

Is Interfacial Tension of a Liquid-Air Interface Thermodynamically a Cyclic Process?

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Abstract

Brønsted ($\log k_B = \beta \text{p}K_a^{\text{HB}} + C$) and Taft ($\log k = \rho^* \sigma^* + \log k_o$) equations are applied to the interfacial tension data of N-substituted anilines. The significance of the values of Brønsted β (-0.096) and Taft ρ^* (0.091) are explained in terms of little proton transfer from the acid to the aniline is accelerated by electron donating groups and the deprotonation of protonated aniline is accelerated by electron withdrawing groups. Since ~~any~~ thermodynamic property associated with any kind of reaction is a point group and the very fact that the similar values of Brønsted β and Taft ρ^* with opposite sign is an indication of that the total process taking place at the aniline-air interface is a cyclic one.

Keywords

Brønsted Equation, Taft Equation, Interfacial Tension, Surface Tension, Cyclic process

1. Introduction

The interest in the application of Linear Free Energy Relationships to surface tension data [1-5] and nucleophilic solvation of aliphatic ammonium ions [6] has been ever increasing from our laboratory. In the present article we have given a trial to apply Brønsted and Taft equations to interfacial tensions of some N,N-disubstituted anilines. To our knowledge the present study on the application of Brønsted equation to interfacial tensions is first of its kind in literature. The opposite trend of Brønsted β and Taft ρ^* are explained based on thermodynamic considerations.

2. Experimental Data Source

Data on interfacial tensions of N,N-disubstituted anilines is from reference [7] and references cited therein. The $\text{p}K_a$ and Taft σ^* values of N,N-disubstituted anilines are from

reference [8]. All the linear correlations were done using the KaleidaGraph software, Reading, PA, USA. The figure is drawn using chemdraw software.

3. Discussion

The main difference between surface tension and interfacial tension is: surface tension is defined to a single liquid surface which is in contact with a gas phase usually air, whereas the interfacial tension is defined to the interface of two immiscible liquids. Surface tension is actually a derivation of interfacial tension where force from the second surface is negligible or zero. Therefore surface tension of pure liquid is nothing but the interfacial tension of liquid-air interface because the surface tension of air is zero. The reason for the surface tension of air is zero that the surface tension needs a surface, and for a surface there must be two different phases in contact with each other. Gases do not form inter-phase surfaces. And that the surface tension is caused by inter-molecular forces that keep flowing molecules together. Such forces do not exist in the gas phase as the gas thermodynamically is assumed to be a dilute system.

As explained in the above paragraph the figure 1 shows the typical example of aniline-air interfacial system.

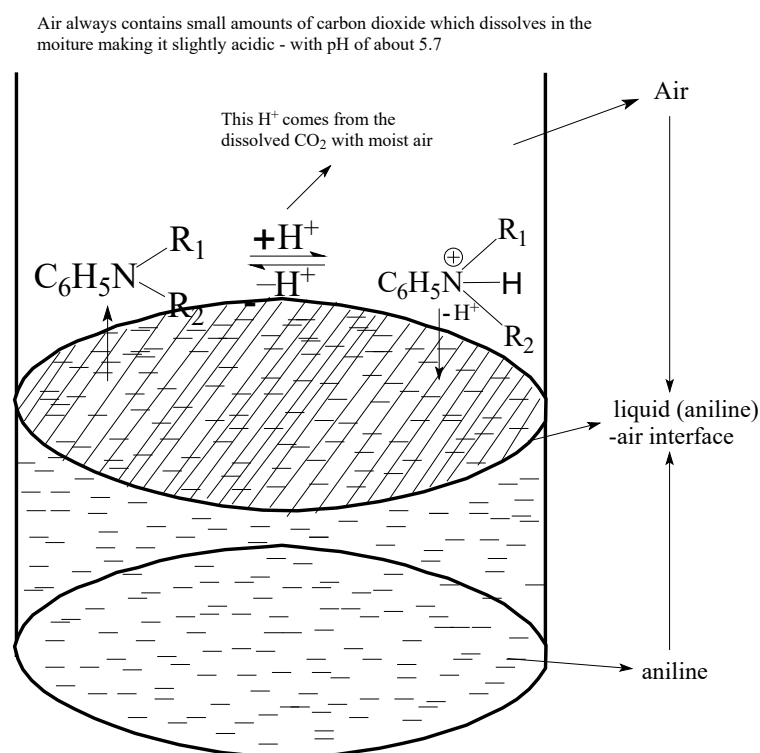
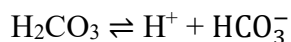
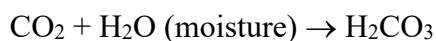


