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Ponderal Substituent Effect due to Alkyl Substitution in 1-Alkanes: Quantitative Correlations with Physical Constants

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Ponderal substituent effect due to changing alkyl substitution is demonstrated on the physical properties—vapour pressure, viscosity, diamagnetic susceptibility and polarizability—of 1-alkanes. The ponderal parameter log $(1/\mu)$ has been shown to give linear correlation with a function of the corresponding physical constant, in each case. The correlation is justified as consequence of substituent mass effect on the vibrational component of the *covalent* molecular interactions between the alkane molecules, created by dispersion forces.

INTRODUCTION

Ponderal* (mass) substituent effect due to alkyl substitution has been demonstrated in a number of solvation-based chemical reactions and equilibria in alcoholic solvents[1]. Changes in alkyl substitution had been made in solvent alcohols rather than in solutes. Alcohols of normal series and α-series were used. In each of the systems, the substituent effect, represented by the changes in *reactivity parameters*, log k^* or log K^*, was linearly correlated to the ponderal parameter, log $(1/\mu)$, where μ is the reduced molecular weight of the solute and the solvent given by $\mu = (M_1M_2)/(M_1 + M_2)$, M_1 and M_2 being the molecular weights of the solute and the solvent respectively.

Similar alkyl substituent effect was also reported[1, 2] in the solubilities of organic and inorganic (complex) solutes in alcoholic solvents wherein the *solubility parameters* showed equally good linear correlation with the function log $(1/\mu)$.

Later it has also been shown that the physical properties of alcohols—vapour pressure, viscosity, surface tension, diamagnetic susceptibility and polarizability—are also susceptible to ponderal substituent effect due to alkyl groups. In this instance, the reactivity parameters—parameters representing energy changes during the physical processes—were shown as functions of the corresponding physical constants.[3] And these functions showed good linear correlation with the ponderal parameter log $(1/\mu)$, but only for alcohols of normal series and not for alcohols of the α-series [in which steric effect could have been interfering[3].

In the present work, an attempt is made to see if ponderal effect is observable due to alkyl substitution in a *non-polar* system and if so whether a similar linear correlation is obtained with the ponderal parameter. The system chosen is a homologous series of alkanes. As in the case of pure alcohols[3], substituent effect

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*k representing the rate constant and K, the equilibrium constant.

was studied on the physical properties—vapour pressure, diamagnetic susceptibility, polarizability, viscosity and surface tension; the reactivity parameters (or activation energy-parameters) for the physical changes are shown to be functions of corresponding physical constants (cf. next section); the ponderal parameter log $(1/\mu)$ reduces to log $(2/M)$* where M is the molecular weight of the alkane, which is both the solute and the solvent in the pure alkane systems.

Parameters of Physical Properties for Correlation

Vapour Pressure: The experimental parameter of vapour pressure of a liquid, at 1 atm pressure, is the normal boiling point, T_b. At the normal boiling point any energy consumed is totally used up for the process of vaporization, so that the "energy of vaporization" is the activation energy (of vaporization) for breaking the intermolecular forces in a liquid, thereby converting them to vapour state. This activation energy has, as its components, the enthalpy of activation (ΔH_r) and entropy of activation (ΔS_r). By Clayperon equation these are related by[4]

$$\Delta S_{vap} = (\Delta H_{vap}/T_b), \quad \text{at } T_b.$$

For non-polar systems, as the alkanes are, at ordinary temperatures and pressures, ΔS_{vap} is constant at approximately 21 e.u. The activation energy is then simply the enthalpy of vaporization. From the above equation,

$$\Delta S_{vap} = \text{constant} = (\Delta H_{vap}/T_b)$$

so that

$$\Delta H_{vap} = \text{constant}, T_b$$

which is a linear relationship. Therefore T_b *can be a parameter for the activation energy of vapourization.* The ponderal parameter log $(1/\mu)$ is plotted against the energy parameter, T_b, in Fig. 1, with the relevant data in Table-1. A good linear plot is obtained for the linear, normal series of 1-alkanes but not for the branched, α-series.

