

Correlation of the isosteric heat of adsorption of organic molecules over zeolites with equalized electronegativity and chemical hardness

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Abstract. Considering the direct correlation between charge transfer and heat of adsorption, we have equated the isosteric heat of adsorption (Q_{st}) with Nalewajski's charge transfer equation involving equalized electronegativities and chemical hardness given in the literature. The equation is then tested and compared with the experimental heat of adsorption values of organic molecules over zeolites given in the literature with the average percentage deviation of 15.9. Other similar types of equations of charge transfer affinity are also tested. Various semi-empirical equations based on Barrer's approach of the determination of Q_{st} and neural network method have been proposed, tested and compared for the first time.

Keywords. Isosteric heat of adsorption, charge transfer, equalized electro negativity, chemical hardness, zeolites.

1. Introduction

Parr and Pearson originally related the charge transfer (ΔN) process to the electronegativity (c) and chemical hardness (h).^{1–3} This method is based on the equalization of electronegativities proportional to the electron charge variation between the non-interacting atoms by introducing the core polarization energy term, i.e., the effect of nuclear interaction on the charge transfer. Pearson³ and Klopmann⁴ included both Coloumbic interaction and covalent interaction in the charge transfer term. Based on these developments, Komorowski⁵ further simplified the equation by considering the identities of chemical approximation. Komorowski⁵ defined the term charge transfer affinity using thermodynamic considerations. As well is known and discussed,⁶ chemical potential is the negative value of the electronegativity; so it may be logical to correlate charge transfer to the thermodynamic quantity, like heat of adsorption, with appropriate coefficients. Parr and Chattaraj⁷ discussed the principle of maximum hardness and the relation between charge transfer and chemical hardness.^{7,8}

In this paper, we report for the first time, correlation of isosteric heat of adsorption (Q_{st}) of organic mole-

cules over zeolites with the charge transfer equation using appropriate coefficients. The attempt is to understand the trend in the various sorption systems. Various semi-empirical equations based on Barrer's approach of the determination of Q_{st} and the neural network method have been proposed, tested and compared.

2. Methods

Originally Parr and Pearson¹ proposed the following equation,

$$\Delta N = (c_C - c_D)/[2(h_C + h_D)], \quad (1)$$

where c and h are electronegativity and chemical hardness of the interacting species C and D respectively. ΔN is the charge transfer. Based on this equation, Nalewajski² introduced the following equation,

$$\Delta N = (c_C - c_D) + 2(a_D \Delta Z_D - a_C \Delta Z_C)/[2(h_C + h_D)], \quad (2)$$

where a is the polarizability, which considers the nuclear polarization.

Based on Klopmann's⁴ suggestion regarding the inclusion of the covalent bonding, while expressing exchange the integral, Pearson³ proposed the following equation,

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$$\Delta N = 2(\mathbf{c}_C - \mathbf{c}_D)/[(\mathbf{h}_C + \mathbf{h}_D) - (1/R) - 2\mathbf{b}(N_C N_D)^{1/2}], \quad (3)$$

where \mathbf{b} is the electron exchange integral for a two-centre particle system, and R is the distance between the two interacting systems. Considering the chemical approximations, Komorowski⁵ introduced the equation,

$$\Delta N = [(c_C/h_D) - (c_D/h_C)]/[(h_C/h_D) + (h_D/h_C)]. \quad (4)$$

In our studies on correlating the isosteric heat of adsorption, we have tested these equations. The Nalewajski equation has shown the best fit to our data of the sorption of C₁ to C₅ aliphatics and benzene on zeolites. The following type of equation has been considered:

$$\Delta H = A[(c_C - c_D) + 2(a_C - a_D)]/2(h_C + h_D) + B, \quad (5a)$$

$$\Delta H = A(\Delta N) + B, \quad (5b)$$

where c_C and c_D are equalized electronegativities of zeolites and adsorbates respectively, a_C and a_D are polarizabilities and h_C and h_D are equalized chemical hardness values of zeolites and adsorbates respectively. A and B are constants.

