Chemistry: Bulgarian Journal of Science Education *Volume 29 Number 4, 2020* *Природните науки в образованието*

Teaching Experiment in Science
Учебен експеримент в природните науки

ATTENUATION EFFECT IN ALIPHATIC ACIDS EXTENDED TO ALKANES THE CARBON ACIDS VIA THE ALIPHATIC ALCOHOLS: AN EDUCATIONAL PERSPECTIVE IN CHEMISTRY

[1)]R. Sanjeev, [2)]V. Jagannadham
[1)]Geethanjali College of Engineering and Technology (India)
[2)]Osmania University (India)

Abstract. A simple, new, lucid and an improved version of a protocol over Andrew William's treatment is presented in this article for the evaluation of the attenuation effect of methylene group on the deprotonation process of aliphatic acids RCOOH – $RCOO^-$ + H^+ and extended to aliphatic alcohols and alkanes; the carbon acids.

Keywords: attenuation effect; methylene group; aliphatic acid dissociation equilibriums, Taft r*

Introduction

Aliphatic acid dissociation equilibriums and their chemical reactivity is well explained on the basis of well established acid and base catalyzed hydrolysis of substituted aliphatic ester derivatives by Taft equation (Taft, 1952a; 1952b; 1953) in terms of two parameters the Taft substituent constant (s*) and the Taft reaction constant (r*). Thus the Taft equation in terms of only polar sensitivity factors in aliphatic acid dissociation equilibriums is:

$$\log K_x = \log K_{CH_3} + \rho^*\sigma^* \tag{1}$$

K_X and K_{CH} K_{CH} are the acid dissociation constants of substituted acids and acetic acid respectively. The Taft reaction constant (r*) is a measure of the magnitude of the polar effect of structure on the aliphatic acid dissociation equilibriums. The steric effects are assumed to be negligible because the distance between the dissociable hydrogen and the substituent is quite appreciable.

Methods

All calculations and curve fittings were done by KaleidaGraph software version 4.1 supplied by Synergy Software INC., Reading, PA, USA. All chemical structures were drawn using "Chemdraw" software.

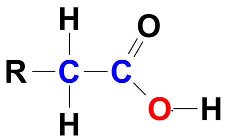
Discussion

The attenuation effect may be explained as a systematic depletion of the transmitting power of a polar effect through increasing number of methylene groups between the dissociable hydrogen and the substituent. On this aspect few publications have appeared in literature from our group (Jagannadham, 2009; Sanjeev & Jagannadham, 2017; Sanjeev et al., 2014; 2020).

Owing to his observations and formulation of a strong empherical relation that explains the attenuation effect in aromatic systems, Andrew Williams (2003) has come up with another empherical equation for aliphatic systems, Eq. (2).

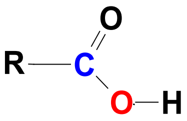
$$\rho^* \sim 0.8(2.0)^{(2 - i)} \tag{2}$$

Here "i" is the number of methylene groups or the number of carbon atoms between the atom bearing the dissociable hydrogen and the substituent R ($R\text{-}(C)_i\text{-}XH$)$^{1)}$ (Williams, 2003). Here one must bear in mind that the number "i" is not the number of methylene groups between the dissociable proton and the substituent as mentioned above in the first paragraph of our "discussion", but in the contention of Williams it is the number of the methylene groups or the number of carbon atoms between the *atom* bearing the dissociable hydrogen that is the "oxygen" in *red* in the structures I and II and the substituent R ($R\text{-}(C)_i\text{-}XH$)$^{1)}$ (Williams, 2003). Using Eq. (2), the predicted values of Taft **r*** for substituted acetic acids (RCH_2CO_2H, i = 2, the *blue* carbons in the structure I and formic acids (RCO_2H), i = 1, again the *blue* carbon in the structure II) are 0.8 and 1.6 respectively. And these values are well agreed with the observed values of 0.67 and 1.62, respectively (Perrin et al., 1981).



