Stoichiometric Investigations of the Liquid State IV[*1]. *Viscosity of Associated Liquid*

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(Received May 9, 1957)

It is well known that viscosity of pure liquid is generally expressed by eq. (1), according to Eyring's absolute reaction rate theory.

$$\eta = \frac{hN}{V} e^{\Delta F^{\neq}/RT} \qquad (1)$$

where h is Planck's constant, N, Avogadro's number, $\Delta F^{\neq}$, standard free energy of activation per mole, and

$$\Delta F^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad (2)$$

Ep. (1) can be rewritten as eq. (3)

$$\eta = \left[\left(\frac{hN}{V}\right) e^{-\Delta S^{\neq}/R}\right] e^{\Delta H^{\neq}/RT} \qquad (3)$$

where $\Delta H^{\neq}$, standard energy of activation per mole and $\Delta S^{\neq}$ standard entropy of activation per mole.

In general, the temperature variance of the frequency factor of eq. (3) is very little compared with that of the exponential energy factor. Therefore, eq. (1) can be rewritten as eq. (4).

$$\eta = A e^{E_{vis}/RT} \qquad (4)$$

where E_{vis} is activation energy per mole for viscous flow.

In the case of associated liquid, Eyring and others[1)] thought that E_{vis} depends upon temperature because of the destruction of hydrogen bond with increase in temperature. They showed that E_{vis} decreases with the increase of temperature in the case of water, ethylene glycole and glycerin, but said nothing about typical associated liquid such as saturated alcohol and fatty acid. Thereafter, investigations concerning the viscosity of associated liquid[2-4)] are unexpectedly few. The present author discussed the reasonableness of classifying associated liquid into two kinds from analysis of sound velocity in liquid in the previous paper[5)]. In the other paper[6)], an empirical method for calculating the degree of association of associated liquid of the first kind was proposed. In this paper, detailed analysis of viscosity of associated liquid is presented.

Method and Result

E_{vis} can be calculated by eq. (5) from eq. (4).

[*1] The third paper of this series, *Bull. Chem. Soc. Japan*, **27**, 306 (1954).

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1) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes" p. 477 (1941).

2) O. Kimura, *J. Chem. Soc. Japan*, **63**, 1068 (1942).

3) Y. Wada, *J. Phys. Soc. Japan*, **4**, 136 (1949).

4) L. Grunberg, and A. H. Nissan, *Trans. Faraday Soc*,, **45**, 125 (1949).

5) K. Tyuzyo, This Bulletin **27**, 306 (1954).

6) K. Tyuzyo, *Kolloid-Z*, **131**, 40 (1953).

TABLE I

E_{vis}, A AND DIELECTRIC CONSTANT OF ASSOCIATED LIQUID

Substance	E_{vis} (Kcal/mole)	A	Range (°C)	Dielectric constant	temp. freq.
	saturated fatty acid				
formic acid	3.35	5.63×10^{-5}	8~100[a]	58.5	16 0
acetic acid	2.66	1.29×10^{-4}	31~119	6.17	20 0
propionic acid	2.47	1.63 〃	17~137	3.1	room. temp. λ=83 cm
n-butylic acid	2.81	1.25 〃	18~156	3.0	room. temp. 0
n-valeric acid	3.27	8.24×10^{-5}	16~90[a]		
n-caproic acid	3.57	7.06 〃	〃		
n-heptylic acid	3.84	6.05 〃	20~90		
n-caprylic acid	4.18	4.07 〃	50~90		
n-pelargonic acid	4.58	3.11 〃	20~90		
n-capric acid	4.76	2.71 〃	50~70		
n-lauric acid	5.10	2.69 〃	50~160		
n-myristic acid	5.34	2.46 〃	60~90		
n-palmitic acid	5.54	2.40 〃	70~95		
n-stearic acid	5.74	2.26 〃	70~98		
	saturated aliphatic alcohol				
methyl alcohol	2.61	6.92×10^{-5}	0~60	31.8	19 0
ethyl alcohol	3.57	2.74 〃	10~90	25.8	20 0
propyl alcohol	4.39	1.24 〃	10~96	21.3	19 0
n-butyl alcohol	4.64	1.07 〃	10~114	19.1	19 0
n-amyl alcohol	5.20	7.30×10^{-6}	12~80	16.0	room temp. 0
n-hexyl alcohol	5.40	4.97 〃	25~50		
n-heptyl alcohol	5.76	3.63 〃	25~90		
n-octyl alcohol	5.99	3.13 〃	15~90		
n-cetyl alcohol	6.86	2.74 〃			
	others				
hydrogen cyanide	1.64	1.15×10^{-4}	0~20	ca. 95	21 λ=84cm.
hydrogen fluoride	1.69	1.19 〃	−90~20	83.6	0 0
formamide	4.10	3.07×10^{-5}	0~120	111.5	20 0
water	varies with temperature	varies with temp.		81	19 0
ethylene glycole				38.7	
glycerine				63	−50 0
aniline				7.21	20 $0\sim4\times10^{8}$
ammonia				25	−77.7 0

