Quantitative structure and retention relationships for gas chromatographic data: Application to alkyl pyridines on apolar and polar phases

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Abstract

Quantitative structure and retention relationships (QSRR) have been developed to model gas chromatographic retention data of alkyl pyridines on apolar (branched alkane) and polar (primary alcohol) stationary phases. The retention properties analyzed are Kovats retention index, I; partial molar enthalpy, ΔH; partial molar entropy, ΔS and partition coefficient, $\log K$. Using the seven valence molecular connectivity indices (χ) calculated for the 18 alkyl pyridines, regression models are generated to predict the retention properties. The best model (model A) obtained with the descriptors $^1\chi_P^V$, $^3\chi_P^V$ and $^6\chi_{CH}^V$ was unable to produce a satisfactory statistical performance and correct order of elution. The model has been modified (model B) by including steric parameter s, which has been empirically derived by considering the steric effects due to the presence of alkyl groups at the *ortho* and *meta* positions. The modified model predicts the correct order of elution for all the alkyl pyridines and good correlation coefficients, r. The r values obtained for I, ΔH, ΔS and $\log K$ are: $r = 0.955$, 0.975, 0.984 and 0.955 (model A) become $r = 0.999$, 0.996, 0.990 and 0.999 (model B) on the apolar stationary phase and $r = 0.931$, 0.926, 0.911 and 0.931 (model A) become $r = 0.999$, 0.992, 0.958 and 0.999 (model B) on the polar stationary phase.
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Keywords: Valence molecular connectivity indices; Kovats retention index; Partial molar thermodynamic properties; Gas chromatography; QSRR; Alkyl pyridines

1. Introduction

Valence molecular connectivity indices are very popular chemical graph theoretical descriptors and have been proved to be useful in the studies of quantitative structure and retention relationships (QSRR) [1–4]. These descriptors are derived directly from molecular structural formula which encodes the size, branching, cyclic nature and the presence of heteroatom in any organic molecule. The application of QSRR models to describe Kovats retention indices and partition coefficients has been extensively reported in the literature [5–12]. In most of these studies better predictions have been observed when connectivity indices are combined with any other parameter such as electronic descriptor [5,6], molecular surface area [13], weighted holistic invariant molecular descriptor [9], steric factor [11], boiling point, etc.

In this study, retention data of alkyl pyridines determined in the apolar hydrocarbon and in polar primary alcohol stationary phases are subjected to QSRR models. Here, we proposed two models for the prediction of gas chromatographic retention properties viz., Kovats retention index, partial molar enthalpy, partial molar entropy and partition coefficient on an apolar and a polar stationary phases of alkyl pyridines. In model A, three valence connectivity indices are selected from a pool of seven, based on the criteria that the best regression equation should give highest correlation coefficient with minimum number of descriptors. In model B, along with the descriptors used in model A, a steric parameter is included. The statistical performance of model B has been found to be more satisfactory than model A.

Alkyl pyridines are employed in the preparation of pyridinium compounds which are in turn used as corrosion inhibitors in different media [14]. The corrosion inhibiting efficiency is controlled by the position and length of alkyl group attached to the pyridine. QSRR models of alkyl pyridines are useful to predict the inhibiting efficiency and to modify the

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positions of alkyl groups to attain the desired effect. The predictions can also be used to relate chemical reactivity, catalytic ability, and bioactivity of alkyl pyridines with their structures. The alkyl pyridines are widely used in various fields as acid scavengers, solvents in acylation reactions, in extraction of antibiotics, starting materials for agrochemicals and pharmaceuticals, precursors for herbicides and insecticides [15].

2. Experimental and calculations

Kovats retention indices, I; partial molar enthalpies, ΔH; partial molar entropies, ΔS and partition coefficients, log K, of alkyl pyridines measured by gas chromatography on the stationary phases apolar (C78) and polar (POH) were taken from Reddy et al. [16]. C78 (19,24-dioctadecyldotetracontane, $C_{78}H_{158}$) is a branched alkane and POH (18,23-dioctadecyl-hentetracontan-1-ol, $C_{77}H_{155}OH$) is a primary alcohol, which has been formed by replacing one of the $-CH_3$ groups of C78 with OH group. Both the stationary phases have the same form and nearly the same size. The retention data measured at 403.15 K with C78 and POH in packed columns are used in this analysis [16]. The partition coefficient of alkyl pyridines between ideal gas phase and liquid stationary phase were evaluated using the equations:

$$\log K = -\frac{\Delta\mu}{2.303RT} = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (1)$$

where $\Delta\mu$ is standard chemical potential difference, $R = 1.987$ cal K^{-1} mol^{-1} and $T = 403.15$ K. The valence molecular connectivity indices of path (χ_P^V), cluster (χ_C^V), path cluster (χ_{PC}^V) and cyclic (χ_{CH}^V) for different orders are calculated using hydrogen depleted molecular graphs of alkyl pyridines [1]. The nth order connectivity index is given by:

