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동공부피 분포의 계산결과에 미치는 표면장력의 곡률 의존도 효과

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Effect of Curvature Dependency of Surface Tension on the Result of Pore-Volume Distribution Analysis

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요 약 질소의 흡착 등온곡선을 이용하여 흡착체의 동공부피 분포를 계산하는 과정에서 표면장력의 곡률 의존도 고려 효과를 조사하였다. 즉, 장세헌 등에 의한 표면장력의 곡률 의존도 식과 켈빈 식으로부터 주어진 압력에서의 켈빈반경을 구하고, 이것으로부터 흡착체의 동공부피 분포를 계산하였다. 이와 같이하여 얻은 계산 결과를 표면장력의 곡률 의존도를 고려하지 아니한 종래방법에 의한 계산 결과와 비교하였다.

일반적으로 곡률 의존도를 고려해주면 동공부피 분포 곡선의 극대부분이 큰 동공 쪽으로 이동한다. 또한 모세관 응축이 일어나는 상대압력이 종래까지 생각했던 것보다 훨씬 낮아지고 있다. 이러한 효과들은 흡착체의 동공들이 미세해 질수록 더욱 현저하게 일어난다.

Abstract The significance of the curvature dependency correction of surface tension is studied in calculating the pore volume distribution of porous adsorbent from nitrogen adsorption isotherm. That is, Kelvin radii are calculated with curvature dependent surface tension values calculated by Chang et al, and then with these Kelvin radii, pore volume distributions of three porous adsorbents, silica alumina (steam deactivated), silica gel (Davidson 59), and silica gel (Mallinckrodt Standard Luminescent), are calulated. The results are compared with those obtained by the previous method in which surface tension is taken as constant and also with the others obtained by the modelless method proposed by Brunauer et al. The maximum point of the distribution curve shift to the larger pore radius, when the curvature dependency is considered. Furthermore, the relative pressure at which capillary condensation commences is by far the lower than that accepted previously. This effect becomes significant as the pore radius approaches to the micropore range.

Introduction

The method of pore volume distribution calculation of porous substances from the nitrogen adsorption isotherm is developed by Barrett, Joyner, and Halenda[1]. And various refinements have been mabe by many authors[2,3,4]. Accord-

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ing to this method, i) average radius of pores in which capillary condensation takes place at a given finite pressure range is calculated by the use of Kelvin equation, and ii) the amount of capillary condensate in the pore of given radius, hence the pore volume, is calculated from the nitrogen adsorption isotherm.

The amount of nitrogen adsorbed at a given pressure consists of two contributions, one due to the capillary condensation and the other due to the increased multilayer physisorption on the walls of comparatively large vacant pores. Cranston and Inkley[2] have investigated the statistical thickness (t) of physisorbed layer on a number of non-porous adsorbents and found that it was converging to a constant value at a given pressure. Assuming an independency of the statistical thickness on the curvature of the walls of adsorbents, they have calculated the contribution of condensate to the total amount of adsorbate at a given pressure, and obtained pore volume distribution curves for a number of adsorbents.

Broekhoff and deBoer[4], upon the consideration of thermodynamic stability of the physisorbed layer, have shown that the statistical thickness should depend on the curvature of the walls on which physisorption takes place. However, they have shown that the formal thickness of the adsorbed layer on the walls of relatively narrow cylindrical pore is approximately equal to the statistical thickness of the adsorbed layer on the flat surface. In such pores, capillary condensation is expected to take place, before the formal thickness deviates appreciably from the statistical thickness.

On the other hand, the curvature effect on the surface tension is very significant as the curvature increases to the order of 10^6 cm^{-1}. Therefore, the vapor pressure in equilibrium with the curved surface, which is obtained from the Kelvin equation, is quite different depending whether the curvature effect of surface tension is considered or not. For an example, when the pore diameter is about 30 A, the equilibrium relative vapor pressure is less than 0.130 as can be seen in *Table* 1, whereas it is 0.350 if the surface tension is assumed to be independent of the curvature.

In this work, pore volume distribution is calculated using the Kelvin equation with curvature dependent surface tension, and the result is compared with the one obtained with the Kelvin equation in which constant surface tension is assumed.

Curvature Dependency Correction

The radius of closed-end cylindrical pore is calculated by the use of Kelvin equation,

$$r = t - \frac{2\gamma V_m}{RTln(P/P_o)} \qquad (1)$$

Here, P_o and P are the saturation vapor pressure and the vapor pressure at which the capillary condensation takes place in a pore of radius r, respectively; V_m, the molar volume of the liquid; and γ, the surface tension of the curved liquid surface. In the application of this equation, the curvature dependency of the surface tension should be known. The effect on the liquid density may be neglected.