a) $\log\eta$ vs. $1/T$ somewhat curves.

$$E_{vis} = \frac{\mathrm{d}\ \ln\eta}{\mathrm{d}(1/T)}\times R \tag{5}$$

When $\ln\eta$ vs. $1/T$ is linear, E_{vis} it constant, independent of the temperature. In Table I, E_{vis} and A of several kinds of associated liquid are shown. In the table, dielectric constant is also shown, to be used aftewards*.

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* Viscosity and dielectric constant are adopted from the following literatures.
International Critical Tables; *Landolt-Börnstein, Phys.-Chem Tabellen*; D'Ans-Lax, *Taschenbuch für Chemiker und Physiker*.

Discussion

(1) Classification of associated liquid.—It is clear from Tab. I, that associated liquid can be distinguished clearly into two classes. E_{vis} of one class is constant, independent of the temperature, that of the other class decreases with increase in temperature. Several examples are shown in Fig. 1. In the figure, formic acid and methyl alcohol belong to the former, whereas water and aniline to the latter. Therefore, the author proposes to classify associated liquid into two groups, as shown below. This method of classification is almost consistent with that based on sound velocity discussed in the previous paper5). This method is also almost completely consistent with that of Ewell and others7).

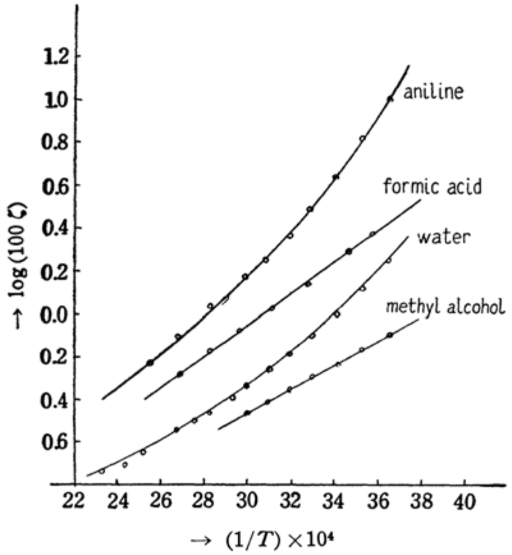

Fig. 1. Viscosity vs. temperature of several associated liquids.

a) *Associated liquid of the first kind*

E_{vis} is constant, independent of the temperature as high as the boiling point. In this class of associated liquid, associated bodies can be distinguished clearly from one another, owing to the strong hydrogen bond. Each associated body flows as a unit without destroying hydrogen bond on viscous flow.

Example: saturated fatty acid, saturated alcohol*, hydrogen cyanide, hydrogen flouoride, formamide.

b) *Associated liquid of the second kind*

E_{vis} decreases with increase in temperature. In this class of associated liquid, there are no distinguishable associated bodies owing to the weak hydrogen bond. The whole liquid makes a three-dimensional network structure and hydrogen bond is destroyed on viscous flow. This flow mechanism is consistent with that of Eyring and others1).

Examples: water, ethylene glycole, glycerin, ammonia, aniline.

