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실리카의 표면 히드록시기와 피흡착질의 질량의존성에 의한 상호작용

김 종 택 · 서 은 덕*

경북대학교 공업화학과
*경남대학교 화학공학과

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Mass Dependent Interaction Between Surface Hydroxyl Groups of Silica and adsorbed Molecules

Jong Taik Kim and Eun Deock Seo*

Department of Industrial Chemistry, College of Engineering
Kyungpook National University
**Department of Chemical Engineering, College of Engineering*
Kyungnam University

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Abstract: A quantitative relationship of mass dependent interaction between surface hydroxyl groups of silica and homologous series of adsorbed molecules, $\Delta\nu_{OH_1} - \Delta\nu_{OH_X} = 1/2\,C \cdot \ln(m_X/m_1)$, was derived from collision theory and Hammett σ substituent constants. This relationship was in good agreement with the results reported in literatures in either adsorption at liquid/solid interface or at vapor/solid interface and the adsorption mechanism could be characterized from the slopes of the equation by plotting the value of $\Delta\nu_{OH_1} - \Delta\nu_{OH_X}$ against $\ln(m_X/m_1)$. Also, good correlation between pKa and $\Delta\nu_{OH_1} - \Delta\nu_{OH_X}$ was confirmed as $pKa_1 - pKa_X = -\rho/f \cdot s(\Delta\nu_{OH_1} - \Delta\nu_{OH_X})$ and $pKa_1 - pKa_X = 1/2\ s \cdot \log(m_1/m_X)$.

1. INTRODUCTION

To investigate an interfacial interaction of filler particle with polymer in polymer composite, it is essential to understand the nature of filler interacting with matrix. In this article, we chose silica as a filler, and various organic compounds as analogous polymer materials interacting with silica, in which we concentrated our attention to the behavior of surface hydroxyls of silica.

The i.r. absorption of surface hydroxyl groups of silica is know to shift to a lower frequency due to the absorption on the surface[1,2]. The i.r. frequency shifts have frequently been attributed to hydrogen bonding between the adsorbates and surface hydroxyls. The extent of frequency shift is a measure of interaction of adsorbates with hydroxyl groups of silica. There have, however, been few attempts to derive a quantitative model concerning the nature of the interaction. One of the most successful model is that of charge transfer theory[3,4].

In this paper, a quantitative model which correlate frequency shifts of silica with the mass of adsorbates was derived from collision theory and Hammett equation.

2. THEORY

2-1. Adsorption at the Vapor/Solid Interface

It has been reported that the frequency shifts of surface hydroxyl group of silica could be correlated with the Hammett substituent constant of adsorbate molecules[5,6]. If $\Delta\nu_{OH}$ is directly proportional to Hammett σ constant, then we get the following equation,

$$\Delta\nu_{OH} = f \cdot \sigma_x \quad \cdots\cdots (1)$$

where f is proportional constant and x is 1.2.3 ……
From the Hammett equation,

$$\log (k_x / k_o) = f \cdot \sigma_x \quad \cdots\cdots (2)$$

wher is a function of the reaction and variable with the reaction conditions and k_x, k_o are rate constants of adsorption of substituent and reference material, respectively, we can get the equation for a series of compounds,

$$\log (k_1 / k_2) = \rho\ (\sigma_1 - \sigma_2) \quad \cdots\cdots (3)$$

Another equation obtained from Eq(1) and Eq(3),

$$\log (k_1 / k_2) = (\rho / f)\ (\Delta\nu_{OH_1} - \Delta\nu_{OH_2}) \quad \cdots\cdots (4)$$

where k_1, k_2 are a rate constants of adsorption for adsorbate 1 and 2, respectively, can be substituted by the Arrhenius equation, $\ln k = \ln A - E/RT$. Then the Eq(4) will be at constant temperature.

$$C(\Delta\nu_{OH_1} - \Delta\nu_{OH_2}) = \ln (A_1/A_2) + (E_2 - E_1)/RT \quad (5)$$

where C is $2.303(\rho / f)$.
Assuming the homologous series of compounds are physically adsorbed and have similar donor orbital to interact with surface hydroxyl of silica, the difference of activation energy, E_2-E_1, between homologous series of adsorbates can be ignored[7,8] to have the following.

