Stoichiometric Investigations of the Liquid State. V[*1]. *Vaporization Phenomenon of Associated Liquids*

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Reasonablesness of classifying associated liquids in two kinds was discussed in the previous paper[1]. In that paper, a method for determining the degree of association of associated liquid of the first kind from viscous flow was proposed and the association state was discussed in detail.

In this paper, a method for determining the degree of association from energy of vaporization and a method for calculating energy of hydrogen bond are proposed.

Energy of vaporization of *n*-paraffin

Relation between energy of vaporization at boiling point of *n*-paraffin ($E_{vap,b}$ in Kcal./mole) and molar volume at room temperature (V in cc./mole) is shown in Fig. 1. The following equation is established approximately in the range of V larger than 250.

$$E_{vap,b}=16\log V-28.4 \qquad (1)$$

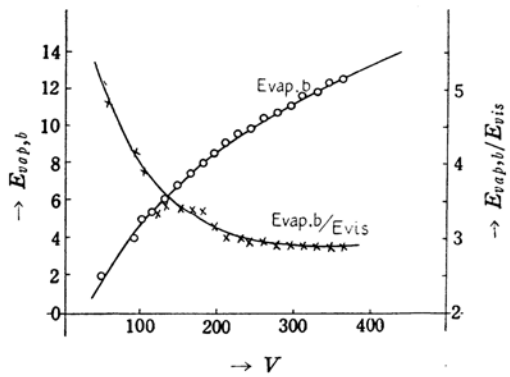

Fig. 1. $E_{vap,b}$ and $E_{vap,b}/E_{vis}$ vs. V of *n*-paraffins.

Relation between $E_{vap,b}/E_{vis}$ and V is shown in Fig. 1. This ratio decreases with increase in V and converges to about 2.8. $\log(E_{vap,b}/E_{vis}-2.80)$ vs. $\log V$ is approximately linear as is shown in Fig. 2. Eq. 2 is established from this.

$$E_{vap,b}/E_{vis}=2.80+(100/V)^2 \qquad (2)$$

This equation is applicable at least in the range of V from 60 to 370. According

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1) K. Tyuzyo, This Bulltein, **30**, 782 (1957).

to Eyring et al.[2], $E_{vap,b}/E_{vis}$ is about 3.5 for unassociated liquid, but this relation is not established rigorously as is shown in Fig. 1.

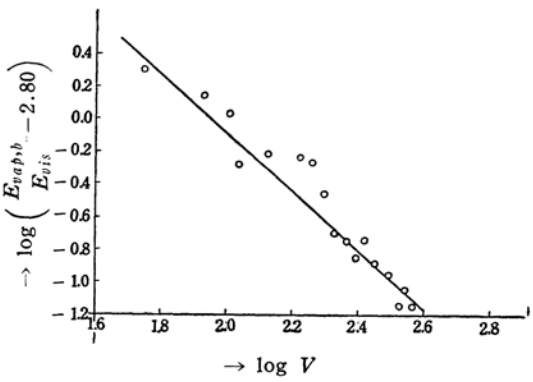

Fig. 2. $\log\left(\frac{E_{vap,b}}{E_{vis}}-2.80\right)$ vs. $\log V$ of n-paraffins.

Method for calculating degree of association of associated liquids of the first kind from energy of vaporization

Viscous flow of associated liquids of the first kind is closely analogous to that of n-paraffin as is shown in the previous paper. Therefore, if an associated body transfers from liquid to vapor phase without dissociation during vaporization, eq. 1 may be established between molar volume of associated body and energy of vaporization of this process. At the same time, eq. 2 may be established among this energy of vaporization, molar volume of associated body and energy of activation of viscous flow. Namely, when the molar volume of an associated body and the energy of vaporization of this process are respectively termed as V_a (cc/mole) and $E_{vap,a}$ (Kcal./mole), then

$$E_{vap,a}=f(V_a)$$
$$=16\log V_a-28.4 \text{ for } V_a>250 \quad (3)$$
$$E_{vap,a}=E_{vis}\cdot[2.80+(100/V_a)^2] \quad (4)$$
$$V_a=n\times V \quad (5)$$

where n is degree of association and V is normal molar volume.