In Table II, values of hydrogen bond energy are shown10). In general, hydrogen bond energy of the associated liquid of the first kind is somewhat larger than that of the associated liquid of the second kind except hydrogen cyanide. However, the idea that this small difference in hydrogen bond energy causes the above-mentioned fundamental difference of the behavior of viscous flow is quite questionable. Details of hydrogen bond energy may be discussed in the next paper of this series.

TABLE II

ENERGY OF HYDROGEN BOND

Substance	State	Method	Energy (Kcal./mole)
HF	gas	vapor density	6～10
Fatty acid	gas	vapor density	7～9
Alcohol	liquid	heat of vapor	6～7
	gas	heat conduct.	7～8
HCN	gas	vapor density	3～4
Water	s, l, g	heat of vapor second virial	4～5
	gas	second virial	3～4
Ammonia	liquid	dielectric const.	6
	solid	heat of sublim.	1.3
Acetamide	solid	heat of sublim.	3.5
Aniline		partition coeff. (CCl_4—H_2O)	1.93

(2) **E_{vis} of unassociated liquid.**—In this paragraph, E_{vis} of unassociated liquid is treated in outline, in order to clarify the structure and the degree of association of associated liquid of the first kind.

a) *E_{vis} of n-paraffin*

Relation between E_{vis} and molar volume (V)* at room temperature of *n*-paraffin is shown in Fig. 2. In this figure, E_{vis} is

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7) R. H. Ewell, J. M. Harrison and L. Berg, *Ind. Eng. Chem.*, **36**, 871 (1944).

* In some papers8,9), it is said that E_{vis} of fatty acid and alcohol varies with temperature but this variance is little. Moreover, E_{vis} is dependent upon temperature with some degree even in *n*-paraffin. Therefore, it is reasonable to regard E_{vis} of fatty acid and alcohol as being independent of temperature at this time.

8) A. Bondi, *J. Chem. Phys.*, **14**, 591 (1946).

9) T. A. Litovitz, *J. Chem. Phys.*, **20**, 1088 (1952).

10) L. N. Fergusson, "Electron Structures of Organic Molecules", p. 57 (1952); S. Seki, *Chem. and Chem. Ind., Japan*, **6**, 217 (1953).

* Molar volume at 50°C is adopted in the case of higher members.

calculated from recent data[11]. From this figure, eq. (6) is obtained.

$$E_{vis}(\text{Kcal/mole}) = 5.18 \log V(\text{cc/mole}) - 9.07 \qquad (6)$$

Eq. (6) is applicable at least to the range of V from 80 to 570. It is natural that eq. (6) is not applicable when viscous flow becomes segmental because of independence of E_{vis} upon V in such a region.

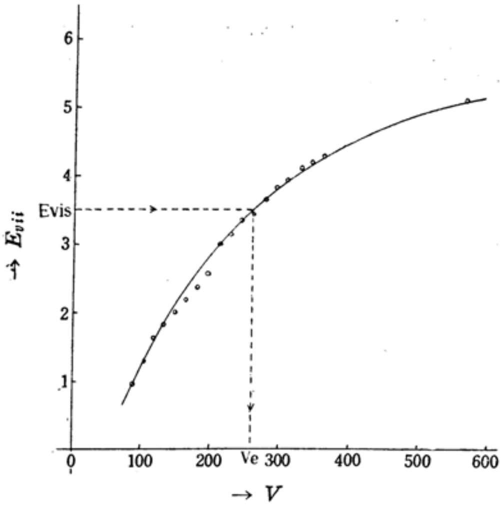

Fig. 2. E_{vis} vs. V of *n*-paraffins.

b) E_{vis} *of unassociated liquid except n-paraffin*

E_{vis} of unassociated liquid is compared with that of *n*-paraffin. Results are summarized as follows.

