Liquid-Phase Capillary Condensation and Adsorption Isotherm

Minoru Miyahara, Masahito Kato, and Morio Okazaki
Dept. of Chemical Engineering, Kyoto University, Kyoto 606-01, Japan

A "capillary condensation" in liquid phase was analyzed theoretically and experimentally, in which a solute in solvent could be separated out as a liquid into small pores by capillary effect. The "liquid-phase capillary condensation" is defined as capillary phase separation. The separated phase is counted as "adsorbed" amount on porous materials. The relation between the concentration and a critical radius of the phase separation was derived. A new method to estimate liquid-phase adsorption isotherms of adsorbates with limited solubility from pore-size distribution of solids is based on this concept. The amount absorbed consists of the separated phase and adsorption on surface expressed with a single parameter. While the surface adsorption alone could not explain measured isotherms, this model showed good agreements between experimental and estimated isotherms for adsorption of four kinds of aromatic compounds from aqueous solution onto three categories of porous solids to demonstrate the significance of the capillary phase separation. The applicability of the method to solid solutes is also discussed.

Introduction

Pore sizes as well as the physicochemical nature of solids play an important role in many fields such as physical adsorption, chemisorption, and catalysis. In gaseous-phase adsorption, the so-called Kelvin condensation, or capillary condensation may contribute to the amount adsorbed appreciably in higher range of the relative pressure, especially for mesoporous solids. The capillary condensation can be interpreted as follows: the vapor-liquid equilibrium of the adsorbate is deviated from that with a flat liquid surface by the curvature of the liquid surface which results from the contact with walls of the narrow pores. This phenomenon is reversely utilized for characterization of porous solids (for example, Barrett et al., 1951; Wheeler, 1955; Cranston and Inkley, 1957; Dollimore and Heal, 1964), especially in the mesopore range, which is now quite popular and getting more like a routine work. The effect of pore sizes on the adsorption in liquid phase, however, still remains unclear. Only a limited number of research results have lighted up the effect and hence almost no guideline has been established for the desirable nature of the pore structure of an adsorbent in liquid-phase adsorption.

A similar situation in liquid phase to the capillary condensation of gaseous phase may be as follows: a hindered liquid-liquid equilibrium could stand within a pore because of the presence of a curved interface of the two liquid phases. In other words, a solute-rich phase could be equilibrium with a solvent-rich phase at a lower concentration than the saturated. Patrick and co-workers (Patrick and Jones, 1925; Patrick and Eberman, 1925) first suggested the possibility of this phenomenon and intuitively proposed a Kelvin-type equation for the relation between the pore radius and the concentration. However, no sound basis for derivation of the equation nor quantitative tests with experimental data were presented. In spite of its importance not only in the field of adsorption but also in many relevant fields, no significant advance seems to have been made since then. As a matter of fact, many prominent books on adsorption did not mention the phenomenon, except the one by Kipling (1965). As a result, the nature of this phenomenon remains unclear. Here we call this phenomenon capillary phase-separation (CPS).

If such a solute-rich phase holds within a pore at a concentration less than the saturation, the apparent amount absorbed in liquid phase consists of at least two *adsorption* modes, namely, one associated with the affinity to the surface itself

---

Correspondence concerning this article should be addressed to M. Miyahara.
Current address of M. Kato: Ajinomoto Co., Inc., Yokka-ichi 510, Japan.

and the other with the CPS. Hence, the knowledge of the relation between the concentration and the curvature enables us to interpret the adsorption isotherms of adsorbates with limited solubilities onto porous solids to some extent, especially in higher range of relative concentration.

The purpose of this work has been to clarify the effect of pore characteristics of a solid on liquid-phase adsorption isotherms for solutes with limited solubility, through a quantitative treatment of the relation between the curvature of the interface and the concentration. Further, utilizing this concept, we have proposed a method to estimate liquid-phase adsorption isotherms from the information of pore characteristics, especially from nitrogen isotherms. The method is successfully applied to adsorption isotherms of aromatic compounds from aqueous solution.

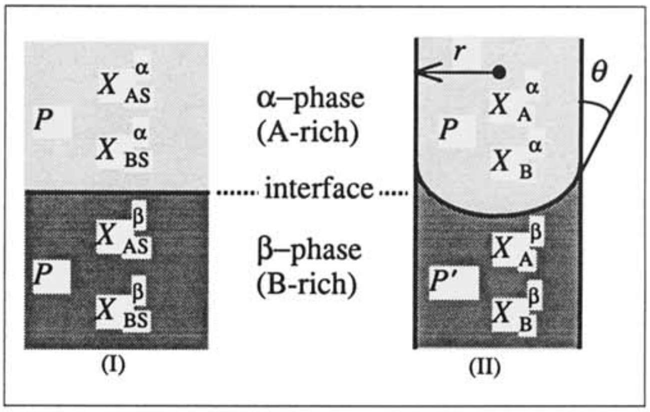

Figure 1. Liquid-liquid equilibria with flat and curved interfaces.

Liquid-Liquid Equilibrium with Curved Interface

Suppose that we have two equilibrium states including components A and B as shown in Figure 1, namely, one with a flat interface and the other with a curved one existing within a pore which has a cylindrical shape, as an example, with radius r. The interface with the interfacial tension σ contacts to the wall with the contact angle θ. The components A and B correspond to a solvent and an adsorbate, respectively, in the case of adsorption. Besides, α-phase corresponds to a bulk phase and β-phase contributes to the amount adsorbed.

