



Application of Non-Linear Hammett Relationship to Surface Tensions and Dipole Moments in Estimating the Associative Behavior of Phenols: A Chemical Educational Article to Graduate Students

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Non-linear Hammett relationship was applied to surface tensions (γ) and dipole moments (μ) of some *meta* and *para* substituted phenols. The non-linearity of $\log \gamma$ versus Hammett σ correlation was explained in terms of Eötvös constant, Ramsay-Shields equation, Trouton's rule, order of association, sandwich type molecular pairs and number of hydrogen bond donor-acceptor sites (H_{ad}). And non-linearity of $\log \mu$ versus Hammett σ correlation was explained in terms of the net bulk property of the entire molecule and not based on a chemical property like a localized reaction center.

Keywords: Hammett equation, Eötvös constant, Ramsay-Shields equation, Trouton's rule, Dipole moments, Phenol.

INTRODUCTION

Hammett equation is an efficient tool in predicting the reaction mechanisms of several organic reactions¹⁻⁵. Ever since its discovery⁶ about 80 years ago its use among physical-organic chemists and physical chemists is still afresh. However there were some reactions which deviate from linearity of Hammett $\rho\sigma$ plot and documented by Schreck⁷. An example of such non-linear Hammett $\rho\sigma$ plot is that reported by Crowell and his associates⁸ in the reaction of aromatic aldehydes with *n*-butyl amine. This was interpreted in terms of the change in the rate determining step from reversible addition of amine to aldehyde to the subsequent dehydration step which is favored by electron donating substituents. Hancock *et al.* had tried to explain the V-shaped Hammett locus based on the same explanations of change in mechanisms of Wolf-Kishner reaction of hydrazones⁹ and U-shaped Hammett locus for the rates of solvolysis and thiosulfate reactions of α -chloro toluenes¹⁰. Another notable example of this kind was from our laboratory¹¹ where in the Hammett plot was again non-linear for the reactions of mono anion and di anion of peroxo monosulfate with benzaldehydes. Even there were non-linear Hammett correlations observed on physical properties also. For example, quantitative solubility-structure relationships for several *meta* and *para*-substituted benzoic acids in benzene and in cyclohexane¹² and in 1,4-dioxane and tetrahydrofuran¹³ were

studied. Such kind of studies using physical properties like melting points and dipole moments of benzoic acids was even reported from our laboratory¹⁴. Predicting the associative behavior of alcohols using available data on surface tensions¹⁵ and of several amines using available data on dipole moments¹⁶ from literature is a major breakthrough from our laboratory. There were several other reports on non-linear Hammett correlations in literature¹⁷⁻³³ and even non-linear Taft correlations for the first time from our laboratory³⁴ on the reactions of *N*-substituted benzyl amines with benzyl bromide in methanol.

EXPERIMENTAL

Data on surface tensions of phenols is from reference³⁵ and references cited therein. The Hammett σ values are from references^{1,2}. Thermo chemical data is from reference³⁶. All the linear correlations and the polynomial correlations were done using the KaleidaGraph software, Reading, PA, USA.

RESULTS AND DISCUSSION

By definition the surface tension is a measure of the work that must be done to bring a molecule from the interior to the surface against the attractive cohesive forces in the bulk of the substance. Solids also possess the property of surface tension much the same as liquids have and sometimes to a greater extent. That such a surface effect exists with solids is shown

by the smoothening of surfaces of solids by sintering at temperature well below the melting points of the solids. The tendency of solids to absorb all sorts of substances or their own substances on their surfaces is another manifestation of surface tension in solids. As an example if a block of a solid substance say a NaCl crystal is cut a new crystal-gas interface is created and hence there will be increase in surface free energy of the solid. The newly cleaved surface of solid may not be immediately in equilibrium configuration unlike in the case of liquids. Therefore the free energy required to create such a new surface may not give the direct measure of the surface tension of the solids. However methods are available to measure the surface tensions of solids under achieved equilibrium conditions. One such good method was the measure of the rate of the shrinkage of fine wires or thin foils³⁷. And usually the surface tensions of solids are measured at high temperatures³⁸. The surface tension of solids was dealt in detail by Shuttleworth³⁹.