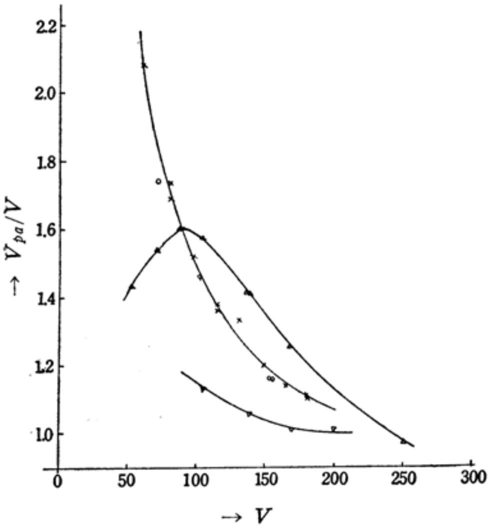

Fig. 3. V_{pa}/V vs. V of polar liquids.

×: ester ○: ketone
△: alkyl-chloride ▽: ether

i) Compared with the same value of V, E_{vis} of branched aliphatic compounds is almost the same as that of linear aliphatic compound within ±10%. This means that the influence of branching upon E_{vis} is very small.

ii) Compared with the same value of V, E_{vis} of polar compounds is greater than that of *n*-paraffin, but this difference decreases rapidly with higher homologous members and is almost zero in the region of V greater than 200. Fig. 3 shows this relation. In the figure, abscissa is V and ordinate is the ratio of V of *n*-paraffin having the same value as E_{vis} of the polar compound (hereafter, V_{pa}) to V of the polar compound.

iii) Compared with the same value of V, E_{vis} of cyclic compounds having no substituted group is much greater than that of *n*-paraffin. Namely, $V_{pa}/V \fallingdotseq 2.0$, independent of polarity. This is shown in Table III. It is clear from this fact that rigidity of structure has great influence upon viscous flow.

TABLE III

V_{pa}/V OF CYCLIC COMPOUND WITH NO SUBSTITUTED GROUP

Substance	V	E_{vis}	V_{pa}/V
Benzene	89	2.52	2.0
Cyclohexane	108	2.90	1.9
Dioxane	85.4	2.88	2.4
Thiophene	78.7	2.17	1.9
Pyridine	80.8	2.48	2.2
Cycopentane	94	1.88	1.4
Biphenyl	155	3.61	1.8

iv) V_{pa}/V decreases rapidly with increase of the number of substituted group of cyclic compound. Some examples are shown in Table 4.

TABLE IV

INFULENCE OF SUBSTITUTED GROUP OF CYCLIC COMPOUND UPON V_{pa}/V

Substance	V	E_{vis}	V_{pa}/V
Benzene	89	2.52	2.0
Toluene	106	2.90	1.9
Ethyl benzene	122	2.17	1.3
n-Butyl benzene	156	2.03	0.9
Cyclohexane	108	2.90	1.9
Methyl cyclohexane	128	2.50	1.4
1, 2-Dimethyl cyclohexane	144	2.35	1.2

(3) **Entropy of activation, $\varDelta S^{\neq}$ of viscous flow of unassociated liquid**—$\varDelta S^{\neq}$ is calculated as follows.

In eq. (4),

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[11] "Selected Values of Properties of Hydrocarbons", (National Bureau of Standards), 1947.