I

i = 2 (two blue carbon atoms)



II

i = 1 (one blue carbon atom)

Making Taft plots for substituted acetic acids, RCH_2CO_2H and formic acids, RCO_2H, we found that the Taft r* values 0.75 and 1.6 respectively (present work). William's treatment is good as long as these two examples are used. But Eq. (2)

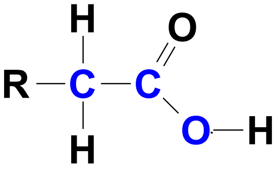
fails when the treatment is extended to alcohols and the alkanes, the carbon acids and with higher "i" values.

Different Taft plots including alcohols with i =1 and alkanes with i = 0; pK_a versus Taft s* were made and presented in Tables 1-7 and Figures 1-7. Applying William's empherical equation, Eq. (2), a plot of Taft r* versus i is shown in figure 8 with the corresponding data in table 8 with the inclusion of aliphatic alcohols and the alkanes (the carbon acids). The correlation is very poor (r = 0.4757).

In the present work William's treatment is further extended by including aliphatic alcohols and the alkanes (the carbon acids) with a different but modified equation, Eq. (3).

$$\rho^* = m1 + m2^*e^{-m3^*i} \tag{3}$$

Here m1, m2 and m3 are arbitrary constants. And "i" is as usual the number of methylene groups or the number of carbon atoms between the dissociable hydrogen (*not the atom to which dissociable hydrogen attached*) and the substituent. With this new definition "i" would be 3 for acetic acid as an example, as shown in structure III.



III

i = 3, two blue carbon atoms and the blue oxygen atom

Table 1. Taft s* and pK_a data of substituted carbon acids, i = 0

Sl. No.	**R—H**			
	R	Taft s*	pK_a	**Taft ρ* = 12.12**
1	$(CH_3)_3$-	-0.30	53.0	
2	$(CH_3)_2CH$-	-0.19	51.0	
3	$CH_3CH_2CH_2$-	-0.12	51.0	
4	CH_3CH_2-	-0.10	51.0	
5	CH_3-	0.00	50.0	
6	$C_6H_5CH_2$-	0.22	34.0	
7	$C_6H_5CH=CH$-	0.41	43.0	
8	H	0.49	36.0	
9	$CH_2=CH$-	0.56	50.0	
10	C_6H_5-	0.60	43.0	
11	$C_6H_5C°C$-	1.35	23.0	
12	CH°C-	2.18	25.0	
13	CCl_3-	2.65	15.7	

A plot of Taft r* versus i is shown in Fig. 9 with the corresponding data in table 8 with the inclusion of aliphatic alcohols (i = 1) and the alkanes (i = 0, the carbon acids). The correlation is very good (r = 0.9989). A similar study was manifested by one of the authors (VJ) earlier (Jagannadham, 2009) in the study of attenuation effect in benzoic acids and was extended to benzenes, the aromatic carbon acids (in the present work it is alkanes, the aliphatic carbon acids) itself via phenols (in the present work it is alcohols).

