Adsorbed Water in Soil as Interpreted by Its Potentials Based on Gibbs Function

Gibbs 함수의 포텐샬로 해석한 토양 흡착수

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ABSTRACT : Usual experimental adsorption isotherms as a function of relative humidity were constructed from adsorbed water contents in soils, which were kept more than 2 days in vacuum desiccators with constant humidities controlled by sulfuric acids of various concentrations. From the experimental data, the adsorption surface areas were calculated on the basis of the existing adsorption theory, such as Langmuir, BET, and Aranovich. Based on the Gibbs function describing chemical potential of perfect gas, the relative humidities in the desiccators were transformed into their chemical potentials, which were assumed to be the same as the potentials of equilibratedly adsorbed water in soils. Moreover, the water potentials were again transformed into the equivalent capillary pressures, heads of capillary rise, and equivalent radius of capillary pores, on the basis of Laplace equation for surface tension pressure of spherical bubbles in water. Adsorption quantity distributions were calculated on the profile of chemical potentials of the adsorbed water, equivalent adsorption and/or capillary pressures, and equivalent capillary radius. The suggested theories were proved through its application for the prediction of temperature rise of sulfuric acid due to hydration heat. Adsorption heat calculated on the basis of the potential difference was dependant on various factors, such as surface area, equilibrium constants in Langumuir, BET, etc.

요약 : 황산 농도를 달리하여 습도를 조절한 진공 데시케이터에 2일간 평형시키어 토양에 흡착시킨 수분 함량으로 상대 습도의 함수로서의 흡착 등온 실험 성적을 얻었다. Langmuir, BET, Aranovich 등의 흡착 이론식에 따라 흡착 표면적을 계산하였다. 완전 기체의 화학 potential과 관련된 Gibbs 함수에 따라 데시케이터 안에 상대 습도를 화학 Potential로 변환시키고 토양에 평형적으로 흡착시킨 수분 포텐샬과 동일하게 취급하였다. 더욱이 이 값을 다시 물속 구형 거품의 내부 압력에 관한 Laplace 표면 장력식을 적용하여 대등한 모세관 압력, 모세관 수두, 모세관 직경으로 변환하였다. 흡착수의 화학 포텐샬, 흡착 또는 모세관 압력, 대등 모세관 직경의 단층에 분포한 흡착 물량을 계산하였다. 제시된 이론으로 황산의 수화 온도 상승을 산출하여 제시된 이론을 증명하였고 포텐샬 차이를 기초로 하여 계산된 흡착열은 Langumir, BET 의 흡착 표면적, 평형상수 등의 인자에 영향을 받음을 보이었다.

INTRODUCTION

The universe is a complicated fields of forces, including electricity, gravitation, and magnetism, etc. The displacement of matter in the force fields is accompanied with the change of their energy levels, which is expressed in terms of potential. Therefore, most of natural phenomena as well as

water adsorption in soil can be described by the changes of potential energy. But most of the existing adsorption isotherms, for example, Langumuir, BET, Aranovich, deal only with chemical equilibrium applying mass action law, although their adsorption models were branched off each others in terms of the number of adsorbing layers or free spaces in them. They are all based on simple assumptive models and their fitness does not cover full moisture regime in soil. Especially in the agricultural moisture regime, these isotherms all deviate from reality.

Water potential is very important, because moisture movement in soil is described as a function of its gradients and hydraulic conductivity. Moreover, we may assume the adsorbing surface is not so uniform as assumed in the model of Langumuir, BET, or Aranovich. If we assume that there are many micropores on adsorption surface, the potential theory of capillary water may be applied better than the simple mass action law. The relationship of moisture against water potential can provide additional information about soil adsorbents. Approximate adsorption energy, adsorption pressure, and pore size distributions can be reached, which are important soil characteristics.

The aim of the present work was to characterize the relationship between adsorbed soil moisture and its water potential and to evaluate adsorption pressure or equivalent capillary water pressure or capillary radius of the adsorbed water.