V_a satisfying both eq. 3 and 4 can be obtained as is shown in Fig. 3. In the figure, curve-(a) is common for all associated liquids of the first kind and is expressed by eq. 3. Curve-(b) is characteristic for each associated liquid and is expressed by eq. 4. V_a is obtained from intersecting point of curve-(a) and (b). Then n is calculated from eq. 5.

Degree of association obtained from this method is termed as n_v and given in Table I. In the Table, n values from literature are also shown. It is clear from

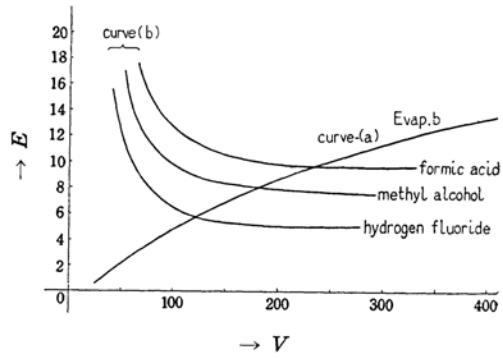

Fig. 3. Calculation of degree of association of formic acid, methanol and hydrogen fluoride.

TABLE I
DEGREE OF ASSOCIATION CALCULATED FROM EQ. 3 AND 4

Substance	V	V_v	n_v	n
saturated fatty acids				
formic acid	37.7	246	6.5	polymer
acetic acid	57.2	186	3.3	polymer
propionic acid	74.6	173	2.3	2
n-butylic acid	91.9	198	2.2	〃
n-valeric acid	108.7	238	2.2	〃
n-caproic acid	125.0	270	2.2	〃
n-heptylic acid	141.9	296	2.1	〃
n-caprylic acid	158.6	336	2.1	〃
n-pelargonic acid	174.5	394	2.2	〃
n-capric acid	196.2	423	2.2	〃
n-lauric acid	229.8	482	2.1	〃
n-myristic acid	270.4	523	1.9	〃
n-palmitic acid	304.6	564	1.9	〃
n-stearic acid	338.9	603	1.8	〃
saturated aliphatic alcohols				
methanol	40.5	182	4.5	5.0
ethanol	58.3	270	4.6	4.7
propanol	75.0	367	4.9	4.7
n-butanol	92.0	403	4.4	—
n-pentanol	107.7	500	4.6	—
n-hexanol	125.2	534	4.3	—
n-heptanol	140.7	606	4.3	—
n-octanol	156.7	673	4.3	—
n-cetanol	285	(955)	3.4	—
others				
hydrogen cyanide	38.5	118	3.1	3
hydrogen fluoride	20.4	122	6.0	6∼10
formamide	39.9	328	8.2	—

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

the table that n_v is quite consistent with n. Litérature of the n value is referred to in the previous paper. It may be understood from these facts that viscous flow of associated liquid of the first kind is closely analogous to that of n-paraffin.

A new method for calculating energy of hydrogen bonds

Vaporization process of associated liquid of the first kind is schematically shown in Fig. 4. In the figure,

State A: liquid system composed of 1 mole of associated body of n-mer just before vaporization

State B: hypothetical gas system composed of 1 mole of associated body of n-mer just after vaporization

State C: hypothetical liquid system composed of n/n' mole of associated body of n'-mer just before vaporization

State D: gas system composed of n/n' mole of associated body of n'-mer just after vaporization

E_1: dissociation energy of 1 mole of associated body of n-mer of liquid into n/n' mole of associated body of n'-mer of the liquid

E_2: Energy of vaporization of n/n' mole of associated body of n'-mer of the liquid

E_3: dissociation energy of 1 mole of associated body of n-mer of the gas into n/n' mole of associated body of n'-mer of the gas

E_4: energy of vaporization of 1 mole of associated body of n-mer of the liquid. This value is different from $E_{vap,a}$ in the preceding paragraph. Namely, E_4 is energy of vaporization at observed boiling point, compared with $E_{vap,a}$ which is energy of vaporization at the boiling point of n-paraffin corresponding to V_a.

