenzene	C_6H_5I	94.1	111.4	44.1	0.41	0.414
Fluorobenzene	C_6H_5F	75.1	93.8	69.0	0.51	0.514
Pyridine	C_5H_5N	66.4	80.5	48.8	0.42	0.435
Piperidine	$C_5H_{11}N$	79.7	99.0	59.3	0.51	0.477
Aniline	C_6H_7N	77.4	91.1	35.7	0.37	0.374
Methylaniline	C_7H_9N	92.6	108.9	40.4	0.39	0.397
o-Toluidine	C_7H_9N	90.5	107.4	37.5	0.41	0.383
Dimethylaniline	$C_8H_{11}N$	107.3	126.8	46.0	0.42	0.423
Nitromethane	CH_3NO_2	42.6	53.6	48.5	0.44	0.433
Nitrobenzene	$C_6H_5NO_2$	86.0	102.0	38.2	0.40	0.387
o-Nitrotoluene	$C_7H_7NO_2$	99.3	117.9	41.9	0.43	0.404
m-Nitrotoluene	$C_7H_7NO_2$	100.0	118.5	38.9	0.42	0.390
Methylacetate	$C_3H_6O_2$	61.6	79.8	73.5	0.57	0.529
Ethylacetate	$C_4H_8O_2$	76.4	98.1	79.0	0.59	0.548
Ethylether	$C_4H_{10}O$	77.2	103.8	138	0.72	0.716
Acetylacetone	$C_5H_8O_2$	84.5	103.2	53.9	0.48	0.456
Propylacetate	$C_5H_{10}O_2$	91.3	114.6	80.3	0.56	0.552
Butylacetate	$C_6H_{12}O_2$	106.1	133.4	82.6	0.60	0.560
Benzaldehyde	C_7H_6O	85.3	101.5	43.7	0.41	0.412
Amylacetate	$C_7H_{14}O_2$	120.0	148.8	83.0	0.58	0.561
Acetophenone	C_8H_8O	97.8	117.1	43.6	0.45	0.412
Carbondisulphide	CS_2	47.8	60.3	59.0	0.46	0.477

also L according to (1). The uncertainty regarding V_0 is due among other things to errors in the critical temperature values available. Nevertheless, V_0 cannot be computed with greater accuracy than 0.5 %, even in favourable cases with a correct value for the critical temperature. But even a small error in V_0 has relatively great effect on L, owing to the fact that the difference $V_T - V_0 = V_a$ is only 20—30 % of V_T. From this it follows that neither V_a nor L can be given with greater accuracy than about 2 %. This explains why only two decimal places have been included in Table 1 for L values computed according to equation (1).

As regards the accuracy possible in the free length computed according to (4) from compressibilities, it should be noted that the uncertainty respecting L is probably always of the order of 1 %. This is due to several contributing factors, one being that the internal compressibility of the molecules may be thought to have a disturbing effect. With macromolecular solutions correction should be made for the relatively high internal compressibility of these molecules (10^{-11} cm^2/dyne).

ISOTHERMAL COMPRESSIBILITY OF NORMAL LIQUIDS AT 20° C

It is interesting to see whether there exists for the isothermal compressibility a relation similiar to that demonstrated for the adiabatic. The isothermal compressibility β_{is} is related to the adiabatic β_{ad} through the expression $\beta_{is} = \gamma\beta_{ad}$, where $\gamma = c_p/c_v$ is the ratio of the specific heats of the liquid. As it is not possible to obtain γ directly, the isotermal compressibility has been computed for 40 organic liquids from the relation usually employed $\beta_{is} = \beta_{ad} + T\alpha^2/\varrho c_p$ where T is the absolute temperature, α the coefficient of cubic expansion, ϱ the density and c_p the heat capacity at constant pressure. Some examples of the values used and results obtained are assembled in Table 2. In Figure 3, β_{is} has been plotted as a function of L. It will be seen that for most of the substances there applies a relation of the type

$$\beta_{is} = k \cdot L^p \tag{5}$$

where $p = 2.058$ and $\log k = 7.012$ for c.g.s. units at 20° C. For many of the substances, however, the deviation from the straight line is greater than was the case with the adiabatic compressibility. On closer investigation of these deviating substances it appears to be common for them that the ratios of the specific heats differ considerably from $\gamma = 1.3$, which is about the value for most organic liquids. There does not exist any simple generally applicable relation between γ and L. Thus the investigation suggests that the isothermal compressibility does not follow (5) so well as the adiabatic follows equation (4).