In the present work Hammett plot of $\log \gamma$ vs. σ is presented in Fig. 1. Surprisingly there was a correlation between surface tensions of phenols with Hammett substituent constants with two straight lines one with negative slope for electron donating substituents and the other with positive slope for electron withdrawing substituents (Fig. 1). The surface tensions of different phenols are from literature^{40,41}. Though the correlation coefficients are away from unity, the trends are certainly unmistakable. The prime reason for little poor correlation of Hammett equation on physical properties is due to the fact that application of Hammett and/or Taft equations are for only 'localized reaction sites' in elucidating the reaction mechanisms. But the physical properties are not only part of 'localized reaction sites' in case of solubilities and are for the entire bulk of the molecule. Thus the surface tension of a solid not only depends on a particular functional group in a molecule but also on shape, orientation and several attractive and repulsive forces of the entire molecule with its neighbouring molecules. Though the correlations are little poor the surface tensions are fairly good indications of the application of the Hammett equation.

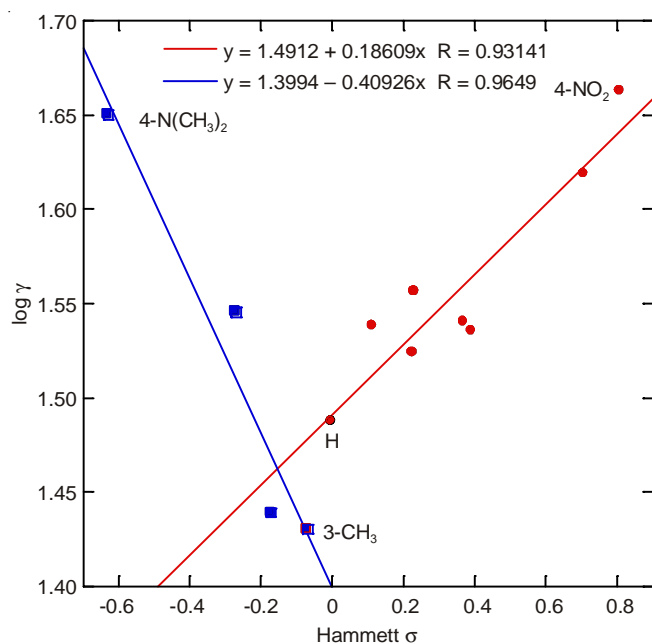


Fig. 1. Plot of $\log \gamma$ vs. Hammett σ for phenols

Usually the non-linear Hammett correlations^{7-11,17-33} or Taft correlations³⁴ on rates of chemical reactions were explained in terms of change in reaction mechanisms or shift of the rate determining step in a multi-step reaction. And the same were observed on solubilities of benzoic acids in benzene^{12,13} because these are not completely physical properties as the solubility would be a function of ionizing capacity and ionization is a chemical property which depends on the dielectricity of the solvent and it will be taking place at a localized ionization site. This was explained as a measure of the tendency of the interaction of π -electron cloud of benzene with the benzoic acid¹². Now we explain the non-linearity of Hammett correlation of surface tensions in terms of sandwich type molecular pairs, Eötvös constant, Ramsay-Shields equation, order of association, Trouton's rule and number of hydrogen bond donor-acceptor sites (Had).

Sandwich type molecular pairs: It was a good correlation between surface tensions of phenols with Hammett substituent constants with two straight lines one with negative slope for electron donating substituents and the other with positive slope for electron withdrawing substituents (Fig. 1). Surface tensions of phenols first decreased with increasing Hammett σ values starting from 4-N,N-dimethylamino group and then started increasing from 3-methyl group to 4-nitro group. The break in the Hammett correlation is in between 3-methyl ($\sigma = -0.07$) and H ($\sigma = 0.00$) groups. And this is very much clear in the second order polynomial plot where the break is if not exactly at hydrogen but closer to hydrogen than 3-methyl group (Fig. 2) though the correlation coefficient is away from unity. This is usually observed in non-linear Hammett correlations⁷⁻³⁴.

