

Ponderal Effect due to Alkyl Substitution on Physical Constants of Alcohols—A Quantitative Correlation

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The parameter of ponderal substituent effect, $\log(1/\mu)$, has been shown to give good linear correlations with functions of various physical constants for alcohols of normal series. The functions, in all cases, apparently represent hydrogen-bond strength under the different circumstances of different physical processes. The correlation is therefore suggested to be of ponderal effect on H-bonding.

INTRODUCTION

Ponderal substituent effect on solvation bonds due to alkyl substitution in solvent molecules has been reported, using alcohols as solvents, by the author¹. A parameter of the effect, $\log(1/\mu)$ —where μ is the reduced molecular weight of the solute and the solvent, given by $\mu = M_1M_2/(M_1 + M_2)$, where M_1 and M_2 being the molecular weights of the solute and the solvent respectively—has been quantitatively correlated to reactivity parameters in a number of (11) solvation-dependent reactions in the alcoholic solvents¹⁻⁵. The correlation has been theoretically justified on the basis of substituent mass effect on the vibrational energy of the solvation bond, the weakness and the length of the solvation bond keeping the otherwise stronger polar and steric substituent effects minimal.

Against this background it seemed logical that under the same or similar circumstances it would be possible to observe ponderal effect on intermolecular hydrogen bonds in alcohols. For, H-bonds also are covalent in character; weaker than regular covalent bonds; and therefore longer. It could be possible to get quantitative correlation as well, with the ponderal parameter.

The difference will have to be in the experimental parameters. For example, in the case of solvation bonds, the function $\ln k$ (k being rate constant), linearly related to activation energy (through the relationship $k = Ae^{-\Delta E/RT}$) represented the changes in activation energy due to changing alkyl substitution and could be used as experimental parameter; but, for pure liquid alcohols only physical constants or their functions can be used as experimental parameters. Since H-bonds are indeed broken (or formed) during physical changes, if the functions of physical constants are so chosen that they are linearly related to the minimum energy required for H-bond breaking—which will be the “activation energy” for the physical change—they could be used as experimental parameters, for correlations with the ponderal parameter. This was done as given, for the various physical constants, in the ‘Mathematical work-up’.

Also, unlike in the case of a solvation bond which is formed between solute and solvent molecules, the H-bond in pure alcohols is formed between identical molecules. Therefore, in the determination of ponderal parameter, $\log(1/\mu)$,

where $\mu = M_1M_2/(M_1 + M_2)$, M_1 is taken as equal to M_2 , M_1 and M_2 being the molecular weights of the two identical alcohol molecules, held together by H-bonding (even though there can be more than two involved). Thus the value of reduced molecular weight μ becomes

$$\mu = (M_1/M_2)/(M_1 + M_2) = M^2/2M = (M/2), \quad \text{where } M_1 = M_2 = M.$$

Mathematical Work-up

Boiling point: When a liquid boils, its molecules get converted to vapour state from liquid state; and the molar energy of vaporization, ΔE_{vap} , at a particular temperature, is the energy required to convert one mole of liquid to its vapour at that temperature. Since conversion of liquid to vapour at constant temperature and constant pressure constitutes solely the process of breaking of intermolecular forces of attraction in the liquid, ΔE_{vap} may be called *the activation energy of vaporization, for a liquid at its normal* boiling temperature*. For alcohols, in which the major intermolecular force, by far, is hydrogen bonding, ΔE_{vap} represents the activation energy required for breaking of intermolecular hydrogen bonding. Any change in substituent effect due to changing alkyl substitution in the alcohol molecules (along a series of alcohols) on the strength of the hydrogen bonding must therefore cause corresponding changes in the value of ΔE_{vap} at the normal boiling point.

Activation energy of vaporization, ΔE_{vap} , can be related to the vapour pressure of a liquid by the following equation^{2a} (which is a form of Clausius-Clapeyron equation).

$$p_{\text{vap}} = c_1 \dagger, e^{-\Delta E_{\text{vap}}/RT} \quad (1)$$

where p_{vap} is the vapour pressure of the liquid at T , the temperature, c_1 being a constant at constant temperature and R , the gas constant. The equation relates ΔE_{vap} to vapour pressure at constant temperature. A relationship between ΔE_{vap} and normal boiling temperature, T_b , of the liquid is derived as below.