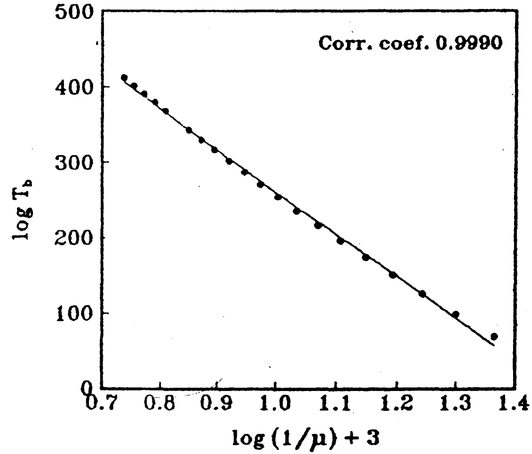

Fig. 1. Plot of log $(1/\mu)$ *vs.* T_b

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*In the solute-solvent system $\mu = M_1M_2/(M_1 + M_2)$. In a system of pure solvents the intermolecular bonding is between identical (solvent) molecules so that $M_1 = M_2 = M$ and thus $\mu = (M^2/2M) = (M/2)$.

Diamagnetic susceptibility and polarizability: As has been shown in the case of alcohols[3] when a fluid is placed in a magnetic or electrical field any intermolecular bonding breaks down and the molecules get reoriented in the applied field. The minimum energy required for the process is the activation energy for magnetization (ΔE_m) or for polarization (ΔE_p) respectively. The physical constants molar diamagnetic susceptibility ($-\chi_m$) and molar polarizability (α) can be related to the activation energies by

$$-\chi_m = Ae^{\Delta Em/RT}$$

and $$\alpha = Ac^{\Delta Em/RT} \text{ respectively}$$

TABLE-1

DATA FOR LINEAR CORRELATION BETWEEN PONDERAL PARAMETER, log (1/μ) AND FUNCTIONS OF (a) NORMAL BOILING POINT (b) DIAMAGNETIC SUSCEPTIBILITY (c) POLARIZABILITY AND (d) VISCOSITY, IN ALKANES OF NORMAL SERIES

Sl. No.	1-Alkane	m.w.	log (1/μ) + 3	T_b [a]	log $(-\chi_m)^{*\,b}$	log $Z^{*\,c}$	log (η) + $1^{*\,d}$
1.	Ethane (C_2H_6)	30.068	1.823	–	1.428	–	–
2.	Propane (C_3H_8)	44.094	1.657	–	1.587	1.212	–
3.	Butane (C_4H_{10})	58.120	1.537	–	1.702	1.316	–
4.	Pentane (C_5H_{12})	72.146	1.443	–	1.789	1.400	0.350
5.	Hexane (C_6H_{14})	86.172	1.366	68.7	1.870	1.477	0.477
6.	Heptane (C_7H_{16})	100.198	1.300	98.5	1.930	1.537	0.588
7.	Octane (C_8H_{18})	114.224	1.243	125.6	1.985	1.594	0.706
8.	Nonane (C_9H_{20})	128.25	1.193	150.8	2.034	1.641	0.823
9.	Decane ($C_{10}H_{22}$)	142.276	1.148	174.1	2.077	1.683	0.923
10.	Undecane ($C_{11}H_{24}$)	156.31	1.107	195.9	2.120	1.722	1.041
11.	Dodecane ($C_{12}H_{26}$)	170.34	1.070	216.3	–	1.759	1.141
12.	Tridecane ($C_{13}H_{28}$)	184.37	1.035	235.4	2.187	1.792	1.237
13.	Tetradecane ($C_{14}H_{30}$)	198.39	1.004	253.5	2.221	1.824	1.328
14.	Pentadecane ($C_{15}H_{32}$)	212.42	0.974	270.6	–	1.852	–
15.	Hexadecane ($C_{16}H_{34}$)	226.45	0.946	286.8	2.273	1.879	1.482
16.	Heptadecane ($C_{17}H_{36}$)	240.47	0.920	302.0	–	1.906	–
17.	Octadecane ($C_{18}H_{38}$)	254.50	0.895	316.3	–	–	–
18.	Nonadecane ($C_{19}H_{40}$)	268.53	0.872	329.9	–	1.954	–
19.	Ercosane ($C_{20}H_{40}$)	282.55	0.850	343.0	–	–	–
20.	Docosane ($C_{22}H_{46}$)	310.61	0.809	368.6	–	2.016	–
21.	Tricosane ($C_{23}H_{48}$)	324.63	0.790	380.0	–	–	–
22.	Tetracosane ($C_{24}H_{50}$)	338.66	0.771	391.3	–	–	–
23.	Pentacosane ($C_{25}H_{52}$)	352.69	0.754	401.9	–	–	–
24.	Hexacosane ($C_{26}H_{54}$)	366.71	0.737	412.2	–	–	–