$$\Delta\nu_{OH_1} - \Delta\nu_{OH_2} = (1/C) \ln\ (A_1 / A_2) \quad \cdots\cdots (6)$$

From collision theory, the collision factor A is given by

$$A = [(d+d')^2 / 4]\ [8\pi kT(m+m')/mm']^{\frac{1}{2}} \quad \cdots (7)$$

where d, d' and m, m' are diamters and masses of colliding molecules, respectively. When a series of gas molecules adsorbed on the silica surface the adsorption processes may be considered simply as a bimolecular reaction[8]. The ratio of collision factor for adsorbate 1 and 2 colliding with silica is reduced to Eq(8) by taking account the diameters and masses of silicaa, adsorbate 1 and 2 into the Eq(7) and the mass and diameter of silica particle are large enough for the collision compared to that of adsorbate 1 and 2.

$$A_1 / A_2 = (m_2 / m_1)^{\frac{1}{2}} \quad \cdots\cdots (8)$$

For the case of silica disc on which adsorbate molecules collide, the number of collisions per unit times per unit area of surface of silica is given by

$$Z = P / (2\pi mkT)^{\frac{1}{2}} \quad \cdots\cdots (9)$$

The ratio of collision factors at constant temperature gives the same result obtained from Eq(8).
From Eq(6) and Eq(8), a general form for mass dependent interaction between surface hydroxyl groups of silica and adsorbed molecules is deduced,

$$\Delta\nu_{OH_1} - \Delta\nu_{OH_x} = (1/2C) \ln\ (m_x / m_1) \quad \cdots\cdots (10)$$

wher x is 1,2,3,.....

It is interesting to examine the relationship between pKa and frequency s shift of adsorbate. By the use of Hammett equation, it is also possible to derive the relationship.

$$\log(k_x/k_0)=\log(K_x/K_0) \quad \cdots\cdots (11)$$

where K and k is an equilibrium constant and rate constant respectively. Considering the adsorption reaction as a charge transfer reaction and putting acid dissociation constant, Ka, in the place of the equilibrium constant, K, we have,

$$\log(K_x/K_0) = S\ \log(Ka_x/Ka_o) \quad \cdots\cdots (12)$$

where S is a function of the reaction.

Besides, the Eq(4) and Eq(12) give

$$pKa_i - pKa_x = (-\rho/f \cdot S)\ (\Delta\nu_{OH_i} - \Delta\nu_{OH_x}) \quad \cdots (13)$$

where x is 1,2,3, ...

And this reduce Eq(10) to have

$$pKa_i - pKa_x = (1/\tau S)\ \log(m_1/m_x) \quad \cdots\cdots (14)$$

2-2. Adsorption at the Liquid/Solid Interface

With respect to the adsorption of homologous series of adsorbates on silica took place at the liquid/solid interface, a few works on the frequency shifts correlated with the Hammett σ substituent constants[9] were reported[10,11]. Since there is no fundamental difference between a reaction in the solutions and in the gaseous state[8,12], the forgegoing discussions could be applied in this system by modifying, Eq (1) as follows

$$\Delta\nu_{OH} = f' \cdot \sigma \quad \cdots\cdots (15)$$

Replacing f′ in the place of f in Eq (10) and Eq (13), these equations seems very applicable form of expressions as already discussed,

2-3. Adsorption of Polymer on Silica at the Liquid/Solid Interface

It was well known that the rate constant was independent of molecular size in polymerization reaction[13]. As the molecular size increase along with the polymerization process, the rate constant approaches to constant value. When the adsorption of a polymer of different molecular weight takes place on silica, it is assumed that the rate constant of the adsorption remains unchanged with molecular weight variation. Then we have

$$k_1 = k_2 \quad \cdots\cdots (16)$$

where k_1 and k_2 are the rate constants of the adsorption of polymer of molecular weight 1 and 2, respectively. This fact can be proved by examination of Eq (3) in which the values of σ_1 and σ_2 are much the same for the same polymer of only different in molecular weight, since its chemical composition and structure are exactly the same with each other. So we can expect the result

$$\Delta\nu_{OH_1} = \Delta\nu_{OH_2} \quad \cdots\cdots (17)$$

The result obtained in this manner means that the strenght of the interaction between polymer and silica is independent of molecular weight of polymer. More generally speaking, the strength of interfacial energy between polymer and reinforcing filler in polymer composite is not affected by molecular weight of polymer but polymer itself.