E_5: energy required to produce n/n' mole of associated body of n'-mer of gas from 1 mole of associated body of n-mer of the liquid

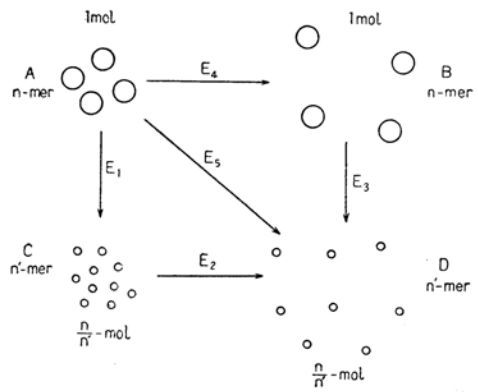

Fig. 4. Schematic representation of the vaporization process of the associated liquid of the first kind.

It is clear that the following equations are established.

$$E_4+E_3=E_1+E_2=E_5 \tag{6}$$

$$E_5=n\cdot\Delta E_{vap} \tag{7}$$

where ΔE_{vap} is observed energy of vaporization at an observed boiling point in Kcal./mole.

If the associated state is linear chain association,

$$E_3=N_A\cdot\left[(n-1)-\frac{n}{n'}(n'-1)\right]\cdot\varepsilon_{hb} \tag{8}$$

where ε_{hb} is energy of hydrogen bond per bond and N_A Avogadro's number. Namely,

$$E_3=\left(\frac{n}{n'}-1\right)\cdot E_{hb} \tag{9}$$

where E_{hb} is energy of hydrogen bond per mole in Kcal.

If the associated state is ring-like dimer association and $n=2$, $n'=1$,

$$E_3=2\cdot E_{hb} \tag{10}$$

E_4 can be calculated as follows. This is the energy of vaporization per mole of asociated body of n-mer at observed boiling point. It is widely known that the following equation is established between heat of vaporization and temperature for unassociated liquid[3].

$$\frac{\Delta H}{\Delta H_b}=\left(\frac{1-T/T_c}{1-T_b/T_c}\right)^{0.38} \tag{11}$$

where ΔH and ΔH_b are the heat of vaporization at T and T_b in °K respectively and T_c is critical temperature in °K. Therefore, energy of vaporization at T can be given by eq. 12.

$$\Delta E=(\Delta E_b+RT_b)\left(\frac{1-T/T_c}{1-T_b/T_c}\right)^{0.38}-RT \tag{12}$$

On the other hand, the following equations are established between T_b, T_c and V for n-paraffin.

$$T_c=664\log V-906 \tag{13}$$

$$T_b=620\log V-975 \tag{14}$$

It is clear from the previous paper and the preceding paragraph that an associated

3) K. M. Watson, *Ind. Eng. Chem.*, **35**, 398 (1943); K. Sato, *Kagaku Kogaku* (*Chemical Engineering*), **18**, 266 (1954) (in Japanese).

body of the first kind shows an analogous behavior to that of *n*-paraffin of equal molar volume. Therefore, critical temperature and boiling point of the associated body may be calculated by eq. 13 and 14. These are termed as $T_{c,a}$ and $T_{b,a}$. Then, E_4 can be calculated by inserting $T_{c,a}$ and $T_{b,a}$ in eq. 12 and adopting observed boiling point as T. Namely,

$$E_4=(\Delta E_{b,a}+RT_{b,a})\left(\frac{1-T_b/T_{c,a}}{1-T_{b,a}/T_{c,a}}\right)^{0.38}-RT_b \tag{15}$$