Tolman[5], and Buff and Kirkwood[6] have derived a curvature dependent surface tension equation. Chang et al[7] have also obtained a similar result according to the theory of significant liquid structure;

$$\gamma = \frac{\gamma_\infty}{1-\frac{2\delta}{r-t}} \qquad (2)$$

where, γ_∞ is the surface tension of the flat surface: δ is the distance between the surface of separation and the surface of tension accord-

ing to Tolman, and the unimolecular thickness acording to Chang et al. The unimolecular thickness can be calculated from the geometrical consideration of molecular packing and solid density. Combining equations (1) and (2), the following equation is obtained.

$$r = t - 2\delta - \frac{2\gamma_\infty V_m}{RT\ln(P/P_o)} \qquad (3)$$

Using this equation, the radius (r) of the closed-end cylindrical pore in which capillary condensation takes place at the relative vapor pressure (P/P_o) can be calculated. This radius is converted into the pore diameter and the result is tabulated in the first columm of *Table* 1.

According to Cranston and Inkley, the closed-end cylindrical pore volume (V_{12}) whose pore diameters are in the range of d_1 through d_2 is calculated from the following equation;

$$V_{12} = R_{12}\left(v_{12} - k_{12}\sum_{d_2+\frac{1}{2}\Delta d}^{d_{max}} \frac{d-2t_{12}}{d^2} V_d \Delta d\right) \qquad (4)$$

where,

$$R_{12} = \frac{r_2 - r_1}{\int_{r_1}^{r_2} \frac{(r-t_r)^2}{r^2} dr}$$

$$k_{12} = 4(t_2 - t_1)$$

$$t_{12} = \frac{1}{2}\left(t_1 + t_2\right)$$

Table 1. Vanlues of P/P_0, R_{12} and k_{12} for standard increments of pore diameter.

d	P/P_0	k_{12}	R_{12}	d	P/P_0	k_{12}	R_{12}
313.4	0.931			123.4	0.809		
			1.203			1.30	1.449
303.4	0.929			113.4	0.787		
		0.50	1.209			1.44	1.482
293.4	0.926			103.4	0.764		
		0.52	1.215			1.60	1.520
283.4	0.924			93.4	0.734		
		0.54	1.221			1.80	1.565
273.4	0.921			83.4	0.696		
		0.56	1.228			2.08	1.619
263.4	0.918			73.4	0.646		
		0.58	1.235			2.44	1.682
253.4	0.915			63.4	0.578		
		0.60	1.243			1.40	1.736
243.4	0.911			58.4	0.535		
		0.62	1.251			1.56	1.775
233.4	0.907			53.4	0.484		
		0.65	1.261			1.76	1.814
223.4	0.902			48.4	0.423		
		0.68	1.270			2.00	1.852
213.4	0.897			43.4	0.350		
		0.71	1.281			2.34	1.882
203.4	0.891			38.4	0.265		
		0.75	1.293			2.86	1.890
193.4	0.885			33.4	0.168		
		0.79	1.306			1.34	1.873
183.4	0.879			31.4	0.130		
		0.84	1.320			1.49	1.847
173.4	0.871			29.4	0.090		
		0.89	1.336			1.68	1.799
163.4	0.861			27.4	0.058		
		0.95	1.353			1.93	1.729
153.4	0.850			25.4	0.035		
		1.02	1.373			2.26	1.628
143.4	0.838			23.4	0.016		
		1.10	1.395				
133.4	0.824						
		1.19	1.420				

Table 2. The function $(d-2t)/d^2$ for mean values of t and d in each standard increment of pore diameter. (multiply the value by 10^{-2})

