

Dipole moments and melting points and their unsolved miracles on the application of hammett equation

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Abstract: Application of Hammett equation to structure-reactivity correlations of a “localized reaction site” in elucidating the reaction mechanisms of several organic reactions is a very well-known phenomenon in physical-organic chemistry class-room of senior undergraduate and graduate level students. This is a testament of purely chemical phenomena. There were two successful reports in literature on the application of linear and non-linear Hammett equation to claim to be physical property of solubilities of benzoic acids. In this article we tried to apply the same to the dipole moments and melting points of some benzoic acids and however premature and unsolved.

Keywords: Hammett Equation, Melting Points Of Benzoic Acids, Dipole Moments Of Benzoic Acids, Structure-Reactivity Correlations

1. Introduction

Quantitative solubility-structure relationships for several meta- and para-substituted benzoic acids in benzene and in cyclohexane¹ and in 1, 4-dioxane and tetrahydrofuran (THF)² were studied. Even the application of Hammett equation to melting points of some benzene derivatives were touched and left without any reasonable arguments³. Katritzky et al gave a one line concluding argument on the application of QSPR models to the melting points of benzene derivatives in terms of molecular packing and intermolecular interactions⁴. The V-shaped locus in the Hammett plot was not noticed in the study of effect of substituents on dipole moments of benzoic acids⁵. In this the non-linearity is concluded in terms of poor correlation, hence no arguments were offered. In the present article we were tempted to apply the Hammett equation to the dipole moment and melting point data of benzoic acids but still it kept us under skepticism.

2. Discussion

Though lately the application of structure-reactivity correlations in the form of either linear or non-linear Hammett equation is not being observed in chemical literature, there

are many still unsolved applications in this aspect with several physical properties such as dipole moments, melting points, surface tension, viscosities and several other physical properties as a function of Hammett substituent constants. Our recent experience in this field⁶⁻¹² and in the interpretation of Marcus equation (a special type of linear free energy relationship) to electron transfer reactions between carbon centered free radicals and aromatic systems¹³, prompted us to take up the title subject and if possible to offer any reasonably intelligent explanations. In the study of quantitative solubility-structure relationships for several meta- and para-substituted benzoic acids in benzene and in cyclohexane¹, Hancock et al observed that there was no significant correlation between $\log X_B$ alone or $\log X_C$ alone with Hammett's σ . Here X_B and X_C are the solubilities of benzoic acids in benzene and cyclohexane. However they observed a linear correlation between $\log (X_B/X_C)$ and Hammett's σ . They explained this as a measure of tendency of the interaction of π -electron cloud of benzene with the benzoic acid. And the same studies by these people in 1,4-dioxane and THF were performed² and they have observed a V-shaped locus when $\log (X_D/X_C)$ were plotted against σ . Here X_D is the solubility of benzoic acids in dioxane and X_C is from reference 1. Hancock et al had tried to explain this V-shaped Hammett locus based on the same explana-

tions of change in mechanisms of Wolf-Kishner reaction of hydrazones¹⁴ and U-shaped Hammett locus for the rates of solvolysis and thiosulfate reactions of α -chloro toluenes¹⁵ for two sets of electron donating and electron withdrawing of substituents. But it was difficult to make any reasonable explanations due to complexity of several factors which affect the solution processes. Later Schreck¹⁶ had described this in an article on non-linear Hammett relationships as what appears to be the only physical property that gives a non-linear Hammett plots. But 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 gets support from the variation of Hammett ρ with solvent polarity^{17,18}.

3. Dipole Moments

To our view it may not be unreasonable to assume that the dipole moments and melting points 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 mo-

ments¹⁹. In all the molecules these individual moments are constant but may not be taken as universal²⁰. 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 zero²¹. If we introduce a substituent with or without hetero atom in to the benzene ring the dipole moment would be > 0 ²⁰. 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 example²², 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 benzoic acid is again 1.78 D⁵. Hence the dipole moments of substituted benzoic acids either with electron donating or electron withdrawing substituents would be more than that of benzoic acid itself⁵. Surprisingly there was a good correlation between dipole moments of benzoic acids 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 (Figure 1).

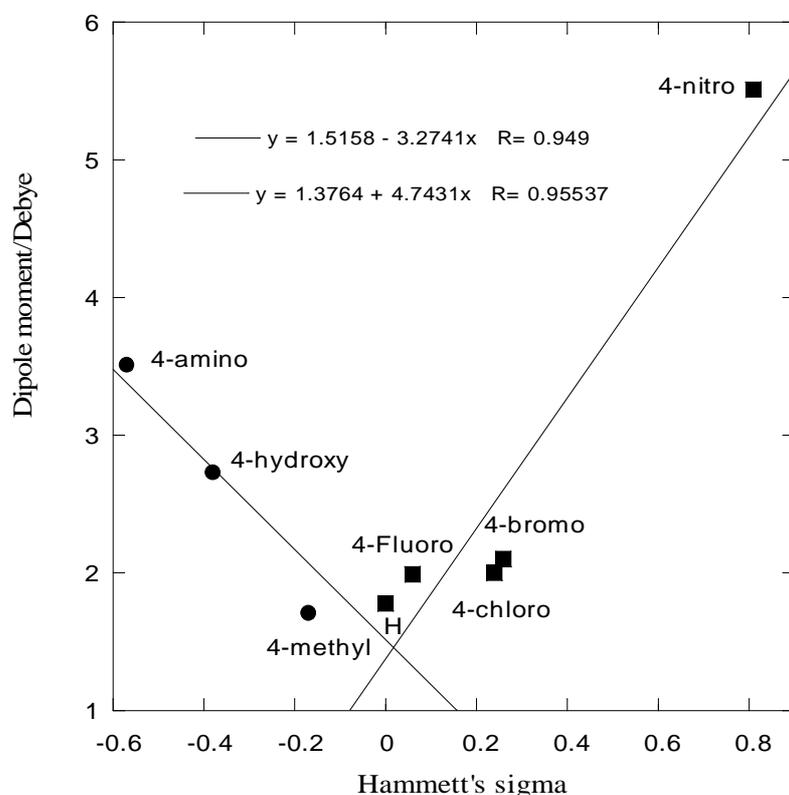


Figure 1. Hammett plot: dipole moments of benzoic acids versus Hammett's sigma.