Table 2. Examples of values used for calculating isothermal compressibilities and obtained intermolecular free lengths of some organic liquids at 20° C.

Substance	c_p 10^{-7}	a 10^{-3}	γ	Compressibility β_{is} 10^{-12} cm²/dyne	Intermolecular free length, L 10^{-8}cm	
					Calc. from V_0 and V_T	Calc. from β_{is}
Pentane	2.332	1.608	1.354	200.0	0.74	0.759
Hexane	2.249	1.350	1.279	166.3	0.70	0.694
Heptane	2.225	1.244	1.276	137.8	0.64	0.633
Octane	2.205	1.160	1.256	124.8	0.60	0.603
Benzene	1.737	1.215	1.438	93.3	0.50	0.524
Cyclohexane	2.118	1.20	1.33	103.8	0.55	0.552
Toluene	1.676	1.099	1.373	89.9	0.49	0.514
Ethylbenzene	1.712	0.957	1.281	82.5	0.49	0.493
Nitromethane	1.725	1.19	1.44	69.6	0.44	0.454
Nitrobenzene	1.503	0.83	1.29	49.3	0.40	0.384
Aniline	2.072	0.850	1.280	45.7	0.37	0.370
Pyridine	1.775	1.03	1.37	66.6	0.42	0.445
Carbontetrachloride	0.846	1.22	1.45	103.7	0.51	0.551
Chloroform	0.942	1.26	1.50	99.7	0.52	0.541
Ethylbromide	0.904	1.42	1.53	129.2	0.56	0.614
Carbondisulphide	0.996	1.18	1.55	91.4	0.46	0.519

In stating this, however, it should be remembered that the accuracy of the computed isothermal values is much lower than the accuracy of the adiabatic values. In what follows we shall deal chiefly with the adiabatic compressibility.

DEPENDENCE ON TEMPERATURE

Plentiful data are available for many liquids regarding the dependence of the adiabatic compressibility on temperature in the range 0—50° C (Freyer *et al.*[11]; Lagemann *et al.*[9]). This makes possible a study of the dependence of the constants p and k on temperature. The values computed are given in Table 3. The compressibility values at 0° C appear to be of low accuracy, so that the values for p and k at this temperature are comparatively uncertain. For purposes of comparison p and k are also given for the isothermal compressibility computed from liquids with values for γ in the neighbourhood of 1.3.

If another definition than (1) for the free length is desired, say L_{hex}, the constants p and k can be converted with the aid of equation (4). It has not

Table 3. Values of the constants p and k in c.g.s. units for adiabatic and isothermal compressibilities at various temperatures.

Temp. °C	Adiabatic compressibility		Isothermal compressibility	
	p	log k	p *	log k *
0	(2.010)	(6.543)	(2.003)	(6.605)
10	2.041	6.778	2.028	6.787
20	2.082	7.097	2.058	7.012
25	2.106	7.274	2.073	7.131
30	2.128	7.459	2.089	7.246
40	2.174	7.820	2.121	7.490
50	2.220	8.181	2.155	7.750

* Computed from liquids with a ratio of specific heats of about $\gamma = 1.3$.

been possible to find any definition for L which makes p and k independent of temperature.

