269. *Viscosity and Molecular Association. Part I.*

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The relationships previously published by the author are extended to associated liquids, and a viscometric method of calculating degrees of association of alcohols and amines is presented. For ten lower alcohols, the degrees of association are largely independent of temperature over the temperature ranges examined.

In previous publications (*J.*, 1946, 573; 1947, 822), the author advanced the equations :

$$\log_{10}\eta\sqrt{v} = c + k(T_c/T - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$\log_{10}\eta\sqrt{v} = \alpha + \beta/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$\log(\phi\sqrt{d}/\phi_c\sqrt{d_c}) = a \log p/p_c \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or

$$\log_{10}\phi\sqrt{d} = b + a \log_{10}p \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where η, ϕ, v, d, and p are the viscosity, fluidity, specific volume, density, and vapour pressure respectively at absolute temperature T; α, β, and k are constants. The suffix $_c$ denotes critical values.

$c = \log_{10}\eta_c\sqrt{v_c}$ was shown to be ~ 0.067 (η in 10^3 poises) for non-associated substances. Equation (3) also leads to a sensibly constant figure (~ 1.256) for $\eta_c\sqrt{v_c}$. As previously indicated, the two figures are somewhat different.

(1) or (2) may be converted into (3) or (4) by means of the equation

$$\log_e p = c - E/\boldsymbol{R}T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

so that $a = 4.571\beta/E$. (5) was shown to hold for non-associated liquids with satisfactory accuracy from temperatures somewhat below the b. p. to the critical point. At temperatures sufficiently below the b. p., E becomes equal to L, the latent heat of vaporisation of 1 g.-mol.

It was further shown that for non-associated substances, with the exception of a few possessing highly symmetrical molecules, $a \sim 0.220$.

The molecular weight in the liquid state for an associated substance may be greater than that in the vapour state, but we may assume that $4.571\beta/L' = 0.220$, where L' is the g.-mol. latent heat of the association complex *per se*. It is well known that the latent heat of an associated substance is greater than that of a normal liquid at the same temperature. It includes not only the energy used to overcome the intermolecular forces, but an additional amount absorbed in the breaking up of the complex into monomers. Assuming the latter to be x cals. per unit formula weight, we may write $L' = \gamma(L - x)$, where γ is the degree of association and L is the latent heat of vaporisation of the associated substance per formula weight, so that $4.571\beta/\gamma(L - x) = 0.220$. But $4.571\beta = aL$, therefore $aL/\gamma(L - x) = 0.220$, or, more accurately,

$$aE/\gamma(E - x) = 0.220 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It has been shown by Kistiakowsky (*Z. physikal. Chem.*, 1923, **107**, 65) that the g.-mol. latent heat of a non-associated substance at its b. p., T_b, is given by a modified Trouton relationship :

$$L_b = 2.303\boldsymbol{R}T_b \log_{10}82.07T_b \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The value of L_b so calculated for an associated liquid is less than the experimental value, and it is suggested that the difference between them is equal to the value of x at the b. p. Hence γ at the b. p. can be calculated from (6).

A less restricted and probably more reliable method is presented below.

Association in alcohols is generally assumed to be due to the formation of " hydrogen bonds " (see below). Let h be the heat liberated in the formation of N such bonds. Then the total heat absorbed in the breaking up of the complex into monomers is, per formula weight, $(\gamma - 1)h/\gamma$, *i.e.*,

$$x = (\gamma - 1)h/\gamma \text{ or } h = x\gamma/(\gamma - 1)$$

Values of h so determined are tabulated below, together with values of γ_b. The values of E used in (6) are the mean figures over the temperature ranges in question. Strictly, E_b should have been used; however, the temperature ranges are such that (5) may be considered accurate. In any case, small variations in E do not significantly affect the numerical values of γ. In most cases mean figures of L_b taken from the results of several workers have been used in the calculations, references to which are given as footnotes to the table.