$$\chi^V = (\delta_i^V \delta_j^V \cdots \delta_{n+1}^V)^{-1/2} \quad (2)$$

where n refers to the number of bonds connecting the path and the summation goes over all the paths of that type in the molecule. δ_i^V is the valence delta of atom i defined by the equation:

$$\delta_i^V = \frac{Z^V - h}{Z - Z^V - 1} \quad (3)$$

where Z and Z^V are the atomic number and the number of valence electrons of atom i, respectively, h is the number of hydrogen atoms attached to atom i. Seven possible connectivity indices calculated for the 18 alkyl pyridines are given in Table 1. As an example the method of calculation of connectivity indices for 3-methyl pyridine is shown below. The values in parenthesis are δ_i^V.
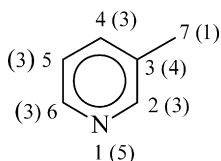
$$^1\chi_P^V = \frac{2}{\sqrt{3 \times 5}} + \frac{2}{\sqrt{3 \times 3}} + \frac{2}{\sqrt{3 \times 4}} + \frac{1}{\sqrt{4 \times 1}} = 2.2604$$

$$^2\chi_P^V = \frac{2}{\sqrt{5 \times 3 \times 3}} + \frac{1}{\sqrt{3 \times 3 \times 3}} + \frac{2}{\sqrt{3 \times 3 \times 4}}$$
$$+ \frac{2}{\sqrt{3 \times 4 \times 1}} + \frac{1}{\sqrt{4 \times 3 \times 5}} = 1.5304$$

$$^3\chi_P^V = \frac{2}{\sqrt{5 \times 3 \times 3 \times 3}} + \frac{2}{\sqrt{3 \times 3 \times 3 \times 4}} + \frac{1}{\sqrt{3 \times 3 \times 4 \times 1}}$$
$$+ \frac{2}{\sqrt{3 \times 4 \times 3 \times 5}} + \frac{1}{\sqrt{1 \times 4 \times 3 \times 5}} = 0.8094$$

$$^4\chi_P^V = \frac{4}{\sqrt{5 \times 3 \times 3 \times 3 \times 4}} + \frac{1}{\sqrt{3 \times 3 \times 3 \times 4 \times 1}}$$
$$+ \frac{1}{\sqrt{3 \times 3 \times 3 \times 4 \times 3}} + \frac{1}{\sqrt{1 \times 4 \times 3 \times 5 \times 3}}$$
$$+ \frac{1}{\sqrt{3 \times 5 \times 3 \times 3 \times 3}} = 0.4481$$

$$^3\chi_C^V = \frac{1}{\sqrt{3 \times 4 \times 1 \times 3}} = 0.1667$$

$$^4\chi_{PC}^V = \frac{1}{\sqrt{3 \times 3 \times 4 \times 3 \times 1}} + \frac{1}{\sqrt{3 \times 4 \times 1 \times 3 \times 5}} = 0.1707$$

$$^6\chi_{CH}^V = \frac{1}{\sqrt{5 \times 3 \times 3 \times 3 \times 4 \times 3}} = 0.0248$$

Some of these descriptors will encode similar information about the molecule and it is possible that they may intercorrelate. The correlation matrix shown in Table 2, revealed that only the pair $^3\chi_C^V$ and $^4\chi_{PC}^V$ has intercorrelation. Consequently, $^3\chi_C^V$ has been deleted from the set of independent variables and using the remaining descriptors, linear regression models are formed in step wise addition of each descriptor and in different combinations using *Origin* software. The choice of selection of the best model has been judged by considering correlation coefficients, standard deviations and Fisher's F values. In Fig. 1, it has been shown that the variation of r with the number of Chi parameters indicates that there is no much improvement in r after three independent Chi parameters used in the regression equation. The r values are slightly different for different combinations used under each set of Chi parameters. The ideal model is one that has high r and F values and low standard deviations, σ, with the least number of descriptors. In the process of the development of model A, the data of the four properties are regressed independently by multiple linear regression analysis using only the connectivity indices. It has been found that the best possible regression is obtained with $^1\chi_P^V$, $^3\chi_P^V$ and $^6\chi_{CH}^V$ for the four properties studied here. In the regressions with the other combinations of connectivity indices, the statistical performance is relatively lower. Since model A is unable to predict satisfactory results, the model has been developed further by considering the steric effects. An empirical method has been proposed to include the effects due to steric hindrance produced by the alkyl groups at the *ortho* and *meta* positions. For each alkyl group, the retention index difference, δI, between *ortho* and *para*, and between *meta* and *para* substituents has been calculated using retention index of the alkyl pyridine on C78 as well as on POH phases. For any alkyl group (methyl or