3. RESULTS AND DISCUSSION

Applicability of these equations proposed should meet the limiting assumptions; homologous compounds of similar donor orbital and neglecting the difference of activation energy. Beside the condition, the steric effect has to be excluded not to disterb overlapping between dornor and acceptor orbital. Within the conditions, linearity is supposed to be obtainable by these equations on plotting observed data.

On the case of aromatic molecules adsorbed on silica at the vapor/solid interface, the observed shifts in absorption maxima and the related data for the adsorption are listed in Table 1., in which frequency shifts are cited from the data of pohle[5]. All the values listed are adjusted to $\theta = 0.3$ except a,a,a-trifluorotoluene, chlorobenzene, brombenzene and iodobenzene which are asjusted $\theta = 0.5$.

The calculated ρ,f and correlation coefficients are also listed. The validity of the equations proposed in this paper is well manifested by plotting $\Delta\nu_{OH_1} - \Delta\nu_{OH_X}$ which designated as $\Delta\Delta\nu_{OH}$ against ln (m_x/m_1) in accord with Eq (10), Moreover, an adsorption mechanism of adsorption site may be deduced by plotting Eq (10) and that is proved to be very reasonable. And a logical outcome of using reaction function for the adsorption

Table 1. Frequency Shifts and Related Data for the Adsorption of Aromatics on Silica

adsorbate	$\Delta\nu_{OH}$**	$\Delta\Delta\nu_{OH}$***	$\ln(m_x/m_l)$	f[a]	(f/ρ)[b]	ρ[c]	R[d]	R[e]
Benzene	119	0	0					
Toluene	136	-17	0.165					
m-Xylene	153	-34	0.306	-76.2	-501.9	0.2	-1.00	0.94
Mesitylene	171	-52	0.431					
Hexamethylbenzene	197	-78	0.731					
Fluorobenzene	63	56	0.193					
Hexafluorobenzene	25	94	0.836	-70.1	279.6	-0.3	0.99	1.00
a,a,a-Trifluorobenzene*	33	86	0.606					
Chlorobenzene	100	-19	0.366					
Bromobenzene	110	-9	0.700	-74.7	-109.7	0.7	-0.99	0.90
Iodobenzene	114	-5	0.961					

* Porous glass, all the rest silica.

** cited from reference 5. *** $\Delta\nu_{OH_1} - \Delta\nu_{OH_X}$

a; calculated from the data of reference 5.

b; calculated from the slope of Eq (10).

c; calculated from f and (f/ρ).

d; correlation coefficient calculated from the data of $\Delta\Delta\nu_{OH}$ and $\ln(m_x/m_l)$.

e; correlation coefficient calculated from the data of ionization potential and M.P.K. parameter listed in reference 6.