THEORY

Water potential

Energy level can not be expressed in absolute value, but in relative quantity as a difference from the established standard level. Gibbs function describes the free energy level, $G(p_g)$ of perfect gas at pressure, p_g by the differences from the standard energy level, $G(p_{0,g})$ at standard pre-

Table 1. Notations and dimensions

Notation	Description
a, a_m	Adsorbed amount, Maximum adsorbed amount[mg/g]
C	Proportionality constant in BET, dimensionless
g	Gravitational acceleration [9.8 m/sec]
$G(p_g), G(p_{0,g})$	Gibbs free energy of perfect gas at pressure p, at standard pressure, [joule]
H	Capillary rising head [m]
k	Equilibrium constant for Langumuir, dimensionless
$p_g, p_{0,g}$	Gas pressure at p, at standard state [Nm^{-2}]
p, p_s	Vapour pressure above the surface of the adsorbed or capillary water, Saturated vapour pressure of free water. [Nm^{-2}]
$p_{free,wat}, p_{dspres}$	Free water pressure, Water pressure depressed by capillary action or adsorption. [Nm^{-2}]
p_a	Air pressure above meniscus, [Nm^{-2}]
r	Capillary radius [m]
V_{wat}, V_g	Volume of water, gas or vapour [m^3/mole]
μ, μ_i	Chemical potential at p, at standard pressure. [Joule/mole]
ε	Difference of chemical potential from standard state or water potential [joule/mole]
γ	Surface tension [N/m]
ρ	Density of water [kg/m^3]

ssure, $p_{0,g}$ and at constant temperature of T.

$$G(p_g) = G(p_{0,g}) + nRT \ln \left(\frac{p_g}{p_{0,g}}\right) \qquad (1)$$

The standard condition is established usually at a pressure of exactly one bar, $p_{0,g}$ for Gibbs function. But it may be set at any convenient pressure, for example, at saturated water vapour pressure, p_s of free water in order to express the potential of adsorbed or capillary water in soil in comparison with free water.

In the case of one mole, equation (1) may be writen as following;

$$\varepsilon = \mu - \mu_0 = RT \ln \frac{p}{p_s} \qquad (2)$$

Th quantity, μ is called the chemical potential and ε is the potential difference from the standard. When the standard is that of free water, ε is shortly called the water potential compared to that of free water surface and its value may be expressed in various units, for example, in joule/mole, capillary water head, adsorption pressure, or equivalent capillary radius etc.

Pressure head from water potential

At equilibrium, the level of Gibbs free energy of gas phase of water is the same as that of liquid phase, therefore there is no apparent water movement between gas phase and liquid phase of water. At equilibrium, the chemical potential, μ_g of gas phase, ie water vapour above the meniscus or adsorbed water surface are equal to that of water, μ_{water} on meniscus surface or adsorbed surface. Therefore, for any change that preserves equilibrium, the change in one is equal to the change in other: $d\mu_g = d\mu_{water}$.

At constant temperature, the change of Gibbs free energy or chemical potential can be expressed as $d = V$ dp. When the pressure on water is increased by $d\ p_{water}$ due to a reversible movement of molecules, its chemical potential changes by V_{water} $d\ p_{water}$. The change in the pressure of the water vapour, $d\ p_g$ corresponds to a change in its chemical potential of $V_g d\ p_g$. Therefore,

$$V_{water}\ d\ p_{water} = V_g\ d\ p_g \qquad (3)$$

If the water vapour is assumed to be a perfect gas, equation (3) can be arranged as following;

$$dp_g/p_g = V_{water}\ dp_{water}/RT \qquad (4)$$

By integration of equation (4) from free water pressure, $p_{freewater}$ to the pressure, $p_{depress}$ depressed by capillary action or adsorption, we can get the vapour pressure, p above the meniscus or adsorbed surface in equilibrium.

Table 2. The relationship between soil air humidity and soil water potentials expressed by various ways in non−agricultural regime.