The chemical potentials, μ, of each component in both states are considered with the following assumptions: Molar volumes, ν, of dilute components are approximated as that of the infinite dilution, and those of concentrated components as that of pure states, and they are constant against pressure. Equating corresponding potentials, we obtain:

$$\mu_A^o+\nu_A^o(P-P_o)+RT\ln a_{AS}^{\alpha}=\overset{*}{\mu}_A+\overset{*}{\nu}_A(P-P_o)+RT\ln a_{AS}^{\beta} \quad (1)$$

$$\overset{*}{\mu}_B+\overset{*}{\nu}_B(P-P_o)+RT\ln a_{BS}^{\alpha}=\mu_B^o+\nu_B^o(P-P_o)+RT\ln a_{BS}^{\beta} \quad (2)$$

$$\mu_A^o+\nu_A^o(P-P_o)+RT\ln a_A^{\alpha}=\overset{*}{\mu}_A+\overset{*}{\nu}_A(P'-P_o)+RT\ln a_A^{\beta} \quad (3)$$

$$\overset{*}{\mu}_B+\overset{*}{\nu}_B(P-P_o)+RT\ln a_B^{\alpha}=\mu_B^o+\nu_B^o(P'-P_o)+RT\ln a_B^{\beta} \quad (4)$$

Subtracting Eq. 1 from Eq. 3:

$$RT\ln\frac{a_A^{\alpha}}{a_{AS}^{\alpha}}=\overset{*}{\nu}_A(P'-P)+RT\ln\frac{a_A^{\beta}}{a_{AS}^{\beta}} \quad (5)$$

Similarly from Eqs. 2 and 4:

$$RT\ln\frac{a_B^{\alpha}}{a_{BS}^{\alpha}}=\nu_B^o(P'-P)+RT\ln\frac{a_B^{\beta}}{a_{BS}^{\beta}} \quad (6)$$

The mechanical balance of phases is expressed by the Young-Laplace equation:

$$P'-P=-2\sigma\cos\theta/r \quad (7)$$

For the activities, Raoult's law is assumed for concentrated components and Henry's law for dilute components. Then the ratios of the activities can be substituted by the ratios of mole fractions. Thus:

$$\frac{X_A^{\alpha}}{X_{AS}^{\alpha}}=\frac{X_A^{\beta}}{X_{AS}^{\beta}}\exp(-\phi_A) \quad (8)$$

$$\frac{X_B^{\alpha}}{X_{BS}^{\alpha}}=\frac{X_B^{\beta}}{X_{BS}^{\beta}}\exp(-\phi_B) \quad (9)$$

where

$$\phi_A=\frac{2\sigma\overset{*}{\nu}_A\cos\theta}{rRT} \quad (10)$$

$$\phi_B=\frac{2\sigma\nu_B^o\cos\theta}{rRT} \quad (11)$$

Since $X_A^{\alpha}=1-X_B^{\alpha}$ and $X_A^{\beta}=1-X_B^{\beta}$, Eq. 8 can be rearranged to be:

$$X_B^{\beta}=1-(1-X_B^{\alpha})\frac{X_{AS}^{\beta}}{X_{AS}^{\alpha}}\exp(\phi_A) \quad (12)$$

Substituting Eq. 12 into Eq. 9 and rearranging, we obtain the equation for the relation between the concentration and the curvature as follows:

$$\frac{X_B^{\alpha}}{X_{BS}^{\alpha}}=\frac{X_{AS}^{\alpha}-X_{AS}^{\beta}\exp(\phi_A)}{X_{AS}^{\alpha}X_{BS}^{\beta}\exp(\phi_B)-X_{BS}^{\alpha}X_{AS}^{\beta}\exp(\phi_A)} \quad (13)$$

Equation 13 corresponds to the Kelvin equation of gaseous phase. A rather complicated form is obtained because two components contribute to the phase equilibrium in liquid phase. For the other shape of the pore, the corresponding curvature should be substituted for $2\cos\theta/r$.

To simplify Eq. 13, a few more assumptions are made: $\theta=0$, the solubility of A in β-phase is small so that the ratio $X_B^{\beta}/X_{BS}^{\beta}$ is close to unity, and the concentrations of B-component in α-phases are small so that the ratio $X_B^{\alpha}/X_{BS}^{\alpha}$ can be approximated by relative concentration C/C_S. The resulting equation is:

$$\frac{C}{C_s}=\exp\left(-\frac{2\sigma v_B^o}{rRT}\right) \tag{14}$$

Now we obtain the same equation as that proposed by Patrick and Eberman (1925). One has to be careful whether Eq. 14 holds in a given system. All the assumptions made above except the one related to the contact angle are valid if each phase can be treated as an ideal dilute solution. Hence, the equation is applicable to aqueous solutions of, for example, aromatic compounds or aliphatic compounds because they have quite small solubilities in general.

The derivation made so far is for liquid-liquid equilibrium. However, almost the same treatment could be made for solid-liquid equilibrium. In this case, β-phase consists of only the B component in general. Then, Eq. 14 might be applicable to solid-liquid equilibria as far as the concave interface, as shown in Figure 1, and the mechanical balance between the phases hold. The applicability will be discussed later.

Method of Estimating Liquid-Phase Adsorption Isotherms

The solute-rich phase of the hindered liquid-liquid equilibrium within a pore would be counted as adsorbed amount at a lower concentration than the saturated. Accordingly, the total amount adsorbed consists of two modes of *adsorption*, namely, the *real* adsorption which arises from physicochemical nature of the adsorbent surface, and the apparent amount which arises from the pore characteristics of the adsorbent especially in the mesopore range. This concept is quite the same as that employed in pore analysis of mesoporous solids by physisorption of gas. The two adsorption isotherms, namely, the isotherm in liquid phase and that in gaseous phase can now be connected by the pore-size distribution function. Hence, a liquid-phase adsorption isotherm can be estimated by taking the reversed procedure of pore analysis starting from the pore-size distribution.

Among the existing pore analysis methods, the one proposed by Dollimore and Heal (1964) was used to determine the distribution in this study. The determined distribution should be recognized as an *effective* pore-size distribution because the pores may not be cylindrical as assumed.