3. Results and discussion

Barrer and coworkers have determined the isosteric heat of adsorption (Q_{st}) of many adsorbates over zeolites using the following (9),

$$Q_{st} = j_D + j_R + j_P + j_{F-Q}, \quad (6)$$

where j_D = dispersion energy, j_R = repulsion energy, j_P = polarization energy and j_{F-Q} = quadrupole interaction energy. Experimentally and routinely Q_{st} is determined by using the Clausius–Clapeyron equation for adsorption.⁹

For the estimation of isosteric heat of adsorption, we have considered the following parameters: e/K and s , the Lennard–Jones (L–J) parameters, (ST) = surface tension, (Z/r) = electrostatic potential and a = polarizability. The isosteric heat of sorption has been estimated by applying the multi-parametric equation with these input parameters,

$$Q_{st} = A(e/K) + B(s) + C(Z/r) + D(ST) + E(a) + F. \quad (7)$$

Equation (7) with $A = 0.7772$, $B = 7.727$, $C = 8.719$, $D = 4.313$, $E = 0.3455$ and $F = -29.84$ represents the data with percent average absolute deviation (\bar{e}), the correlation coefficient (R) and standard deviation (s) of 22.2%, 0.8770 and 15.8 respectively over a data set of 94 points.

Adsorption of aliphatic hydrocarbons, C₁ to C₅, benzene and inorganic molecules like CO₂ and NH₃ over various zeolites including Y-zeolite (14 zeolites) was studied by an artificial neural network. The input parameters are as given in (7). The percent absolute average deviation over 94 data points was 13.4. A plot of the Q_{st} – values calculated by the methods of artificial neural nets (ANN) and multi-linear regression MLR, (7) vs the experimental values is illustrated in figure 1. A glance at the figure reveals the points represented by ANN to be closer to the diagonal (points falling on which indicate perfect agreement between the experimental and calculated Q_{st} values) compared to those of MLR. This implies better representation of the data by ANN compared to that of MLR. Further support to the superiority of ANN lies in the lower (\bar{e}) (percent average absolute deviation) and s (standard error) values and higher values of the correlation coefficient (R) determined for the ANN method compared to those

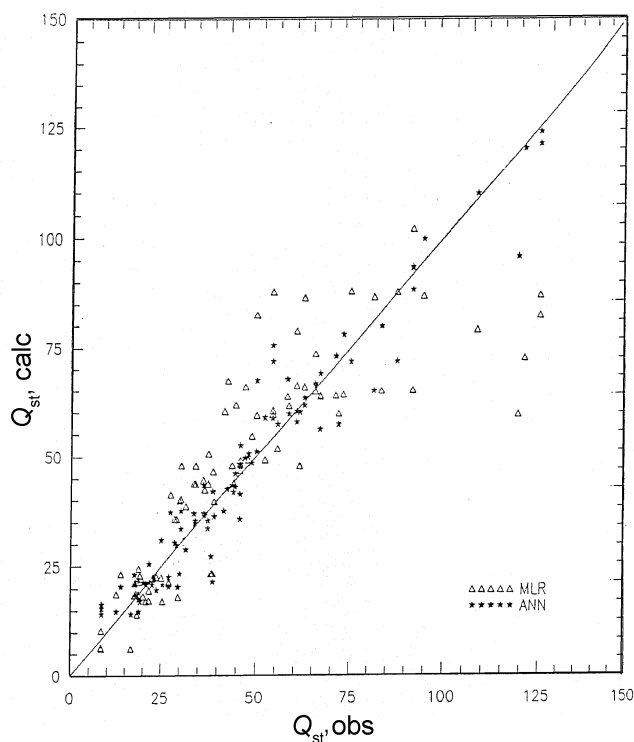


Figure 1. Graphical representation of Q_{st} data.

of MLR. Comparative values of those statistical parameters are (\bar{e}): 13.4% (ANN) and 22.2% (MLR); s : 6.8 (ANN) and 15.8 (MLR) and R : 0.9714 (ANN) and 0.8770 (MLR). The activation function used in the error back-propagation ANN method is the sigmoid model. Further detailed analysis of the results obtained from the ANN method has revealed the order of significance of the several variables influencing Q_{st} as:

$$ST > z/r > e/k > s > a.$$

We have correlated Q_{st} with the Nalewajski charge transfer term in the case of organic molecules sorbed over zeolites. Charge transfer was determined by the equation based on equalized electronegativity (c), chemical hardness (h) and polarizability (a). The percent average deviation was about 15.9%. The results and various methods are summarized in table 1. It can be seen from the table that the most comprehensive study on Q_{st} including both organic and inorganic adsorbates (with as many as 94 data points) has been the approach of using e/k , s , ST , z/r and a as the variables influencing the adsorption process. In the case of organic adsorbates, the concept of charge transfer function is a useful approach.