The relationship between vapour pressure of liquids, p_{vap} , and their boiling points, T_b (boiling point increasing with decreasing vapour pressure and *vice versa*) may be represented by

$$p_{\text{vap}} = c_2 \cdot (1/T_b) \quad (2)$$

where c_2 is the constant of proportionality. Next, taking a liquid to be at its normal boiling point, equation (1) is rewritten, substituting for both p_{vap} and T_b from equation (2), as

$$c_2/T_b = c_1' \cdot e^{(-\Delta E_{\text{vap}}/R)(p_{\text{vap}}/c_2)} \quad (3)$$

where c_1' is constant at constant pressure (while c_1 in equation (1) was constant at constant temperature). [This is applicable, also since c_1 at 1 atm. pressure is given by (see foot note on previous page)

*Under pressure of 1 atm.

†The value of c_1 is evaluated^{2a} by putting T as the normal boiling temperature, T_b , and p_{vap} as equal to 1 atm, to be $c_1 = 1 \text{ (atm)} \cdot e^{+\Delta E_{\text{vap}}/RT}$.

$$c_1 = 1 \text{ (atm)} \cdot e^{+\Delta E_{\text{vap}}/RT_b}$$

where it represents, at pressure of 1 atmosphere—the applied pressure being equal to vapour pressure—the molar energy of vaporization (activation energy of vaporization for us) of a liquid at its normal boiling point, which is a characteristic property of the liquid and hence of constant value (T and p_{vap} being constant at normal boiling point)].

Next, since T in equation (3) is the normal boiling point, p_{vap} is equal to 1 atmosphere and this is true for any liquid so that we can write for p_{vap} at 1 atm

$$c_1/T_b = c'_1 \cdot e^{-(\Delta E_{\text{vap}}/Rc_2)}, \quad p_{\text{vap}} = 1$$

Taking logarithm on both sides,

$$\ln c_2 - \ln T_b = \ln c'_1 - (\Delta E_{\text{vap}}/Rc_2)$$

$$-\ln T_b = \ln (c'_1/c_2) - (\Delta E_{\text{vap}}/Rc_2)$$

Since R, c'_1 and c_2 are all constants, the equation is one for a straight line as

$$\Delta E_{\text{vap}} = A + B \ln T_b \quad (4)$$

where $A = Rc_2 \ln (c'_1/c_2)$ and $B = Rc_2$ are both constants.

Equation (4) thus shows that the logarithm of the normal boiling point of a liquid is linearly related to the activation energy of vaporization of the liquid and therefore can be used as a parameter of that activation energy, ΔE_{vap} .

We now have a quantitative parameter for ΔE_{vap} , which is a function of normal boiling point and which would reflect the changes in the ΔE_{vap} due to changing substituent effects on H-bonding in the alcohol. If changing of alkyl substituents does produce ponderal substituent effect on H-bonding, and therefore on ΔE_{vap} , the parameter $\ln T_b$ must give linear correlation with the ponderal parameter $\log (1/\mu)$. The result of the attempt at this correlation is a very good straight line-plot as shown in Fig. 1, for alcohols of normal series. A similar correlation is, however, not obtained for alcohols of α -series.

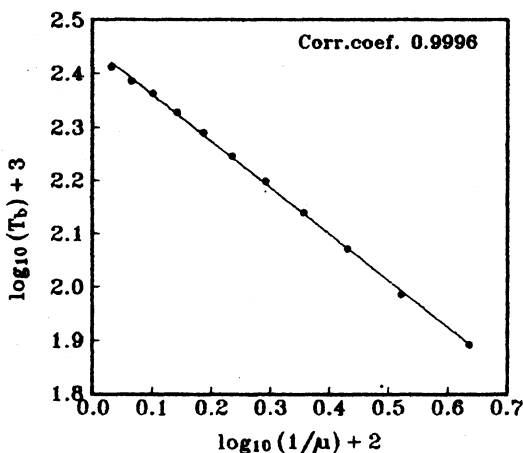


Fig. 1. Plot of $\log (1/\mu)$ vs $\log (T_b)$

Viscosity: In a flowing liquid, as an upper plate of liquid moves relative to a lower plate, the association bonds—mainly H-bonds in the case of alcohols—get stretched and eventually broken. This causes resistance to flow and viscosity is a measure of the resistance. The energy required to overcome this resistance—the “activation energy of flow”, ΔE_f , is related to the coefficient of viscosity, η , by the equation^{2b}:

$$\eta = Ae^{\Delta E_f/RT} \quad (4)$$

where A is Arrhenius constant, R the gas constant and T, the temperature. It follows that

$$\Delta E_f/RT = -\ln A + \ln \eta \quad (5)$$

and thus, at constant temperature, $\ln \eta$ is linearly related to ΔE_f . Therefore, as before, ponderal effect due to changing alkyl mass in the alcohol series should, if it is the dominant effect of the substituent, change viscosity in such a way that the parameter $\ln \eta$ is linearly correlated to the ponderal parameter, $\log(1/\mu)$. The good linear correlation obtained for normal alcohol series is given in Fig. 2. No such correlation is obtained for alcohols of α -series.

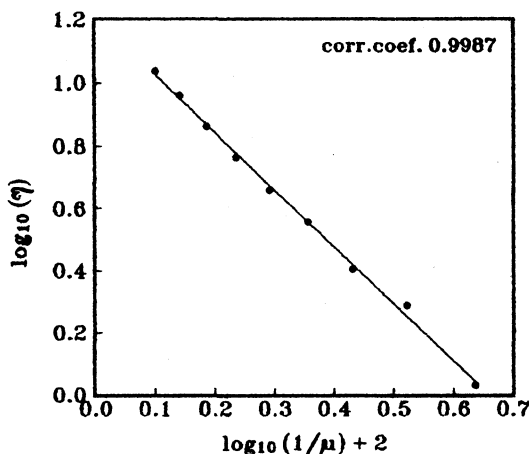


Fig. 2. Plot of $\log(1/\mu)$ vs $\log(\eta)$

Surface tension: Surface tension is the force acting per centimetre length of a liquid film, opposing the increase in area of the film^{2c}. As this area increases, the intermolecular bonds—the H-bonds in the alcohols—get stretched and, at a particular level of bond energy, break. This minimum energy for bond breaking, the “activation energy of surface stretching”, ΔE_s , may be given, as in the case of viscosity, by the equation

$$\gamma = Ae^{\Delta E_s/RT} \quad (6)$$

where γ is the surface tension, T the temperature and A and R constants as in the case of coefficient of viscosity. As before this leads to the linear relationship

$$\Delta E_s/RT = -\ln A + \ln \gamma \quad (7)$$

Again, as before, any ponderal effect due to changing alkyl substitution in alcohol series must get reflected on the activation energy, ΔE_s , leading to a linear

correlation of the parameter $\ln \gamma$ and the ponderal parameter $\log (1/\mu)$. The linear correlation obtained is given in Fig. 3, and no such correlation is obtained for alcohols of α -series.

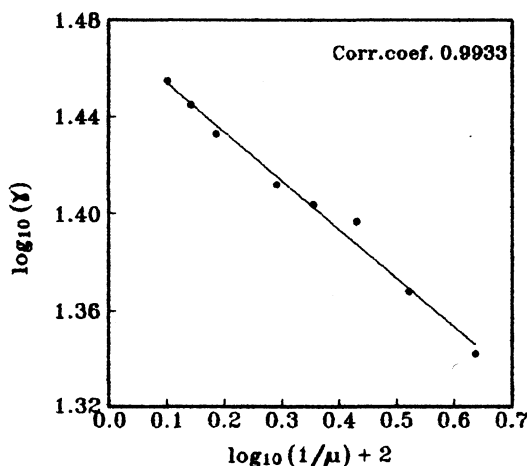


Fig. 3. Plot of $\log (1/\mu)$ vs $\log (\gamma)$

Diamagnetic susceptibility: When a material is placed in a magnetic field H , a magnetization M is induced (in the material) which is related to the applied field by the equation³

