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Behavior of Organic Compounds with Different Functional Groups based on Surface Tension, Ramsey-Shields-EÖTVÖS Constants (*k*), Order of Association (x) and Trouton's Rule

R. SANJEEV[1] and V. JAGANNADHAM[2]*

[1]Department of Chemistry, Geethanjali College of Engineering and Technology, Cheeryal-501301, Telangana, India.
[2]Department of Chemistry, Osmania University, Hyderabad, 500007, India.

Abstract

Hydrocarbons and organic compounds having different functional groups with hetero atoms have shown a discriminative behavior toward surface tension, EÖTVÖS constants (k), order of association (x) and Trouton's rule. This was explained in terms of associative and non-associative behavior of these compounds.

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Introduction

Study on associative properties of aliphatic alcohols[1], aliphatic carboxylic acids[2], phenols[3], and aliphatic amines[4] based on their surface tension data, EÖTVÖS constants (k), order of association (x) and Trouton's rule is a major breakthrough from our laboratory hither to not reported earlier in literature.In the present study, various compounds like hydrocarbons, and compounds having different functional groups with different hetero atoms were taken to see the effect of these groups on surface tension, EÖTVÖS constants (k), order of association (x) and Trouton's rule.

Experimental and Data Source

All the surface tension data used in this article is from reference[2]. The detailed procedure for calculation of various parameters mentioned in table 1 are described in references 1-4.Thermo chemical data is from reference[6]. Taft σ^* values are from reference[7].

CONTACT V. Jagannadhamb jagannadham1950@yahoo.com Department of Chemistry, Osmania University, Hyderabad, 500007, India.

Linear correlation was done using the KaleidaGraph software, Reading, PA, USA.

Discussion

In continuation of our earlier work[1], the present study is to search for the associative and non-associative behavior of hydrocarbons, ethers and organic compounds having different functional groups with hetero atoms based on surface tension, EÖTVÖS constants (k), order of association (x) and Trouton's Rule. As a first observation, figure 1 shows the correlation of surface tensions with Taft σ* (R = 0.9531).

It is interesting to note that there is a clear discrimination between hydrocarbons, ethers and other organic moleculeshavingdifferent functional groups with hetero atoms toward surface tension.At first sight we thought that hydrocarbons (sl. no. 1, 2, 3, 5, 9) and ethers (sl. no. 14, 15) may correlate well with Taft σ* values because their Ramsey-Shields-EÖTVÖS constants (k) are close to 2.12 or little higher[8], and order of association (x) is less than 1. The molecules with Ramsey-Shields-EÖTVÖS constants (k) are close to 2.12 or little higher[8], and order of association (x) is less than 1 are supposed to be normal molecules and they contain identical molecules in the vapor and liquid states, hence they are believed to obey the Taft equation. But to our surprise they did not obey the Taft correlation and fortunately they even did not fall under the category of the other molecules having functional groups with hetero atoms.These molecules did not even obey the Troutons rule[9] (see table 1 for their ΔS_V values). They belong to their own category without any Taft correlation. On the other hand the molecules (sl. no. 10, 11, 12, 13, 16, 19, and 20) which are not supposed to follow the Taft correlation did follow the Taft correlation. The reasons for this inference is that the molecules with functional groups containing hetero atoms and with Ramsey-Shields-EÖTVÖS constants (k) are less than 2.12 and order of association (x) is more than 1 are supposed to be associated. If the molecules are associated the Taft σ* values have no meaning hence no Taft correlation should have been observed. But to our surprise the molecules having functional groups with hetero atoms correlated well (r = 0.9531). These are the molecules (with sl. no. 10, 11, 12, 13, 15, 16, 17 this is a solid, 19, and 20) which are liquids at 20°C belong to one category and have their own path of Taft correlation. Also they obeyed Trouton's rule[9]