Equation (7) holds for a large number of non-associated liquids with an average error of 3%. Taking ethyl alcohol as typical of an associated liquid, we have $L_b = 9429$ cals.; assuming an error of 3%, L_b calculated from (7) = 7160 ± 215 cals., whence $x = 2269 \pm 215$ cals., *i.e.*, $2269 \pm 9.5\%$. An increase of 9.5% in x increases γ by only 2.5%, but increases h by 6% to 5200 cals. It is probable, then, that in general the average error in h so determined is $\sim \pm 6\%$. In individual cases, errors in L_b and hence in h may be substantially greater than this. Further, in (6), 0.220 is only an average value of a; the true value of a for a given substance may differ from this by a few units %. Probably the higher values of h exhibited by the two higher primary alcohols are due to such causes.

TABLE I.

Alcohol.	L_b, exptl.	L_b, calc.	x.	E.	a.	γ.	$\dfrac{h}{100}$.	Refs.
Methyl	8,418	6870	1548	9,133	0·264	1·44	50	1, 2
Ethyl	9,429	7160	2269	10,100	0·321	1·88	48	1, 2, 3
Propyl	9,870	7570	2300	11,180	0·381	2·20	42	1
Butyl	10,460	8050	2410	12,040	0·375	2·13	45	2
Heptyl	12,170	9380	2790	13,820	0·325	1·85	61	1
Octyl	12,680	9820	2860	15,810	0·350	1·94	59	1
*iso*Propyl	9,608	7250	2358	10,520	0·482	2·82	37	1, 2, 3
*iso*Butyl	10,220	7840	2380	11,320	0·476	2·74	38	1, 2
tert.-Butyl *	9,660	7270	2390	10,520	0·571	3·35	34	1
*iso*Amyl	10,540	8360	2180	12,400	0·405	2·23	40	1, 2

(1) " International Critical Tables."
(2) Matthews, *J. Amer. Chem. Soc.*, 1926, **48**, 562.
(3) Parks and Nelson, *J. Physical Chem.*, 1928, **32**, 61.
* See Part II (following paper).

The values of h printed in Table I are strictly those at the b. p. and therefore for primary straight-chain alcohols cover a temperature range of 78—195°. However, they are seen to be constant within the limits of accuracy of the method. Although it is to be expected that h will vary from one alcohol to another to a certain extent, and depend on temperature, it is reasonable to suppose that within such limits the " hydrogen bond " energy for such alcohols is constant at 5000 ± 300 cals. over the temperature range in question. The values for the branched-chain alcohols whether primary, secondary, or tertiary, are similarly constant at 3800 cals.

The heats of sublimation of solid methyl and ethyl alcohols are 9·8 and 11·2 kcals. per formula weight respectively; approximately 3·5 and 5·0 kcals., respectively, may be attributed to van der Waals forces, leaving $\sim 6·2$ kcals. as the energy necessary to disrupt the hydrogen bonds. Assuming complete co-ordination, *i.e.*, one hydrogen bond per formula molecule, this leads to a figure $\sim 6·2$ kcals. for the energy of N such bonds (Pauling, " The Nature of the Chemical Bond ", 1940). The figure agrees tolerably well with the above estimated value of 5·0 kcals.; the difference might well be attributed to the different temperatures appertaining in the two methods of determination.

We can therefore write

$$\gamma = 4\cdot545aE - h/(E - h) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In the general case, a and E are both functions of temperature. If their values at any temperature could be estimated, γ at that temperature could be calculated. Methods of achieving this end are discussed in Part II.

Values of γ calculated from (8) are printed in Table II; they are in close agreement with those previously given, and are probably accurate to $\sim \pm 5\%$.

TABLE II.