Figure 1

Air always contains small amounts of carbon dioxide which dissolves in the moisture present in the air making it slightly acidic. Thus the moisture becomes slightly acidic with a pH of 5.7. This becomes the source of H^+ as shown below:



Anilines are acting as general proton acceptors. As shown in the figure 1 the forward step, i.e. the addition of H^+ to aniline of the equilibrium reaction is taking place at the aniline-air interface pulling the aniline molecules to the interface. As the electron withdrawing groups decrease the electron density on nitrogen in turn increase the pK_a values, protonation is retarded by the electron withdrawing groups R_1 and R_2 . A plot of $\log \gamma$ versus pK_a was linear with a Brønsted β of -0.096 (Table 1, figure 2). The very low value of Brønsted β is an indication of small amount of proton transfer from H_2CO_3 to the aniline.

Table1: Various parameters of N-substituted anilines

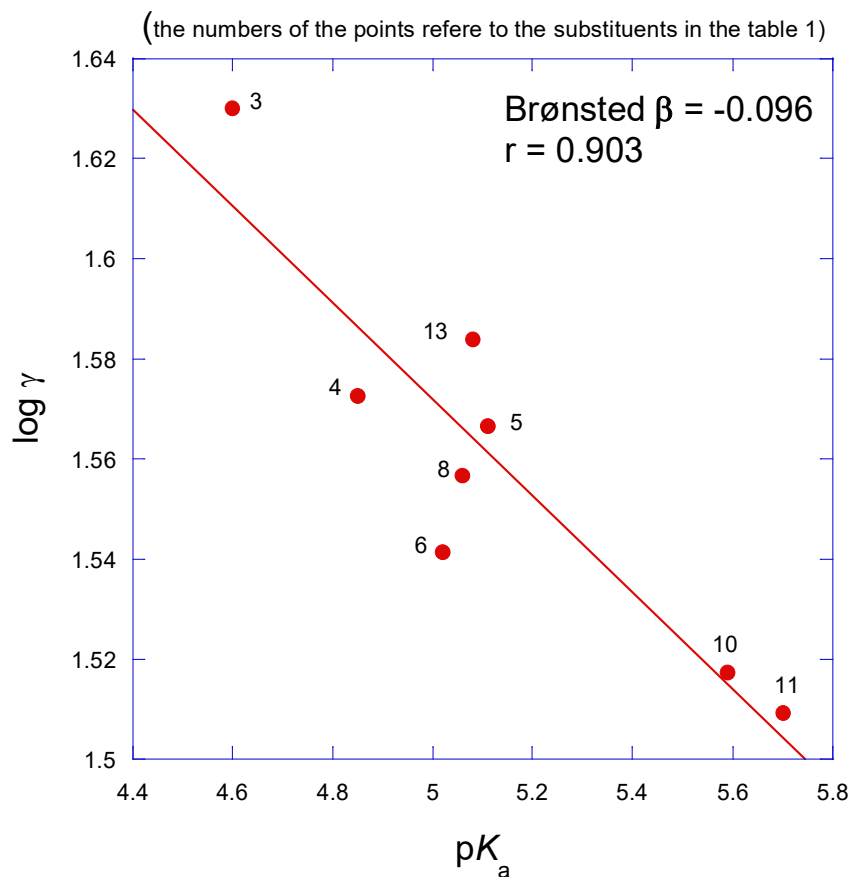
Sl. No.	(XC ₆ H ₄ NR ₁ R ₂)			Taft $\Sigma\sigma^*$ (a)	pK_a (b)	γ at 20°C	$\log \gamma$
	X	R ₁	R ₂				
1	H	H	NH ₂	1.11	5.2	45.56	1.6586
2	H	H	C ₆ H ₅	1.09	0.9 (c)	43.33	1.6368
3	H	H	H	0.98	4.6	42.67	1.6301
4	H	H	CH ₃	0.49	4.85	37.38	1.5726
5	H	H	C ₂ H ₅	0.39	5.11	36.86	1.5666
6	H	H	n-C ₃ H ₇	0.37	5.02	34.79	1.5415
7	H	H	n-C ₄ H ₉	0.36	4.95	33.91	1.5303
8	H	CH ₃	CH ₃	0.00	5.06	36.04	1.5568
9	H	C ₂ H ₅	C ₂ H ₅	-0.20	6.56	34.51	1.5379
10	H	n-C ₃ H ₇	n-C ₃ H ₇	-0.24	5.59	32.92	1.5175
11	H	n-C ₄ H ₉	n-C ₄ H ₉	-0.26	5.7	32.30	1.5092
12	H	i-C ₄ H ₉	i-C ₄ H ₉	-0.26		30.75	1.4878
13	m-CH ₃	H	H		5.08	38.37	1.5840