[a] Normal boiling point (T_b) in °C; Range within 50°C to 420°C.

[b] Molar diamagnetic susceptibility in [$-\chi_m/10^{-6}$ cm^3 mol^{-1}].

[c] Molar polarizability, α = const. Z.

Constant = ($3/4\pi N_0$); N_0 = Avogadro No.

Z = [(ε − 1)(ε + 2)](M/ρ); ε = dielectric constant at 273.2°C; M = Mol. wt.; ρ = density at 20° or 25°C]].

[d] Absolute viscosity in millipascal seconds (mpa. s)

*Values of ($-\chi_m$), (ε), (ρ) and (η) given in Table-2.

TABLE-2
VALUES OF MOLAR DIAMAGNETIC SUSCEPTIBILITY, DIELECTRIC CONSTANT AND ABSOLUTE VISCOSITY

1-Alkanes	Molar diamagnetic susceptibility ($-\chi_m$)	Polarizability (α)			Absolute viscosity (η) at 25°C
		Dielectric constant (ε) at 293.2°K	Density (ρ) at 20°/25°C	Value of Z	
Ethane (C_2H_6)	26.8	–	–	–	–
Propane (C_3H_8)	38.6	1.6678	0.494^{25}	16.286	–
Butane (C_4H_{10})	50.3	1.7697	0.573^{25}	20.710	–
Pentane (C_5H_{12})	61.5	1.8371	0.6262	25.134	0.224
Hexane (C_6H_{14})	74.1	1.8865	0.6548	30.018	0.300
Heptane (C_7H_{16})	85.2	1.9207	0.6837	34.420	0.387
Ocatane (C_8H_{18})	96.6	1.9480	0.6896	39.260	0.508
Nonane (C_9H_{20})	108.1	1.9722	0.7176	43.742	0.665
Decane ($C_{10}H_{22}$)	119.5	1.9853	0.7300	48.186	0.838
Undecane ($C_{11}H_{24}$)	131.8	1.9972	0.7402	52.682	1.098
Dodecane ($C_{12}H_{26}$)	–	2.0120	0.7487	57.388	1.383
Tridecane ($C_{13}H_{28}$)	153.7	2.0213	0.7564	61.906	1.724
Tetradecane ($C_{14}H_{30}$)	166.2	2.0343	0.7620	66.673	1.128
Pentadecane ($C_{15}H_{32}$)	–	2.0391	0.7685	71.109	–
Hexadecane ($C_{16}H_{34}$)	187.6	2.0460	0.7733	75.707	3.032
Heptadecane ($C_{17}H_{36}$)		2.0578	0.7780	80.575	
Nonadecane ($C_{19}H_{40}$)		2.0706	0.7855	89.912	
Docosane ($C_{22}H_{46}$)		2.0840	0.7944	103.78	

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

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

and

$$\ln \alpha = \ln A + (\Delta E_p/RT).$$

The equations, representing linear relationships, show that ln ($-\chi_m$) *and* ln (α) *can be the experimental parameters of* ΔE_m *and* ΔE_p which change with increasing alkyl substitution in the alkanes.