TABLE V
ENTROPY OF ACTIVATION OF VISCOUS FLOW OF UNASSOCIATED LIQUID

Substance	A	$\Delta S^{\ddagger}$ (E.U./mole)
Methane	1.09×10^{-4}	−0.93
Carbon tetrachloride	1.23 〃	−2,21
Benzene	8.71×10^{-5}	−1.32
Cyclohexane	6.76 〃	−1.21
Dioxane	9.16 〃	−1.40
Carbon disulfide	4.25×10^{-4}	−3.71
Toluene	1.55 〃	−2.83
Acetone	1.95 〃	−2.56
Methyl ethyl ketone	1.55 〃	−2.76
Ether	1.55 〃	−2.71
n-Ethyl valeriate	1.32 〃	−3.20
n-Butyl valeriate	1.12 〃	−3.23
n-Butyl butylate	1.32 〃	−3.37
n-Amyl n-butylate	1.20 〃	−3.38
Ethyl chloride	2.29 〃	−2.80
Ethylene chloride	2.95 〃	−3.10
Chloroform	2.82 〃	−3.46
n-Propyl chloride	1.32 〃	−2.14
Ethyl bromide	1.55 〃	−2.13
Thiophene	1.62 〃	−2.40
Pyridine	1.41 〃	−2.20
Ethane	2.49 〃	−3.06
Propane	2.69 〃	−3.57
n-Butane	1.94 〃	−3.19
n-Pentane	1.36 〃	−2.76
n-Hexane	1.34 〃	−2.99
n-Heptane	1.33 〃	−3.20
n-Octane	1.29 〃	−3.34
n-Nonane	1.23 〃	−3.44
n-Decane	1.15 〃	−3.45
n-Undecane	7.13×10^{-5}	−2.68
n-Dodecane	6.70 〃	−2.69
n-Tridecane	6.11 〃	−2.64
n-Tetradecane	6.40 〃	−2.87
n-Pentadecane	5.53 〃	−2.69
n-Hexadecane	4.92 〃	−2.57
n-Heptadecane	4.72 〃	−2.59
n-Octadecane	4.13 〃	−2.44
n-Nonadecane	4.34 〃	−2.65
n-Eicosane	3.65 〃	−2.40
	Average	−2.9

$$A=\frac{hN}{V}e^{-\Delta S^{\ddagger}/R} \tag{7}$$

Inserting numerical values of R, h, N into eq. (7),

$$\Delta S^{\ddagger}=-11.1-4.6\log(VA) \tag{8}$$

$\Delta S^{\ddagger}$ is easily calculated from eq. (8). Results are shown in Table V. It is clear from the table that

a) $\Delta S^{\ddagger}$ is almost constant and approximately equal to −2.9 E.U./mole, irrespective of polar and non-polar liquid except spherical molecules.

b) $\Delta S^{\ddagger}$ of spherical molecules is abnormal and approximately equal to −1.0∼−2.0 E.U./mole. Abnormality of E_{vis} of spherical molecules is already shown by Eyring and others¹²⁾. It is very interesting that $\Delta S^{\ddagger}$ of spherical molecules is also abnormal as is shown above.

(4) **Method for calculating degree of association of associated liquid of the first kind.**—As is shown in (1), hydrogen bond is not destroyed on viscous flow of associated liquid of the first kind. Then, it is probable that viscous flow of this kind of associated liquid is quite analogous to that of unassociated liquid. Therefore, degree of association is calculated by the following method, on trial⁶⁾.

a) *Method based on* E_{vis}

It is already shown that relation between E_{vis} and V at room temperature for *n*-paraffin is as Fig. 2 and expressed by eq. (6). V of *n*-paraffin, corresponding to E_{vis} of associated liquid of the first kind, can be obtained from Fig. 2 or eq. (6). This is termed V_e. Then, degree of association is calculated by eq. (9). Degree of association calculated by eq. (9) is termed as n_e.

$$n_e=V_e/V \tag{9}$$

where V is normal molar volume.

n_e is shown in Table VI. n_s in the table is referred to in the next paragraph. Degree of association from literature is also shown in the table. The following points are clear from the table.

i) n_e is surprisingly consistent with value from literature.

ii) It is possible to calculate easily the degree of association which has not been known until now.

iii) The n_e values for formic and acetic acid are much greater than 2 on the contrary to propionic acid and higher members of saturated fatty acid. This means that the state of association is different from each other. Investigation of the state of association in the pure liquid state is very rare. But according to the investigation of infra-red spectra by Batuev¹⁴⁾, formic and acetic acid make linear chain association and propionic acid and higher members make ring-like dimer association,

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12) H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936); R. H. Ewell and H. Eyring, *J. Chem. Phys.*, **5**, 726 (1937).

13) W. Kauzmann and H. Eyring, *J. Am. Chem. Soc.*, **62**, 3113 (1640).

14) M. I. Batuev, *Chem. Abst.*, 1936, 2994, 2995, 6154(1947).