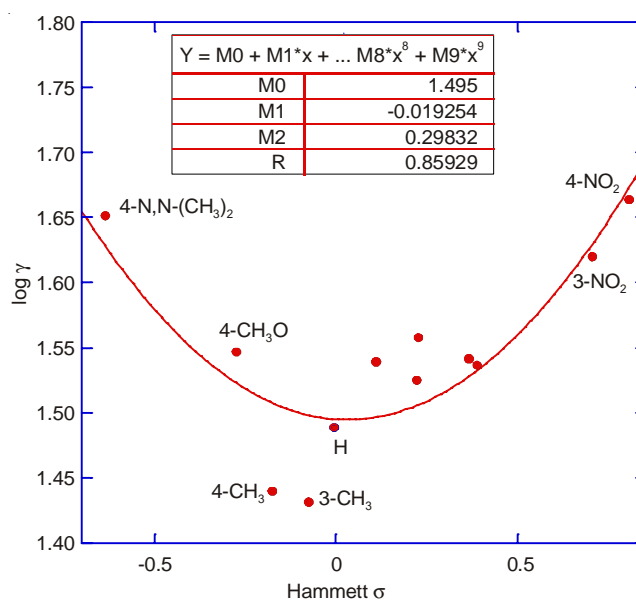


Fig. 2. 2nd Order polynomial correlation of $\log \gamma$ vs. Hammett σ

From the above two plots (Figs. 1 and 2) it is clear that the phenol either with much electron donating substituent [(4-N,N-(CH₃)₂)] or with much electron withdrawing substituent (4-NO₂) had higher surface tensions (Table-1) than any other substituted phenols used in the present work. This is explained as follows in terms of sandwich type molecular pairs: Both 4-N,N-dimethyl amino and 4-nitro phenols had a total of H_{ad}

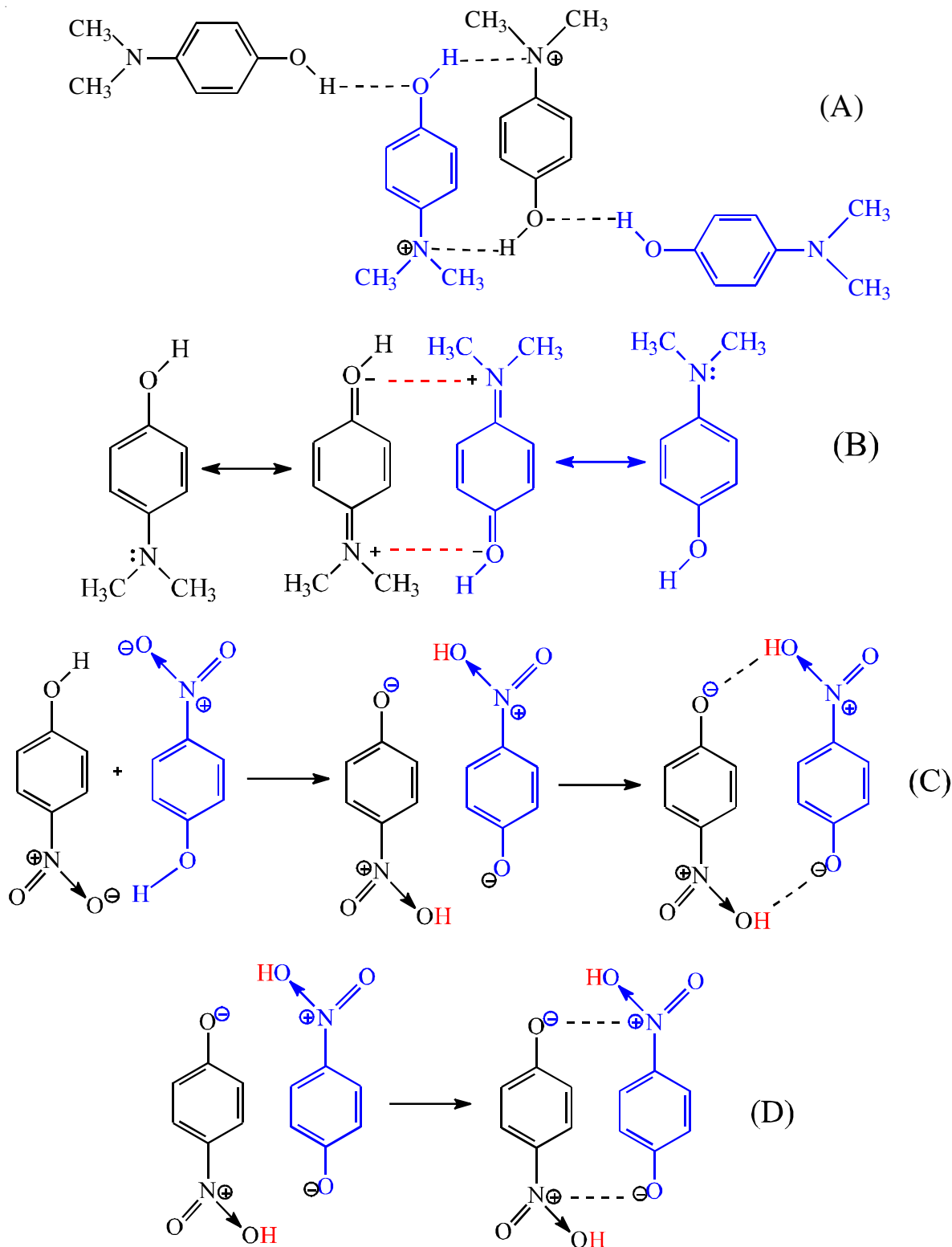
of 3 and 4 respectively (Table-1). Where $H_{ad} = H_a + H_d$, H_a is hydrogen bond acceptor site and H_d is hydrogen bond donor site. Hence both these phenols can form associated molecules the so called sandwich type aggregates as shown in **Scheme-I**.