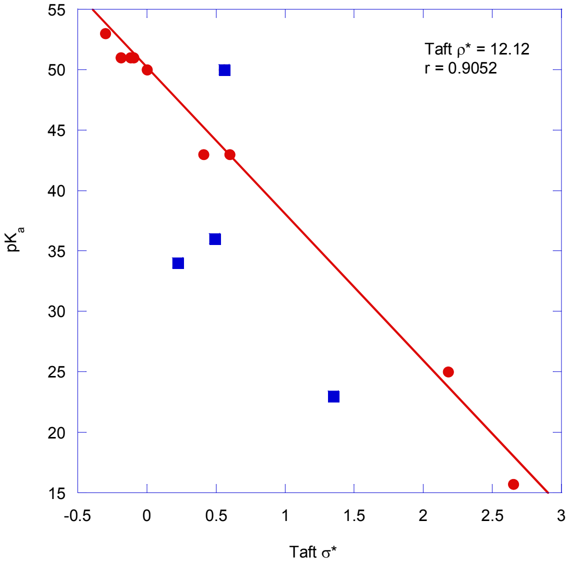


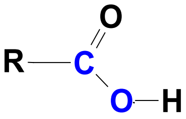
Figure 1. Plot of pK_a vs. Taft σ^*

The attempt in the present work on the evaluation of attenuation effect in aliphatic systems gave an encouragement for studying attenuation effect in different proton dissociation equilibriums to be brought on one rope which includes the nitrogen acids and sulfur acids and even the molecules containing the carbons with different hybridizations other than sp3.

Table 2. Taft s* and pK_a data of substituted aliphatic alcohols, i = 1, blue oxygen

Sl. No.	**R-O-H**			
	R	Taft s*	pK_a	
1	$(CH_3)_3$-	-0.30	16.54	Taft ρ* = 3.54
2	$(CH_3)_2CH$-	-0.19	16.50	
3	$CH_3CH_2CH_2$-	-0.12	16.00	
4	CH_3CH_2	-0.10	16.00	
5	CH_3	0.00	15.54	
6	CF_3CH_2-	0.90	12.43	

Table 3. Taft s* and p*K*$_a$ data of substituted formic acids, i = 2, one blue carbon and one blue oxygen

Sl. No.				
	R	Taft s*	pK$_a$	
1	$CH_3CH_2CH_2$-	-0.12	4.82	Taft ρ* = 1.6
2	CH_3CH_2-	-0.10	4.88	
3	CH_3-	0.00	4.75	
4	H	0.49	3.77	
5	$ClCH_2$-	1.05	2.86	
6	$CNCH_2$-	1.30	2.43	
7	Cl_2CH-	1.94	1.29	
8	Cl_3C-	2.65	0.65	