For the estimation of liquid-phase isotherms, the information of the amount of the *real* adsorption is needed. This amount could be measured by adsorption experiments employing a nonporous solid. However, only a limited number of the measurements has been made so far, especially in higher range of relative concentration, as reported by Valenzuela and Myers (1989). It would be convenient if this amount could be expressed by a simple equation with less number of unknown parameters. Among the existing equations for surface adsorption (for example, Frenkel, 1946; Halsey, 1948; Jura and Harkins, 1944), the amount was assumed to follow the Frenkel-type formula:

$$t=t_o\left[\ln\frac{X_{BS}^{\alpha}}{X_B^{\alpha}}\right]^{-1/3}\cong t_o\left[\ln\frac{C_s}{C}\right]^{-1/3} \tag{15}$$

The equation is thought to be appropriate for a solute with nonspecific interaction, for example, van der Waals forces. For a solute with specific interaction with surface, Eq. 15 may fail to express the real adsorption. The validity of this formula was examined using graphite as a nonporous solid and will be discussed later.

Since the pore-size calculation from nitrogen adsorption also gives the surface area distribution, the amount adsorbed on the surface of a given range of pore radius can be calculated with the available area and Eq. 15.

Using Eq. 15, we have only one unknown parameter, t_o, for the estimation of liquid-phase adsorption isotherms from the pore-size distribution function. Hence, in principle, the isotherm could be estimated with only one measured point for a given system. The t_o value might be unique for a given combination of solution and base material of adsorbent by definition. The characteristics of the parameter will be discussed later.

The liquid-phase adsorption isotherms were estimated with the reversed procedure of the pore analysis of Dollimore and Heal (1964). It is briefly explained below. The CPS phase could be approximated as a pure phase of adsorbate in this calculation because of the small solubility of water into the β-phase. A postulated value of t_o enabled the following calculation. The calculation started from a saturated state in which all the pores were filled with adsorbate. The pore-size distribution obtained from nitrogen adsorption consists of some groups of pores with finite ranges in pore radius. First, the group of pores with the largest radii was subjected to consideration to give a calculated point of adsorption isotherm, at which this group of pores had no CPS phase and the real adsorption only existed. Other groups of pores, with smaller radii, had CPS within the pores. The concentration corresponding to this condition could be calculated since the lower limit of the pore radius of this group, r_{p1}, should satisfy the equation:

$$r_{p1}=r+t \tag{16}$$

and since both the critical radius r and the thickness t are functions of the concentration as given by Eqs. 13 or 14 and 15. The amount adsorbed at this concentration could be calculated by knowing the difference from the saturation, ΔV_1, which should be the volume of the CPS phase in this range of pores, ΔV_{c1}:

$$V_1=V_{\text{sat}}-\Delta V_1=V_{\text{sat}}-\Delta V_{c1} \tag{17}$$

The corresponding mass was calculated using the density of the adsorbate.

The second point could be calculated similarly but the procedure was somewhat complicated because the difference in the surface adsorption in the first group of pores ΔV_{s1} contributed to the total difference in addition to the volume of the CPS phase in the second group of pores:

$$V_2=V_1-\Delta V_2=V_1-(\Delta V_{c2}+\Delta V_{s1}) \tag{18}$$

Similarly, we could calculate the $(i+1)$th point from the volume of the CPS phase in the $(i+1)$th group of pores ΔV_{ci+1} and the difference in surface adsorption in larger pores ΔV_{si}:

$$V_{i+1}=V_i-\Delta V_{i+1}=V_i-(\Delta V_{ci+1}+\Delta V_{si}) \tag{19}$$

Table 1. Physical Properties of Adsorbates

Adsorbate	Molecular Weight (kg/mol)	Density[*] (kg/m^3)	Interfacial Tension with Water Phase[**] (N/m)	Saturated Conc. with Water[†] (mol %)
Nitrobenzene	123.11×10^{-3}	1.19×10^{3}	25.7×10^{-3}	0.0320
Benzene	78.11×10^{-3}	0.86×10^{3}	34.1×10^{-3}	0.0422
Aniline	93.13×10^{-3}	1.01×10^{3}	5.8×10^{-3}	0.768
Benzonitrile	103.12×10^{-3}	0.99×10^{3}	28.0×10^{-3}[‡]	0.084[s]
Benzoic Acid	122.13×10^{-3}	1.32×10^{3}	22.2×10^{-3}[+]	0.072[**]
p-Nitrotoluene	137.13×10^{-3}	1.16×10^{3}	26.9×10^{-3}[+]	0.0065[s]

[*] Daubert and Danner (ed.), 1985.
[**] Hata (ed.), 1984.
[†] Sørensen and Arlt, 1979.
[‡] Reddy Karri and Mathur, 1988.
[+] estimated by the method of Nakai, 1969.
[s] measured in this work.

As the calculation proceeded, ΔV_{si} consisted of more number of contributions since pores only with the surface adsorption increased. The calculation proceeded until the concentration became small enough so that the CPS phase would not contribute to the amount adsorbed, usually around $C/C_s = 0.2$. Note that the estimated isotherms consist of discrete points since the calculation procedure is based on the discrete data points of pore-size distribution. For more details, the pore-size calculation by Dollimore and Heal (1964) should be referred to.

The t_o was chosen to show the best fit of the calculated isotherm to the experimental data. The validity of the determined value of t_o is discussed later.

Experimental

The physical properties of the adsorbates used are summarized in Table 1. In addition to the four adsorbates which have liquid-liquid equilibrium with water, benzoic acid, and *p*-nitrotoluene were used to examine the applicability of the method to solid solutes. The reagents of research grade provided by Wako Pure Chemicals Inc. were used with no further purification. The adsorbents are also summarized in Table 2. The SPs, whose chemical structure is of stylene-divinylbenzene block co-polymer, and ECs (electric conductive porous carbonblacks) are typical mesoporous solids. So the CPS would show a large contribution for these adsorbents. In addition to porous adsorbents of different origin, a nonporous solid was employed to examine the validity of using Eq. 15 for the statistical thickness of the adsorbed layer in liquid phase. Before experimental usage, the carbonaceous adsorbents were washed with distilled water and evacuated at 383 K for 24 h while the macroreticular adsorbents were washed first with methanol before done with distilled water, and then evacuated at 333 K for 48 h.