Relative Humidity (RH, %)	Chemical potential difference ($-\varepsilon$ joule/mole)	pressure (-bar)	Capillary radius (nano meter)
99	25	14.2	104
94	154	87.2	17
84	434	246.5	6
74	751	425.7	3.5
64	1113	631	2.3
54	1536	871	1.7
44	2047	1160	1.3
34	2690	1525	0.97
24	3559	2017	0.73
14	4904	2780	0.53
4	8028	4551	0.33

* Surface tension of water, $7.275 * 10$ N/m

$$\ln \frac{p}{p_s} = \frac{V_{water}}{RT}(p_{freewater} - p_{depress})$$

$$= \triangle p_{water} \frac{V_{water}}{RT} \qquad (5)$$

The dimension of $\triangle p_{water}\ V_{water}$ is the same as ε in equation (2) and so equation (5) is the same as equation (2). $\triangle p_{water}$ is the pressure head.

Equivalent capillary radius and head

In the case of capillary water, the water potential, $\triangle p_{water}\ V_{water}$ or ε can be expressed by capillary rising head or capillary radius. According to Atkins, capillary rise of water is described by the following Laplace equation, when the meniscus is concave as the case of water in soil;

$$p_{depress} = p_{air} - \frac{2\gamma}{r} \qquad (6)$$

and it can be expressed by the capillary rising head;

$$p_{depress} = p_{aor} - \rho\ gH \qquad (7)$$

where $p_{depress}$ is water pressure below the menis-

Table 3. The relationship between soil air humidity and soil water potentials expressed by various ways in agricultural regime.

Head (-m)	pressure (-bar)	capillary radius	Chemical potential difference (-ε, joule/mole)	Relative Humidity (RH, %)
150	15	99nm	26.4	98.93
120	12	123nm	21.1	99.14
50	5	296nm	8.82	99.64
10	1	1.48μm	1.76	99.92
3.3	1/3	4.49μm	0.58	99.97
1	0.1	14.8μm	0.17	99.99
0.5	0.05	29.6μm	0.088	99.99
0.2	0.02	74.2μm	0.0352	99.99
0.02	0.002	742μm	0.0035	99.99
0	0.002	0.0002	7.42mm	0.00035	99.99

cus, p_a is outside pressure above the meniscus, γ is surface tension of water (7.275 * 10⁻¹ N/m), γ is the radius of the capillary tube, ρ is density of water, g is gravitational acceleration, and H is capillary rising head.

Linking above equations, soil water potential may be expressed in various way on the basis of following equation;

$$RT \ln\frac{p}{p_s} = \varepsilon = \triangle p_{water}V_{water} = V_{water}\frac{2\gamma}{r}$$
$$= V_{water}\rho gH \qquad (8)$$

Experimental proof for the relation between vapour pressure and chemical potential

Now, we may call p in equation (8) the indicator for the free energy difference from standard state. The concept can be applied for the calculation of adsorption energy distribution. For example, the concept may also be applied to measure the chemical potential decrease during hydration by sensible hydration heat. When we add water in sulfuric acid, the hydration heat can be calculated as following, using equation (8) related with chemical potential.

$$hydration\ heat = \int_0^w \frac{RT}{18}\ln(\frac{p(w)}{p_s})dw \qquad (9)$$

where $p(w)$ is vapour pressure as a function of water amount, w added into concentrate sulfuric acid. The vapour pressure, $p(w)$ can be calculated through the concentration-density table and the density-water activity table for sulfuric acid solution in CRC.

The adsorption energy as defined the free energy difference from that of free water, that is the heat of adsorption, can be expressed in the same way.

For Lagumuir adsorption as $\frac{p'}{p_s} = \frac{a/a_m}{k(1-a/a_m)}$

Adsorption energy=

$$\int_{w_1}^{w_2} \frac{RT}{18}\ln(\frac{a/a_m}{k(1-a/a_m)})da \qquad (10)$$

We can also calculate numerically the adsorption energy on the basis of the experimental isotherms. Equation (9) and (10) are impossible, when a or p equals zero.

Adsorption distribution on the intensity profile of energy potential

Adsorption isotherms describes the cumulative quantity of adsorbate on the profile of water potential expressed in terms of vapour pressure, although the potential can be expressed in various ways.

Distribution function can be obtained from cumulative function through differentiation. The adsorption quantity distribution is the same as the slopes of experimental adsorption isotherm arranged as a function of the water potential transformed from the vapour pressures. The adsorption energy distribution can be calculated on the basis of adsorption quantity distribution.