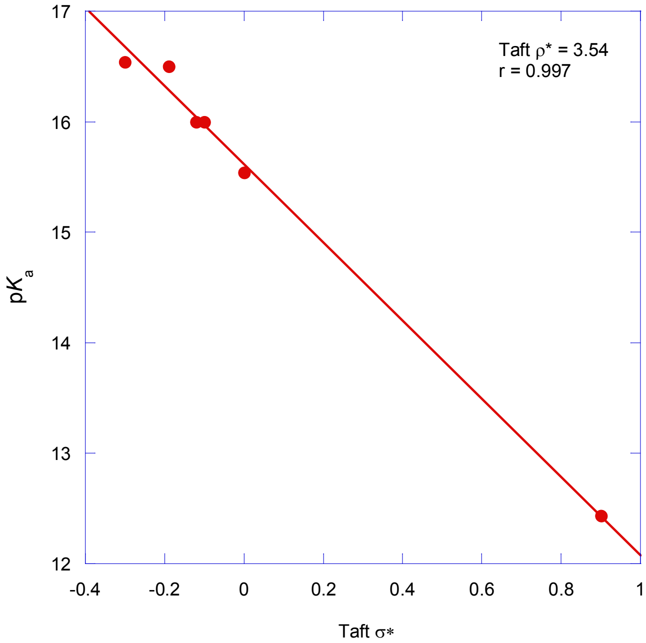


Figure 2. Plot of pK$_a$ vs. Taft s*, i =1

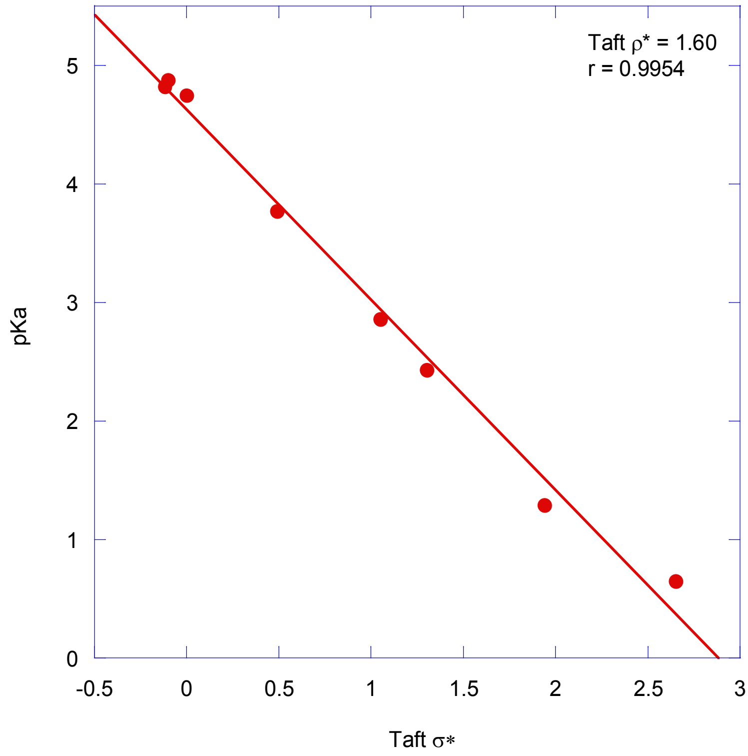
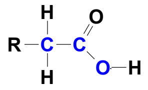


Figure 3. Plot of pK_a vs. Taft s*, i = 2

Table 4. Taft σ* and pK_a data of substituted acetic acids, i = 3, two blue carbons and the blue oxygen

Sl. No.				
	R	Taft s*	pKa	Taft ρ* = 0.75
1	C_2H_5	-0.10	4.82	
2	CH_3	0.00	4.88	
3	H	0.49	4.75	
4	Br	2.84	2.86	
5	Cl	2.96	2.86	
6	F	3.21	2.66	
7	CN	3.30	2.43	
8	NO_2	4.00	1.68	

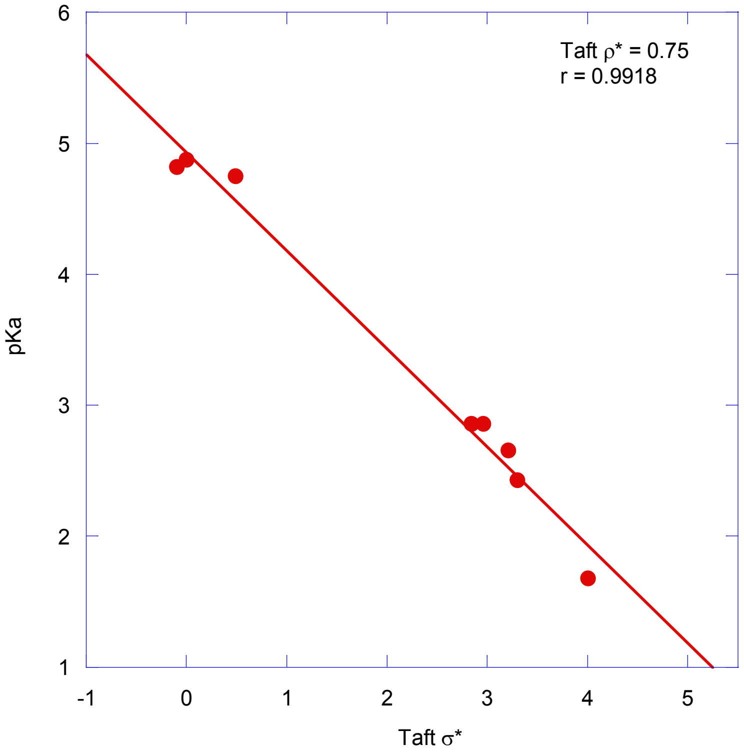
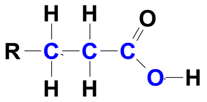