	T, °K.	P, atm.	k.	a.	$\eta_c\sqrt{v_c}$ from (1).	$\eta_c\sqrt{v_c}$ from (3).	Error, % : in (2).	in (4).	γ.	Temp. range, °C.	Refs. η.	p.
NEt₃	535	—	0·7206	0·214	1·096	—	0·0	—	0·96	0—100 E	1	—
NPhMe₂	688	35·8	0·7780	0·2214	1·234	1·311	0·1	0·4	1·00	60—189 C	1, 2	1
NPhMeEt	700 *	—	0·8340	0·238	1·129	—	0·2	—	1·10	109—195 E	2	—
NPhEt₂	705	29·4 *	0·7909	0·2126	1·321	1·445	0·5	0·5	0·96	100—188 C	2	1
o-C₆H₄Me·NMe₂	671 *	32·4 *	0·8433	0·239	1·187	1·265	0·3	—	1·10	72—182 B	2	2
p-C₆H₄Me·NMe₂	700 *	32·4 *	0·7661	0·212	1·199	1·250	0·0	—	0·96	101—204 B	2	2
m-C₆H₄Me·NEt₂	714 *	—	0·8714	0·241	1·191	—	0·1	—	1·11	115—218 E	2	—
(Averages)	—	—	—	0·225	1·193	—	—	—	1·03	—	—	—
AcOH	595	57·2	0·9206	0·2596	1·321	1·396	0·3	0·2	—	20—110 A	3	2
Et·CO₂H	612	53·0	0·8279	0·2112	1·390	1·511	0·5	0·8	0·96	20—140 A	3	3
Pr·CO₂H	628	45·1 *	0·9317	0·2200	1·339	1·489	0·4	0·8	1·00	50—160 A	3	4
Prⁱ·CO₂H	609	45·1 *	0·9074	0·2162	1·416	1·534	0·3	0·5	0·98	40—140 A	3	3
(Averages)	—	—	—	0·227	1·366	1·482	—	—	·0·98	—	—	—
NHPr₂	550	—	0·8543	0·245	1·104	—	0·2	—	1·15	20—104 E	2	—
NHBu₂	599 *	—	0·8553	0·234	1·236	—	0·0	—	1·08	83—151 E	2	—
NHPhMe	702	51·3	0·8602	0·2364	1·133	1·207	0·5	0·1	1·09	95—180 C	2	1
NHPhEt	711 *	36·1 *	0·8764	0·2434	1·016	1·145	0·3	0·1	1·13	100—196 C	2	1
NHPhPr	723 *	—	0·8642	0·246	1·122	—	0·3	—	1·14	106—210 E	2	—
NHPhBu	741 *	—	0·8644	0·242	1·119	—	0·3	—	1·12	99—221 E	2	—
(Averages)	—	—	—	0·241	1·122	1·176	—	—	1·12	—	—	—
NH₂Ph	699	52·4	1·0320	0·2914	1·081	1·206	0·1	0·1	1·39	105—169 D	4	2, 4
o-C₆H₄Me·NH₂ ...	713 *	40·7 *	0·9860	0·2767	1·081	1·233	0·1	0·2	1·31	102—193 C	4	5
m-C₆H₄Me·NH₂ ...	713 *	40·7 *	0·9479	0·2619	1·059	1·197	0·2	0·1	1·23	101—193 C	4	5
p-C₆H₄Me·NH₂ ...	714 *	40·7 *	0·9917	0·2786	0·9928	1·130	0·2	0·1	1·32	136—190 C	4	5
o-C₆H₄Cl·NH₂ ...	730 *	—	0·9105	0·269	1·143	—	0·7	—	1·28	61—189 E	4	—
o-C₆H₄(OMe)·NH₂	737 *	—	1·0060	0·294	1·056	—	0·1	—	1·42	124—210 E	4	—
NH₂Bu	516 *	—	1·1100	—	1·040	—	0·3	—	—	19—73 —	4	—
(Averages)	—	—	—	0·279	1·191	1·191	—	—	1·32	—	—	—
MeOH	513	78·7	1·0267	0·2636	1·128	1·218	0·2	0·3	1·44	0—60 A	3	2
EtOH	516	63·1	1·3742	0·3206	1·200	1·415	0·7	1·0	1·91	0—70 A	3	2
PrOH	537	49·9	1·7350	0·3812	0·9051	1·251	0·3	0·9	2·33	0—90 A	3	2
PrⁱOH	508	53·0	2·1798	0·4825	0·6699	0·8590	0·6	0·4	2·87	0—80 A	3	6
BuOH	560	48·4	1·7587	0·3752	0·8166	1·148	0·3	1·0	2·21	0—100 C	3	7
BuⁱOH	538	48·0	2·2106	0·4756	0·6320	0·9690	1·0	0·3	2·74	10—100 A	3	3
AmⁱOH	580	42·0 *	1·9448	0·4048	0·5999	0·9988	1·8	0·5	2·21	10—130 A	3	3
C₆H₁₃·OH	611 *	37·8 *	1·7136	0·3772	0·7406	1·017	2·0	0·2	2·17	35—155 A	5	8
C₇H₁₅·OH	634 *	35·8 *	1·6230	0·3248	0·7004	1·133	1·8	0·2	1·75	40—140 C	1	7
C₈H₁₇·OH	660 *	33·6 *	1·8970	0·3500	0·4093	0·9895	1·9	0·3	1·87	20—100 C	1	7
CH₂:CH·CH₂·OH	545	59·0 *	1·4174	0·3360	0·8902	1·073	0·2	0·3	2·02	0—90 D	3	9