(a)Taft $\Sigma\sigma^*$ values are computed by adding the Taft σ^* values of the respective substituents. And these values are from Taft, R. W. J. *Am. Chem. Soc.* **1952**, 74, 2729, Taft, R. W. J. *Am. Chem. Soc.* **1952**, 74, 3120, Taft, R. W. J. *Am. Chem. Soc.* **1953**, 75, 4538.

^(b)pK_a values are from the compilation of Williams: https://www.chem.wisc.edu/areas/reich/pkatable/pKa_compilation-1-Williams.pdf

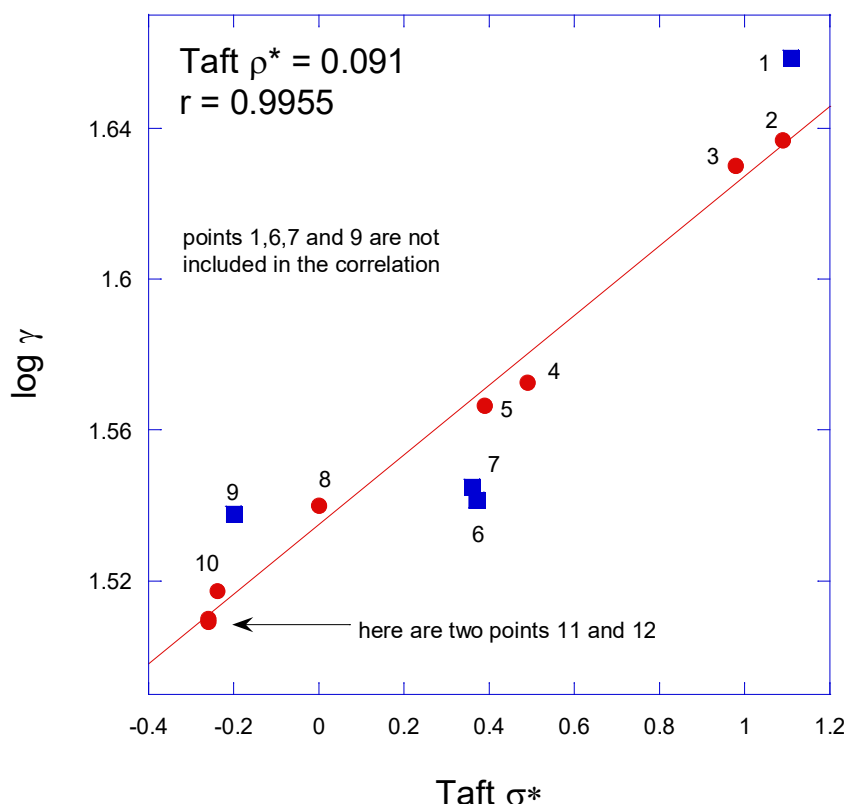
^(c)pK_a was reported as 1.0 in this link: http://www.fao.org/fileadmin/templates/agphome/documents/Pests_Pesticides/JMPR/Evaluation01/07_Diphenylamine.pdf, and as 0.8 in the link: <https://pubchem.ncbi.nlm.nih.gov/compound/Diphenylamine#section=Dissociation-Constants>. Hence an average of 0.90 is taken.