Table 2. Physical Properties of Adsorbents

Adsorbent	Class	Nitrogen Surface Area (m^2/kg)	Pore Volume (m^3/kg)
EC	Porous	670×10^{3}	0.72×10^{-3}
EC600JD	carbonblack	$1{,}100\times10^{3}$	1.32×10^{-3}
SP900	Macroreticular	580×10^{3}	0.84×10^{-3}
SP206	adsorbent	430×10^{3}	0.42×10^{-3}
LGK-1	Activated	$1{,}000\times10^{3}$	0.55×10^{-3}
LGK-3	carbon	$1{,}460\times10^{3}$	0.84×10^{-3}
Graphite	Nonporous carbon	9.9×10^{3}	—

The measurements were made by a batch adsorption method. The adsorbent was added to 300 mL solution in an Erlenmeyer flask stopped by a teflon-sealed screw cap to prevent solutes from evaporative loss. The flask was shaken in a thermostatted bath for 7 days. The initial and equilibrium concentration was determined by an ultraviolet spectrophotometer (Shimadzu UV-260). The amount adsorbed was calculated by a mass balance: $q = L(C_i - C)/W$.

Nitrogen adsorption isotherms at 78 K were measured by an automated sorption measuring apparatus, BELSORP produced by Bel Japan, Inc. The principle of the measurement was the volumetric method. A review for such instruments is given by Mikhail and Robens (1983).

Results and Discussion

Estimation of liquid-phase adsorption isotherms

The pore-size distributions of the adsorbents were determined from nitrogen adsorption isotherms, as shown in Figure 2. All the porous solids more or less showed hysteresis. The distributions shown in the figure were calculated using adsorption branches of the isotherms. The question concerning

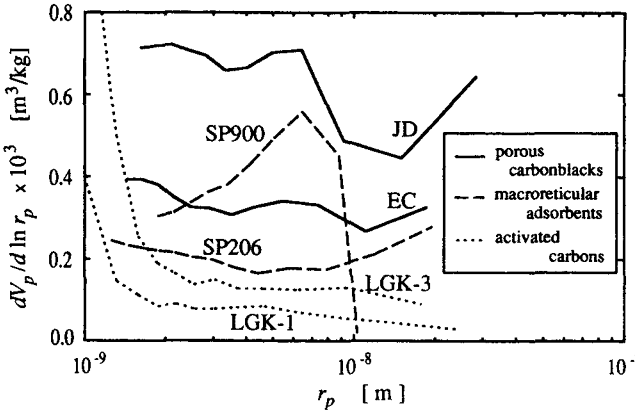

Figure 2. Pore-size distributions from nitrogen adsorption.

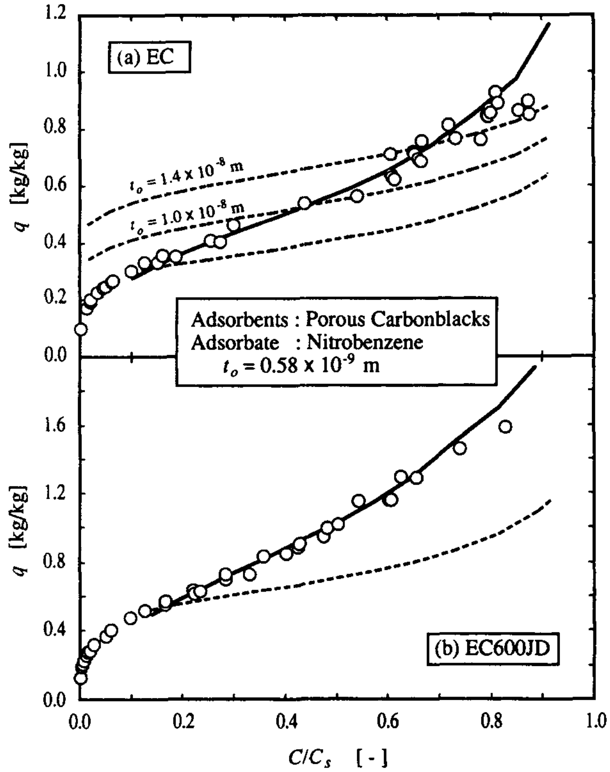

Figure 3. Adsorption isotherms for nitrobenzene from aqueous solution onto ECs.

which branch to use for pore-size calculations has been under discussion for many years. However, the purpose of the calculation made here is not to determine the pore-size distribution itself but to obtain information for the estimation of liquid-phase adsorption isotherms. The adsorption branches of the hysteresis were used here for the "pore-size" calculation since liquid-phase adsorption isotherms in general are considered to be that of the adsorption branch of the hysteresis, if any. The obtained distribution should be considered as a projection of the nitrogen isotherm which reflects adsorption characteristics related to pore structure of the adsorbent. We could at least expect from Figure 2 that the CPS phase would contribute to the amount adsorbed for the porous carbonblacks and the macroreticular adsorbents since they had relatively large distribution in the so-called mesopore range.

The experimental and estimated results of the adsorption of nitrobenzene from aqueous solution onto porous adsorbents are shown in Figures 3-5. Each figure shows the results of two solids of different pore characteristics but of the same origin. Separate determinations of t_o for two solids of a group showed similar values to each other. Then, a common value of the parameter t_o was used for each group of adsorbents of the same origin. The solid lines show the estimated results based on the present method while the broken lines, for reference, show estimation using Eq. 15 only. As seen from the figures, the solid lines agree fairly well with the experimental data of various kinds of the adsorbents to show the validity of the method proposed.