Due to this association several molecules become one aggregated molecule and whose surface tensions would normally be more than the non-associated molecule. The order

of association (x) could be calculated using Ramsay-Shields equation⁴²:

Eötvös⁴³ had suggested the following equation that explains the effect of temperature on surface tension (γ):

$$\gamma \left(\frac{M}{\rho_l} \right)^{2/3} = k(t_c - t) \quad (1)$$



Scheme-I

TABLE-1
 VARIOUS PHYSICAL PARAMETERS OF PHENOLS

S. No.	X	σ	γ	k	μ	x	H_a	H_d	H_{ad}	ΔS_v^\ddagger
1	4-N(CH ₃) ₂	-0.63	44.1*	-	NA	-	2	1	3	97
2	4-CH ₃ O	-0.27	35.1	1.51	NA	1.66	2	1	3	97
3	4-CH ₃	-0.17	27.5	2.00	1.58	1.09	1	1	2	NA
4	3-NH ₂	-0.165	-	-	1.85	-	-	-	-	-
5	3-CH ₃	-0.07	26.9	2.06	1.61	1.04	1	1	2	NA
6	H	0.00	30.7	2.11	1.55	1.00	1	1	2	100
7	3-CH ₃ O	0.12	34.5	1.86	NA	1.22	2	1	3	NA
8	4-Cl	0.23	33.4	2.24	2.25	0.92	1	1	2	96
9	4-Br	0.23	36.0	2.21	2.15	0.94	1	1	2	97
10	3-Cl	0.37	34.6	2.26	2.11	0.91	1	1	2	-
11	3-Br	0.39	34.3	2.13	NA	0.99	1	1	2	96
12	3-NO ₂	0.71	41.6	1.38	4.47	1.9	3	1	4	NA
13	4-NO ₂	0.81	46.0	1.87	5.43	1.21	3	1	4	102

X = The substituent in phenol, σ = Hammett substituent constant, γ (dyn/cm) = Surface tension at 120 °C, at this temperature 3-methoxyphenol is only the liquid and all other phenols are solids, *<http://www.chemspider.com/Chemical-Structure.20816.html> - temperature not known, however from the knowledge of other phenols the available value is taken, k = EÖTVÖS constant, μ (Debye) = Dipole moment, x = Order of association, H_a = Hydrogen acceptor site, H_d = Hydrogen donor site, H_{ad} = total of H_a and H_d , ΔS_v^\ddagger (J K⁻¹ mol⁻¹) = Entropy of vaporization, NA = Not available in literature.