The dipole moments of different benzoic acids are from references 5 and 20. Though the correlation coefficients are bit away from unity, the trends are unmistakable. Therefore the dipole moments are fairly good indications of application of the Hammett equation. We claim this is the first observation on the application of Hammett equation to a physical property like dipole moments.

4. Melting points

A century ago Lindemann had put forward a theoretical basis to predict the bulk melting point of crystalline materials²³. According to his theory, the average amplitude of thermal vibrations increases with increase in temperature. Melting of the crystalline solid would start when the amplitude of vibration becomes large enough for adjacent atoms to partly occupy the same space. The Lindemann prediction states that melting is expected when the root mean square vibration amplitude exceeds a threshold value. According to equipartition theorem²⁴ assuming all atoms in crystalline substance vibrate with same frequency, ν , the estimated average thermal energy was given by the following equation.

$$E = 4\pi^2 m \nu^2 u^2 = k_B T \quad (1)$$

Where m is the atomic mass, ν is the frequency, u is the average vibration amplitude, k_B is the Boltzmann constant, and T is the absolute temperature. If the threshold value of u^2 is replaced by $c^2 a^2$ where ' c ' is the Lindemann constant and ' a ' is the atomic spacing, then the equation for melting point is given by:

$$T_m = \frac{4\pi^2 m \nu^2 c^2 a^2}{k_B} \quad (2)$$

On right hand side of equation 2 only the quantity ' m ' is variable assuming the atomic spacing ' a ' in a molecule to be constant and as others are all constants. Therefore as molecular mass of a molecule consisting of several atoms increases the average thermal energy required for a crystalline substance to melt increases to break more number of bonds. Hence among the all the substituted benzoic acids, un-substituted benzoic acid would have a lower melting point and other substituted benzoic acids whether they had electron donating or electron withdrawing substituent would have higher melting points. Again surprisingly there was a good correlation between melting points of benzoic acids 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 (Figure 2).

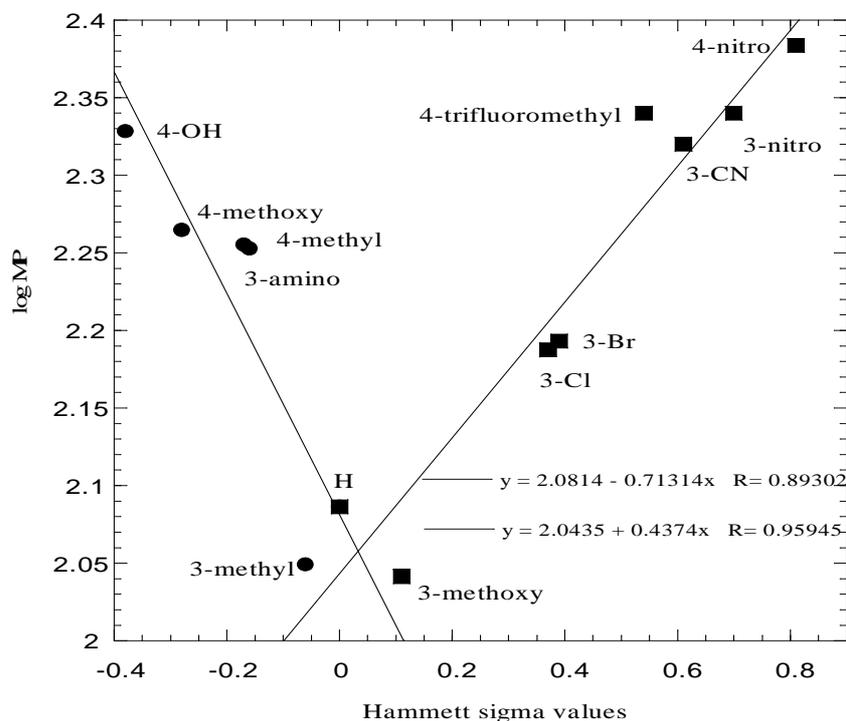


Figure 2. Hammett plot of log (melting point) of benzoic acids versus Hammett substituent constant.

The melting points used in this Hammett correlation are from 'Google search Engine' using the molecular formula of each benzoic acid.

It has to be realized that the original Lindemann's model

for vibrational melting, like many of his successor Scientists, refers only to a crystal with the simple structure. Crystals containing big molecules exhibit complex vibrations. This may rule out any simple rule of lattice stability, determined

merely by vibrational amplitudes of the molecular centers of mass. Furthermore, the Lindemann model is based on harmonic forces whereas melting must involve bond breaking. This is another serious defect of the model. The other defect of the model is that melting is described in terms of individual atomic property, i.e. mean square amplitude of vibration, while a phase transition is a cooperative bulk process. In addition, the Lindemann model did not include the idea of the melting transition must involve both solid and liquid phases. Nevertheless the predictive success of the Lindemann melting criterion lent support to the belief that melting could be a gradual process, beginning within the solid at temperatures below the melting point. With these defects in Lindemann's theory, it may be premature to apply the Hammett equation to the melting point data but we have given a trial for another physical property of melting point.

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