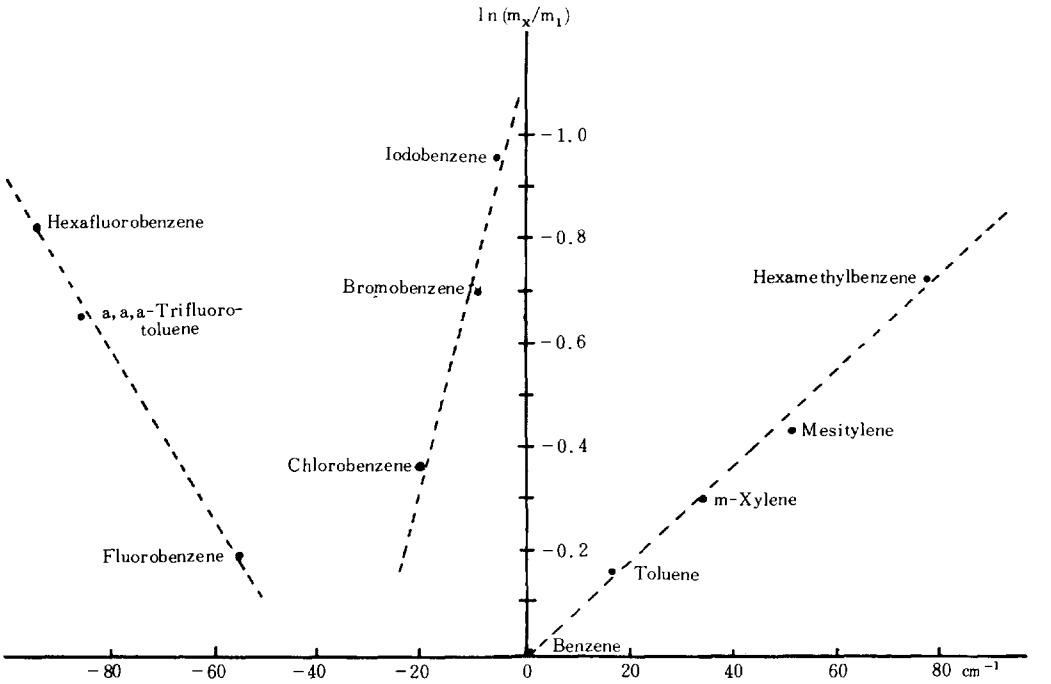

Fig. 1. Linear relationship of alkylbenzenes, fluoroaromatics and halogenoaromatics between $\Delta\nu_{OH_1} - \Delta\nu_{OH_X}$ and $\ln(m_x/m_l)$.

is established. In Table 1, the observed values of reaction function for alkylbenzenes, fluoroaromatics and halogenoaromatics are 0.2,-0.3 and 0.7, respectively. The point of which they differed was regarded to the different adsorption mechanisms of those adsorbates.

From the slopes of the straight lines in Fig. 1., adsorbates are characterized in three groups, i.e, alkylbenzenes, halogenoaromatics and fluoroaromatics as well. And thus it is able to relate the three groups distinguished by the difference in slopes to the molecular structures and adsorption mechanism.

It is well known that the adsorption mechanism of benzene and alkylbenzenes is ascribed to from O-H... π bridges whereas that of fluoroaromatics is due to O-H...F atoms[5,6,14]. It is reasonable to expect that the ρ value of fluoroaromatics should be the same as that of alkylbenzenes if the adsorption of fluoroaromatics takes place through O-H... π bridge. Furthermore, the straight lines of fluoroaromatics should pass through the origin of the coordinate in Fig. 1. However, the ρ values of these two groups are different with each other, and the straight line of alkylbenzenes pass through the origin of the coordinate while fluoroaromatics does not.

It was reported[5] that the adsorption of halogenoaromatics took place via O-H... π bridge. If it is true, the straight line of halogenoaromatics should pass through the origin of the coordinate as alkylbenzenes, and value of halogenoaromatics

Table 2. Frequency Shifts and Related Data for the Adsorption of Various Molecules on Silica

adsorbate	$\Delta\nu_{OH}$	$\Delta\Delta\nu_{OH}$[b]	$\ln(m_x/m_l)$	R	pKa	ΔpKa[d]
$(CH_3)_2O$	420[a]	0	0		-3.83[c]	0
$(C_2H_5)_2O$	445	-25	0.475	-0.99	-4.1	0.27
$(C_3H_7)_2O$	470	-50	0.796		-4.40	0.57
$CH_3Si(OCH_3)_3$	363[a]	0	0			
$(CH_3)_2Si(OCH_3)_2$	403	-40	-0.125	0.99		
$(CH_3)_3Si(OCH_3)$	477	-114	-0.268			
$SiCl_4$	25[a]	0	0			
CH_3SiCl_3	57	-32	-0.128	1.00		
$(CH_3)_2SiCl_2$	90	-65	-0.275			
$(CH_3)_3SiCl$	135	-110	-0.447			
CCl_4	40[a]	0	0			
$CHCl_3$	48	-8	-0.254			
CH_2Cl_2	72	-32	-0.594	0.99		
CH_3Cl	106	-66	-1.115			
n-C_5H_{12}	30[a]	0	0			
n-C_6H_{14}	37	-7	0.178	-1.00		
n-C_7H_{16}	45	-15	0.329			
Ar	8[e]	0	0			
Kr	16	-8	0.741	-0.99		
Xe	19	-11	1.190			

a,e ; cited from the data of reference 15 and 16, respectively.

b ; $\Delta\nu_{OH_1} - \Delta\nu_{OH_X}$ c; ref. 16. d; $pKa_1 - pKa_x$

R; correlation coefficient calculated from $\Delta\Delta\nu_{OH}$ and $\ln(m_x/m_l)$.