If the effect produced due to alkyl substitution on the activation energies of the two processes is ponderal, each of the parameters, ln ($-\chi_m$) and ln (α) must show linear correlation with the ponderal parameter, log $(1/\mu)$. The straight line plot obtained for ln $(-\chi_m)$ *vs.* log $(1/\mu)$ for 1-alkanes is given in Fig. 2 and relevant data in Tables 1 and 2. In the second case the molar polarizability, α, is however determined using the relationship

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

where ε is the dielectric constant, N_0 is the Avagadro number, M the mol. wt. and ρ the density. As the term $(3/4\pi N_0)$ is constant, this equation is rewritten as

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

where $Z = [(\varepsilon - 1)/(\varepsilon + 2)](M/\rho)$ and ln Z is plotted against the ponderal parameter log $(1/\mu)$ in place of ln α. The plot for the normal series of alkanes is given in Fig. 3 and relevant data in Tables 1 and 2.

Viscosity: Again, as shown in the case of alcohols[3] the absolute viscosity, η, represents the minimum energy required to overcome the resistance offered by a fluid to flow or 'the activation energy of flow', ΔE_f, and is given by the equation[5]

$$\eta = Ae^{+\Delta E(f)/RT}$$

where A, R and T are the same constants, as given earlier. Therefore,

$$\ln \eta = \ln A + \Delta E_f/RT$$

and ln η can be the experimental parameter of the activation energy of flow. The plot of ln η vs. log $(1/\mu)$ is shown in Fig. 4, with relevant data in Tables 1 and 2 for 1-alkanes, the linearity of which indicates that the alkyl substituent effect on viscosity of n-alkanes is ponderal.

Surface tension, γ, though changed with changing alkyl substitution, a similar function of it, ln γ, did not give the linear correlation in 1-alkanes whereas such a correlation was obtained for alcohols. Also these correlations were not obtained for branched alkanes of α-series as was the case also for alcohols of the α-series.

RESULTS AND DISCUSSION

The ponderal effect has hitherto[1–3] been demonstrated on solvation bonds and hydrogen bonds, both of which are recognized as being covalent in character. The dispersion forces in non-polar systems—such as the alkanes—are however treated as molecular "interactions" which are electrostatic in character, the interaction energy being given by[4]

$$E_d = -(3/4)h\nu_0 \cdot (\alpha_0^2/r^6) \qquad (1)$$

where $h\nu_0$ stands for ionization energy, α_0 for polarizability and r for the distance between the two (temporary) dipoles, held together by dispersion forces. Molecular mass does not figure in the equation because the energy is taken as totally electrostatic.

The very good linear plots shown in Figs. 1–4, between the (experimental) energy parameters of the physical processes, which involve the breaking of dispersion forces, and the ponderal parameter, log $(1/\mu)$, clearly shows that these *intermolecular dispersion forces in non-polar systems do depend on molecular mass; and that the dependence is quantitative.* Such quantitative dependence is possible only if the *ponderal effect is the major effect on the molecular interaction, due to alkyl substitution.*

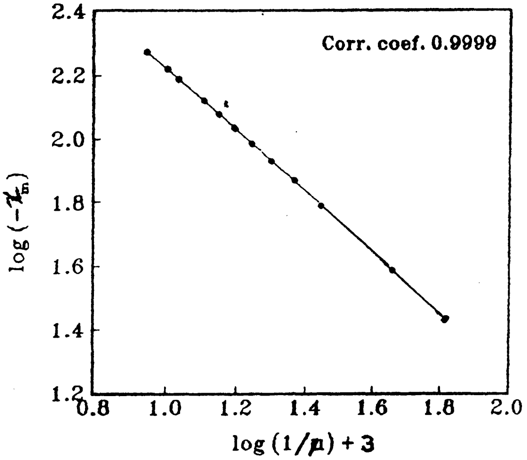

Fig. 2. Plot of log (1/μ) *vs.* log ($-\chi_m$)

