



# Non-Linear Taft Relationship applied to surface tensions of aliphatic acids: Inter-molecular hydrogen bonding versus intra-molecular hydrogen bonding

Sanjeev Rachuru<sup>a</sup>, Jagannadham Vandanapu<sup>b,\*</sup>, Adam A. Skelton<sup>c</sup>

<sup>a</sup> Department of Chemistry, Geethanjali College of Engineering and Technology, Cheeryala-501301, Rangareddy Dist., Telangana, India

<sup>b</sup> Department of Chemistry, Osmania University, Hyderabad 500007, India

<sup>c</sup> Department of Pharmacy, School of Health Science, University of KwaZulu-Natal, Durban, South Africa

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## ABSTRACT

Hammett and Taft equations in their most basic forms are linear free energy relationships between standard free energies of two reaction series. Therefore any chemical or physical property inherently associated with any of the thermodynamic property like enthalpy  $H$ , free energy  $G$ , internal energy  $E$  or entropy  $S$  are subjected to substituent effects. One such physical property is the surface tension. Surface tension is a kind of surface free energy ( $G$ ) of any liquid and is also supposed to be effected by the structure of liquids. Hence the present study has been selected to see the effect of substituents on surface tension of some aliphatic acids. The quick glance at the present study ended up with a non-linearity of Taft equation to the surface tension data of aliphatic acids. Hence Non-Linear Taft Relationship (NLTR) was applied to surface tensions ( $\gamma$ ) of some aliphatic acids. The non-linearity of  $\log \gamma$  versus Taft  $\sigma^*$  correlation was explained in terms of inter-molecular hydrogen bonding versus intra-molecular hydrogen bonding and in terms of steric effects.

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## 1. Introduction

Though the Hammett [1] and Taft [2] equations are nearly more than seventy five years old, they enjoyed outstanding application for predicting the organic reaction mechanisms among physical organic chemists. Ever since the Hammett [1] and Taft [2] equations were developed, there were several hundreds of reactions in literature, for which the Hammett and Taft reaction constants ( $\rho$  and  $\rho^*$ ) were reported. Though the application of Linear Free Energy Relationships to chemical reactions [3–24] and physical properties [25–30] is quite promising in its nature, application of non-linear Taft equation to the reactions of benzyl bromide with  $N$ -substituted benzyl amines is first of its kind in literature and of recent origin from our laboratory [31]. In the present article we have tried to apply non-linear Taft equation to physical properties like surface tensions of some aliphatic acids. To our knowledge the present study is first of its kind in literature. The non-linearity of Taft correlation was explained in terms of inter-molecular hydrogen bonding versus intra-molecular hydrogen bonding of the aliphatic acids and in terms of steric effects.

## 2. Experimental data source

Data on surface tensions of aliphatic acids is from reference [32] and references cited therein. The Taft  $\sigma^*$  values of alkyl substituted acids are from references [33,34] and of halogen substituted acids are from reference [35]. Thermo chemical data is from reference [36]. All the linear correlations were done using the KaleidaGraph software, Reading, PA, USA.

## 3. Discussion

A molecule in the bulk of a liquid is completely surrounded by other molecules; therefore it is attracted equally in all directions. While a molecule on the surface has an attraction inward because the number of molecules per unit volume is greater in liquid than in vapor because vapor is a dilute system. Due to this inward pull, the surface of the liquid always tends to contract to have minimum possible area. In order to extend the area of the surface, it is necessary to do work, to bring molecules from the bulk of the liquid into the surface, against the inward attractive force. The work required to increase the surface area by 1 sq. cm is called surface free energy [37].

As a result of this tendency to contract, a surface behaves as if it were in a state of tension. If a cut were made along any line in the surface, a force would have to be applied to hold the separate portions of the surface together. This force is proportional to the length of the cut and its value per unit length is called surface tension or interfacial tension ( $\gamma$ ).