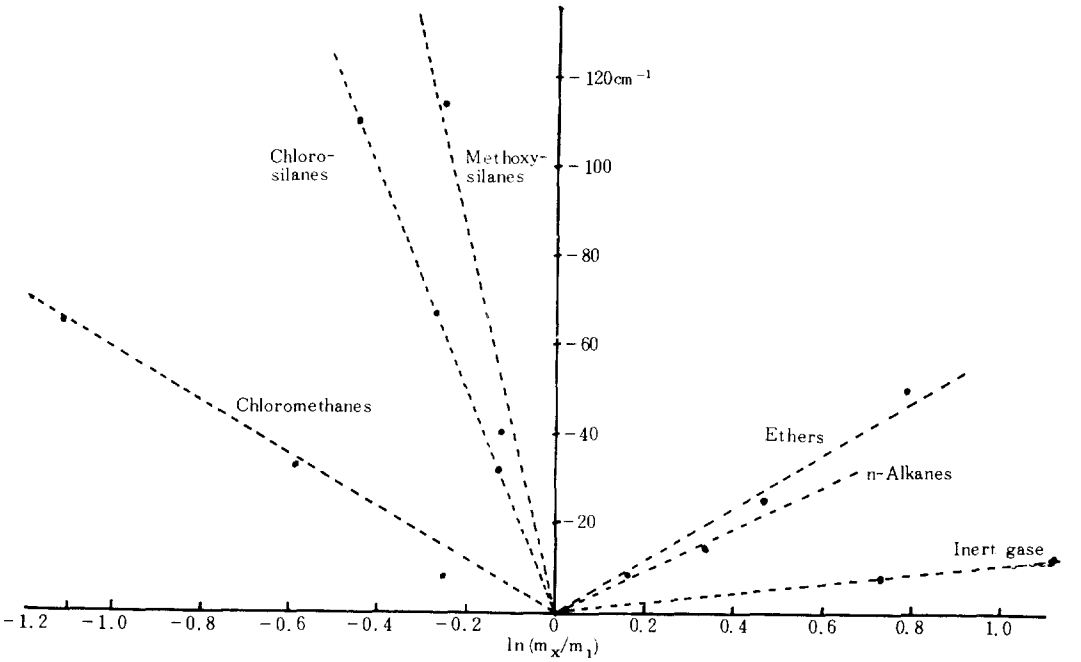

Fig. 2. Linear relationship of n-alkanes, inert gases, chloromethanes, chlorosilanes and methoxysilanes between $\Delta\nu_{OH_1} - \Delta\nu_{OH_X}$ and $\ln(m_x/m_1)$.

should have the same value as that of alkylbenzenes.

Pohle[5] concluded that the adsorbates which have different slopes plotted with M.P.K. parameters against ionization potentials have distinguished adsorption mechanism due to the different overlap integral. This was manifested by the slope, calculated from Pohle's paper, have different values. Futhermore, frequency shift of chlorobenzene due to the adsorption on silica is similar to that of methylchloride (106cm)[1] in which the adsorption probably occur through Cl atom. However, Pohle proposed that the adsorption site of chlorobenzene was phenyl ring. Considering the case of methylchloride which does not have phenyl ring, it is hard to count Pohle's theory as logical. Consequently the adsorption mechanism of halogenoaromatics is not via O-H... π bridge. Thus it is able to conclude that the adsorption mechanism could be deduced by plotting the equations proposed in this paper.

In Table 2., frequency shifts and related data of n-alkanes, chlorinated methanes, ethers, silanes and inert gases are listed and also illustrated in Fig. 2, in which we can observe the straight lines plotted by Eq (10). Accordingly, the adsorbates listed in Table 2. also show the validity of the equations proposed.