The significance of the contribution of CPS is demonstrated in more detail in Figure 3a, in which some other broken lines with different values of t_o were calculated. As seen, the surface

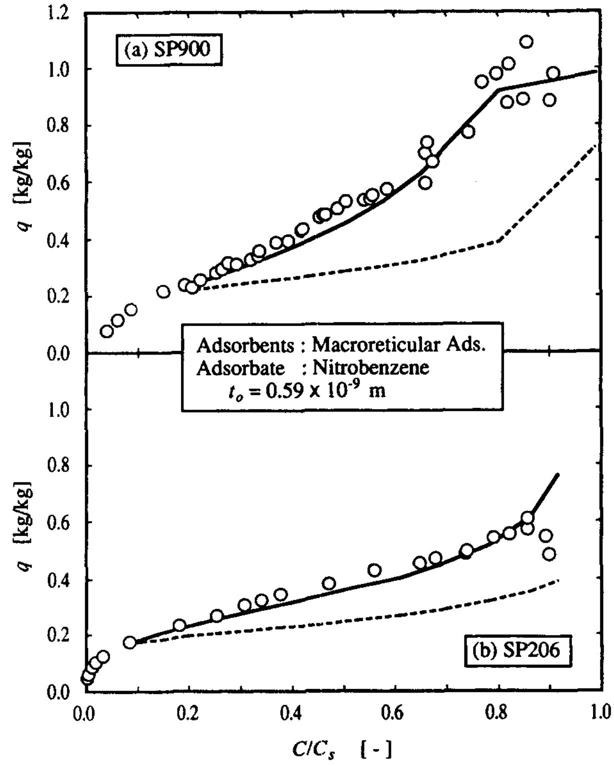

Figure 4. Adsorption isotherms for nitrobenzene from aqueous solution onto SPs.

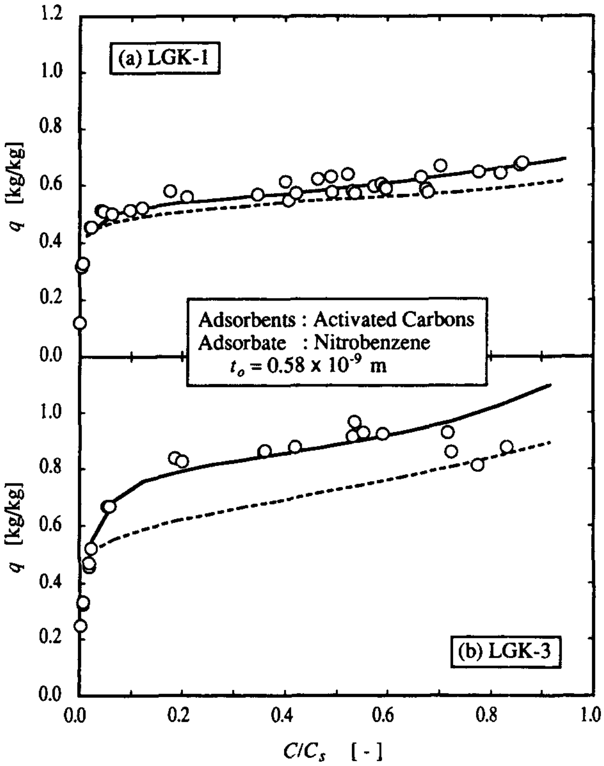

Figure 5. Adsorption isotherms for nitrobenzene from aqueous solution onto LGKs.

adsorption alone could not explain the steep rise of the experimental data. Attempts with surface adsorption alone failed similarly in other systems though only one broken line is shown in the figures.

EC600JD in Figure 3b has almost twice larger pore volume than EC, which resulted in almost twice larger amount of adsorption from solution. Here a single value of t_o is surely enough for the two sets of experimental results of different pore-size distributions with the same chemical composition.

A similar result was obtained for macroreticular adsorbents, as shown in Figure 4. This pair of porous solids have a rather distinct difference in the pore-size distribution, as shown in Figure 2. The success in the estimation well demonstrates the validity of the present method. Though the base material of the adsorbents which consists of aromatic rings and aliphatic chains is quite different from that of ECs in the sense of carbon/hydrogen ratio, the t_o value is quite close to that of ECs.

As for activated carbons, a strongly activated one, LGK-3, was used in addition to its original one, LGK-1. Because of increased mesopore volume LGK-3 shows a greater change of amount adsorbed than LGK-1 in Figure 5. It should be noted here that the broken lines lie below the solid lines because the broken lines show the contribution of the surface adsorption and are not comparable ones with the "standard isotherms" as in the t-plot by Lippens and de Boer (1965) and α_s-plot by Sing (1970).

The t_o obtained here shows just the same value as that of ECs. This result is quite reasonable because ECs and LGKs are supposed to have quite similar chemical composition. The estimation was successful also for this kind of solids. However, one problem on applying the method to activated carbons should be pointed out here.

The concept of the capillary phase-separation is based on an interpretation of the liquid-liquid equilibrium with the classical thermodynamics. It explains equilibrium between *phases* in principle. We should not extend this concept into a pore of the so-called micropore range because a group of molecules can no more behave as a *phase* in such a narrow pore. Hence, the contribution of the CPS is limited to the mesopore volume of a given adsorbent. As expected, the contribution of the CPS was small for activated carbons, as shown in Figure 5, which resulted in small changes of the amount adsorbed in the concentration range considered. The method provides relatively small advantage for such microporous solids though the estimated results agreed well with the experimental data. For mesoporous solids, on the other hand, the amount adsorbed varied significantly in the concentration range, as shown in Figures 3 and 4. The method is of greater practical use for these kinds of adsorbents.