d	313.4—153.4	153.4—83.4	83.4—53.2	53.4—48.4	48.4—43.4	43.4—38.4
313.4—303.4	0.301	0.306	0.310	0.311	0.311	0.313
303.4—293.4	0.310	0.315	0.319	0.320	0.321	0.323
293.4—283.4	0.320	0.325	0.330	0.331	0.332	0.334
283.4—273.4	0.331	0.336	0.341	0.342	0.344	0.345
273.4—263.4	0.342	0.348	0.353	0.354	0.356	0.357
263.4—253.4	0.354	0.360	0.366	0.367	0.369	0.370
253.4—243.4	0.367	0.374	0.380	0.381	0.383	0.385
243.4—233.4	0.380	0.388	0.395	0.396	0.398	0.400
233.4—223.4	0.395	0.404	0.411	0.413	0.415	0.417
223.4—213.4	0.411	0.421	0.429	0.430	0.432	0.435
213.4—203.4	0.429	0.439	0.448	0.450	0.452	0.454
203.4—193.4	0.448	0.459	0.469	0.471	0.473	0.476
193.4—183.4	0.468	0.481	0.492	0.494	0.497	0.500
183.4—173.4	0.491	0.505	0.517	0.519	0.522	0.526
173.4—163.4	0.515	0.531	0.545	0.548	0.551	0.555
163.4—153.4	***	0.561	0.576	0.579	0.583	0.587
153.4—143.4		0.593	0.611	0.614	0.619	0.624
143.4—133.4		0.630	0.650	0.654	0.659	0.665
133.4—123.4		0.671	0.694	0.699	0.705	0.712
123.4—113.4		0.718	0.745	0.751	0.758	0.766
113.4—103.4		0.772	0.804	0.811	0.819	0.828
103.4—93.4		0.833	0.873	0.881	0.891	0.902
93.4—83.4		***	0.953	0.964	0.976	0.990
83.4—73.4			1.049	1.063	1.078	1.096
73.4—63.4			1.165	1.182	1.202	1.226
63.4—58.4			1.267	1.289	1.315	1.355
58.4—53.4			***	1.370	1.400	1.435
53.4—48.4				***	1.496	1.538
48.4—43.4					***	1.654
						***

Table 2. continued

d	38.4—33.4	33.4—31.4	31.4—29.4	29.4—27.4	27.4—25.4	25.4—23.4
313.4—303.4	0.314	0.315	0.316	0.317	0.318	0.319
303.4—293.4	0.324	0.325	0.326	0.327	0.328	0.329
293.4—283.4	0.335	0.336	0.337	0.338	0.339	0.340
283.4—273.4	0.347	0.348	0.349	0.350	0.351	0.352
273.4—263.4	0.359	0.360	0.361	0.363	0.364	0.365
263.4—253.4	0.372	0.374	0.375	0.376	0.378	0.379
253.4—243.4	0.387	0.388	0.390	0.391	0.392	0.394
243,4—233.4	0.402	0.404	0.405	0.407	0.408	0.410
233.4—223.4	0.419	0.421	0.422	0.424	0.429	0.428
223.4—213.4	0.437	0.440	0.441	0.443	0.445	0.447
213.4—203.4	0.457	0.460	0.461	0.463	0.465	0.468
203.4—193.4	0.479	0.482	0.484	0.486	0.488	0.491
193.4—183.4	0.503	0.506	0.508	0.510	0.513	0.516
183.4—173.4	0.530	0.533	0.535	0.538	0.541	0.544
173.4—163.4	0.559	0.563	0.566	0.568	0.572	0.575
163.4—153.4	0.592	0.597	0.599	0.603	0.606	0.610
153.4—143.4	0.630	0.634	0.638	0.641	0.645	0.650
143.4—133.4	0.672	0.677	0.681	0.685	0.690	0.695
133.4—123.4	0.720	0.726	0.730	0.735	0.741	0.747
123.4—113.4	0.775	0.782	0.788	0.793	0.800	0.807
113.4—103.4	0.839	0.848	0.854	0.861	0.869	0.878
103.4—93.4	0.915	0.926	0.934	0.942	0.951	0.962
93.4—83.4	1.006	1.020	1.029	1.036	1.051	1.064
83.4—73.4	1.117	1.134	1.145	1.158	1.173	1.190
73.4—63.4	1.253	1.276	1.291	1.308	1.327	1.350
63.4—58.4	1.379	1.407	1.426	1.448	1.484	1.500
58.4—53.4	1.477	1.524	1.533	1.558	1.600	1.621
53.4—48.4	1.588	1.628	1.656	1.686	1.721	1.779
48.4—43.4	1.715	1.765	1.799	1.836	1.879	1.929
43.4—38.4	1.861	1.924	1.967	2.014	2.068	2.131
38.4—33.4	***	2.110	2.165	2.226	2.296	2.377
33.4—31.4		***	2.324	2.400	2.486	2.585
31.4—29.4			***	2.509	2.607	2.720
29.4—27.4				***	2.739	2.869
27.4—25.4					***	3.033
25.4—23.4						***