Using (5) the sorption of CH_4 , C_1 – C_6 aliphatics and C_6H_6 over various zeolites like NaY, CaY, NaX, LaY, CaA, NaL, HL, Chabite has been tested. The percent average absolute deviation is 15.0. The values of A and B are 0.5424 and 18.00 respectively. Thirty-five data points are considered.⁹ As an approximation ΔZ is considered to be unity.

Based on the principle of maximum hardness, we have correlated the difference of chemical hardness of products and reactants with the isosteric heat of adsorption,

$$\Delta h = [(N_i + N_D)/(N_i/h_{Ci} + N_D/h_D)] - (h_{Ci} + h_D), \quad (8)$$

$$\Delta H = A + B\Delta h, \quad (9)$$

where N_i is the number of cations, N_D = number of the adsorbed molecules, $h_{(Ci)}$ = hardness of the cation and h_D = the hardness of the adsorbed molecule. In this equation only the localized cation–adsorbate interaction has been considered. The values of constants A and B are 37.92 and -0.5745 respectively. Using (9), 35 data points are tested with percent average absolute deviation of 41.3. If we exclude CH_4 (spherical symmetry) as an adsorbate molecule, the

percent average absolute deviation decreases to 26.8. Among the aliphatic organic molecules (C_n), the percent average deviation decreases with increase of ‘ n ’, i.e. the length of molecule (considering as a cylinder).

Considering zeolite as a whole (statistical model) reacting with adsorbate molecule, the equation may be written as,

$$\Delta h = [(C + D)/(C/h_C + D/h_D)] - (h_C + h_D), \quad (10)$$

where C = number of atoms in unit cell of the zeolite, D = number of atoms in the adsorbate and h_C and h_D are the equalized hardness values of zeolite and the adsorbate respectively. The values of constants A and B are 542.7 and 85.43 respectively using (9). Using (9), 35 data points are tested with percent average absolute deviation of 33.6. Excluding CH_4 molecule, the percent average deviation decreases to 28.4. Δh is also determined by considering C = number of ions and atoms in zeolites, and (9) is tested. With $A = 570.4$ and $B = 90.15$, the percent absolute average deviation is 32.9. While excluding CH_4 (of spherical symmetry) the percent average deviation is 28.3.

We have reported the concept of equalized molar refraction.¹⁰ Considering these $R_{M(eq)}$ values, we have determined c , h and a using following equations,

$$c = a + b(R_M)^{2/3}, \quad (11)$$

$$h = a' + b' (R_M)^{-1/3}, \quad (12)$$

$$a = a'' + b'' (R_M), \quad (13)$$

Using these c , h and a values, charge transfer, ΔN , is determined and correlated to heat of adsorption, ΔH (Q_{st}) values. The corresponding percent average absolute deviation is 15.5, tabulated in table 2.

In the analyses discussed so far, in correlating Q_{st} (ΔH) with ΔN or Δh , the shape factor for adsorbates has not been considered. The shape factor may affect the extent of the contribution of the vibrational mode. Pitzer¹¹ quantified the deviation from the sphericity of molecules and named the same the ‘‘acentric factor’’, w by using the equation,

$$w = -\log P_{(R)}^0 \text{ (at } T_R = 0.7) - 1, \quad (14)$$

where P^0 = vapour pressure and T_R = reduced temperature = (T/T_C) . The values of acentric factor are

Table 1. Various methods to determine isosteric heat of adsorption.