In order to specify the interaction of adsorption, they are subdivided into specific and nonspecific, interactions. The interactions of n-alkanes and inert gases are classified as nonspecific whereas ethers, chloro and methoxy silanes as specific. The plots of data listed in Table 2 show excellent linearity regandless of specific or nonspecific, and the slopes of straight lines manifested excellently to meet correlation coeffi-cients which approach to 1.

Fig. 3-4 also show that linearities are readily established between $\Delta\Delta\nu_{OH}$ and pKa, and between pKa and $\ln(m_x/m_1)$ in accord with Eq (13) and Eq (14) with correlation coeffecient of 1. From the fact, it is evident that the validity of Eq (13) and Eq (14) is also very clear.

Here, we find frequency shifts to be proportional to pKa of adsorbates and the frequency shift

is able to be regarded as a means of measuring ability of charge transfer of donor adsorbates to silica. The godd correlation between the pKa of alcohols and phenols and frequency shifts are observed to indicate the molecules form moderately strong hydrogen bonds[18].

Data listed in Table 3 were obtained from the adsorption took place at the liquid/solid interface; i.e, nitrobenzene adsorbed on silica in heptane, pyridine derivatives in CCl_4. The Fig. 5-8 were figurixed from the data listed in Table 3. As was expected, these figures show good linearity plotted according to the Eq (10), Eq (13), and Eq (14) in which f should be replaced with f'. The validity of the relationships proposed seems fairly appropriate for the adsorption at the liquid/solid interface as well as at the vapor/solid interface. Adsorption site of nitrobenzene derivatives or pyridine derivatives seems N atom rather than phenyl ring or methoxy group or else[9,19]. It is interesting to note that the value of nitrobenzene derivatives, 0.2, is exactly same as that of pyridine derivatives. Considering ρ is a function of reaction and experiment was carried out in a similar condition, it is rather logical to have the same values.

The equations discussed so far can be represented by means of activated complex theory

$$\lambda = \lambda (kT/h) e \Delta S^*/R \; e^{-\Delta H^*} RT \quad \cdots\cdots (18)$$

where λ is transmission coefficient and this factor is expected to be a function of particular state, which is usually hard to know and is assumed to be unity. The difference in activation energy between homologous series of adsorbates is assumed to be ignored and the logarithm of the quotient of two rate constants for adsorbate 1 and 2 yields

$$\ln (k_1/k_2) = (\Delta S_1^* - \Delta S_2^*)/R \quad \cdots\cdots (19)$$

And the Eq (4), Eq (10) and Eq (19) becomes

$$\Delta S_1^* - \Delta S_2^* = 2.303 \rho R/f \cdot (\Delta \nu_{OH_1} - \Delta \nu_{OH_2})$$
$$= R/2 \cdot \ln (m_2/m_1) \quad \cdots\cdots (20)$$

In physical adsorption it is known that the adsorbed film is mobile and the entropy change for activation is given by Eq (21)[8].

$$\Delta S^* = -R \ln [(2\pi mkTe)^{\frac{1}{2}}/h] \quad \cdots\cdots (21)$$

The difference between ΔS_1^* and ΔS_2^* gives the

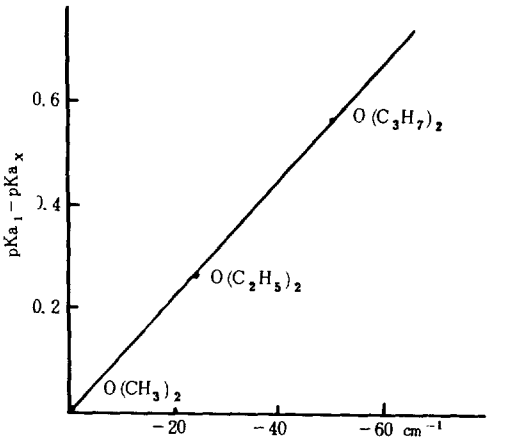

Fig. 3. Linear relationship of ethers between $\Delta \nu_{OH_1} - \Delta \nu_{OH_X}$ and $pKa_1 - pKa_x$.