Table 1
Valance connectivity indices and steric parameter values of alkyl pyridines

S. no.	Solute name	$^1\chi^V$	$^2\chi^V$	$^3\chi_P^V$	$^4\chi_P^V$	$^3\chi_C^V$	$^4\chi_{PC}^V$	$^6\chi_{CH}^V$	s
1	Pyridine	1.8497	1.0246	0.5665	0.3126	0.0000	0.0000	0.0287	0
2	2-Methyl pyridine	2.2705	1.4711	0.8128	0.4481	0.1291	0.1491	0.0248	1
3	3-Methyl pyridine	2.2604	1.5304	0.8094	0.4481	0.1667	0.1707	0.0248	0.05
4	4-Methyl pyridine	2.2604	1.5246	0.8469	0.4264	0.1667	0.1925	0.0248	0
5	2,3-Dimethylpyridine	2.6871	1.9057	1.2712	0.5646	0.2561	0.5331	0.0215	1.05
6	2,4-Dimethylpyridine	2.6812	1.9746	1.0522	0.5667	0.2958	0.3186	0.0215	1.0
7	2,5-Dimethylpyridine	2.6812	1.9769	1.0592	0.5417	0.2958	0.3198	0.0215	1.05
8	2,6-Dimethylpyridine	2.6912	1.9203	1.0276	0.6793	0.2582	0.2782	0.0215	2
9	3,4-Dimethylpyridine	2.6771	1.9599	1.3008	0.5429	0.2888	0.3145	0.0215	0.05
10	3,5-Dimethylpyridine	2.6711	2.0396	1.0117	0.6228	0.3333	0.3157	0.0215	0.10
11	2-Ethylpyridine	2.8311	1.6746	1.0884	0.6073	0.0913	0.1967	0.0248	1.25
12	3-Ethylpyridine	2.8211	1.7148	1.1310	0.6073	0.1179	0.2386	0.0248	0.10
13	4-Ethylpyridine	2.8211	1.7090	1.1576	0.6575	0.1179	0.2539	0.0248	0
14	2-Propylpyridine	3.3311	2.0711	1.2106	0.7591	0.0913	0.1699	0.0248	1.25
15	4-Propylpyridine	3.3211	2.1055	1.2880	0.8381	0.1178	0.2194	0.0248	0
16	2,3,6-Trimethyl pyridine	3.1079	2.3549	1.4893	0.7562	0.3852	0.4074	0.0186	2.05
17	2,4,6-Trimethyl pyridine	3.1019	2.4273	1.2258	1.0434	0.4249	0.4249	0.0186	2.0
18	4-*tert*-Butylpyridine	3.5104	1.6526	1.5463	0.7533	1.0833	0.1933	0.0248	0

ethyl or propyl) and on any phase, δI is given by:

$$\delta I_x = I_{para} - I_x \qquad (4)$$

where x is either *ortho* substituent or *para* substituent.

It is assumed that the steric effect at the *ortho* position is maximum, at *meta* position is minimum and at *para* position it is negligible. The δI_x is a measure of steric hindrance, which increases from methyl to ethyl and afterwards it became constant. The δI_{ortho} values are plotted as a function of number of carbon atoms of the alkyl group in Fig. 2, which shows that δI_{ortho} values for ethyl and propyl is almost same. Based on this

Table 2
Correlation matrix for the valence connectivity indices of alkyl pyridines