Method	Equation	\bar{e}	R	s	Data points
Semi empirical method (A) based on Barrer's approach	$Q_{st} = A(\mathbf{e}/k) + B(\mathbf{s}) + C(z/r) + D(\mathbf{a}) + E(\mathbf{m}) + F(Q) + G$	17.4	0.9067	5.5	43
Method (1) + surface tension	$Q_{st} = A(\mathbf{e}/k) + B(\mathbf{s}) + C(z/r) + D(\mathbf{a}) + E(\mathbf{m}) + F(Q) + G(\text{ST}) + H$	14.9	0.9227	5.1	43
Method (1) + ST and without dipole interaction	$Q_{st} = A(\mathbf{e}/k) + B(\mathbf{s}) + C(z/r) + D(\mathbf{a}) + E(\text{ST}) + F$	15.8	0.9092	5.7	43
Based on Nalewajski charge transfer function	$\Delta\mathbf{h} = [(N_i + N_D)/(N_i/\mathbf{h}_{Ci} + N_D/\mathbf{h}_D)] - (\mathbf{h}_{Ci} + \mathbf{h}_D)$ $\Delta H = A\Delta\mathbf{h} + B$	15.9	0.7071	11.2	35
Based on neural network method	$\mathbf{e}/k, \mathbf{s}, \text{ST}, Z/r, \mathbf{a}$ are inputs	13.4	0.9436	6.8	94

\bar{e} = percentage average absolute deviation; R = correlation coefficient; s = standard error; ST = surface tension

Table 2. Representation of the isosteric heat of adsorption (Q_{st}) data using charge transfer (ΔN) equations.

ΔN (in terms of \mathbf{c}, \mathbf{h} and \mathbf{a})	Proposed by	% Average absolute deviation		
		ΔN in \mathbf{c}, \mathbf{h} and \mathbf{a}	ΔN based on equalized R_M	Using (15)
$[(\mathbf{c}_C - \mathbf{c}_D)/2(\mathbf{h}_C + \mathbf{h}_D)]$	Parr and Pearson ¹	40.9	33.1	20.1
$[2(\mathbf{c}_C - \mathbf{c}_D)/\{(\mathbf{h}_C + \mathbf{h}_D) - (1/R)\}]$	Pearson ³	40.7	33.2	19.8
$[\{(\mathbf{c}_C/\mathbf{h}_D) - (\mathbf{c}_D/\mathbf{h}_C)\}/\{(\mathbf{h}_C/\mathbf{h}_D) + (\mathbf{h}_D/\mathbf{h}_C)\}]$	Komorowski ⁵	39.7	20.3	19.3
$(\mathbf{c}_C - \mathbf{c}_D) + 2(\mathbf{a}_D - \mathbf{a}_C)/2(\mathbf{h}_C + \mathbf{h}_D)$	Nalewajski ²	15.9 ($R = 0.7071$)	16.4 ($R = 0.6846$)	15.8 ($R = 0.8583$)

R = correlation coefficient

taken from Reid.¹² Considering the acentric factor \mathbf{w} , in addition to the charge transfer, ΔN , an equation of the type,

$$\Delta H = Q_{st} = A' + B' \Delta N + C' \mathbf{w}, \quad (15)$$

has been proposed and tested. The overall percent deviations obtained by the use of (15) are about 15.8% as reported in table 2. Although the average absolute deviation (\bar{e}) obtained by using Nalewajski's charge transfer function expressed in terms of (\mathbf{c}, \mathbf{h} and \mathbf{a}) and equalized R_M are 15.9% and 16.4% respectively using (5b). Inclusion of the acentric factor \mathbf{w} in the correlation using (15) substantially improves the correlation coefficient from 0.6846 to 0.8583. Since a value of $\mathbf{g} > 0.8$ is acceptable as an indication for reasonable correlations, it is essential to use the acentric factor in addition to the Nalewajski charge-

transfer function in correlating Q_{st} . Hence, the consideration of the shape of the molecules quantified by a parameter like \mathbf{w} substantially improves the correlation of ΔH (heat of adsorption).

4. Conclusions

(1) Nalewajski charge transfer (ΔN) term expressed either as a function of \mathbf{c}, \mathbf{h} and \mathbf{a} or as a function of the quantities derived from the equalized molar refraction represents the Q_{st} data reasonably well.

(2) Considering the shape effect of the adsorbates in addition to the ΔN term improves the representation of the data on the isosteric heat of adsorption of zeolites.

(3) It is possible to estimate the isosteric heat of adsorption from the properties of zeolites and adsorbates with reasonable accuracy using the artificial neural network method.

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