\* Corresponding author.

E-mail addresses: [rachuru1sanjeev1@rediffmail.com](mailto:rachuru1sanjeev1@rediffmail.com) (S. Rachuru), [jagannadham1950@yahoo.com](mailto:jagannadham1950@yahoo.com) (J. Vandanapu), [Skelton@ukzn.ac.za](mailto:Skelton@ukzn.ac.za) (A.A. Skelton).

Having clearly described what interfacial tension and surface free energy in the foregoing paragraphs [37], we would like to observe the correlation of the interfacial tension of several aliphatic acids with Taft substituent constants ( $\sigma^*$ ). We are well aware of the fact that application of structure-reactivity correlations of a 'localized reaction site' in elucidating the mechanisms of several organic reactions is very well known. This applicability is for chemical reactions. But the application of structure-reactivity correlations to physical properties is extremely uncommon. Hanock et al. [25,26] studied the quantitative solubility-structure relationship for several *meta* and *para* substituted benzoic acids in benzene and cyclohexane. But solubility is not a completely physical property. Solubility is a function of ionizing capacity and ionization is a chemical property which depends on the dielectricity of the solvent; further it will be taking place at a localized ionization site.

In the present work three Taft plots of  $\log \gamma$  vs  $\sigma^*$  were presented in Fig. 1, Fig. 2 and Fig. 3. Surprisingly there was a correlation between surface tensions of aliphatic acids with Taft substituent constants,  $\sigma^*$  with two straight lines one with positive slope ( $r = 0.9799$ ) for electron donating substituents and the other with negative slope ( $r = 0.9267$ ) for electron withdrawing substituents (Fig. 1 without  $\text{CF}_3\text{COOH}$  in the correlation, Fig. 2 without tri-chloro and di-chloro acetic acids in the correlation  $r = 0.9799$  and  $r = 0.9984$  and Fig. 3 without  $\text{CF}_3\text{COOH}$ ,  $r = 0.9799$  and  $r = 0.9267$ ). In Fig. 1, though formic acid contains an electron withdrawing substituent ( $\text{H}$ ,  $\sigma_{\text{H}}^* = 0.49$ ) but it correlated along with the electron donating substituents. The numbers 1–15 in the three figures represent the substituent R given in the Table 1. And there was no correlation between both order of association ( $x$ ) and EÖTVÖS constant ( $k$ ) with Taft  $\sigma^*$ . (See Fig. 4.)

The order of association ( $x$ ) could be calculated using Ramsay-Shields equation [38]:

Eötvös [38] had suggested the following equation that explains the effect of temperature on surface tension ( $\gamma$ ):

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

where 'M' is the molecular weight of the liquid, ' $\rho_l$ ' is the density, ' $t_c$ ' is the critical temperature, ' $t$ ' is temperature in centigrade and ' $k$ ' is the Eötvös constant. For most of the liquids ' $k$ ' works out to be about 2.12 in the cgs system. Such liquids are considered to be normal liquids and

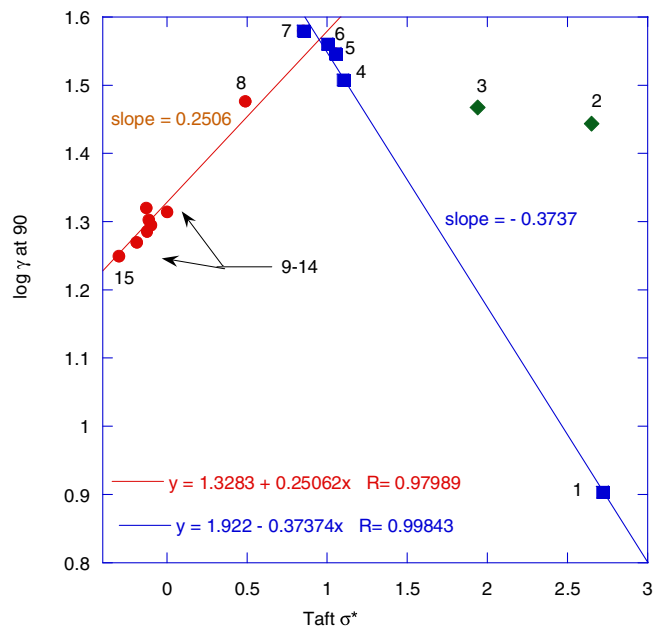


Fig. 2. Plot of  $\log \gamma$  vs Taft  $\sigma^*$ .