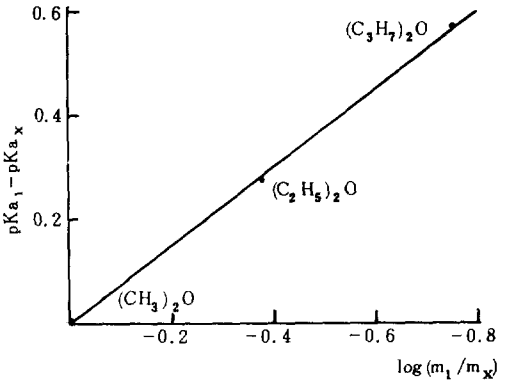

Fig. 4. Linear relationship of ethers between $pKa_1 - pKa_x$ and log (m_1/m_x).

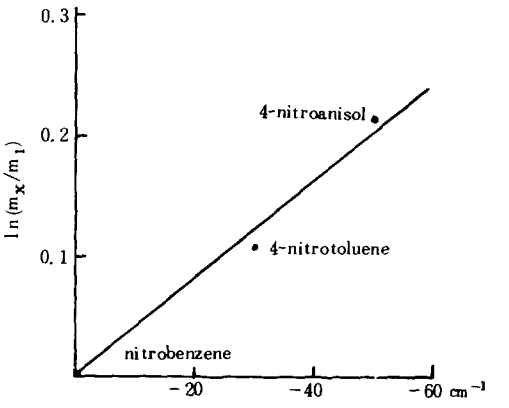

Fig. 5. Linear relationship of aromatic nitrocompounds between $\Delta \nu_{OH_1} - \Delta \nu_{OH_X}$ and ln (m_x/m_1).

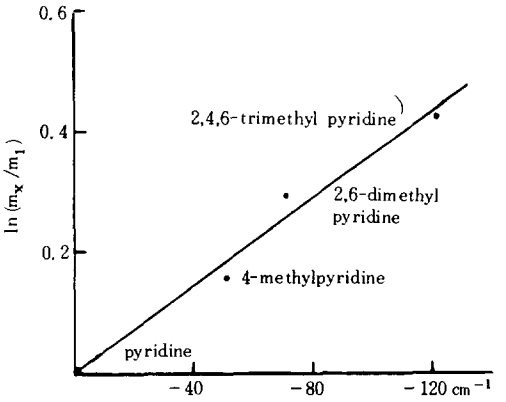

Fig. 6. Linear relationship of pyridine derivatives between $\Delta\nu_{OH_1} - \Delta\nu_{OH_X}$ and ln (m_X/m_1).

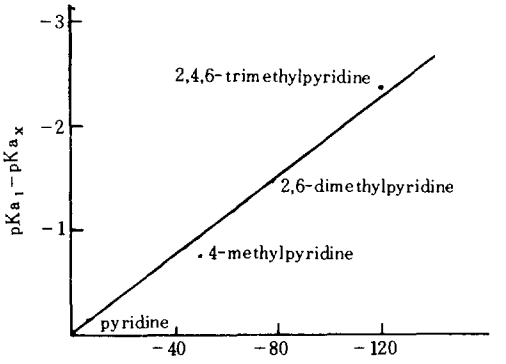

Fig. 7. Linear relationship of pyridine derivatives between $\Delta\nu_{OH_1} - \Delta\nu_{OH_X}$ and $pKa_1 - pKa_X$.

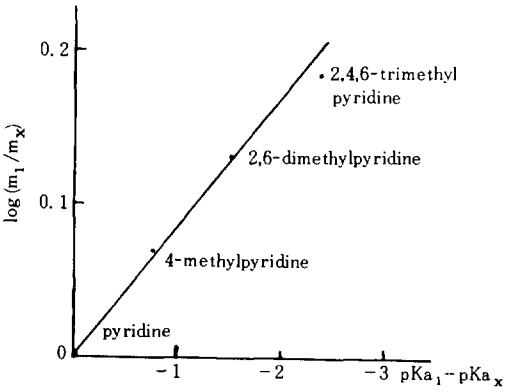

Fig. 8. Linear relationship of pyridine derivatives between $pKa_1 - pKa_X$ and $\log(m_1/m_X)$.

same result as the right term of Eq (20), to prove the equations proposed in this paper as reasonable.