where,

$$\Delta E_{b,a}=[2.80+(100/nV)^2]\cdot E_{vis} \tag{16}$$

$$T_{b,a}=620\log(nV)-975 \tag{17}$$

$$T_{c,a}=664\log(nV)-906 \tag{18}$$

TABLE II
CALCULATION OF ENERGY OF HYDROGEN BOND

Substance	E_{vis}	ΔE_{vap}	V	T_b	$T_{b,a}$	$T_{c,a}$	n	n'	E_{hb}	lit. for n'
saturated aliphatic alcohols										
methanol	2.61	7.73	40.5	338	440	631	5	1	7230	(4)
ethanol	3.57	8.75	58.3	351	532	732	〃	〃	7440	〃
propanol	4.39	9.08	75.0	370	615	804	〃	〃	6800	〃
n-butanol	4.64	9.60	92.0	391	637	864	〃	〃	7420	〃
n-pentanol	5.20	10.25	107.7	411	698	907	〃	〃	7420	〃
n-hexanol	5.40	10.75	125.2	429	715	951	〃	〃	8030	〃
n-heptanol	5.76	11.30	140.7	449	749	985	〃	〃	8270	〃
n-octanol	5.99	11.70	156.7	468	778	1017	〃	〃	8520	〃
saturated fatty acids										
formic acid	3.35	4.77	37.7	374	508	728	7	2	8430 3610	(5)
acetic acid	2.66	5.03	57.2	391	432	586	3	1.8	8580 360	(6)
propionic acid	2.47	6.48	74.6	414	412	586	2.3	(1.4)	11150 2600	
n-butylic acid	2.81	9.16	91.9	437	449	605	2	1.1	11300 5650	(7)
n-valeric acid	3.27	9.60	108.7	460	500	651	〃	(1)	8200 4100	
n-caproic acid	3.57	(9.96)	125.0	478	532	690	〃	(1)	7850 3930	
n-heptylic acid	3.84	(10.40)	141.9	496	558	725	〃	1	7860 3930	(7)
n-caprylic acid	4.18	(10.85)	158.6	512	594	756	〃	(1)	7120 3560	
n-pelargonic acid	4.58	(11.28)	174.5	527	633	784	〃	(1)	5990 3000	
n-capric acid	4.76	(11.86)	196.2	541	653	816	〃	(1)	6530 3270	
n-lauric acid	5.10	12.58	229.8	574	688	864	〃	(1)	7030 3520	
n-myristic acid	5.34	13.50	270.4	601	709	911	〃	(1)	8700 4350	
n-palmitic acid	5.54	(14.01)	304.6	628	731	944	〃	(1)	9380 4690	
n-stearic acid	5.74	14.56	338.9	658	747	974	〃	(1)	10480 5240	
others										
hydrogen cyanide	1.64	6.05	38.5	299	306	462	3	1.1	7070	(8)
hydrogen fluoride	1.69	6.46	20.4	293	315	481	6	1.8	14000	(9)

4) L. Grunberg and A. H. Nissan, *Trans. Faraday Soc.*, **45**, 125 (1949).
5) R. Wolff, *Angew. Chem.*, **67**, 89 (1955).
6) M. Toda, Structure of Liquid, p. 51 (1949) (in Japanese); Ref, (6).
7) R. E. Lundin, F. E. Harres and L. K. Nash, *J. Am. Chem. Soc.*, **74**, 743 (1952).
8) W. F. Giauque and R. O. Ruehervin, ibid., **61**. 2626 (1939).
9) J. Simon and J. H. Hildebrand, ibid., **46**, 2183 (1924); R. W. Long, J. H. Hildebrand and W.E. Morrell, ibid., **65**, 182 (1943).
10) S. Seki, *Chemistry and Chemical Industry*, **6**, 182 (1953) (in Japanese); L. N. Fergusson, Electron "Structures of Organic Molecules," p. 57 (1952).

TABLE III
ENERGY OF HYDROGEN BOND

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

Following equations may be deduced from equation 6, 7, 9, 10 and 15.