	$^1\chi^V$	$^2\chi^V$	$^3\chi_P^V$	$^4\chi_P^V$	$^3\chi_C^V$	$^4\chi_{PC}^V$	$^6\chi_{CH}^V$
$^1\chi^V$	1						
$^2\chi^V$	0.651	1					
$^3\chi_P^V$	0.898	0.652	1				
$^4\chi_P^V$	0.864	0.770	0.733	1			
$^3\chi_C^V$	0.523	0.246	0.611	0.399	1		
$^4\chi_{PC}^V$	0.611	0.33	0.749	0.463	0.934	1	
$^6\chi_{CH}^V$	−0.366	−0.832	−0.529	−0.544	−0.339	−0.415	1
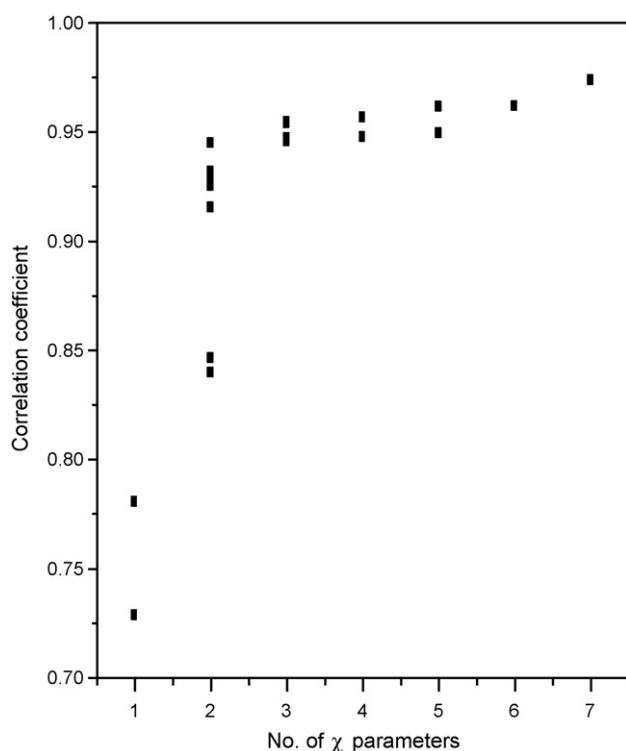
Fig. 1. Variation of r values with the number of Chi parameters.
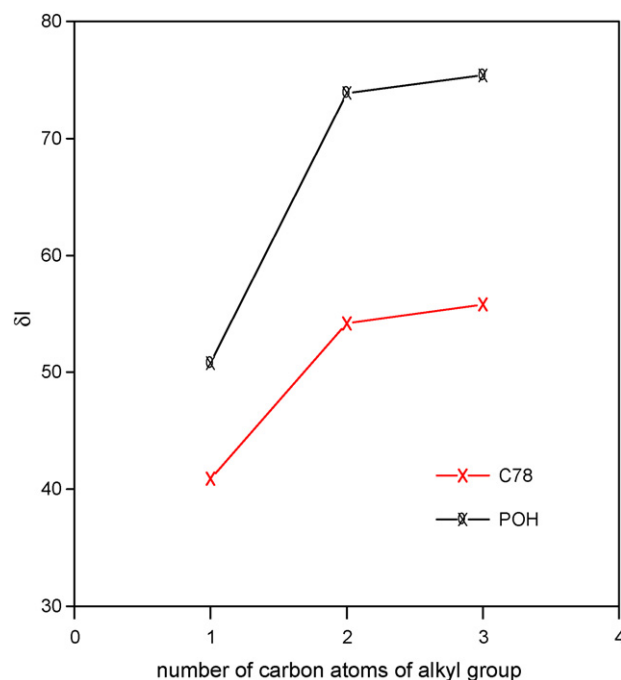
Fig. 2. Plot of δI_{ortho} as a function of number of carbon atoms in the alkyl group.

observation it is made possible to express the steric hindrance in terms of an empirical steric parameter s. The s value given for each *ortho* substituted methyl group is 1 and for each *ortho* substituted ethyl or propyl group is 1.25. Similarly, s value given for each *meta* substituted methyl group is 0.05 and for each *meta* substituted ethyl or propyl group is 0.10. The steric parameter s is included in to model A as an additional parameter and obtained model B. The s values are given in Table 1.

3. Results and discussion

The experimental data I, ΔH, ΔS, and log K; used in the regression analysis are given in Table 3 for C78 and in Table 4 for POH stationary phases at 403.15 K. Model A with the descriptors $^1\chi_P^V$, $^3\chi_P^V$ and $^6\chi_{CH}^V$ has been employed to predict the retention properties of alkyl pyridines on both the phases by

multiple linear regression analysis. The results of the regression equations for apolar C78 phase are:

$$I = 538.6 + 95.1\,^1\chi_P^V + 163.4\,^3\chi_P^V - 2458.8\,^6\chi_{CH}^V,$$
$$r = 0.955,\ \sigma = 27.7,\ F = 49 \tag{5}$$

$$\Delta H = -6800.1 - 1198.0\,^1\chi_P^V - 880.0\,^3\chi_P^V + 84734.9\,^6\chi_{CH}^V,$$
$$r = 0.975,\ \sigma = 205.9,\ F = 90 \tag{6}$$

$$\Delta S = -18.5 - 1.77\,^1\chi_P^V - 0.12\,^3\chi_P^V + 177.3\,^6\chi_{CH}^V,$$
$$r = 0.984,\ \sigma = 0.203,\ F = 146 \tag{7}$$

$$\log K = -0.362 + 0.260\,^1\chi_P^V + 0.450\,^3\chi_P^V - 7.15\,^6\chi_{CH}^V,$$
$$r = 0.955,\ \sigma = 0.076,\ F = 49 \tag{8}$$

Table 3
Retention index, I; partial molar enthalpy, ΔH; partial molar entropy, ΔS; and partition coefficient, log K, calculated using model B and the observed data of alkyl pyridines on C78 at 403.15 K