References.—*Viscosity* (η). (1) From the compilation of Bingham and Spooner, *Physics*, 1933, **4**, 387. (2) Friend and Hargreaves, *ibid.*, 1944, **35**, 619. (3) Thorpe and Rodger, *Phil. Trans.*, 1894, **185**, 397; 1897, **189**, 71. (4) Friend and Hargreaves, *Phil. Mag.*, 1944, **35**, 57. (5) Hovorka, Lankelma, and Stanford, *J. Amer. Chem. Soc.*, 1938, **60**, 820.
Vapour pressure (*p*). (1) Nelson and Wales, *ibid.*, 1925, **47**, 868. (2) " International Critical Tables." (3) Schmidt : taken from " Physico-Chemical Tables " (Castell-Evans, Griffin and Co. Ltd., 1902). (4) Ramsay and Young, *ibid.* (5) Berliner and May, *J. Amer. Chem. Soc.*, 1927, **49**, 1007. (6) Parks and Barton, *ibid.*, 1928, **50**, 25. (7) Butler, Ramchandani, and Thomson, *J.*, 1935, 280. (8) Hovorka *et al., loc. cit.* (9) Stull, *Ind. Eng. Chem.*, 1947, **39**, 517.

A similar treatment for amines is ruled out on account of the fact that the values of *x* are so much smaller owing to lower degrees of association that even an approximate evaluation of *h* is impossible. However, the energy of the bond N—H---N will be less than that of O—H---O (Pauling, *op. cit.*) ; an arbitrary figure of 2 kcals. has been assumed in this paper as probably being near the true value (that in solid ammonia has been stated to be 1·3 kcals.). The degrees of association of amines are found to be so much lower than those of alcohols that even if a value of *h* 50% lower be assumed, the consequent difference in the evaluation of λ is only ∼3%. Thus for aniline we get *h* = 2 kcals., γ = 1·39 ; *h* = 1 kcal., γ = 1·35 ; *h* = 3 kcals., γ = 1·44.

Values of β and *a* of equations (2) and (4) respectively are printed in Table II, together with corresponding values of $\eta_c\sqrt{v_c}$. The constants were evaluated by application of Campbell's " zero sum " method (*Phil. Mag.*, 1920, **39**, 177 ; 1924, **47**, 816). Critical temperatures and pressures were taken from the " International Critical Tables " except those marked *, which were calculated from Hertzog's parachor–critical temperature–critical pressure relationships (*Ind. Eng. Chem.*, 1944, **36**, 997). The critical pressures so calculated are probably much less

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reliable than the critical temperatures.   Cols. 7 and 8 show the average percentage deviations between the experimental values of $\eta\sqrt{v}$ and those calculated by means of (2) and (4) respectively.

The nature of the experimental data is such as to necessitate evaluation of a by a number of different procedures.   The procedure adopted for a particular substance is indicated as in a previous paper (*J.*, 1947, 822) by the letters A, B, C, and D in the table.   In a few cases (E) vapour-pressure data are lacking, so a has then been calculated from β and the b. p. of the substance (*ibid.*).

$$\text{Now} \qquad \frac{\mathrm{d}\,\log_{10}\phi\sqrt{d}}{\mathrm{d}\,\log_{10}p} = \frac{\mathrm{d}\,\log_{10}\phi\sqrt{d}}{\mathrm{d}(1/T)} \cdot \frac{\mathrm{d}(1/T)}{\mathrm{d}\,\log_{10}p} = a$$

