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ADSORPTION EQUILIBRIA OF HYDROCARBON GASEOUS MIXTURES CONTAINING POLAR COMPONENTS

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Adsorption equilibria were measured for binary systems of hydrocarbon gaseous mixtures containing polar components. Three different adsorbents were used: molecular sieve 13X, activated carbon G-2X and molecular sieving carbon MSC-5A. The experimental results were compared with results calculated according to two currently adopted prediction methods: the ideal adsorbed solution model and the two-dimensional fluid model.

The adsorption equilibria of molecular sieve 13X were in good agreement with the predictions from both models. However, neither model was found to give a good fit with the adsorption equilibria obtained with the other adsorbents.

It is shown that the adsorption equilibria of activated carbon G-2X can be well predicted by a modified two-dimensional fluid model which takes into account the distribution of the local molecular concentration. The experimental results obtained from molecular sieving carbon MSC-5A are considered to be accounted for by the nonuniformity of the adsorption energy.

Introduction

Gas adsorption phenomena have been widely utilized in separation processes. Knowledge of the adsorption equilibria is essential for the design of these processes.

To explain adsorption equilibria, a number of models have been proposed. However, lack of experimental data has made it difficult both to develop a model and to evaluate models in the literature. This deficiency is particularly conspicuous in the adsorption of multi-component systems.

Experimental work in the past has mainly used mixtures of inorganic substances with low molecular weight or of nonpolar light hydrocarbons. There has been only a little work done on mixtures of polar and nonpolar components. In these systems, the interaction of the components in the adsorbate might be expected to cause non-ideality of the adsorbed phase. This would have a significant effect compared with that exerted on the adsorption equilibrium by the adsorbate-adsorbent interaction, which has been insufficiently investigated.

Another area of difficulty lies in the nonuniformity of adsorption energy, which arises from its dependency on the adsorbent employed. Furthermore, it should be kept in mind that the non-ideality of the adsorbed phase also depends upon the adsorbent. Therefore, it seems important to obtain experimental data for different types of adsorbents.

In the present work, adsorption equilibria have been measured, using three different types of adsorbents for binary systems of hydrocarbon mixtures

Table 1. Experimental conditions

$P=4.0\,\mathrm{kPa};\ T=303.15\,\mathrm{K}$

Component 1	Component 2	Adsorbent
Methanol	Acetone	
Methanol	Benzene	MS-13X*
Acetone	Benzene	
Acetone	n-Hexane	
Methanol	Acetone	
Methanol	Benzene	
Methanol	n-Hexane	G-2X**
Acetone	Benzene	
Acetone	n-Hexane	
Methanol	n-Hexane	
Acetone	n-Hexane	
Methanol	Acetone	MSC-5A***
Methanol	Benzene	
Acetone	Benzene	

Hydrocarbons used were all special grade agents (Takeda Chemical Industries Co., Ltd.).

* MS-13X: molecular sieve 13X (Linde Co.).

** G-2X: activated carbon G-2X (Takeda Chemical Industries Co., Ltd.).

*** MSC-5A: molecular sieving carbon MSC-5A (Takeda Chemical Industries Co., Ltd.).

containing polar components. The experimental results are explained by taking into account the effects of adsorbate interaction and the nonuniformity of adsorption energy.

1. Experimental Procedure

Adsorption equilibria were measured under the condition of constant total pressure using a volumetric apparatus, as in the previous work.[6] To confirm the attainment of adsorption equilibrium, the present work used two different methods of introducing the component gases of a binary system.[6] That is, results obtained from experiments where both components of a binary system were mixed prior to their introduction into the adsorption column were compared with those where one component of a binary system was first brought into contact with the adsorbent before the introduction of the second component. If equilibrium had been established the same adsorption values should have been obtained. The composition of the gas phase was analyzed by gas chromatography, and the amount of each component adsorbed was determined by material balance from the P-V-T values and the compositions of the gas phase. A detailed description of experimental procedure can be found elsewhere.[6]

The experimental conditions are summarized in **Table 1**. Adsorption temperature was 30°C and total pressure was 4 kPa. Combinations of two components from among methanol, acetone, n-hexane and ben-
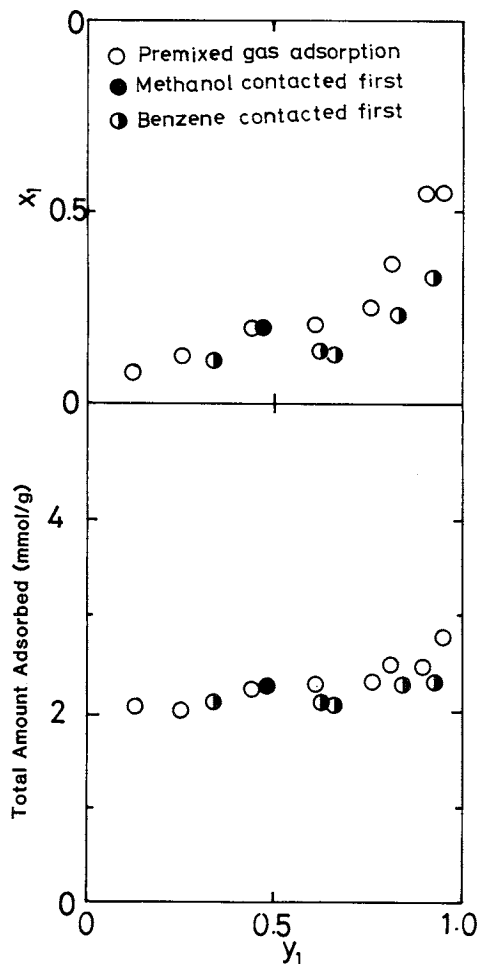

Fig. 1. Experimental results of methanol(1)–benzene(2) system for MSC-5A.

zene were used as binary gaseous mixture systems. The adsorbents adopted were molecular sieve 13X, molecular sieving carbon MSC-5A and activated carbon G-2X. Molecular sieve 13X is a polar adsorbent and the others are non-polar types.