Solute no.	I_{cal}	I_{obs}	ΔH_{cal} (cal mol^{-1})	ΔH_{obs} (cal mol^{-1})	ΔS_{cal} (cal mol^{-1} K^{-1})	ΔS_{obs} (cal mol^{-1} K^{-1})	log K_{cal}	log K_{obs}
1	718.3	723.4	−6957	−7032	−16.712	−16.839	0.118	0.132
2	801.8	802.2	−7965	−7948	−18.149	−18.105	0.348	0.353
3	843.6	843.4	−8252	−8242	−18.333	−18.314	0.464	0.467
4	847.9	843.1	−8272	−8199	−18.329	−18.219	0.476	0.464
5	931.1	933.9	−9194	−9255	−19.559	−19.678	0.705	0.716
6	921.0	919.5	−9177	−9182	−19.645	−19.679	0.677	0.676
7	919.1	920.0	−9162	−9237	−19.631	−19.807	0.673	0.677
8	875.4	870.1	−8870	−8816	−19.461	−19.387	0.551	0.543
9	976.9	982.8	−9501	−9535	−19.742	−19.747	0.832	0.852
10	958.6	961.4	−9444	−9413	−19.833	−19.719	0.782	0.793
11	888.3	886.9	−8797	−8770	−19.122	−19.065	0.586	0.587
12	941.8	938.6	−9153	−9136	−19.331	−19.324	0.734	0.729
13	947.7	941.1	−9188	−9071	−19.342	−19.133	0.750	0.735
14	969.2	976.5	−9597	−9609	−20.085	−20.024	0.808	0.831
15	1029.1	1032.3	−9989	−10169	−20.302	−20.708	0.974	0.986
16	999.4	1000.5	−10034	−10063	−20.778	−20.842	0.893	0.899
17	986.9	986.6	−10013	−9982	−20.881	−20.818	0.859	0.860
18	1070.8	1067.3	−10315	−10219	−20.583	−20.400	1.088	1.081

Table 4
Retention index, I; partial molar enthalpy, ΔH; partial molar entropy, ΔS; and partition coefficient, log K, calculated using model B and the observed data of alkyl pyridines on POH at 403.15 K

Solute no.	I_{cal}	I_{obs}	ΔH_{cal} (cal mol^{-1})	ΔH_{obs} (cal mol^{-1})	ΔS_{cal} (cal mol^{-1} K^{-1})	ΔS_{obs} (cal mol^{-1} K^{-1})	log K_{cal}	log K_{obs}
1	781.6	786.8	−8085	−8144	−18.999	−19.037	0.244	0.256
2	863.9	867.0	−9021	−9146	−20.297	−20.518	0.469	0.477
3	918.1	915.7	−9553	−9594	−20.855	−21.021	0.617	0.609
4	922.9	917.8	−9581	−9573	−20.878	−20.942	0.630	0.615
5	1001.9	1003.8	−10365	−10437	−21.929	−21.999	0.846	0.851
6	992.9	992.3	−10390	−10426	−21.997	−22.115	0.822	0.821
7	990.4	990.2	−10361	−10358	−21.966	−21.971	0.815	0.814
8	934.4	933.5	−9831	−9733	−21.414	−21.134	0.663	0.659
9	1060.7	1068.9	−10924	−10951	−22.511	−22.464	1.006	1.028
10	1042.4	1041.8	−10894	−10691	−22.534	−22.157	0.957	0.955
11	946.1	941.8	−9786	−9569	−21.076	−20.611	0.694	0.685
12	1014.4	1009.0	−10431	−10353	−21.745	−21.725	0.880	0.866
13	1021.6	1015.7	−10488	−10476	−21.800	−21.944	0.899	0.885
14	1026.3	1030.6	−10599	−10607	−21.934	−22.083	0.914	0.924
15	1102.2	1106.0	−11302	−11324	−22.655	−22.093	1.120	1.128
16	1065.8	1062.0	−11089	−10972	−22.921	−22.603	1.021	1.008
17	1054.6	1057.7	−11115	−11360	−22.999	−23.619	0.991	0.998
18	1143.2	1143.0	−11604	−11708	−22.933	−23.426	1.232	1.230

The results for the polar POH phase are:

$$I = 622.2 + 79.0\,^1\chi_P^V + 192.2\,^3\chi_P^V - 2531.0\,^6\chi_{CH}^V,$$
$$r = 0.931, \ \sigma = 35.4, \ F = 30 \tag{9}$$

$$\Delta H = -7811.1 - 956.3\,^1\chi_P^V - 1365.1\,^3\chi_P^V + 71151.3\,^6\chi_{CH}^V,$$
$$r = 0.926, \ \sigma = 366.2, \ F = 28 \tag{10}$$

$$\Delta S = -20.25 - 1.37\,^1\chi_P^V - 0.99\,^3\chi_P^V + 144.08\,^6\chi_{CH}^V,$$
$$r = 0.911, \ \sigma = 0.507, \ F = 23 \tag{11}$$

$$\log K = -0.191 + 0.217\,^1\chi_P^V + 0.522\,^3\chi_P^V - 6.976\,^6\chi_{CH}^V,$$
$$r = 0.931, \ \sigma = 0.096, \ F = 30 \tag{12}$$