LIQUID MIXTURES

To investigate whether equation (4) is applicable to liquid mixtures, determination of compressibilities has been made in a number of these by measuring sound velocities with an interferometer. This instrument has been described in an earlier work (Jacobson [12]). The compressibility was obtained to an accuracy of 0.1 %. Liquids with widely differing free lengths were taken for the different mixing experiments. The results are given in Tables 4—7. In order to make possible a computation of L from molar volumes, the definition (1) has been revised to make it useable for mixtures as follows

$$L = \frac{2[1/\varrho - \{(w_1 V_{01}/M_1) + (w_2 V_{02}/M_2)\}]}{(w_1 Y_1/M_1) + (w_2 Y_2/M_2)} \tag{6}$$

where ϱ is the density of the mixture, w, V_0 and Y are the weight fraction, the zero volume and the internal surface of the two liquids with the subscripts 1 and 2. As will be seen from Tables 4—7 the agreement is very good between the free lengths computed from the compressibility according to (4) and from molar volumes as per (6). The average error is 0.8 % for all 16 mixtures investigated. The greatest deviations were demonstrated for the mixtures of methylene iodide and ethyl ether. The compressibility for this series of mixtures has been plotted in Figure 4 as a function of the free length. The reason for the relatively large errors in these experiments is without doubt largely due to the evaporation of the ether in the course of the measurements.

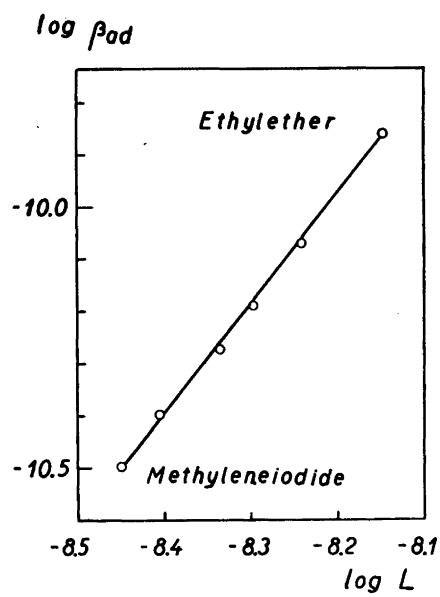

Fig. 4. Adiabatic compressibilities as a function of intermolecular free lengths in mixtures of methylene iodide and ethyl ether at 20° C.

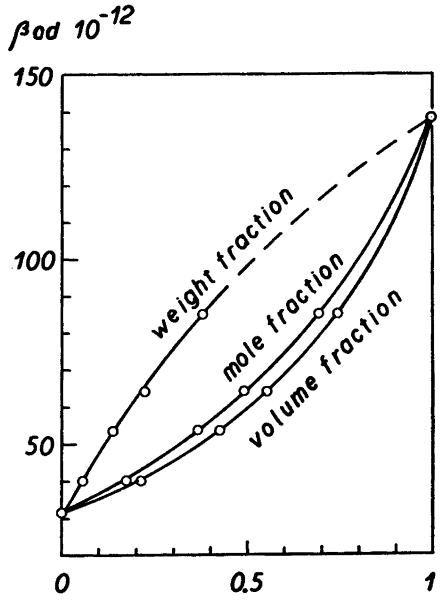

Fig. 5. Adiabatic compressibilities plotted as functions of different concentration units of mixtures of methylene iodide and ethyl ether at 20° C.

As regards the mathematical treatment of the measurement results with liquid mixtures the following should be stated. In Figure 1 the compressibilities of pure liquids have been plotted as a function of the free lengths. If two liquids are mixed then, provided equation (4) is valid, points for a series of mixtures should fall on the straight line between the points for the respective pure liquids. Owing to errors in V_0 and consequently in L, this line does not usually coincide with the line drawn in Figure 1 corresponding to $p = 2.082$ and $\log k = 7.097$. One must therefore for numerical treatment of the results compute new values for p and k for each series of mixtures of two liquids. These values are obtained by (4) from the values for the compressibilities and free lengths of the two pure liquids concerned. The values for the free lengths of the different mixtures can then be computed from their compressibilities (equation (4)). These will then be comparable with those computed according to the definition (6). In the experiment with the mixtures of methylene iodide and ethyl ether the values obtained were $p = 2.1103$ and $\log k = 7.3310$.

There is another and equally good manner in which to surmount this difficulty which arises because of errors in V_0 for the pure liquids. It is possible

Table 4. Experimental and calculated values for different fractions by weight of toluene in pentane at 20° C.