they have identical molecules in all the three states. Further study on Eötvös equation was made by Ramsay and Shields [38], who found that the experimental results for a number of liquids could be better explained by this relationship:

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

This equation indicates that the surface tension becomes zero at a temperature 6 °C below the critical point. Ramsay and Shields 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.

Calculation of ' $x$ ' the order of association:

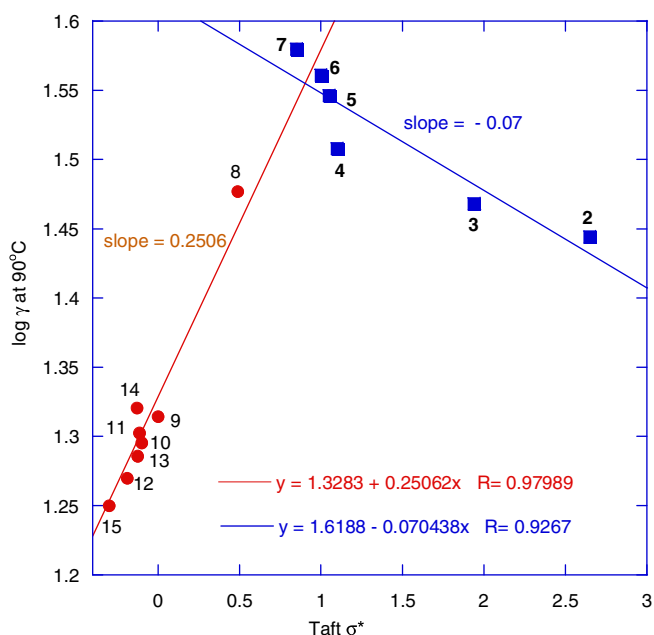


Fig. 1. Plot of  $\log \gamma$  vs Taft  $\sigma^*$ .

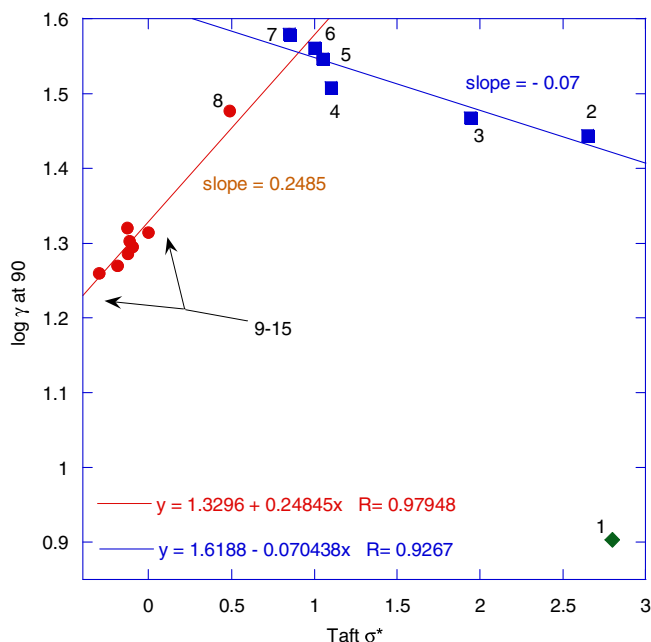


Fig. 3. Plot of  $\log \gamma$  vs Taft  $\sigma^*$ .

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