MATERIALS AND METHODS

The experimental adsorption isotherms of five

Table 4. The experimental water activity and the equivalent values.

Acid density	Water activity	Equivalent Values		
		Chemical potential difference (-joule/mole)	Capillary pressure (-Bars)	Capillary radius (nano-meter)
1.7870	0.010667	11055.7	6267	0.239
1.7025	0.031387	8427.8	4777	0.314
1.6245	0.072015	6405.7	3631	0.413
1.5655	0.120535	5151.6	2920	0.514
1.4995	0.188915	4057.5	2300	0.625
1.4315	0.313355	2825.4	1601	0.937
1.3900	0.391200	2285.2	1295	1.158
1.3620	0.447776	1956.4	1109	1.353
1.3350	0.505300	1662.0	942	1.593
1.3115	0.55747	1422.8	806	1.861
1.2755	0.64229	1077.9	611	2.456
1.2555	0.69069	901.0	510	2.938
1.2360	0.73228	758.7	430	2.490
1.2045	0.79591	555.8	315	4.764
1.1760	0.84484	410.5	232	6.45
1.1430	0.89514	269.7	152	9.81
1.0920	0.94476	138.4	78.4	19.1
1.0400	0.98000	49.2	27.9	53.8

Table 5. Adsorbed water in the desiccators influenced by humidity (mg/g).

Relative humidity(%)	soil 1	soil 2	soil 3	soil 4	soil 5	silica gel
1.07	5.6	3.9	4.1	4.4	4.6	5.7
3.14	15.3	9.3	9.8	8.1	9.6	11.9
7.20	24.4	20.4	14.2	12.6	14.8	31.1
12.05	30.2	25.1	19.1	16.3	17.9	55.4
18.89	36.6	29.5	21.5	18.6	22.0	102.7
31.33	44.0	38.2	28.4	23.2	27.1	168.1
39.12	46.5	42.1	30.1	25.1	29.9	205.0
44.77	48.4	44.5	31.7	26.0	33.6	233.9
50.52	51.3	49.1	33.5	27.7	35.7	263.2
55.74	58.0	53.8	36.3	29.1	38.2	285.1
64.23	62.1	59.7	39.7	30.7	44.3	309.1
69.07	63.5	65.6	43.1	32.9	47.5	318.1
73.23	66.2	71.8	48.5	36.9	50.4	324.8
79.59	70.4	79.5	54.6	44.5	57.1	330.1
84.48	75.6	94.7	60.6	49.7	61.8	334.2
89.51	80.5	106.8	66.5	59.6	70.7	335.6
94.47	87.3	125.6	75.1	69.5	82.1	336.7
98.00	111.3	158.0	87.5	77.6	104.9	340.9

representative Korean soils and commercial Silica Gel adsorbent (Yakuri Pure Chemicals Co., Osaka, Japan), were built through the vacuum chamber method. The humidity in the vacuum desiccator was controled by sulfuric acid solution in it. The densities of the used acid were determined by weighing method and its equilibrium humidity was calculated based on CRC.

Table 4 shows experimental conditions in terms of acid density, the resulting water activity in the desiccator, the chemical potential difference of the water activity by equation 2, and the pressure head and the equivalent radius of the capillary pores in equilibrium with the water activity calculated by equation (8).

For the experimental proof of the relationship in equation (8) between the vapour pressure in equilibrium and the water potential, numerical

solution of equation (9) was made for the temperature rise due to hydration heat of sulfuric acid solution as shown in program 1. The densest sulfuric acid of 100g contains 97 g of acid and 3 g of water. The applied specific heat 0.4285 cal/gram/ ℃ of pure H_2SO_4 was calculated on the basis of atomic heat capacity of 6 cal/mole/℃ (example, 1=6×3/18 for water, 0.4285=6×7/98 for sulfuric acid). In the program, the integration range was divided into 100 sections for stepwise integration. The program can be understood because of the explanations writen in it.