Figure 4. Plot of pK_a vs. Taft s*, i=3

Table 5. Taft s* and pK_a data of substituted propionic acids, i = 4, three blue carbons and one blue oxygen

Sl. No.				
	R	Taft s*	pKa	
1	$CH_3(CH_2)_3CH_2$-	-0.25	4.90	Taft ρ* = 0.29
2	$CH_3(CH_2)_2CH_2$-	-0.13	4.90	
3	$CH_3CH_2CH_2$-	-0.12	4.88	
4	CH_3CH_2-	-0.10	4.82	
5	CH_3-	0.00	4.82	
6	$ClCH_2$-	1.05	4.52	
7	Cl-	2.96	4.00	

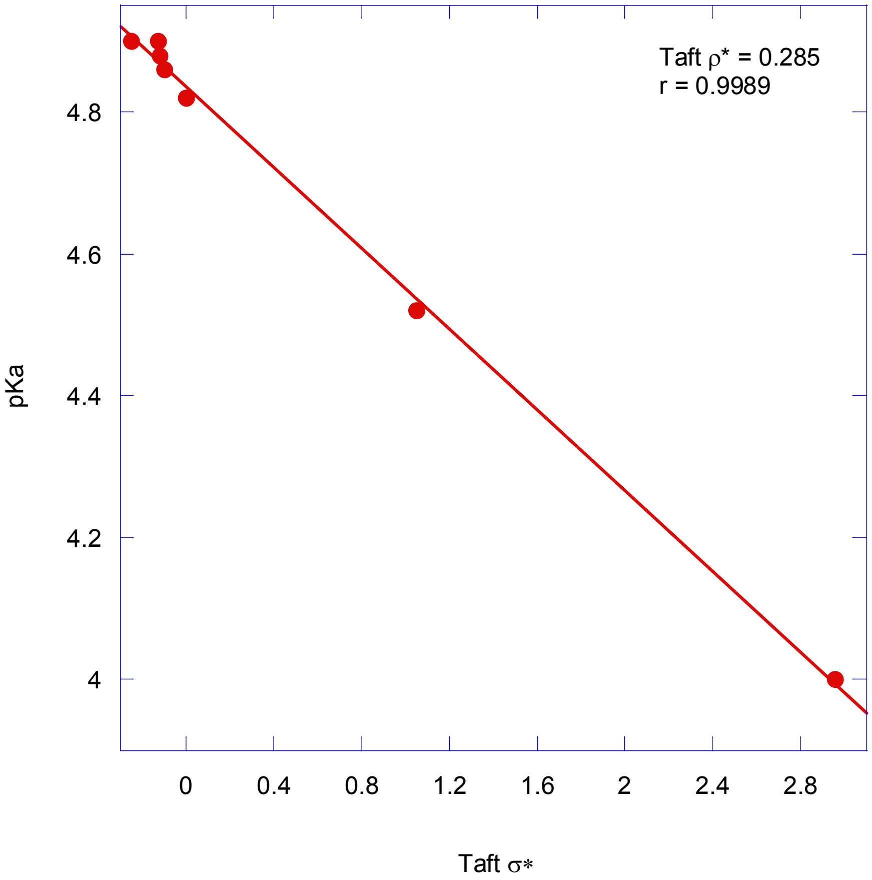
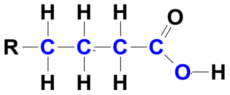


Figure 5. Plot of pK_a vs. Taft s*, i=4

Table 6. Taft s* and pK_a data of substituted butyric acids, i = 5, four blue carbons and one blue oxygen

Sl. No.				Taft ρ* = 0.65
	R	Taft s*	pKa	
1	$CH_3CH_2CH_2$-	-0.12000	4.9000	
2	CH_3CH_2-	-0.10000	4.8800	
3	CH_3-	0.0000	4.8200	