$$M = \chi_m H \quad (8)$$

where χ_m is the molar diamagnetic susceptibility of the material. In a constant field, the series of alcohols, which have very nearly same dipole moment (1.54–1.81 D, due to the common and strong dipole of O—H group), will have their induced magnetization also nearly constant. The measured susceptibility will however depend, apart from the applied field strength or the dipole moment, on the energy required to orient the molecules in the applied field. This orientation will have to be at the expense of breaking the intermolecular forces—which is mainly H-bonding in the alcohols, the strength of which can be different for different alcohols. Therefore χ_m will be, for the alcohol series under a constant applied field, a measure of the minimum energy required for the H-bond breaking-cum-orientation or the “activation energy for magnetization”, ΔE_m . The relationship between the ΔE_m and experimental parameter χ_m can be, as before, given by

$$\chi_m = A \cdot e^{\Delta E_m/RT} \quad (9)$$

so that

$$\Delta E_m/RT = -\ln A + \ln \chi_m \quad (10)$$

Therefore once again any ponderal effect due to alkyl substitution along the alcohol series on the H-bond can be expected to cause changes in ΔE_m and, quantitatively, to give a linear correlation between $\ln \chi_m$ and the ponderal parameter $\log (1/\mu)$. The linear plot obtained is given in Fig. 4, for alcohols of the normal series. The linearity is not obtained for the alcohols of α -series.

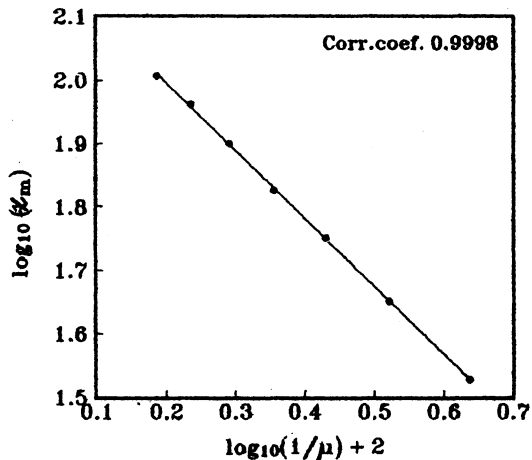


Fig. 4. Plot of $\log(1/\mu)$ vs $\log(\chi_m)$

Dielectric constant or permittivity: When a material is placed in an electrical field its molecules get polarized and the polarization induces a dipole moment which is proportional to the applied field, E , as per the relationship^{2d}.

$$m = \alpha E \quad (11)$$

where m is the induced dipole moment and α , the polarizability. In a strongly polar molecule, like alcohol, polarizability is the sum of distortion polarizability and orientation polarizability, the latter being much larger than the former. The orientation polarizability is known to depend on dipole moment. Therefore for alcohols which have nearly constant dipole moment (due to O—H bond moment), the polarizabilities should not vary significantly due to any dipole moment variations. However, orientation of the O—H dipole involves the breaking of H-bonds also, which, along with orientation, can be subject to the effects of alkyl substituent of the alcohol and therefore vary significantly from alcohol to alcohol. The molar polarizability, α , will then be a measure of the “activation energy for orientation”, ΔE_0 , for the O—H dipole in a constant applied field, as given by the, now familiar, relationship:

$$\alpha = A e^{\Delta E_0/RT} \quad (12)$$

where A and R are the same constants and T , the temperature as before.

It means that

$$\Delta E_0/RT = -\ln A + \ln \alpha \quad (13)$$

and, being linearly related to ΔE_0 , α can be the experimental parameter of ΔE_0 . Molar polarization (α) can be determined applying the relationship^{2d}.

$$[(\epsilon - 1)/(\epsilon + 2)](M/\rho) = (4\pi/3) \cdot N_0 \alpha$$

where ϵ is the dielectric constant, M , the molecular weight and ρ , the density, all of the alcohol; and N_0 is the Avogadro number. If we take

$$Z = [(\epsilon - 1)/(\epsilon + 2)](M/\rho)$$

then,

$$\alpha = \text{constant } Z$$

So that the experimentally determinable parameter, Z , is proportional to α , the polarizability.