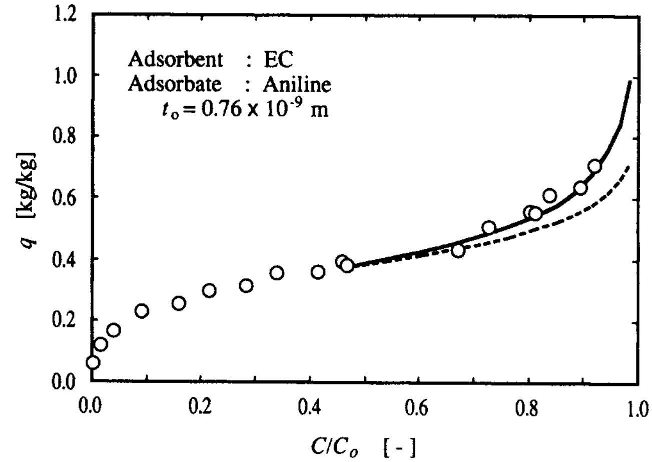

Figure 7. Adsorption isotherm for aniline from aqueous solution onto EC.

Other than nitrobenzene, three more solutes were used as adsorbates, whose adsorption isotherms onto porous carbon-black EC were obtained as Figures 6–8. Since the experimental data for benzene were rather scattered, because of the high volatility of the solutes, quantitative validity of the method was not clear in this case. However, the estimated curve at least followed experimental data qualitatively.

The estimation was made only above $C/C_s \cong 0.5$ in the case of aniline as a solute, as shown in Figure 7. The interfacial tension of aniline-water system is very small compared with other systems examined here. A small interfacial tension in Eq. 13 or 14 brings the critical radius small at a certain relative concentration. As a result, the mesopore region corresponds

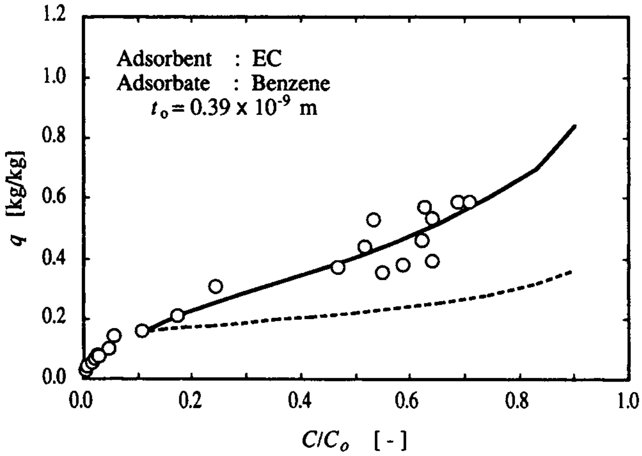

Figure 6. Adsorption isotherm for benzene from aqueous solution onto EC.

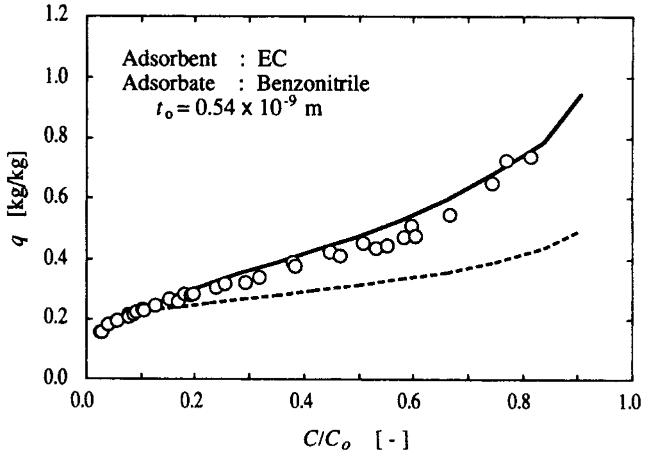

Figure 8. Adsorption isotherm for benzonitrile from aqueous solution onto EC.

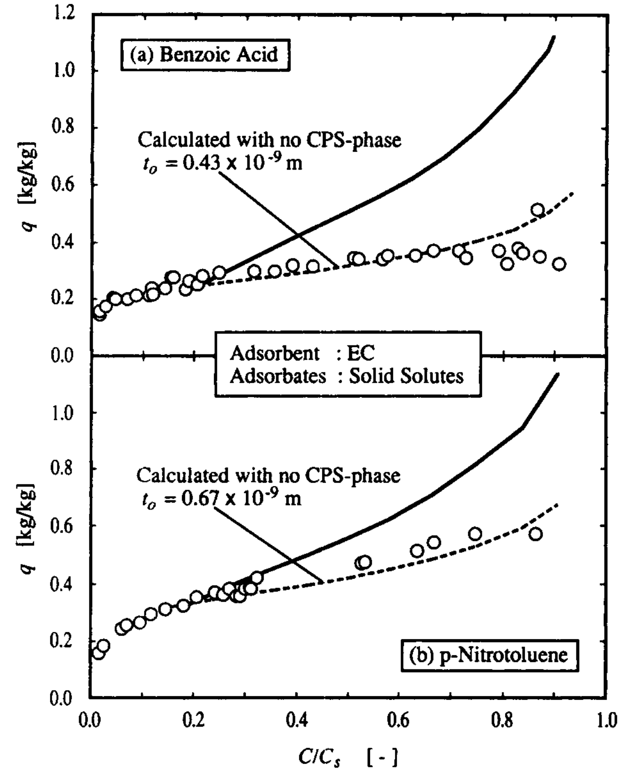

Figure 9. Adsorption isotherms for solid solutes from aqueous solution onto EC.

to a higher range of the relative concentration in this system. The agreement between the solid line and the data was fairly good though the contribution of the CPS was relatively small.