TABLE VI

DEGREE OF ASSOCIATION OF THE ASSOCIATED LIQUID OF THE FIRST KIND

Substance	V	V_e	n_e	V_s	n_s	n	Lit. of n
saturated fatty acid							
formic acid	37.7	251	6.7	303	8.0	Polymer	Batuev[14]
acetic acid	57.2	194	3.4	132	2.3	〃	〃
propionic acid	74.6	179	2.4	105	1.4	2	Batuev[14] &
n-butylic acid	91.9	206	2.2	136	1.5	〃	Gibling[15]
n-valeric acid	108.9	245	2.2	201	1.9	〃	〃
n-caproic acid	125.0	268	2.1	249	2.0	〃	〃
n-heptylic acid	141.9	298	2.1	315	2.2	〃	〃
n-caprylic acid	158.6	337	2.1	426	2.7	〃	〃
n-pelargonic acid	174.5	400	2.3	541	3.1	〃	〃
n-capric acid	196.2 (50°C)	433	2.2	608	3.1	〃	〃
n-lauric acid	229.8 (50°C)	516	2.2	655	2.8	〃	〃
n-myristic acid	270.4 (50°C)	603	2.2	695	2.6	〃	〃
n-palmitic acid	304.6 (50°C)	668	2.2	725	2.4	〃	〃
n-stearic acid	338.9 (50°C)	724	2.1	758	2.2	〃	〃
saturated aliphatic alcohol							
methyl alcohol	40.5	191	4.7	245	6.0	5.0	Eucken[16]
ethyl alcohol	58.3	268	4.6	605	10.0	4.7	〃
propyl alcohol	75.0	367	4.9	1170	15.6	4.7	〃
n-butyl alcohol	92.0	411	4.5	1690	18.4	—	—
n-amyl alcohol	107.7	575	5.3	2610	24.3	—	—
n-hexyl alcohol	125.2	617	4.9	3390	27.0	—	—
n-heptyl alcohol	140.7	741	5.3	4240	29.8	—	—
n-octyl alcohol	156.7	813	5.2	5660	35.6	—	—
n-cetyl alcohol	(285)	1202	4.3	6780	23.0	—	—
others							
hydrogen cyanide	38.5	119	3.1	148	3.8	3	Pauling[17]
hydrogen fluoride	20.4	112	6.0	143	7.1	6~10	Bauer et al[18]
formamide	39.9	331	8.3	553	13.8	—	—

as is generally recognised. This is quite consistent with the above result. The following paragraph (5) may be refered to about this fact.

iv) n_e of saturated aliphatic alcohol is 5, independent of the carbon number. This result is consistent with Eucken's[16].

v) V_e and n_e of stearic acid are 724 and 2 respectively. V_e and n_e of octyl alcohol are 813 and 5.2 respectively. These are quite reasonable values. But n_e of cetyl alcohol is 4.3 and is slightly smaller than 5. From these facts, it can be supposed that the limit of eq. (6) exists between 810 and 1200 of V. Namely, it can be supposed that segmental flow occurs at least in the range of carbon numbers of greater than 50 for n-paraffin. This result is different from Kauzmann and Eyring's[13].

vi) No conclusive method has been so far found for determining degree of association in the pure liquid state. Moreover, accessible methods are all roundabout and complex. Although the above method is quite empirical, it is very effective under such a circum-stance.

b) *Method based on* $\Delta S^{\neq}$

It is shown in Paragraph (3) that $\Delta S^{\neq}$ of unassociated liquid is about -2.9 EU./mole except in the case of spherical molecules. Inserting $\Delta S^{\neq}=-2.9$ in eq. (8), eq. (10) is obtained. V from this is expressed as V_s.

$$V_s=1.70\times10^{-2}/A \qquad (10)$$

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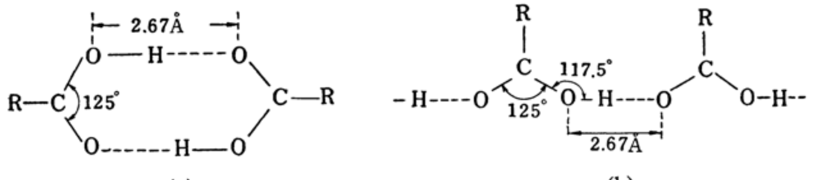
[15] T. W. Gibling *J. Chem. Soc.*, 665 (1942).