It has been shown that $\mathrm{d}\,\log_{10}\phi\sqrt{d}/\mathrm{d}(1/T)$ $(-\beta)$ is sensibly constant for non-associated liquids only at temperatures near the b. p. but increases slowly at lower temperatures (*J.*, 1946, 573).   For most of the alcohols examined, β is not a constant even near the b. p. and increases rapidly as the temperature falls.   On the other hand, $\mathrm{d}(1/T)/\mathrm{d}\,\log_{10}p$ $(-2\cdot303R/E)$ decreases with fall in temperature, the effect being greater for alcohols than for non-associated liquids. The effects are therefore compensatory.   In fact, the average of the mean percentage errors involved in (4) is only $0\cdot5\%$ for the ten alcohols examined as compared with an average of $1\cdot1\%$ involved in (2).   The improvement is particularly noticeable in the higher alcohols, of which *n*-hexyl alcohol is typical (Table III).   These show log $\eta\sqrt{v}$–$1/T$ curves which are markedly convex to the $1/T$ axis.   It seems likely then that (4) is to be preferred to (2), and the former might well prove to be the more fundamental equation.   For this reason it is to be expected that for such liquids the critical values of $\eta\sqrt{v}$ obtained by extrapolation of (2) and (4) will be widely different.   In fact, for amines, but to a less extent for primary straight-chain alcohols, values of $\eta_c\sqrt{v_c}$ from (3) do not differ greatly from the average value for non-associated liquids. On the other hand, with the exception of secondary and tertiary amines, (1) leads to values of $\eta_c\sqrt{v_c}$ noticeably lower than $1\cdot167$, and these are probably unreliable.

It is perhaps surprising that the lower alcohols considered in this paper show degrees of association which do not demonstrably decrease with rising temperature, at least over the ranges examined.   This is in keeping with Rao's conclusion (*J. Indian Chem. Soc.*, 1945, **22**, 260) from dipole-moment evidence that changes in temperature from 5° to 70° show no appreciable changes in the degrees of association of methyl and ethyl alcohol.   In fact, methyl, ethyl, propyl, and *iso*butyl alcohols show linear plots of log η against $1/T$ right down to temperatures of $\sim -75°$ (cf. Andrade, *Phil. Mag.*, 1934, **17**, 698).
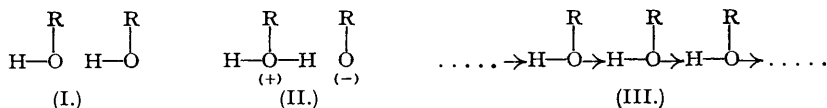
TABLE III.

| Temp.	p, mm.		$\eta\sqrt{v}$, exptl.	$\eta\sqrt{v}$, calc. from (2).	Error, %.	$\eta\sqrt{v}$, calc. from (4).	Error, %.
35°	2·0	(1·94) †	37·92	35·92	+5·5	37·97	−0·1
45	4·4	(3·99)	29·05	28·08	+3·4	28·96	+0·3
55	7·8	(7·78)	22·53	22·29	+1·0	22·51	+0·1
65	14·0	(14·4)	17·86	17·93	−0·4	17·84	+0·1
75	25·9	(25·5)	14·37	14·61	−1·6	14·40	−0·2
85	43·3		11·75	12·04	−2·4	11·80	−0·4
95	71·4		9·76	10·02	−2·5	9·76	±0·0
105	112·7		8·226	8·431	−2·5	8·208	+0·2
115	171·0		7·011	7·153	−2·1	7·018	−0·1
125	251·0		6·053	6·119	−1·1	6·063	−0·2
135	367·0		5·258	5·274	−0·3	5·269	−0·2
145	516·5		4·623	4·580	+0·9	4·620	+0·1
155	714·0		4·104	4·002	+2·5	4·092	+0·3
				Mean	2·0	Mean	0·2

† The vapour pressures given in parentheses are those calculated from the p–T equations of the experimenters.   The actual values at the lower temperatures were not measured with the requisite degree of accuracy.   The former have been used in the calculations entailed in the table.