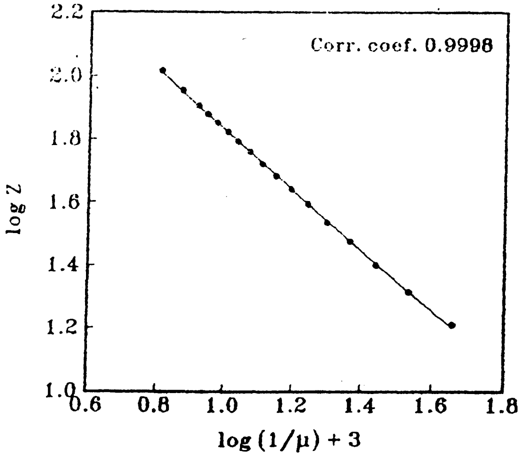

Fig. 3. Plot of log (1/μ) *vs.* log *Z*

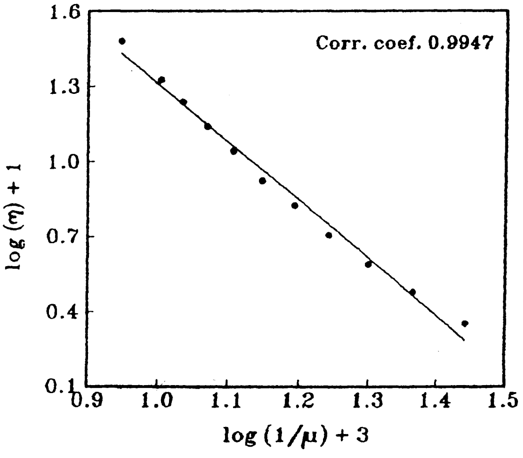

Fig. 4. Plot of log (1/μ) *vs.* log (η)

Secondly, the fact that the ponderal effect has the particular mass function, log $(1/\mu)$, as its parameter has been shown[1] to indicate, on theoretical basis, that the changing of (alkyl) mass has its effect on the *vibrational components* of the activation energies in the various processes, and it is only a covalent bond with *orbital overlap* (of whatever degree) that can have a vibrational component. This means that *the "dispersion forces" or rather the intermolecular bonding created by the dispersion forces, which may be called dispersion bonding, have to be covalent in character.* This is particularly acceptable in the case of alkanes which are made only of carbon and hydrogen atoms both of which tend to form covalent rather than electrovalent bonds.

This argument however does not negate the dependence of dispersion forces on polarizability and inter-dipolar distance (cf. Eq. 1). It could be the polarization that brings the molecules together, and also probably in suitable alignment, for the eventual *orbital overlap and covalent-type interaction*—however weak they may be and however temporary they may be. This is similar to what is recognized as happening in many polar systems where the electrostatic dipole-dipole attraction brings the molecules together, but once within covalent bonding distance with favourable orientation, the interaction changes to one of lower-energy orbital overlap. For example, in pure alcohols, the molecules are attracted to each other and brought closer by virtue of their dipoles in all probability; but they end up forming intermolecular hydrogen-bonding which are covalent in character.

The apparent failure of branched alkanes in giving similar correlations can only be speculated as was done for alcohols of α-series[3]. It is possible that dispersion forces being much weaker than solvation bond are more easily interfered with or overcome by the steric substituent effect. However, sufficient data have not been available for alkanes with regular and systematic changes in alkyl substitution to prove this.

Conclusion

Dispersion forces in 1-alkanes seem to be, like H-bonds in alcohols, covalent in character. And—like H-bonds and solvation bonds of alcohols—they are sensitive to ponderal effect, in a quantitative way, showing similar correlation with the ponderal parameter, log $(1/\mu)$.

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