[16] A. Fucken, *Z. Elektrochem.*. **52**, 255 (1948).

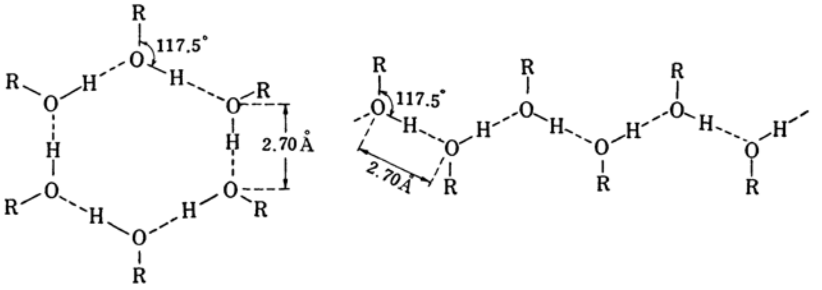
[17] L. Pauling, *Nature of Chemical Bond*, p. 275 (1939).

[18] S. H. Bauer, J. Y. Beach and J. H. Simons, *J. Am. Chem. Soc.*, **67**, 757 (1945).



(a) (b)

Fig. 4. Associated state of saturated fatty acids.



(a) (c)

Fig. 5. Associated state of saturated aliphatic alcohols[20].

In eq. (10), A is obtained from temperature variance of viscosity by eq. (4). Degree of association, n_s may be calculated by eq. (11).

$$n_s = V_s/V \tag{11}$$

where V is normal molar volume. The n_s values are shown in Table VI.

It is clear from the table that n_s is fairly consistent with values from literature, although the agreement is not so good as for n_e. However, n_s of saturated alcohol is quite different from the observed value. The reason for this is not clear, but it may be supposed that polydispersity of association of saturated alcohol[19] in the liquid state may have some influence upon this point.

(5) **Associated state of associated liquid of the first kind.**—In this paragraph, association state of associated liquid of the first kind is discussed in detail.

(a) *formic acid*

According to (4), degree of association of formic acid is 7 to 8. If association state is a ring-like dimer as is shown in Fig. 4-(a), $V_{pa}/V \fallingdotseq 2.0$ from (2)-(b), because this state is non-branched ring. But as

$$E_{vis}=3.35,\ V_{pa}/V=251/2\times37.7=3.3\neq2.0$$

This is unreasonable. Moreover, the dielectric constant is very great (58.5 as is shown Table I), and liquid viscosity is almost the same as that of valeric acid, which is higher than acetic and propionic acid. Considering these facts, it is reasonable that association is chain association as is shown in Fig. 4-(b).

(b) *acetic acid*

According to (4), n is about 3. If association state is ring-like dimer as is shown in Fig. 4-(a), $V_{pa}/V=194/2\times57.2=1.7$. But V_{pa}/V of such a slightly branched ring compound is 1.2 to 1.5 from (2)-(b). Moreover, dielectric constant is comparatively small (6.17 as is shown in Table I) and viscosity is higher than that of propionic acid. Considering these facts, it is reasonable that association state is the mixture of dimer association and chain association as is shown in Fig. 4-(a), (b).

(c) *saturated fatty acid higher than propionic acid.*

According to (4), $n=2$. If association state is a perfect ring-like dimer as is shown in Fig. 4-(a), $V_{pa}/V=1.0$. V_{pa}/V of such a branched ring compound is 1 from (2)-(b). Both these are quite consistent. Moreover, dielectric constant is small (2 to 3 as is shown in Table I). Considering these facts, it is reasonable to assume that association state is dimer association as is shown in Fig. 4-(a).

(d) *saturated alcohol*

According to (4), $n=5$. If association state is ring-like association of $n=6$, $V_{pa}/V=1.0$ from (2)-(b). However, $V_{pa}/V = \frac{5}{6} \neq 1$. Moreover, the dielectric constant

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[19] K. L. Wolf and R. Wolff, *Angew. Chem.*, **61**, 191 (1949).