Figure 2: Plot of log γ versus pK_a N-substitued anilines



The substituents with high σ^* values are electron withdrawing and they reduce the electron density on nitrogen of the aniline. Therefore deprotonation reaction of the equilibrium step shown in the figure at the interface is favored by the electron withdrawing groups R₁ and R₂. Therefore free aniline goes back to the bulk. A plot of log γ versus $\Sigma\sigma^*$ was linear with a Taft ρ^* of 0.091 (Table 1, figure 3). "The four anilines **1**, **6**, **7** and **9** present a large deviation and for this reason, were not used for the correlation shown in Figure 3".

Figure 3: Plot of $\log \gamma$ versus $\Sigma\sigma^*$
(the numbers of the points refer to the substituents in the table 1)



At the interface the conversion of free aniline to anilinium ion is taking place by protonation. And then by deprotonation the protonated anilium ion becomes free aniline. Therefore at first sight it appears that the whole process is assumed to be a cyclic one. This is further explained thermodynamically in the following paragraph.

Both Brønsted equation $\log k_B = \beta \text{p}K_a^{\text{HB}} + C$ and Taft equation (in terms of γ) $\log \gamma = \rho^*\sigma^* + \log \gamma_0$ are linear free energy relationships. k_B is the reaction rate constant for protonation of aniline and K_a^{HB} is the ionization constant of a series of protonated anilines. β is a constant usually called Brønsted β . $\text{p}K_a^{\text{HB}}$ is the negative log of K_a^{HB} . The term “HB” as superscript in K_a^{HB} stands for the protonated aniline. In Taft equation, ρ^* and σ^* are the Taft reaction constant and Taft substituent constant respectively. $\text{p}K_a$ is directly related to free energy change as indicated by the thermodynamic equation $\Delta G = -2.3 \log K_a$. Therefore any amount of free energy change in the protonation step would be a function of that reaction.

And γ is related to K_a by the following equation [9], this equation is used to determine the interfacial tension of a system as a function of pH [9].

$$\frac{\gamma}{\gamma_o} = \frac{H_{aq}^+}{H_{aq}^+ + K_a}$$

Taking logarithms of this equation we get

$$\log \left(\frac{\gamma}{\gamma_o} \right) = \log [H_{aq}^+] - \log [H_{aq}^+ + K_a]$$

$$\therefore \log \gamma = \log [H_{aq}^+] - \log [H_{aq}^+ + K_a] + \log \gamma_o$$

Here γ is related to K_a and K_a is related to ΔG as mentioned above. Therefore the free energy change associated with deprotonation process would be a function of the reverse reaction of the equilibrium step.

The cyclic and non-cyclic processes are very important topics in thermodynamics. Thermodynamically a cyclic process is the one when a system returns to its original state after completing a series of changes. In an ideal cyclic process the initial and the final state is same [10, 11], hence the net change in free energy $\Delta G = 0$

The very fact that both the values of Brønsted β - 0.091 and Taft ρ^* 0.096 are equal and opposite in sign. Therefore the total free energy change associated with protonation and deprotonation processes would be zero. Hence thermodynamically any process with $\Delta G = 0.00$ is a cyclic process.

4. Acknowledgement

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5. Conflict of interest

The authors have no conflict of interest.

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