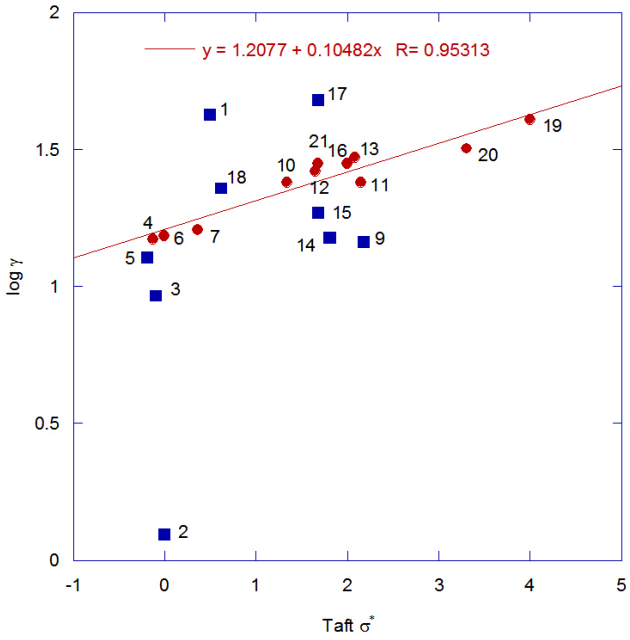

Fig. 1: Plot orf log γ versus T aft σ*

Sl. No.	Compound (CH_3-R)	$\sigma^{*(a)}$	γ (dyn/cm)	*k*	x	H_a	H_d	H_{ad}	Density g/cm^3	BP ^oC	ΔH_V kJ/mol	ΔS_V J(K. mol)$^{-1}$
1	CH_3-H	0.49	42.3	2.18	0.96	0	0	0	0.66	-164	8.2	74.6
2	CH_3-CH_3	0.00	1.24	2.40	0.83	0	0	0	1.28	-89.0	15	80.0
3	CH_3-C_2H_5	-0.1	9.22	1.75	1.34	0	0	0	0.49	-42.0	19	82.5
4	CH_3-n-C_3H_7	-0.12	14.9	98.4[b]	0.003[b]	0	0	0	0.003[b]	-0.50	22.4	82.2
5	CH_3-i-propane	-0.19	12.8	101[b]	0.003[b]	0	0	0	0.003[b]	-11.7	21.3	81.5
6	CH_3-propene	0.0	15.2	108[b]	0.003[b]	0	0	0	0.002[b]	-6.30	22.1	82.9
7	CH_3-propene (cis)	0.36	16.1	2.54	0.76	0	0	0	0.64	3.71	23.3	82.9
8	CH_3-i-propene	NA	14.8	2.75	0.68	0	0	0	0.59	-6.90	NA	NA
9	CH_3-C≡CH	2.18	14.5	2.65	0.72	0	0	0	0.53	-23.2	NA	NA
10	CH_3-OH	1.34	24.0	0.91	3.60	1	1	2	0.79	65.0	35.2	104
11	CH_3CHO	2.15	23.9	1.99	1.10	1	0	1	0.79	20.0	25.8	88.1
12	CH_3COCH_3	1.65	26.3	1.96	1.12	1	0	1	0.79	56.0	29.1	88.4
13	CH_3COOH	2.08	29.5	1.48	1.72	2	1	3	1.05	118	23.7	60.6
14	CH_3OCH_3	1.81	15.0	120[b]	0.002[b]	1	0	1	0.002[b]	-25.0	21.5	86.6
15	$CH_3OCH_2CH_3$	1.68	18.6	2.50	0.84	1	0	1	0.73	56.0	NA	NA
16	CH_3COOCH_3	2.00	28.0	2.39	0.84	2	0	2	0.93	57.0	30.3	91.8
17	CH_3CONH_2	1.68	47.7	1.40	1.86	2	2	4	1.16	221	NA	NA
18	CH_3NH_2	0.62	22.9	1.86	1.21	1	2	3	0.7	-6.32	25.6	96.0
19	CH_3NO_2	4.00	40.7	2.39	0.84	2	0	2	1.14	101	34.0	90.9
20	CH_3CN	3.30	31.8	1.76	1.32	1	0	1	0.79	82.0	29.8	84.0
21	CH_3SH	1.68	28.1	0.88	0.88	0	1	1	0.96	6.00	NA	NA

. [(a)]Taft σ^* values of substituents (R) in blue are from reference 7, NA – not available in literature or the attempts of the authors might have failed to find them. [(b)]If the densities are correct, they are extremely small hence unusual high values were obtained for *k* and x.

(see table 1 for their ΔS_V values). However there is an exception with methanol and acetic acid (sl. no 10 and 13) which did not follow Trouton's rule[9] and their order of association is more than one. And the molecules with very low boiling points and ethers belong to other category. *Note that the explanation given above cannot explain why some molecules like 4, 6 and 7 which are hydrocarbons did correlate in Taft equation along with associative molecules*.

As a conclusion it could be understood that there is a clear distinction between hydrocarbons, ethers and organic compounds having different functional groups with hetero atoms toward surface tension, Ramsey-Shields-EÖTVÖS constants (*k*), order of association (x) and Trouton's rule. The hydrogenacceptor (H_a) and donor (H_d) site values did have a significant influence on the order of association in the case of methanol, acetic acid acetamide and methyl amine (sl. no. 10, 13, 17 and 18).

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