[20] L. Pauling, "Nature of Chemical Bond", p. 285 (1939).

is the greatest for methyl alcohol (31.8) and becomes smaller with increasing number of carbon atom. However, dielectric constants of all these compounds are much greater than those of fatty acid higher than propionic acid. Therefore, it is reasonable that association state is chain association as is shown in Fig. 5-(b). Eucken concluded chain association of $n=5$ for lower alcohols[16]. This conclusion is quite consistent with the above.

(e) *hydrogen fluoride*

According to (4), $n=6\sim7$ and is consistent with the value from literature[18]. If association state is unbranched ring-like association, $V_{pa}/V=2.0$ from (2)-(b). Then from observed E_{vis}, $V_{ag}=V_{pa}/2.0=122/2.0=61$. Therefore. $n=61/20.4\fallingdotseq 3$. This value is unreasonable, on the basis of the ring-like structure and is not consistent with the observed value. Moreover, dielectric constant is very great (83.6 as is shown in Table I). When these facts are considered, it is reasonable that association state is chain association of $n=6\sim7$ as is shown in Fig. 6.

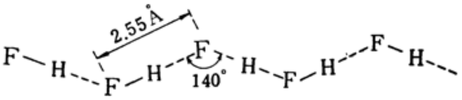

Fig. 6. Association state of hydrogen fluoride[21].

(f) *Hydrogen cyanide*

According to (4), $n=3$ and is consistent with the value from literature[17]. If association state is unbranched ring-like association, $V_{pa}/V=2.0$ from (2)-(b). Then from observed E_{vis}, $V_{ag}=V_{pa}/2.0=59.5$. Therefore, $n=59.5/38.5=1.6$. This value is unreasonable, on the basis of the ring-like structure and is not consistent with the observed value. Moreover, dielectric constant is very great (ca. 95 as is shown in Table I). When these facts are considered, it is reasonable that association state is chain association of $n=3$.

(g) *Formamide*

According to (4), $n=8\sim14$. If association state is unbranched ring-like association, $V_{pa}/V=2.0$ from (2)-(b). Then from observed E_{vis}, $V_{pa}/V=V_{pa}/2=165.5$. Therefore, $n=165.5/39.9\fallingdotseq 4$. A decisive conclusion cannot be made because of the lack of the observed value. The dielectric constant is very great (111.5 as is shown in Table I). Considering these, it is probable that association state is chain association of $n=8\sim14$.

(6) Association degree of alcohols, hydrogen fluoride and hydrogen cyanide from (4) is quite consistent with the observed degree. On the other hand, these liquids are chain association and their dielectric constants are great as is discussed in (5). If the non-polar part is extremely great compared with the polar part of polar liquid, $V_{pa}/V=1.0$ according to (2). But, in the case of the above compounds, polar part is not always extremely small compared with non-polar part. In spite of this, $V_{pa}/V_{ag}=1$ as is shown in (5). A complete explanation of this fact can not be given at present.

Summary

(1) It is concluded from analysis of viscous flow that associated liquid can be classified as follows.

The first kind: Associated bodies can be distinguished clearly from one another, owing to the strong hydrogen bond. Each associated body flows as a unit in the case of viscous flow.

Examples: saturated fatty acid, saturated aliphatic alcohol, hydrogen fluoride, hydrogen cyanide.

The second kind: There are no associated bodies which are distinguished clearly from one another, owing to the weak hydrogen bond. The liquid makes overall three-dimensional network structure. Hydrogen bond is destroyed in the case of viscous flow.

Examples: water, ethylene glycole, glycerin, ammonia.

(2) Influence of branching, polar group and ring upon activation energy of viscous flow of unassociated liquid is discussed.

(3) It is found that entropy of activation of viscous flow of unassociated liquid is constant and equal to ca. -2.9 E.U./mole with some exceptions.

(4) The method for calculating degree of association of associated liquid of the first kind from energy and entropy of activation of viscous flow is presented.

(5) Association state of the first kind liquid is discussed in detail.

The author expresses his sincere thanks to Professor Dr. N. Sata and Mr. M. Okuyama of Osaka University for their kind instruction.

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[21] L. Pauling, "Nature of Chemical Bond", p. 276 (1939),