In the case of polymer adsorption on silica at liquid/solid interface, the frequency shifts do not vary with molecular weight of polymer as the result of Eq (17). This phenomenon also can be explained by application of charge transfer theory which was developed by Mulliken[3] and applied to hydrogen bonding by Puranik and Kumar[4]. The equation is,

$$I = [(5/4)^{\frac{1}{2}} CS\lambda^{\frac{1}{2}}] (\Delta\nu_{OH}/\nu_O)^{\frac{1}{2}} + E_A + W \quad .. (22)$$

For a given polymer, although its molecular weight is different, the composition and structure

Table 3. Frequency Shifts and Related Data for the Adsorption of Various Molecules on Silica in Solution

adsorbate	$\Delta\nu_{OH}$	$\Delta\Delta\nu_{OH}$	$\ln(m_x/m_l)$	R[c]	f	f/ρ	ρ	pKa	ΔpKa
Nitrobenzene	150[a]	0	0						
4-Nitrotoluene	180	-30	0.108	-0.99	-209.5[b]	-1055.7	0.2		
4-Nitroanisole	200	-50	0.218						
Pyridine	766[d]	0	0					5.22[d]	0
4-Methylpyridine	816	-50	0.163					5.98	-0.76
2,6-Dimethylpyridine	836	-70	0.303	0.99	-248.1[e]	-1230.2	0.2	6.72	-1.50
2,4,6-Trimethyl-pyridine	886	-120	0.426					7.59	-2.37

a; cited from reference 10. b; calculated from the data of reference.
c; correlation coefficient between frequency shifts and $\ln(m_x/m_l)$.
d; cited from reference 19. e; calculated from the data of reference 9.

are exactly the same, so that I, ionization potential of donor, of a polymer is not different with molecular weight. Therefore, frequency shift for a polymer of different molecular weight is constant and is independent of molecular weight of polymer. The experimental evidence for the validity of Eq (17) was reported by Fontana and Thomas[21] who carried out experiment for the adsorption of poly (lauryl methacrylate) on Cab-O-Sil in n-dodecane. There was no change obserbed in frequency shifts of surface hydroxyl of silica in-which molecular weights of the polymer were 3.3×10^5 and 1.19×10^6, respectively.

Similarly, Thies[22] reported that there was no change observed in the frequency shifts of carbonyl groups of poly (methyl methacrylate) in which its molecular weights were 8.22×10^5 and 3.20×10^5, respectively.

Though its circumstances are different from our discussions, the experimental results for frequency shifts as a function of size of methanol polymers in solid nitrogen by Van Thel et al.[23] agree with our opinion. They also concluded that an increase in polymer size produced no further change in bond energy or frequency shifts. Consequently, result obtained from Eq (17) can be applied to the composite in which interfacial energy between polymer and filler is independent of molecular weight of the polymer.

Also, results obtained in this paper can be applied to the adsorption of polymers which is the primary step in the formation of all polymeric interfacial bonds such as in adhesion, in coatings, in dispersion stabilization, and in biological membranes. Thus, the study of adsorption of polymers from solution by measuring the degree of frequency shifts of surface hydroxyls is of both academic and practical value.

4. CONCLUSION

We derived a quantitative model correlating i.r. frequency shifts of silica with the molecular properties of adsorbates such as mass, pKa and entropy change of activation by using collision theory and Hammett equation. The results are that $\Delta \nu_{OH_i} - \Delta \nu_{OH_x}$ is directly proportional to ln (m_x/m_i) and pKa. The validity of relationship derived was evidenced by the foregoing results and theoretical classification for a homologous series of adsorbates adsorbed on silica regardless of the vapor/solid interface or the liquid/solid interface. Futher, the adsorption mechanism may be deduced by plotting equations proposed.

From activated complex theory and statistical mechanics, mass dependent interaction of surface hydroxyl could also be directly correlated with the entropy change of activation, ΔS^*, on adsorption.

In the case of the adsorption of polymers the strength of polymeric interfacial bonds is independent of molecular weight.

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