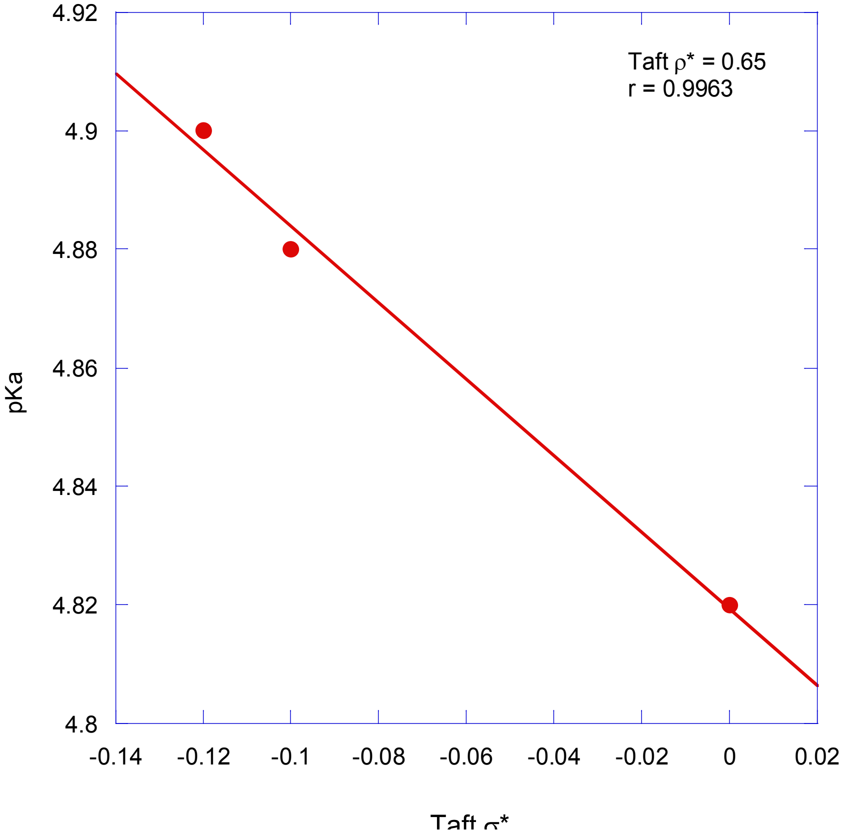
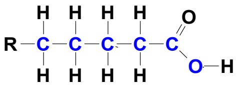


Figure 6. Taft s* and pK_a data of substituted butyric acids, i = 5, four blue carbons and one blue oxygen

Table 7. Taft s* and pK_a data of substituted pentanoic acids, i = 6, five blue carbons and one blue oxygen

Sl. No.				Taft ρ* = 0.18
	R	Taft s*	pKa	
1	$CH_3CH_2CH_2$-	-0.12000	4.90	
2	CH_3CH_2-	-0.10000	4.90	
3	CH_3-	0.0000	4.88	