Now, if, as expected, the activation energy for orientation is affected by the ponderal effect due to changing alkyl substitution, the ponderal parameter, $\log(1/\mu)$, should show linear correlation with $\ln \alpha$ and therefore with the experimental parameter, $\ln Z$. The result of the correlation for normal alcohols is shown in Fig. 5. The linear relationship is not obtained for alcohols of α -series.

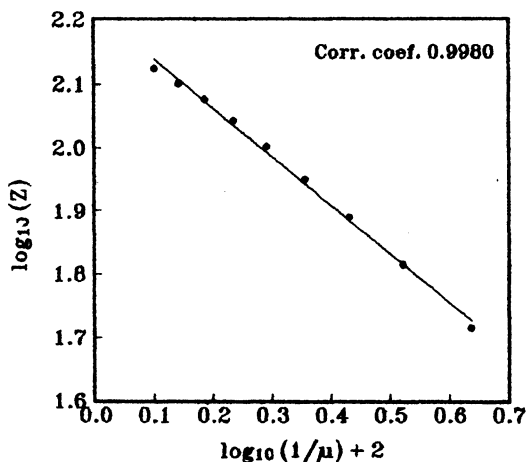


Fig. 5. Plot of $\log(1/\mu)$ vs $\log(Z)$

TABLE-2
DIELECTRIC CONSTANT (PERMITTIVITY) OF ALCOHOLS (ϵ) RELATED TO
POLARIZABILITY FUNCTION Z

Alcohol	$\epsilon(293.2^\circ\text{K}^{4d})$	Molar volume (Mol. wt/density) (density ^{temp}) ^{4a}	$Z^{\#}$	$\log Z$
Ethanol	25.3	58.37 (0.7893 ²⁰)	51.96	0.7157
1-Propanol	20.8	75.15 (0.7997 ²⁵)	65.25	0.8146
1-Butanol	17.84	91.53 (0.8098 ²⁰)	77.69	0.8904
1-Pentanol	15.13 (298.2 K)	108.23 (0.8144 ²⁰)	89.28	0.9508
1-Hexanol	13.03	125.58 (0.8136 ²⁰)	100.51	1.0022
1-Heptanol	11.75	141.38 (0.8219 ²⁰)	110.53	1.0435
1-Octanol	10.30	157.62 (0.8262 ²⁵)	119.18	1.0762
1-Nonanol	8.83	174.36 (0.8273 ²⁰)	126.06	1.1006
1-Decanol	7.93	190.76 (0.8297 ²⁰)	133.13	1.1243

#Polarizability (α) = constant Z (see text); $Z = [(\epsilon - 1)/(\epsilon + 2)](M/\rho)$; $\alpha = (3/4\pi N_o) \cdot Z$

*At higher temperatures, the thermal motions can force the orientation to be random so that there will be no polarization, nor any induced dipole moment.

TABLE-1
 LINEAR CORRELATIONS BETWEEN FUNCTIONS OF PHYSICAL CONSTANTS AND THE PONDERAL PARAMETER FOR ALCOHOLS
 OF NORMAL SERIES*