(i) linear chain association

$$(\Delta E_{b,a}+RT_{b,a})\left(\frac{1-T_b/T_{c,a}}{1-T_{b,a}/T_{c,a}}\right)^{0.38}-RT_b+\left(\frac{n}{n'}-1\right)\cdot E_{hb}=n\Delta E_{vap} \quad (19)$$

(ii) ring-like dimer association

$$(\Delta E_{b,a}+RT_{b,a})\left(\frac{1-T_b/T_{c,a}}{1-T_{b,a}/T_{c,a}}\right)^{0.38}-RT_b+2E_{hb}=2\Delta E_{vap} \quad (20)$$

Using eq. 19 and 20, one of the values, n, n' and E_{hb} can be calculated from the remaining two, when V, E_{vis}, T_b and ΔE_{vap} are known.

In Table II are shown T_b, $T_{b,a}$ and $T_{c,a}$ from eq. 17 and 18, n, n' and E_{hb} from eq. 19 and 20 and literature for n'. Moreover, energy of hydrogen bond from literature is shown in Table III.

The following is clear from the tables.

1) Calculated values of energy of hydrogen bond of alcohols are quite consistent with those from literatures and are independent of the length of carbon chain.

2) Calculated values of energy of hydrogen bond of formic- and acetic acid are quite consistent with those from the literature of the subject if the associated state is linear chain association, but are quite inconsistent if the associated state is ring-like dimer association. This fact suggests linear chain association of these compounds in the liquid state.

3) In propionic- and *n*-butylic acid, E_{hb} values based on linear chain association are too great and those based on ring-like dimer association are too small. This fact suggests mixture of linear chain and ring-like association in the liquid state. These results are quite consistent with those in the previous paper.

4) In higher fatty acids, calculated values of E_{hb} are fairly consistent with those from literature, which assumes linear chain association. However, a decisive answer cannot be given because of the lack of accurate data of degree of association in the gaseous state, n'. E_{hb} based upon ring-like dimer association may be more consistent with the observed value even if n' is slightly greater than unity.

5) Calculated value of E_{hb} of hydrogen cyanide is about two times as great as that from literature. However, accurate data of E_{hb} of this compound are very rare. Moreover, E_{hb} of water is greater than that of hydrogen cyanide from literature, though water belongs to the associated liquid of the second kind and its hydrogen bond is easily destroyed with increase in temperature according to the previous paper. Considering these facts, the E_{hb} value of hydrogen cyanide from literature seems to be too small. A detailed investigation may be required.

6) Calculated value of E_{hb} of hydrogen fluoride is some what greater than that from literature, but the cause is not clear at present. However, the value from literature is not quite accurate.

The starting equation is $E_4+E_3=E_5$ in the above treatment, but it is of course possible to start from the equation, $E_1+E_2=E_5$. However, E_1 does not consist of the energy required to destroy hydrogen bond, because this process is a dissociation reaction in the liquid state. Moreover, eq. 2 which is established in the case of *n*-paraffin is not always applicable to E_2, because E_2 is the energy of vaporization

of a polar liquid. Therefore, the method based on E_1 and E_2 is more difficult than that based on E_4 and E_3. At any rate, it is very remarkable that energy of hydrogen bond can be calculated as shown above, on the assumption that the associated body of the first kind is analogous to *n*-paraffin.

Summary

1) Energy of vaporization of *n*-paraffin is discussed. It is shown that relation between ΔE_{vap} at the boiling point and E_{vis} is different from that of Eyring et al..

2) A new method for calculating the degree of association of the first kind from energy of vaporization is proposed. The degree of association calculated by this method is quite consistent with the result of the previous paper and the value from literature.

3) A new method for calculating the energy of hydrogen bond is proposed. Energy of hydrogen bond obtained by this method is fairly consistent with the value from literature.

4) Considering all results, it can be concluded that the associated body of the first kind shows analogous behavior to *n*-paraffin.

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