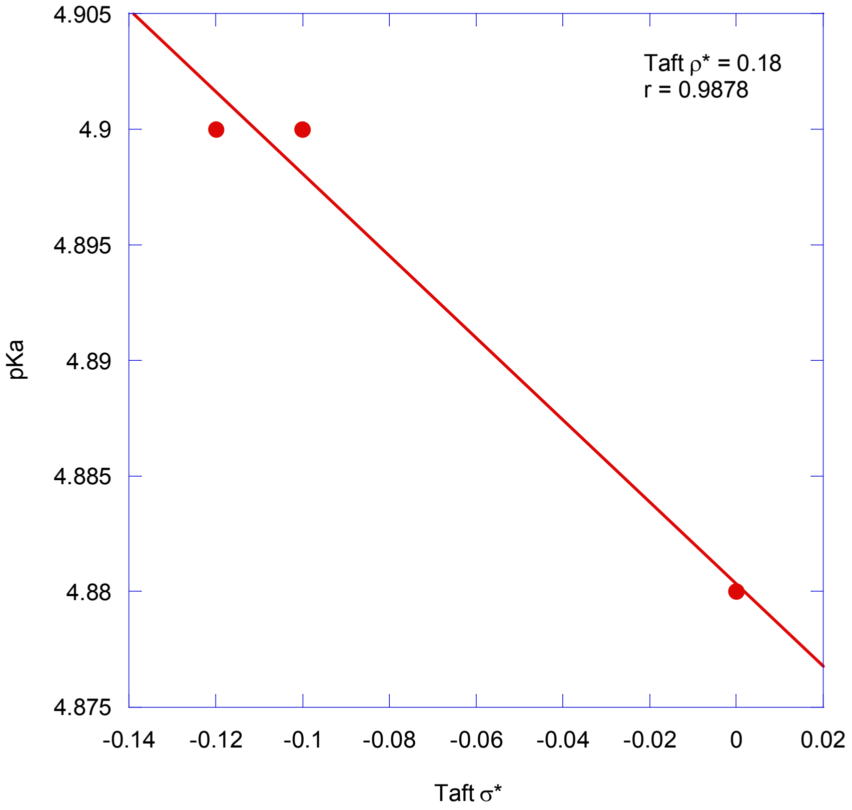


Figure 7. Taft s* and pK_a data of substituted butyric acids, i = 6

Table 8. Data of ‘i’ and Taft r*

i	Taft r*(#)
0.00	12.1
1.00	3.54
2.00	1.60
3.00	0.75
4.00	0.65
5.00	0.275
6.00	0.180

(#)From the plots of pK_a versus Taft s* the slopes are all negative. Yet taking the positive sign for Taft r* values is justified because pK_a = - log K_a.

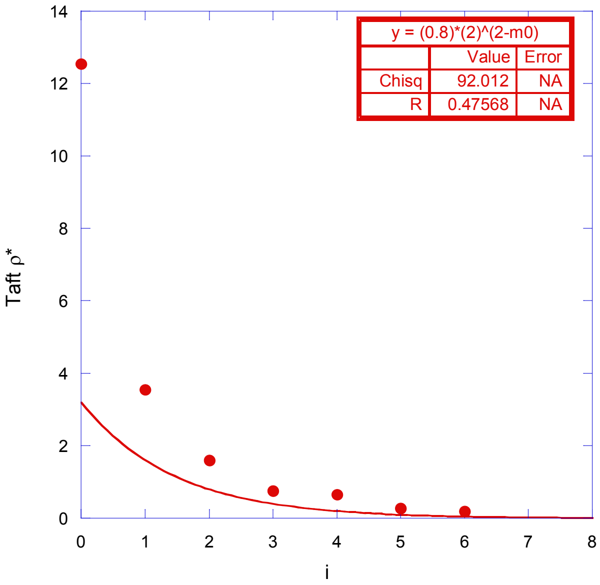


Figure 8. Plot of Taft ρ^* vs. i using Eq. (2)