RESULTS AND DISCUSSION

Table 4 shows the experimental data obtained from the isothermal adsorption in humidity controlled desiccator at room temperature. Among these data, the adsorption values at relative humidity of 98% are very interesting. The biggest moisture adsorption at 98% RH was only 15.8%

for soil 2, which is far lower than the wilting point moisture content of the soil. This point may be considered as a simple proof that soil water regime for plant use locates at soil humidity higher than 98% as shown in Table 2.

From the experimental data, difficulties were found in relation to the roughness of the existing adsorption theory, such as Langmuir, BET, and Aranovich, which may be summarized using following equations in linear forms:

for Langmuir; $\dfrac{p/p_s}{a} = \dfrac{1}{k a_m} + \dfrac{p/p_s}{a_m}$ (11)

for BET; $\dfrac{\frac{p}{p_s}}{a(1-\frac{p}{p_s})} = \dfrac{1}{a_m C} + \dfrac{(C-1)\,p}{a_m C\;\;p_s}$ (12)

for Aranovich; $\dfrac{\frac{p}{p_s}}{a\sqrt{1-\frac{p}{p_s}}} = \dfrac{1}{a_m C} + \dfrac{\frac{p}{p_s}}{a_m}$ (13)

The most characteristic parameters of adsorption is monolayer surface areas, a_m. They were calculated through Gauss method of least squares from the experimental data as shown in Table 6.

Generally, the adsorption isotherms fit with real adsorption of moisture only at low regime of relative humidity. Therefore, only limited number of data, that is 6 or 10 data points in low regime of relative humidity were fed for the calculations. Indeed, the literature states that BET model

Table 6. monolayer surface area determined by various isotherms (m²/g).

000method	Langmuir		BET		Aranovich	
number of data fed	6	10	6	10	6	10
soil 1	203	234	122	97	160	149
soil 2	196	242	110	92	151	149
soil 3	127	151	76	62	100	96
soil 4	100	119	62	50	79	76
soil 5	119	160	73	65	94	102
silica gel	2373	-5333	1055	661	-11179	3667
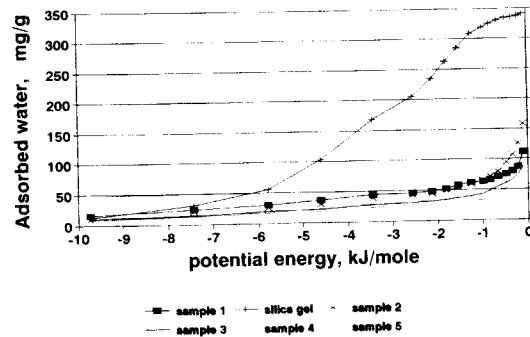
Fig. 1. Cumulative quantity of adsorption on the profile of potential energy.
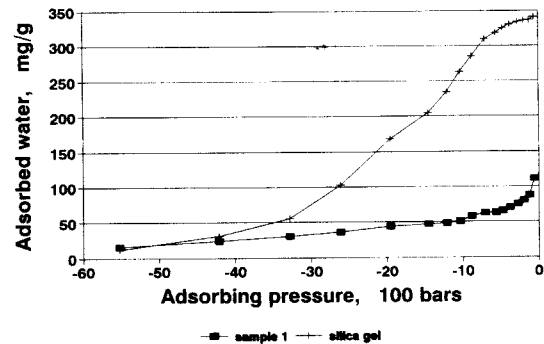
Fig. 2. Cumulative quantity of adsorption on the profile of adsorbing pressure.

works for the adsorption within the range of p/p_0 =0.05~0.35 (Oscik,1982). From the rough estimation of fitting data on the graph, it could be concluded that BET worked in p/p_0 range of about 0. 03~0.32 for the soils studied, whereas Aranovich worked in 0.03~0.65 range.