Association in alcohols and in amines is generally considered (Pauling, *op. cit.*) to be due to the formation of the so-called " hydrogen bond ".   Thus alcohols have two possible structures of similar energy, (I) and (II), the actual molecule being a combination or resonance hybrid of the two.   In this way chains are built up which might extend considerably through the liquid, these being written conventionally as in (III).   The molecules are held together, and the associated system stabilised, by the resonance energy.   Such association occurs readily between

molecules containing the hydroxyl group, for the oxygen atom is both a good " donor " and " acceptor " of electrons.

$$
\begin{array}{ccc}
\underset{\text{H}-\overset{\displaystyle\text{R}}{\underset{|}{\text{O}}}\;\;\text{H}-\overset{\displaystyle\text{R}}{\underset{|}{\text{O}}}}{\text{(I.)}}
&
\underset{\text{H}-\overset{\displaystyle\text{R}}{\underset{|}{\underset{(+)}{\text{O}}}}-\text{H}\;\;\overset{\displaystyle\text{R}}{\underset{|}{\underset{(-)}{\text{O}}}}}{\text{(II.)}}
&
\underset{\cdots\cdots\to\text{H}-\overset{\displaystyle\text{R}}{\underset{|}{\text{O}}}\to\text{H}-\overset{\displaystyle\text{R}}{\underset{|}{\text{O}}}\to\text{H}-\overset{\displaystyle\text{R}}{\underset{|}{\text{O}}}\to\cdots\cdots}{\text{(III.)}}
\end{array}
$$

The position with amines is similar, the resonating structures being (IV) and (V), the hybrid being written as in (VI). However, unlike the R—O (−) ion, the R—NH (−) ion is not readily

(IV.)   (V.)   (VI.)
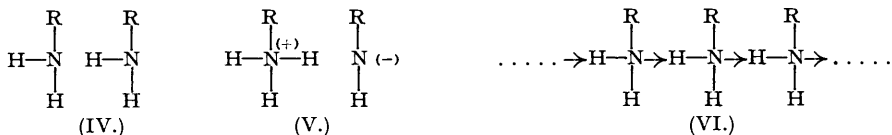
formed, the nitrogen atom being a good donor but a poor acceptor. The resonance energy of primary and secondary amines is thus much less than that of alcohols, and the degrees of association of the former might accordingly be expected to be lower. In fact, the secondary amines in the present work have values of $\gamma \sim 1\cdot12$, showing that they are associated only to the extent of $\sim 12\%$. Primary amines are seen to be somewhat more associated ($\sim 32\%$).

Tertiary amines do not contain the group $> \text{NH}$ and therefore cannot form a hydrogen bond. In fact they exhibit normal values of a and are, if at all, only very slightly associated.

Normal values of a are also exhibited by fatty acids showing that the molecular weight in the liquid state is identical with that in the vapour state. Hence, in view of the fact that vapour-density measurements show them to be dimeric in the vapour state at temperatures near the b. p., they must also be dimeric in the liquid state—a conclusion in harmony with that reached from X-ray diffraction measurements (Glasstone, " Text-book of Physical Chemistry ", Macmillan and Co., Ltd., 1940, p. 501). On the other hand, fatty acids are unique inasmuch as their values of $\eta_c\sqrt{v_c}$ appear to be significantly higher ($\sim 9\%$) than the mean value for normal substances, which of course implies that if the log $\phi\sqrt{d}$–$1/T$ plots continued linear above their boiling points, they would be more viscous at their respective critical temperatures than normal liquids. It is likely, however, that dissociation of the complexes would occur at higher temperatures, proceeding more rapidly in the vapour than in the liquid phase. We might then expect a to increase gradually so that the acids would become increasingly less viscous at a higher rate than previously, thus leading possibly to normal values of $\eta_c\sqrt{v_c}$. Such an explanation would imply that with rising temperature an increasing quantity of heat would be absorbed in breaking up the complexes into monomers. In fact, acetic acid is exceptional inasmuch as its latent heat actually increases slightly with temperature before the normal falling off occurs, and even then decreases more slowly than the latent heats of normal liquids.

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