Fraction by weight	Density$_4^{20}$	Adiab. compress. β_{ad} 10^{-12}cm^2/dyne	Intermolecular free length, L 10^{-8}cm		Deviation %
			Calc. from eq. 6	Calc. from β_{ad}	
0.000	0.6278	147.4	0.706	0.706	—
0.288	0.6838	118.9	0.646	0.639	−1.1
0.509	0.7330	102.2	0.598	0.597	−0.2
0.651	0.7676	91.46	0.568	0.567	−0.2
0.827	0.8151	77.39	0.529	0.525	−0.8
1.000	0.8676	66.09	0.488	0.488	—

Table 5. Experimental and calculated values for different fractions by weight of methylene iodide in ethyl ether at 20° C.

Fraction by weight	Density$_4^{20}$	Adiab. compress. β_{ad} 10^{-12}cm^2/dyne	Intermolecular free length, L 10^{-8}cm.		Deviation %
			Calc. from eq. 6	Calc. from β_{ad}	
0.000	0.7154	138.0	0.714	0.714	—
0.618	1.407	85.02	0.575	0.568	− 1.2
0.787	1.896	64.03	0.505	0.496	− 1.8
0.861	2.237	53.26	0.462	0.455	− 1.5
0.945	2.804	40.05	0.393	0.397	+ 1.0
1.000	3.325	31.81	0.356	0.356	—

Table 7. Experimental and calculated values for different fractions by weight of diphenylmethane in hexane at 30° C.

Fraction by weight	Density$_4^{20}$	Adiab. compress. β_{ad} 10^{-12}cm^2/dyne	Intermolecular free length, L 10^{-8}cm.		Deviation %
			Calc. from eq. 6	Calc. from β_{ad}	
0.000	0.6657	132.0	0.648	0.648	—
0.258	0.7316	105.3	0.596	0.596	0.0
0.514	0.8091	81.82	0.542	0.542	0.0
0.690	0.8706	66.68	0.504	0.502	− 0.4
0.877	0.9489	52.41	0.458	0.459	+ 0.2
1.000	1.002	43.94	0.430	0.430	—

Table 6. Experimental and calculated values for different fractions by weight of pyridine in hexane at 20° C.

Fraction by weight	Density$_4^{20}$	Adiab. compress. β_{ad} 10^{-12}cm^2/dyne	Intermolecular free length, L 10^{-8}cm.		Deviation %
			Calc. from eq. 6	Calc. from β_{ad}	
0.000	0.6701	120.4	0.629	0.629	—
0.277	0.7361	97.29	0.575	0.573	− 0.3
0.494	0.7936	82.94	0.541	0.534	− 1.3
0.688	0.8566	69.50	0.499	0.495	− 0.8
0.856	0.9224	57.53	0.453	0.456	+ 0.7
1.000	0.9816	49.16	0.424	0.424	—

to compute according to (4) and (1) from the compressibilities of these liquids such values for V_0 that when plotted in Figure 1 they fall on the line $p = 2.082$ and $\log k = 7.097$.

The very good agreement between L computed from compressibilities and L computed from molar volumes for mixtures constitutes the strongest evidence of the general applicability and utility of equation (4) for computation of intermolecular free lengths.

ASSOCIATED LIQUIDS

The possibility demonstrated of computing from compressibility data the free lengths between molecules in liquids is of special interest for associated liquids. If the compressibility is plotted in the ordinary way as a function of the free length for associated liquids, without taking into account molecular association, it is found that the points for these always fall to the left of the mean line corresponding to normal liquids in Figure 1. This means that the free length in the liquid, according to the computations (equation (1)) is too small for the empirical relation (4) to hold good. The conditions with the lower fatty acids are shown in Figure 6. If the free lengths are computed by using monomeric molecular weights, then all will fall to the left of the line for normal liquids. But according to current opinion these acids occur at 20° C in associated state as dimers. If this is taken into account and the double molecular weight is used for the computation of L from (1) then all the acids will fall in the neighbourhood of the line for normal liquids. This supports the utility of the method stated here for computation of free lengths from