The BET surface areas for the studied soils vary between 62 to 122m²/g, what is in agreement with literature data (Sokolowska, 1989). Somewhat higher values are calculated from the Aranovich equation: 77~150m²/g. This is consistent with the assumptions on the mechanisms of adsorption process postulated by the above theories. As far as Aranovich postulates vacancies in adsorbed polymolecular layers, more of adsorption is attributed to the surface itself. For BET, more adsorption is regarded to be on poly-
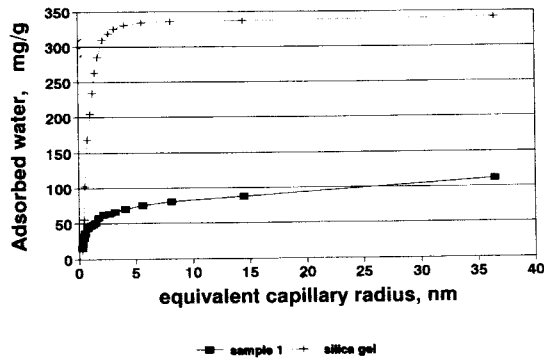
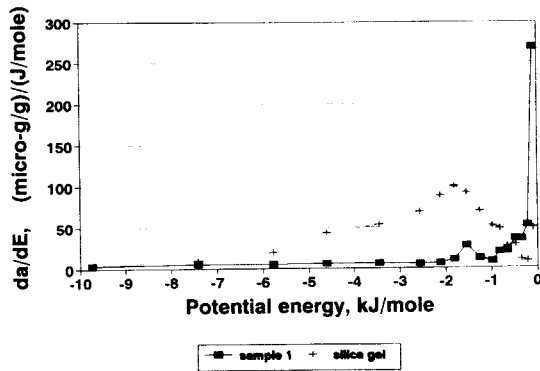Fig. 3. Cumulative quantity of adsorption on the profile of equivalent radius.

Fig. 4. Adsorption distribution on the profile of potential energy.

Fig. 5. Adsorption distribution on the profile of equivalent radius.

layers on it. In the case of Langmuir, the surface area was the largest because all adsorption locates only on mono-layer adsorption on the surface. The variations among the determined surface area show the roughness of existing adsorption models.

If we arrange the experimental data on the scale of other equivalent variables, we can approach other features of adsorption, for example, we can imagine the shape of the adsorbent.

Fig. 1 shows the data in table 4 as arranged on the profile of adsorbed water potential, instead of the usual arrangement on the humidity scale. In these Fig., adsorption characteristics of the 5 soils are very similar to each others. But that of silica gel is quite different from those of soils. And so,
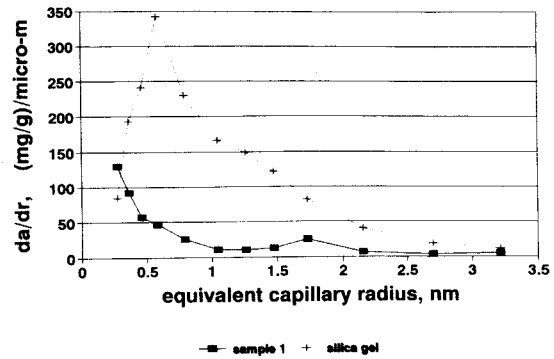
attention was paid only on soil 1 and silica gel for the conveniency in later discussion as shown in Fig. 2. It shows cumulative adsorption properties of soil 1 and silica gel as arranged on the profile of pressure head. But it is the same as Fig. 1, because pressure head is proportional to the chemical potential. And so the pressure head will be omitted in later discussions. Fig. 3 shows cumulative adsorption of water vapour as arranged on the profile of equivalent radius of capillary tube. We can see that there are more micro-pores in silica gel than in soils. Moreover, the dominant radius of the micro-pores is less than 5 nm.

In Fig. 1 and 2, we can see that the increasing rate of adsorption with increasing chemical potential, $da/d\varepsilon$ is far lower for soils than for silica gel up to chemical potential of -1 k joule/mole. It is substantial in the range of -6 to -1 k joule/mole for silica gel. This point indicates that there are many adsorbing sites in silica gel in this regime of water potential. The adsorbing sites may be micro -capillary pores.