In both the stationary phases, the poor correlation coefficients and high standard deviations indicate that the statistical performance of model A is far from satisfactory. Further, when order of elution is analyzed by comparing predicted retention index with the observed values the model predicts correct order of elution only for six solutes. It is evident that the model generated with the connectivity indices alone is unable to do better evaluation for alkyl pyridines. However, the evaluation on apolar phase is slightly better than on polar phase.

Model B consists of four independent variables; three connectivity indices $^1\chi_P^V, ^3\chi_P^V, ^6\chi_{CH}^V$ and one steric parameter, s. The four retention properties are predicted using model B by multiple linear regression analysis. The regression equations for C78 are:

$$I = 808.4 + 149.0\,^1\chi_P^V + 52.4\,^3\chi_P^V - 13776.9\,^6\chi_{CH}^V - 45.8s,$$
$$r = 0.999, \ \sigma = 4.49, \ F = 1511.9 \tag{13}$$

$$\Delta H = -8680.3 - 1574.2\,^1\chi_P^V - 107.3\,^3\chi_P^V$$
$$+ 163603.9\,^6\chi_{CH}^V + 319.6s,$$
$$r = 0.996, \ \sigma = 80.4, \ F = 462.4 \tag{14}$$

$$\Delta S = -19.793 - 2.024\,^1\chi_P^V + 0.395\,^3\chi_P^V$$
$$+ 229.999\,^6\chi_{CH}^V + 0.214s,$$
$$r = 0.990, \ \sigma = 0.164, \ F = 169.5 \tag{15}$$

$$\log K = 0.381 + 0.409\,^1\chi_P^V + 0.144\,^3\chi_P^V$$
$$- 38.354\,^6\chi_{CH}^V - 0.127s,$$
$$r = 0.999, \ \sigma = 0.012, \ F = 1585.2 \tag{16}$$

The results for the polar POH phase are:

$$I = 967.9 + 148.2\,^1\chi_P^V + 50.1\,^3\chi_P^V$$
$$- 17032.4\,^6\chi_{CH}^V - 58.8s,$$
$$r = 0.999, \ \sigma = 4.64, \ F = 1515.9 \tag{17}$$

$$\Delta H = -11204.9 - 1635.2\,^1\chi_P^V + 29.8\,^3\chi_P^V$$
$$+ 213512.9\,^6\chi_{CH}^V + 576.9s,$$
$$r = 0.992, \ \sigma = 129.1, \ F = 194.8 \tag{18}$$

$$\Delta S = -24.787 - 1.768\,^1\chi_P^V + 0.221\,^3\chi_P^V$$
$$+ 311.229\,^6\chi_{CH}^V + 0.606s,$$
$$r = 0.958, \ \sigma = 0.354, \ F = 36 \tag{19}$$

$$\log K = 0.752 + 0.406\,^1\chi_P^V + 0.135\,^3\chi_P^V$$
$$- 46.52\,^6\chi_{CH}^V - 0.160s,$$
$$r = 0.999, \ \sigma = 0.012, \ F = 1671.2 \tag{20}$$

Better correlation coefficients, higher F values and lower standard deviations for the four properties on both the phases indicate that model B shows satisfactory predictions. The predicted retention indices are plotted as a function of observed values in Fig. 3 both for C78 and POH. A comparison of predicted and observed retention index reveals that model B also predicts the order of elution correctly for all the alkyl pyridines on both the phases. The predicted ΔH, ΔS, and $\log K$ values are plotted as a function of observed data in Figs. 4–6, respectively. In all the cases the correlation between observed and calculated values is greater than 0.977 for all the properties and on both the phases. The line drawn in Figs. 3–6 represents an ideal fit where the difference between observed and calculated values is zero. The points around the line will measure the deviations from the observed data. The retention index difference, ΔI between I_{POH} and I_{C78} for any solute is given by:

$$\Delta I = I_{POH} - I_{C78} \tag{21}$$

ΔI^{obs} is plotted as a function of ΔI^{cal} in Fig. 7 with a correlation coefficient, $r = 0.953$. Since the two stationary phases are isosteric, in the calculation of ΔI the structural effects between solute and the stationary phase are eliminated and ΔI will
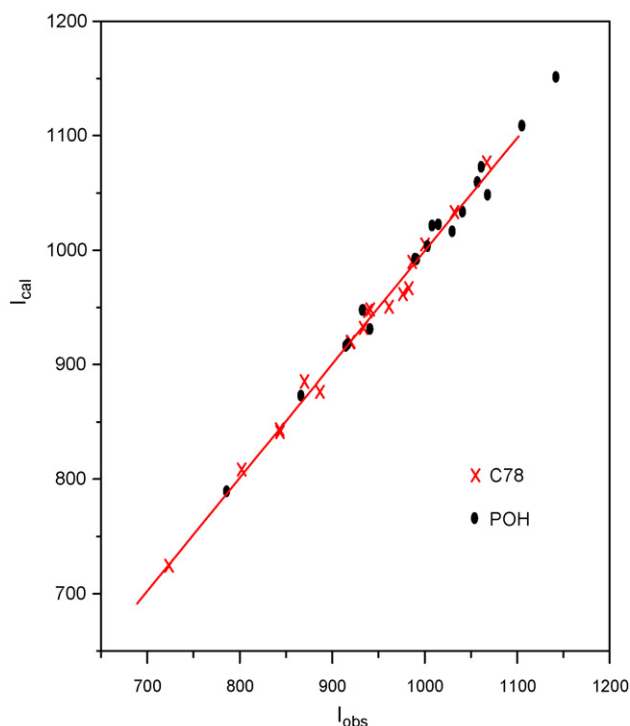

Fig. 3. Plot of calculated retention indices using model B vs. observed values on C78 ($\times$) and on POH ($\bullet$) at 403.15 K.
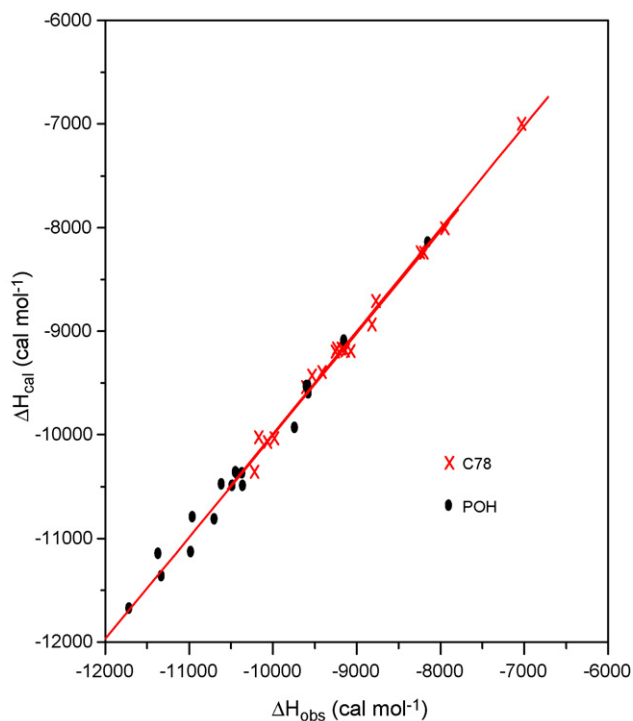
Fig. 4. Plot of calculated partial molar enthalpy values using model B vs. observed values on C78 (×) and on POH (●) at 403.15 K.
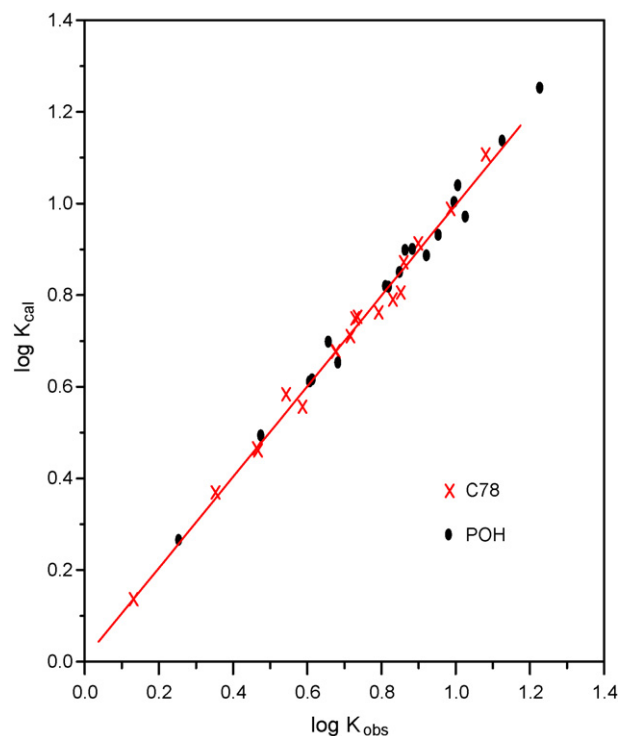