Sl. No.	Alcohol	Mol. wt. ^{4a}	$\log_{10}(1/\mu)$	Boiling point (T_b) ^{4a}	$\log_{10}(T_b)$	Viscosity (η) ^{4b}	$\log_{10}(\eta)$	Surface tension (γ) ^{4c}	$\log_{10}(\gamma)$	Diamagnetic susceptibility ($-\chi_m$) ³	$\log_{10}(\chi_m)$	$\log_{10}(Z)$
1.	Ethanol	46.068	0.6376	78.2	1.892	1.074	0.031	21.97	1.342	33.7	1.528	1.7157
2.	1-Propanol	60.094	0.5222	97.0	1.987	1.945	0.289	23.32	1.368	44.8	1.651	1.8146
3.	1-Butanol	74.120	0.4311	117.7	2.072	2.544	0.406	24.93	1.397	56.4	1.751	1.8904
4.	1-Pentanol	88.146	0.3558	138.0	2.140	3.619	0.559	25.36	1.404	67.0	1.826	1.9508
5.	1-Hexanol	102.170	0.2917	157.6	2.199	4.578	0.661	25.81	1.412	79.5	1.900	2.0022
6.	1-Heptanol	116.200	0.2358	176.4	2.246	5.810	0.764	—	—	91.7	1.962	2.0435
7.	1-Octanol	130.220	0.1863	195.0	2.290	7.288	0.863	27.10	1.433	101.6	2.007	2.0762
8.	1-Nonanol	144.250	0.1419	213.0	2.328	9.123	0.960	27.89	1.445	—	—	2.1006
9.	1-Decanol	158.280	0.1016	231.0	2.364	10.900	1.037	28.51	1.455	—	—	2.1243
10.	1-Undecanol	172.300	0.0647	243.0	2.386	—	—	—	—	—	—	—
11.	1-Dodecanol	186.330	0.0308	259.0	2.413	—	—	—	—	—	—	—

*All physical constants are taken in units in which they are given in the references cited, which are given below:

T_b = Boiling temperature under 1 atm. pressure in degrees centigrade ($^{\circ}\text{C}$).

η = Absolute viscosity at 25°C and 1 atm. pressure given in units of millipascal seconds (mPas)

γ = Surface tension at 25°C and 1 atm. pressure in units of millineutons per metre (mN/m)

χ_m = Molar diamagnetic susceptibility given as $-\chi_m/10^{-6} \text{ cm}^3 \text{ mol}^{-1}$

for Z see Table-2

$\log_{10}(1/\mu)$ is determined from $\mu = (M/2)$ where M is the mol. wt. of the particular alcohol (see text).

Conclusions

First, the good linear plots in Figs. 1–5 support the idea that alkyl substituents do produce, in addition to polar, steric and field effects, a mass or ponderal effect; only, it is not being observed in regular covalent bond-breaking reactions in which the former effects are far stronger. H-bonds provide, like the solvation bonds¹, an environment where polar and steric substituent effects are negligible so that the ponderal effect plays the dominant role.

Secondly, whether it is the H-bond or the solvation bond, apparently so long as the breaking bond is covalent in character and provided that the ponderal effect is observable enough, its parameter, $\log (1/\mu)$, can be linearly correlated to parameters of activation energy. In the case of physical changes these parameters can be functions of physical constants as shown earlier. The correlations can be justified theoretically on the same grounds as reported earlier¹. The reason for the alcohols of α -series failing to give the linear correlations can only be speculated. It is possible that the H-bonds are considerably weaker than most solvation bonds (for which linear correlations are obtained in α -series also) in alcoholic solvents so that the ponderal effect produced is itself smaller. Given that the effect is smaller, the steric effect due to the more symmetrically and closely substituted alkyl groups in the α -series could be greater and overshadowing the ponderal effect, at least sufficiently to prevent the latter from being the *quantitatively* dominant effect.

Thirdly, for liquid-alcohols at least, these correlations explain, *quantitatively*, the “anomalous” character of their boiling points compared to non-associated or non-H-bonded liquids. In other words, they need not be anomalous, if due regard is paid to the H-bond energy, quantitatively.

REFERENCES

1. J.M. Jessy, *Asian J. Chem.*, **12**, 145 (2000).
2. G.W. Castellan, *Physical Chemistry*, Addison-Wesley Publishing Company, Inc., (a) p. 76; (b) p. 575; (c) p. 541; (d) p. 467 (1964).
3. D.R. Lide (Ed.), *Handbook of Chemistry and Physics*, 79th Edn., CRC Press, New York, p. 3-737 (1998–99).
4. Ref. 3, (a) p. 3-1; (b) p. 6-170; (x) p. 6-135; (d) p. 6-142.
5. J.M. Jessy, *Asian J. Chem.*, **13**, 283 (2001).

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