The present method was also successfully applied to the adsorption of benzonitrile solution onto EC, as seen in Figure 8. From Figure 3a and Figures 6-8, the applicability of the present method was confirmed for the adsorption of four different liquid solutes from aqueous solution onto the porous carbonblack EC.

Applicability to solid solutes

A reduction of solubility for solid solutes expressed by Eq. 14 can easily be expected when considering the situation with reversed curvature; a fine particle or an embryo shows greater solubility than a sufficiently large one as often discussed in the field of precipitation. The greater solubility comes from a Kelvin effect which is similar to a larger vapor pressure of fine drops of liquid. Reversely then, a solid with concave interface might have smaller solubility than that with flat interface and thus yield a phase separation in a pore at a smaller concentration than the saturated.

The results of Figure 9, therefore, should be subjected to much discussion, which shows the isotherms for solid solutes as adsorbates onto porous carbonblack EC. Any attempt of calculation with CPS phase showed qualitative disagreement with the measured data. An example of the calculation is shown by the solid lines in the figure which were fitted to the data only in the lower range of the relative concentration where the CPS phase would not contribute to the total amount adsorbed. This means that the amount adsorbed would increase as shown by the solid lines if the CPS phenomena would occur in these systems. However, the experimental data obviously deviate from the solid lines and are rather close to the broken line, which was calculated without the CPS phase. The interfacial tensions were based on an estimation method (Nakai, 1969) and inevitably include some error. However, this magnitude of discrepancy cannot be attributed to the error in this property.

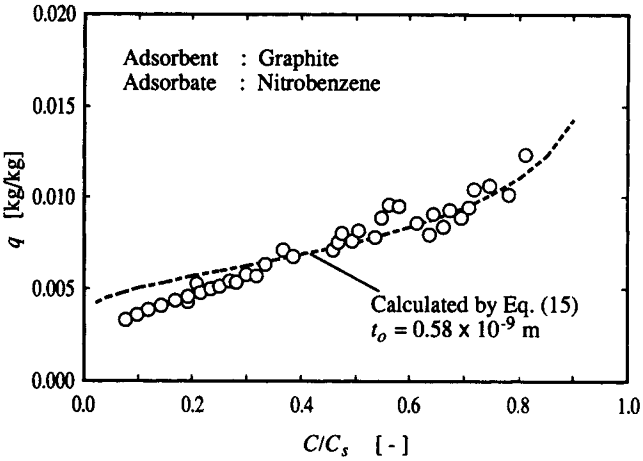

Figure 10. Adsorption isotherm for nitrobenzene from aqueous solution onto graphite.

The solid-liquid equilibrium with curved interface could be expressed by Eq. 14 as far as the concave interface and the mechanical equilibrium through the interface were valid. The discrepancy would tell us that either the shape of the interface or the mechanical balance is, or both of them are, not valid for solid solutes. The mechanical balance might be more complicated because a solid phase could stand with internal stress, which would affect the pressure in the solid phase. As a result, the method is not applicable to the adsorption of solutes with solid-liquid equilibrium. However, it should be noted that a solid solute may have a liquid-liquid equilibrium with a certain solvent as seen in the phenol-water system. In that case, the method is thought to be applicable.

Parameter for statistical thickness of adsorbed phase

The verification of Eq. 15 as an expression for the *real* adsorption amount in liquid phase was tried with nonporous solid. The result of adsorption isotherm of nitrobenzene from aqueous solution onto graphite is shown in Figure 10. The broken line shows Eq. 15 with t_o value of 0.58 nm, which is the one obtained from the estimation for the nitrobenzene-EC system. Though the data were rather scattered because of the only small adsorption amount in this system, the broken line expresses the data fairly well in most parts of the concentration examined. In lower concentration range, Eq. 15 overestimates the amount adsorbed to some extent. The important information for the estimation of liquid-phase adsorption isotherms is the *real* adsorption amount in middle or higher range of the relative concentration. This characteristic of the present method would make the influence of the overestimate quite small. As a whole, the utilization of the Frenkel formula for the adsorption on surface is appropriate for the present method.

The obtained t_o values through the estimation for various combinations of adsorbent and adsorbate are summarized in

Table 3. t_o Values

Adsorbate	Adsorbent	t_o [nm]
Nitrobenzene	EC EC600 JD	0.58
	SP900 SP206	0.59
	LGK-1 LGK-3	0.58
Benzene	EC	0.39
Aniline		0.76
Benzonitrile		0.54

Table 3. The variation of the value is quite small for an adsorbate, nitrobenzene, over the adsorbents used, while it shows relatively large variation over four kinds of adsorbates.

The insensitivity of the t_o value to the adsorbents may be interpreted as follows. In the concentration range studied here the apparent coverage exceeds unity, which implies more opportunity for an adsorbed molecule to interact with other adsorbed molecules. This situation for the molecule reduces the importance of the interaction with the solid surface. As a result, the influence of the adsorbent-adsorbate interaction on the t_o value becomes less important and the adsorbate-adsorbate interaction principally determines the t_o. If a unique value could exist for a given adsorbate, which can be applied to a relatively wide variety of solids, the estimation of liquid-phase adsorption isotherms could be made without any measured data in liquid phase. It would need only the information of the nitrogen isotherms. Direct measurements of liquid-phase adsorption on nonporous solids, however, would be needed to clarify the characteristics of the parameter in more detail.

Other than *a priori* estimation of the liquid-phase adsorption isotherm, the knowledge of the parameter t_o enables us to follow the reversed procedure starting from a liquid-phase adsorption isotherm to obtain the pore-size distribution of the solid in liquid phase. As seen in macroreticular adsorbents, some porous materials swell or shrink when immersed in a solvent. Conventional methods such as the nitrogen adsorption or mercury immersion need evacuation before the measurement. The swollen or shrunken state in a solvent could not be obtained by these methods. Utilization of the CPS concept may enable us to obtain an *in situ* measurement of the pore characteristics of these kinds of porous solids. However, nothing definite can be said in the present state of the research. Further investigation would be needed to clarify the possibility.