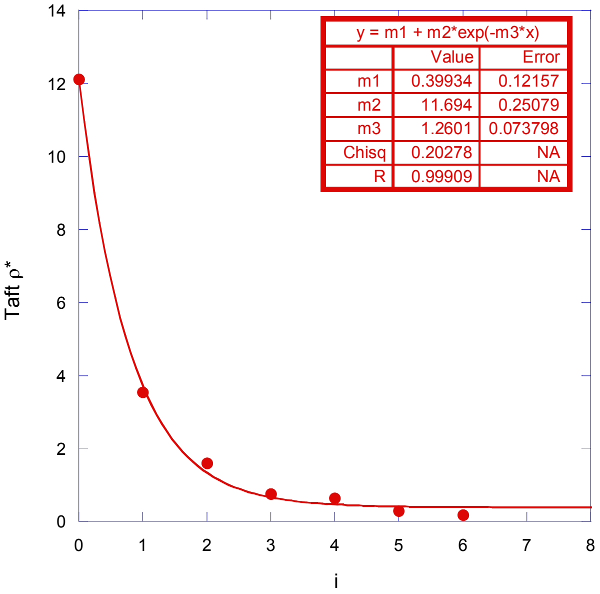


Figure 9. Plot of Taft ρ^* vs. i

The decrease in Taft r* value is more pronounced with increase in the number of atoms between the ionizable proton and the first carbon atom of the substituent when compared to that in aromatic systems (Jagannadham, 2009; Sanjeev & Jagannasdham, 2020). Here it decreased from a value of 12.1 with one atom to 0.275 to 0.18 with five and six atoms. After the number atoms become 5 the Taft r* is approaching zero, Fig. (9). In the aromatic systems the gradual decrease in Hammett r is only by a factor of 2 each time as a function of each methylene group (Jagannasdham, 2009). But in aliphatic systems as in the present work the decrease is 3 – 4 each time and finally approaches zero as ‘x’ approaches 8 (Fig. (9)). This may be because of the larger distance between the substituent attached to aromatic system and the ionizable proton compared to the smaller distance in the aliphatic systems. Hence the *attenuation* effect of substiuents is not much pronounced in aromatic systems compared to that in aliphatic systems.

NOTES

1. The readers are requested to make a note in Eq. (2) that it is not the equality sign it is “~” and reflects its meaning as not exactly the same.

REFERENCES

Jagannadham, V. (2009). The attenuation effect through methylene group. *Bulg. Chem. Commn., 41,* 50 – 53.

Perrin, D.D., Dempsey, B. & Serjeant, E.P. (1981). p*Ka prediction for organic acids and bases.* London: Chapman and Hall.

Sanjeev, R. & Jagannadham, V. (2017). Estimation of Taft ρ* of dissociation equilibriums of methanium Ions RCH4+ the hydrocarbon super acids: a chemical education practice in physical-organic chemistry classroom. *Curr. Phys. Chem.,* 7, 218 – 223.

Sanjeev, R. & Jagannadham, V. (2020). Attenuation effect in twenty one different proton dissociation equilibriums brought on one rope: a chemical education tool for evaluation of pKa of proton dissociation equilibrium of any substituted benzene (XC6H5). *World J. Chem. Educ., 8*(2), 61 – 66.

Sanjeev, R., Jagannadham, V. & Veda Vrath, R. (2014). The attenuation effect through methylene group: part 2. *Bulg. Chem. Commn.,* 46, 375 – 377.

Sanjeev, R., Jagannadham, V. & Ravi, R. (2020). Can non-bonded pair of electrons of Sp3 nitrogen with two single σ-bonds on either side still transmit substituent electronic effects to the reaction rite: reversal of attenuation effect by Sp3 nitrogen – a chemical education perspective. *Chem. Methodologies, 4,* 106 – 114.

Taft, R.W. (1952a). Linear free energy relationships from rates of esterification and hydrolysis of aliphatic and ortho-substituted benzoate esters. *J. Amer. Chem. Soc., 74*, 2729 – 2732.
Taft, R.W. (1952b). Polar and steric substituent constants for aliphatic and o-benzoate groups from rates of esterification and hydrolysis of esters. *J. Amer. Chem. Soc., 74,* 3120 – 3128.
Taft, R.W. (1953). Linear steric energy relationships. *J. Amer. Chem. Soc., 75*, 4838 – 4839.
Williams, A. (2003). *Free energy relationships in organic and bioorganic chemistry.* Cambridge: *Royal Society of Chemistry.*

✉ **V. Jagannadham (corresponding author)**
Department of Chemistry
Osmania University
Hyderabad 500 007, India
E-mail: jagannadham1950@yahoo.com