where 'M' is the molecular weight of the liquid, ' ρ_l ' is the density, ' t_c ' is the critical temperature, ' t ' is temperature and ' k ' is the Eötvös constant. For most liquids ' k ' works out to be about 2.12 in the cgs system. Such liquids are considered to be normal liquids and they have identical molecules in all the three states. Further the study on Eötvös equation was made by Ramsay and Shields⁴². They found that the experimental results for a number of liquids could be better explained by the relation:

$$\gamma \left(\frac{M}{\rho_l} \right)^{2/3} = k(t_c - 6 - t) \quad (2)$$

This equation indicates that the surface tension becomes zero at a temperature 6 °C below the critical point. Ramsay and Shields⁴² had also found that the value of ' k ' works out to be 2.12 for most of the liquids which are normal and non-associative. The less than 2.12 value of Eötvös constant (k) may be an indication of the liquid to be associated. And in the present work it is an indication of the solid with associated molecules. The values of Eötvös constant (k) are presented in Table-1. In the present work for phenols having H_{ad} 3 and 4 had the values of k less than 2.12. Hence di-methyl amino, methoxy and nitro substituted phenols with H_{ad} of 3 and 4 are associated molecules in solid state.

Calculation of ' x ' the order of association:

Let ' x ' be the order of association of associated solid

Therefore ' x ' of its molecules have formed one associated molecule, the molecular weight of the substance in the solid state will be ' xM '.

Taking the eqn. 2

$$\gamma \left(\frac{M}{\rho} \right)^{2/3} = k(t_c - 6 - t)$$

This gives an observed value of k . And for associated molecules, to get order of association, forcing the value of k to be equal to 2.12, the equation would be:

$$\gamma \left(\frac{xM}{\rho} \right)^{2/3} = 2.12(t_c - 6 - t) \quad (3)$$

Dividing equation 3 by the eqn. 2

$$\left(\frac{xM}{\rho} \right)^{2/3} = \frac{2.12}{k} \quad (4)$$

$$\text{or} \quad x = \left(\frac{2.12}{k} \right)^{3/2} \quad (5)$$

The values of ' x ' are presented in Table-1.

It is interesting to observe that in the polynomial plots of log (EÖTVÖS constant, k) and log (order of association, x) versus Hammett σ had the break again near the 'hydrogen' (Fig. 3). The EÖTVÖS constant, k for 4-N,N-dimethyl aminophenol could not be calculated since no data available in literature on the variation of surface tension with temperature or our attempts might have failed.

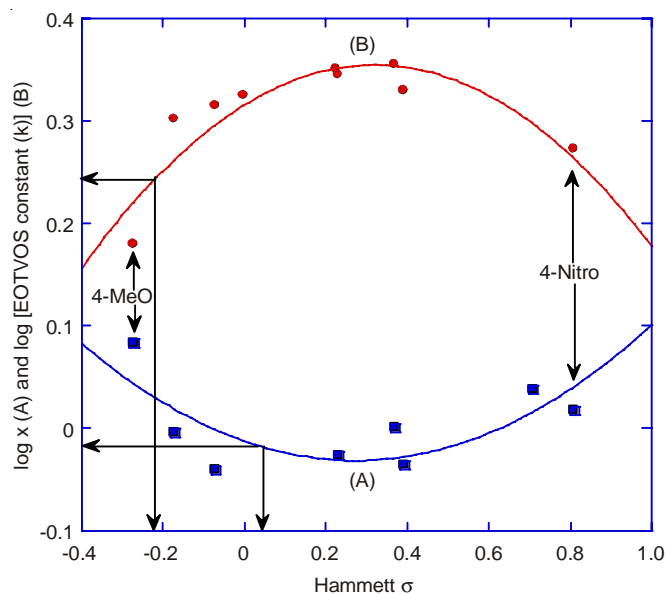


Fig. 3. Plot of log (EÖTVÖS constant, k) and log x (order of association) versus Hammett σ