Here, v_{12} is the total volume of nitrogen adsorbed in the pressure range of consideration; $V_d \Delta d$, the volume of pores having diameters between $\left(d-\frac{1}{2}d\right)$ and $\left(d+\frac{1}{2}d\right)$; d_{max}, the diameter of the largest pore. The values of k_{12} and R_{12} are given in the third and fourth columns of *Table* 1 for suitable pore-diameter increments, and the factor $(d-2t)/d^2$ is given in *Table* 2 for values of d larger than d_2. The second term in the bracket of equation (4) represents the volume of the nitrogen which increases the thickness of the adsorbed layer on the walls of larger vacant pores.

Since equation (4) can be applied to the de-

Table 3. Calculation of pore-size distribution of a silica gel (Davidson 59)

d (Å)	P/P_0	v_{12} (ml/g)	$v_{12}-k_{12}\sum$ (ml/g)	V_{12} (ml/g)	$\sum V_{12}$ (ml/g)	S_{12} (m^2/g)	$\sum S_{12}$ (m^2/g)
313.4	0.931						
		0.0010	0.0010	0.0012	0.0012	0.156	0.156
303.4	0.929						
		0.0013	0.0012	0.0015	0.0027	0.202	0.358
293.4	0.926						
		0.0015	0.0015	0.0018	0.0045	0.252	0.610
283.4	0.924						
		0.0018	0.0017	0.0021	0.0066	0.306	0.916
273.4	0.921						
		0.0018	0.0017	0.0021	0.0087	0.318	1.234
263.4	0.918						
		0.0015	0.0015	0.0018	0.0105	0.284	1.518
253.4	0.915						
		0.0035	0.0035	0.0043	0.0148	0.692	2.210
243.4	0.911						
		0.0033	0.0032	0.0040	0.0188	0.671	2.881
233.4	0.907						
		0.0050	0.0050	0.0062	0.0250	1.087	3.968
223.4	0.902						
		0.0061	0.0061	0.0077	0.0327	1.402	0.370
213.4	0.897						
		0.0100	0.0099	0.0126	0.0453	2.418	7.788
203.4	0.891						
		0.0116	0.0115	0.0147	0.0600	2.972	10.760
193.4	0.885						
		0.0153	0.0151	0.0196	0,0796	4.157	14.917
183.4	0.879						
		0.0281	0.0279	0.0364	0.1160	8.160	23.077
173.4	0.871						
		0.0631	0.0627	0.0828	0.1988	19·663	42.740
163.4	0.861						
		0.2246	0.2237	0.3028	0.5016	76.471	119.211
153.4	0.850						
		0.1967	0.1840	0.2664	0.7680	71.802	191.013
143.4	0.838						
		0.0835	0.0788	0.1098	0.8778	31.791	222.804
133.4	0.824						
		0.0515	0.0456	0.0648	0.9426	20.189	242.993
123.4	0.809						
		0.0263	0.0193	0.0279	0.9705	9.433	252.426
113.4	0.787						
		0.0288	0.0207	0.0307	1.0012	11.337	263,763
103.4	0.764						
		0.0288	0.0195	0.0296	1.0308	12.028	275.791
93.4	0.734						
		0.0225	0.0116	0.0182	1.0490	8.222	284.013
83.4	0.696						
		0.0250	0.0119	0.0192	1,0682	9.811	293,824
73.4	0.646						

sorption branch as well as to the adsorption branch, it is applied to the desorption branches of silica gel (Davidson 59), silica alumina (steam deactivated), and silica gel (Mallinckrodt Standard Luminescent). The procedure of pore volume distribution calculation adopted in this work is the same as the one proposed by Cranston and Inkley except the correction of the curvature dependency of surface tension. The adsorption isotherm for the above three samples have been reported previously by Cranston and Inkley[2], and Brunauer et al[8]. The typical result of calculation for Davidson 59 is given in *Table* 3. The sixth column of the *Table* 3 is the cumulative volume. The seventh column is the inner surface area in square meters per gram of adsorbent, which can be obtained from the fifth column by the use of following equation;

$$S_{12} = \frac{4aV_{12}}{d'} \times 10^4$$

where, d' is the mean diameter of the corresponding region, and "a" is a factor, $1,584 \times 10^{-3}$, which results from the geometrical consideration of close packing. The last column of the table is the cumulative surface area.