As mentioned in the theory section, adsorption isotherms describe the cumulative value and its derivative shows the distribution of adsorbate on the profile of water potential difference from that of free water. And this may be expressed by the equivalent radius of capillary pores. In Fig. 4 and 5, adsorption quantity distribution was shown
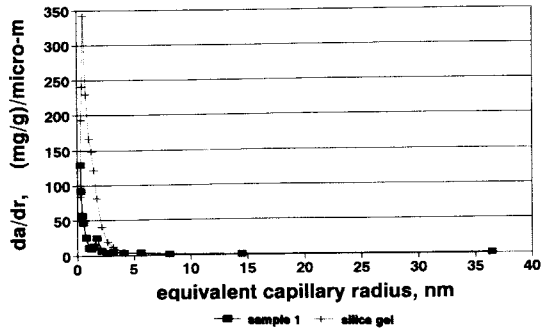
Fig. 6. Adsorption distribution on the profile of equivalent radius.
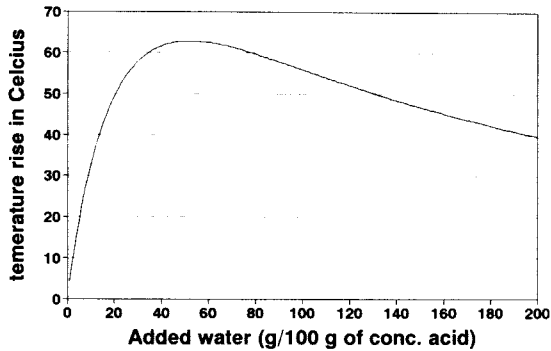

Fig. 7. Temperature rise of conc. sulfuric acid due to hydration heat of added water.

against these variables. In the case of silica gel, substantial amount of adsorbate distributes in the water potential regime of -6 to -1 kjoule/mole, while the adsorbate distribution is very low under 1 k joule/mole in the case of soil.

Fig. 5 and 6 shows more explicitly the nature of the adsorbent in terms of capillary radius. In the case of soil, maximum adsorbate distribution locates at the smallest radius and it is decreasing as the radius is increasing. The dominant radius is slightly bigger than the radius of water molecule, 2 angstrom. Therefore, these regime of small radius may not be capillary regime, but surface adsorption regime. And moisture adsorption in korean soil may be interpreted to be through Wan der Waals forces of surfaces and korean clay may be thought to be flat with negligibleb
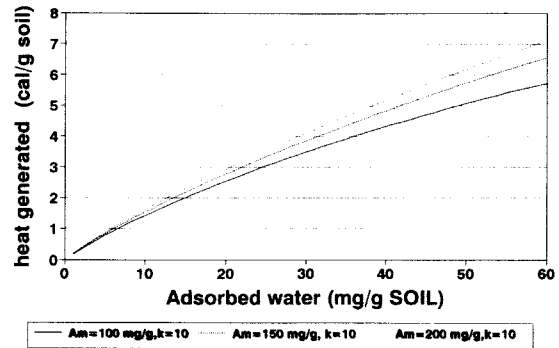
Fig. 8. Heat generation from adsorbed water due to potential decrease by adsorption.

Appendix 1. S/W calculating the temperature rise of H₂SO₄ due to hydration heat.

pores in it. In the case of silica gel, substantial adsorption distributes on the range of 10 to 25 angstrom radius of capillary tube. Therefore, adsorption in silica gel may be thought as capillary holding of water. Silica gel is made from acid precipitates of silicic acid through vacuum dehydration and may contain a lot of micro-pores in it.

The water molecule radius of 2 angstrom was calculated as following;

Volume of water molecule $= 18 * 10^{-6}$ m^3/Avogadro constant

Radius of water molecule = one-third power of one quarter of its volume = 2 angstrom

Final discussion is related with experimental proof of equation (8). The temperature rise due to hydration heat of sulfuric acid is shown in Fig. 7. It was conformed by experiments that the calculated temperature rise fits approximately with experimental results. Therefore, it was concluded that we may apply equation (8) and (10) for the adsorption heat of moisture on soil. Fig. 8 shows adsorption heat as calculated by equation 10. The factor influencing adsorption heat was the maxim amount, a_m of adsorbate on the monolayer adsorbent surface. The equilibrium constant, k also influences the adsorption heat generation, although it is not shown.

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