Trouton's rule: ΔS_v data of phenols is presented in Table-1. Trouton's rule is of interest in the context of latent heats of

vaporization of liquids. It is an empirical rule based on heats of vaporization of a large number of normal liquids at their boiling points. According to this rule the entropy of vaporization is almost the same value, about 85-88 J K⁻¹ mol⁻¹, for various kinds of liquids at their boiling points⁴⁴. Abnormal values of Troutons' rule constant suggest abnormal entropy changes during vaporization of concerned liquids. If the Troutons' rule constant for a liquid is more than the limit of 85-88 J K⁻¹ mol⁻¹ it suggests association of molecules in the liquid form. In fact in the present work the ΔS_v values of strongly electron donating substituent and strongly electron withdrawing substituent are more than the limit of 85-88 J K⁻¹ mol⁻¹ with exception of unsubstituted phenol indicating their association in the solid form.

Dipole moment data correlation: Even the non-linear Hammett correlation of log (dipole moment) versus Hammett σ has a break again at hydrogen (Fig. 4).

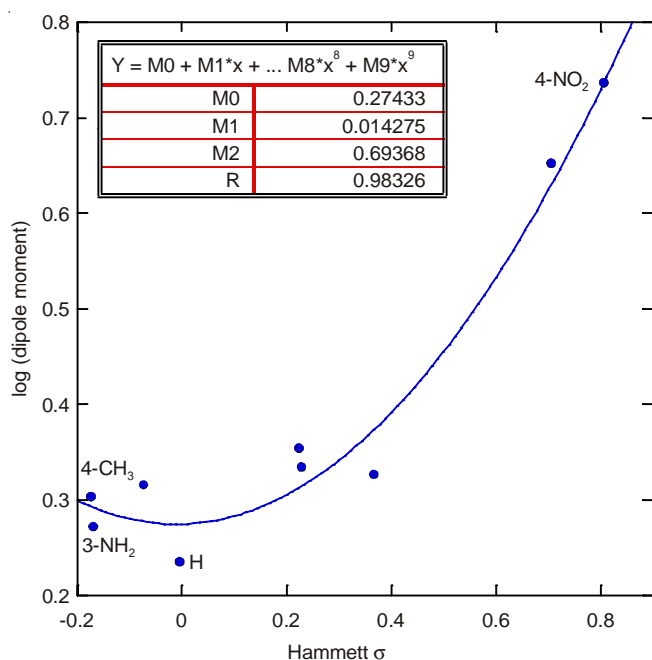


Fig. 4. Plot of log (dipole moment) versus Hammett σ

To our view it may not be unreasonable to assume that the dipole moments to be the purely physical properties. The dipole moment is a property of a molecule that results from charge separation with in a bond of a diatomic molecule containing two hetero atoms. The larger the difference in electronegativities of the two hetero atoms the greater would be the dipole moment. However in polyatomic molecules it is not possible to measure the dipole moment of an individual bond with in a molecule, but one can measure only the total moment of the molecule, which is the vectorial sum of the individual bond moments⁴⁵. In all the molecules these individual moments are constant but may not be taken as universal⁴¹. Therefore one can conclude that the property of the molecule in terms of dipole moment is not like a localized reaction center but it is the bulk property of the entire molecule. The difference between electronegativities of carbon and hydrogen is so small, alkanes or any hydrocarbon molecule had very small dipole moment. For example the dipole moment of benzene is

zero⁴⁶. If we introduce a substituent with or without hetero atom in to the benzene ring the dipole moment³⁹ would be > 0. This is because of the charge separation analogous to resonance in the entire aromatic molecule. Therefore whether the substituent is either electron donating or electron withdrawing the dipole moments of mono substituted benzenes ought to be more than that of benzene because either of the substituents would induce charge separation in the benzene ring. As an example⁴⁷, the dipole moment of toluene is 0.43 D and that of nitrobenzene is 3.93 D. It is a general observation that when a substituent introduced in to benzene ring, having hetero atom other than carbon or hydrogen the dipole moment would be even large. The dipole moment of phenol is again 1.55 D. Hence the dipole moments of substituted phenols either with electron donating or electron withdrawing substituents would be more than that of phenol itself (Table-1) resulting in non-linearity in the Hammett correlation with a break at hydrogen.

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