Fig. 6. Plot of calculated partition coefficient values using model B vs. observed values on C78 (×) and on POH (●) at 403.15 K.
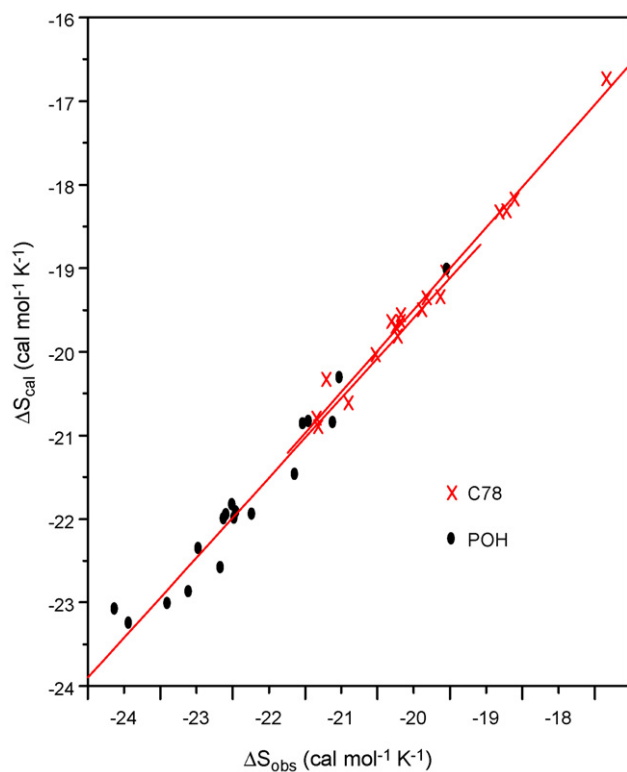
become proportional to only the interaction of solutes with the alcohol group. The satisfactory correlation between ΔI^{obs} and ΔI^{cal} indicate that ΔI^{cal} is also a measure of interaction between solutes and the –OH group.

Fig. 5. Plot of calculated partial molar entropy values using model B vs. observed values on C78 (×) and on POH (●) at 403.15 K.
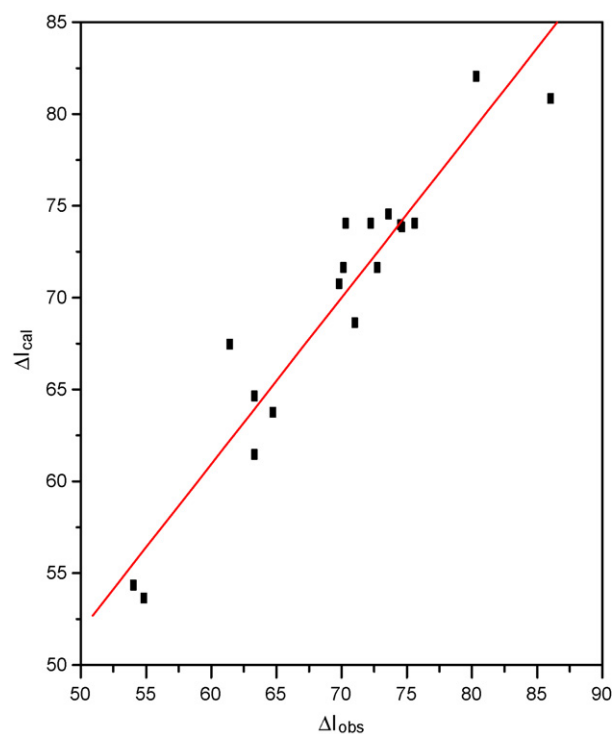

Fig. 7. Plot of ΔI^{obs} as a function of ΔI^{cal} on C78 and POH.

4. Conclusions

The study revealed that the steric factor is an essential descriptor, to be used in the development of QSRR models for alkyl pyridines. The inclusion of steric factor in the model B is equally important whether the stationary phase is apolar or polar. The approach of –N= atom in the alkyl pyridine towards the interacting group in the stationary phase is sterically hindered by the presence of alkyl groups at the ortho position. The steric effect produced by higher alkyl groups is found to be same as that produced by the ethyl group. Further it is observed that when alkyl groups attached to adjacent carbon atoms, retention is increased compared to the alkyl groups attached to alternate carbon atoms in the pyridine ring. For instance retention index values of (a) 2,3-lutidine and 2,4-lutidine are 933.9 and 919.5, (b) 3,4-lutidine and 3,5-lutidine are 982.8 and 961.4 and (c) 2,3,6-collidine and 2,4,6-collidine are 1000.5 and 986.6, respectively. In the models proposed here the descriptor $^3\chi_P^V$ can able to discriminate between these two types of structures.

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