The Result and Discussions

From *Table* 3, cumulative pore volume $V(r)$ is plotted against pore radius r. The pore volume distribution curve, then, can be obtained by converting this plot to the $\Delta V(r)/\Delta r$ versus r curve. *Figures* 1, 2, and 3 are the pore volume distribution curves obtained in this way for the three samples. In each *figure*, both results, one with curvature dependency correction and the other without correction, are shown for comparison. The result with curvature correction is quite similar in its shape to the one without correction, but the maximum has shifted to the larger pore radius side.

The result of this shifting has significant meanings; firstly, the pore volume distribution calculated by the previous method gives a comparatively large negative deviation. In the case of silica alumina, the mean pore radius calculated by the proposed way is about 20 A, while the previous method gives 15 A. This is quite a large relative difference. Secondly, if the curvature dependency of surface tension is taken into account, the micro pore condensation occurs at the further lower relative vapor pressure than that accepted before. In other words, the vapor pressure in equilibrium with the condensate in the pore of given radius would be quite different from the vapor press-

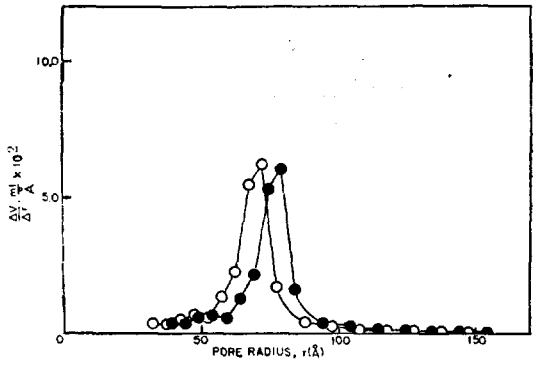

Fig. 1. Pore volume distribution of a silca gel (Davidson 59); ●corrected; ○uncorrected.

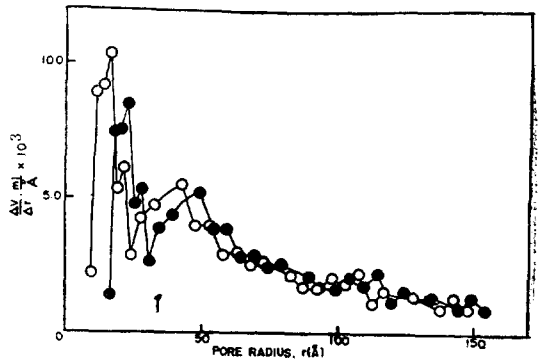

Fig. 2. Pore volume distribution of a silica gel (Mallinckrodt Standard Luminescent): ● corrected; ○ uncorrected.

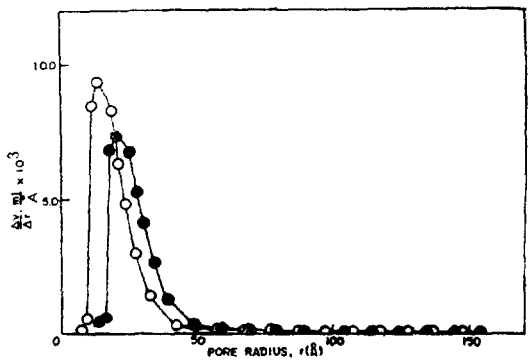

Fig. 3. Pore volume distribution of a silica alumina (heat deactivated); ●corrected; ○uncorrected.

ure calculated assuming the surface tension is constant. This discrepency becomes more prominent as the pore radius approaches to the lower limit of the transition pore. For example, when the pore diameter is about 30 A, relative vapor pressure in equilibrium with the pore condensate is less than 0.13 as can be seen in *Table* 1, whereas it is 0.35 if the surface tension is assumed to be independent of the curvature.

As can be seen from *Figures* 2 and 3, silica gel (Mallinckrodt) and silica alumina have both transition and micro pores. This result coincide with the *t*-plot obtained by Brunauer et al[8]. Although the calculations are performed to the micro pore region, it is meaningless but for the purpose of comparison. It is inadequate to apply the thermodynamically derived Kelvin equation to the micro pores. For Davidson 59, the cumulative surface area is 332.7 m^2/g according to Cranston and 335 m^2/g according to the corrected medelless method of Brunauer. The observed B.E.T. area is 273 m^2/g. The cumulative surface area calculated by the proposed way is very close to the B.E.T. area, being 293.8 m^2/g. The comparison of cumulative surface area of the other two samples to the B.E.T. area is meaningless as these adsorbents have micro pores.

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