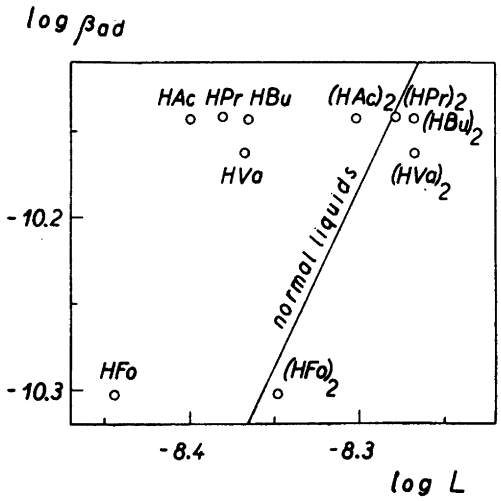

Fig. 6. Adiabatic compressibilities plotted as functions of intermolecular free lengths in fatty acids calculated as monomers and dimers. HFo = formic acid, HAc = acetic acid, HPr = propionic acid, HBu = butyric acid and HVa = valeric acid.

compressibilities and also, of course, the generally accepted opinion of organic acids as dimers.

It is in fact possible to compute in a simple manner association factors if the compressibility and zero volume of the compound are known. It is also possible to study easily association in liquid mixtures. A report on this will be given in a later work, when comparison will be made between association factors computed from different properties and in different ways.

GENERAL DISCUSSION

Compressibilities and ultra sonic velocities have been closely studied by a large number of investigators (Bergmann [8]). Efforts have been made to utilise values obtained to draw conclusions regarding the chemical constitution of the liquids (Parthasarathy [13]; Schaaffs [14]; Rao [15]). The relations obtained, however, have been very complicated or have proved not to be of general application. Thus it has been demonstrated by several authors (Lagemann *et al.*[9]; Weissler [10]; Natta *et al.*[16]) that Rao's molar sound increments are not constant. This is understandable as it has been shown that the compressibility and thus to a large extent sound velocities are dependent on the free length between the molecules. The free length in turn varies, of course, with chemical constitution, but probably not in any simple manner. There seems to be small possibility of finding such a general correlation between free length and chemical constitution.

Detailed studies have also been made of compressibility and sound velocity in liquid mixtures. Attempts have been made to find relations between these properties and the concentration of the components comprised in the mixtures. Various concentration units, such as mole fraction, weight fraction and volume fraction have been tried with the object of finding linear relations with the compressibility (or the sound velocity). It has, however, been possible only in special cases to find such linear relations and these are rather to be regarded as accidental. The shape of the curve obtained when the compressibility (sound velocity) is plotted as a function of the concentration is entirely dependent on the choice of concentration units. This may be seen from Figure 6, in which the compressibility has been plotted as a function of different concentration units in mixtures of methylene iodide and ethyl ether. If the same is done with the sound velocity the curves will be still more complicated. Sometimes such curves are used for drawing conclusions regarding associations in solutions (Parshad[17]). This, according to what is stated above, is not possible. Information regarding association in liquid mixtures can, however, as may be seen from the above, be obtained from compressibility by relation to the intermolecular free length.

SUMMARY

An empirical relation has been demonstrated between the intermolecular free length L in the liquid state and the adiabatic compressibility $\beta_{ad} = kL^p$ where k and p are constants dependent to some extent on temperature. At 20° C $p = 2.082$ and $\log k = 7.097$ for c.g.s. units. The free length is defined as $L = 2\ V_a/Y$ where the available volume $V_a = V_T - V_0$ is the difference between the molar volumes at T°K and O°K. Y is the surface of all the molecules per mole. The relation has been tested for 54 organic non-associated liquids and for 16 liquid mixtures. It has been found that the intermolecular free length can be computed from the relation stated to an accuracy of some few per cent. Association factors in liquids and liquid mixtures can be obtained from compressibility data. The isothermal compressibility follows a relation similar to that stated for the adiabatic but probably with poorer accuracy.

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