Conclusions

The relation between the curvature of an interface of liquid-liquid equilibrium and the equilibrium concentration was derived. The relation suggested the existence of a solute-rich phase within a pore even at a lower concentration than the saturated. Based on this concept, a method to estimate liquid-phase adsorption isotherms of a solute with limited solubility was proposed. Liquid-phase adsorption isotherms of six kinds of solutes from aqueous solutions onto three categories of solids were measured. The comparison of estimated and experimental adsorption confessed fairly good applicability to liquid solutes and implied nonpresence of CPS phenomena for solid solutes investigated. Further, utilizing this concept, we have a possibility to obtain pore characteristics of swollen or shrunk solid immersed in a solvent.

Acknowledgment

This work was supported in part by a Grant-in-Aid for Scientific Research 2750670 from the Ministry of Education, Science and Culture of Japan. The authors are grateful to Mr. Suguru Niwa for the assistance in the experimental work. Acknowledgments are also made to Lion Corp., Mitsubishi Chemical Industries Ltd. and Takeda Chemical Industries Ltd. for providing adsorbents of ECs, SPs, and LGKs.

Notation

a = activity
C = concentration of adsorbate, kg/m^3
C_i = initial concentration, kg/m^3
C_s = saturated concentration of adsorbate, kg/m^3
L = volume of solution in batch experiment, m^3
P = pressure, Pa
P' = pressure in separation phase, Pa
P_o = standard pressure, Pa
q = amount adsorbed, kg/kg
r = radius, m
r_p = pore radius, m
R = gas constant, J/(mol·K)
t = statistical thickness of adsorption in liquid phase, m
t_o = parameter for statistical thickness of adsorption in liquid phase, m
T = temperature, K
v = molar volume, m^3/mol
V = adsorption volume, m^3/kg
V_p = pore volume, m^3/kg
V_{sat} = adsorption volume at saturation, m^3/kg
ΔV = difference in adsorption volume, m^3/kg
ΔV_c = difference in adsorption volume by CPS, m^3/kg
ΔV_s = difference by surface adsorption, m^3/kg
W = adsorbent dosage, kg
X = mole fraction

Greek letters

θ = contact angle, rad
μ = chemical potential, J/mol
σ = interfacial tension, N/m

Subscripts

A = component A
B = component B
S = normal equilibrium

Superscripts

α = solvent-rich phase
β = solute-rich phase
o = pure state
$*$ = infinite dilution

Literature Cited

Barrett, E. P., L. G. Joyner, and P. P. Halenda, "The Determination of Pore Volume and Area Distributions in Porous Substances: I. Computations from Nitrogen Isotherms," *J. Amer. Chem. Soc.*, **73**, 373 (1951).

Cranston, R. W., and F. A. Inkley, *Advances in Catalysis*, Vol. 9, Academic Press, New York, p. 143 (1957).

Daubert, T. E., and R. P. Danner, eds., *Data Compilation Tables of Properties of Pure Compounds*, AIChE, New York (1985).

Dollimore, D., and G. R. Heal, "An Improved Method for the Calculation of Pore Size Distribution from Adsorption Data," *J. Appl. Chem.*, **14**, 109 (1964).

Frenkel, J., *Kinetic Theory of Liquids*, Clarendon Press, Oxford (1946).

Halsey, G., "Physical Adsorption on Non-Uniform Surfaces," *J. Chem. Phys.*, **16**, 931 (1948).

Hata, K., ed., *Kagaku Binran* (*Handbook of Chemistry*), 3rd ed., Chem. Soc. of Japan, Tokyo (1984).

Jura, G., and W. D. Harkins, "A New Adsorption Isotherm Which is Valid over a Very Wide Range of Pressure," *J. Chem. Phys.*, **11**, 430 (1943).

Kipling, J. J., *Adsorption from Solutions of Non-Electrolytes*, Academic Press, London, p. 77 (1965).

Lippens, B. C., and J. H. de Boer, "Studies on Pore Systems in Catalysis: V. The *t* Method," *J. Catalysis*, **4**, 319 (1965).

Mikhail, R. S., and E. Robens, *Microstructure and Thermal Analysis of Solid Surfaces*, John Wiley, New York, p. 31 (1983).

Nakai, T., "Studies of the Estimation of the Interfacial Energy of Embryo in Solid-Liquid Systems," *Bull. Chem. Soc. Japan*, **42**, 2143 (1969).

Patrick, W. A., and D. C. Jones, "Studies in the Adsorption from Solution from the Standpoint of Capillarity: I," *J. Phys. Chem.*, **29**, 1 (1925).

Patrick, W. A., and N. F. Eberman, "Studies in the Adsorption from Solution from the Standpoint of Capillarity: II," *J. Phys. Chem.*, **29**, 220 (1925).

ReddyKarri, S. B., and V. K. Mathur, "Measurement of Interfacial Tension of Immiscible Liquids of Equal Density," *AIChE J.*, **34**, 155 (1988).

Sing, K. S. W., *Surface Area Determination*, D. H. Everett and R. H. Ottewill, eds., Butterworths, London, p. 25 (1970).

Sørensen, J. M., and W. Arlt, "Liquid-Liquid Equilibrium Data Collection: 1. Binary Systems," *Chemistry Data Ser.*, Vol. V, Part I, D. Behrens and R. Eckermann, eds., DECHEMA, Frankfurt (1979).

Valenzuela, D. P., and A. L. Myers, *Adsorption Equilibrium Data Handbook*, Prentice Hall, Englewood Cliffs, NJ (1989).

Wheeler, A., *Catalysis*, Vol. II, Reinhold, New York, p. 116 (1955).

Manuscript received Feb. 16, 1993, and revision received Sept. 27, 1993.