For the estimation of adsorption of the gaseous mixtures, the adsorption of each pure component was also measured.

2. Experimental Results

Figure 1 shows the results of the methanol–benzene system on MSC-5A. The experimental result obtained from bringing methanol into contact with the adsorbent first is consistent with results obtained from using this binary system mixed prior to adsorption. These results, however, did not agree with those obtained when benzene was brought into contact with the adsorbent first. This hysteresis effect was also observed in the acetone–benzene system for the same adsorbent. In both systems, experimental results did not change with longer adsorption time.

Since the hysteresis only occurred during adsorption on MSC-5A, it might be attributed to the surface structure of this adsorbent. However, the

mechanism of the hysteresis phenomenon is not clear.

Except with the methanol–benzene and acetone–benzene systems adsorbed on MSC-5A, no hysteresis effect was observed and the attainment of equilibrium was confirmed. The above equilibrium data are compared in Section 3 with those calculated from the predictive models.

3. Discussion

3.1 Estimation by current methods

Calculations of adsorption equilibria were carried out according to two different types of adsorption models: the ideal adsorbed solution model[7] and the two-dimensional fluid model.[2]

The former model was derived by Myer and Prausnitz[7] and is based upon thermodynamic theory and the assumption of ideality of the adsorbed phase. Since this model is free of any other assumptions, comparisons of the predicted results with the measurements obtained are helpful in inferring the interaction effect of the adsorbate. In addition, it is important to examine the applicability of this model because it has been widely adopted as a prediction method.

The interaction effect of the adsorbate is taken into account in the two-dimensional fluid model[2] on the basis of statistical thermodynamic theory under the assumption of monolayer adsorption. In the present study, some modifications are suggested to the two-dimensional fluid model.

According to de Boer,[2] the partition function of the monolayer-adsorbed phase, consisting of mobile molecules, can be expressed as follows for a binary system:

$$(\text{P.F.}) = \frac{1}{N_1! N_2!} \left(\frac{2\pi m_1 kT}{h^2}\right)^{N_1} \left(\frac{2\pi m_2 kT}{h^2}\right)^{N_2} A_f^{N_1+N_2}$$
$$\times \exp\left(\frac{N_1\phi_1 + N_2\phi_2}{kT} + \frac{U}{kT}\right) \quad (1)$$

where N_i is the number of molecules of component i in the adsorbed phase, m_i the molecular mass of component i, k the Boltzmann constant, h the Planck constant, A_f the free surface area, T the absolute temperature, ϕ_i the adsorption energy of component i, and U the total interaction energy of the adsorbate.

In this work the total interaction energy U is calculated from Eq. (2), which is the attraction term in Peng and Robinson's two-dimensional equation of state.[9]

$$U = \frac{N^2\alpha_m}{\sqrt{2}\,\pi N d_m^2} \ln\frac{1+(2+2\sqrt{2})\theta}{1+(2-2\sqrt{2})\theta} \quad (2)$$

where

$$\theta = \frac{\pi}{4} d_m^2 (N_1 + N_2)/A \quad (3)$$

$$N = N_1 + N_2 \quad (4)$$

and A is the surface area of adsorbent, d_m the mean diameter of adsorbed molecules and α_m the averaged interaction parameter of the adsorbate. The free surface area, A_f, in Eq. (1) is obtained from the following two-dimensional equation of state, which was derived for mobile molecules of hard discs by Henderson.[5] This analytical solution is applicable with good accuracy up to high surface coverages.

$$A_f = A \exp\{-R(\theta)\} \quad (5)$$

where

$$R(\theta) = -1.1925 - 0.043(1-\theta) - 0.743\ln(1-\theta)$$
$$+ 1.257/(1-\theta) - 0.0215/(1-\theta)^2 \quad (6)$$

From Eqs. (1)–(6), the chemical potential of each component in the adsorbed phase is obtained. Assuming that the chemical potential in the gas phase can be approximated by that of ideal gas, the following equation can be derived as the adsorption isotherm for component 1.

$$Py_1 = \frac{N_1}{\xi_1} \exp\left[R(\theta) + \frac{N}{2}\frac{\partial R(\theta)}{\partial\theta}\frac{\partial(N\delta_m^2)}{\partial N_1} \right.$$
$$- \frac{\eta_m}{\delta_m^2}\frac{\partial(N\delta_m^2)}{\partial N_1}\frac{2\theta}{1+4\theta-4\theta^2} - \frac{1}{2\sqrt{2}\,N\delta_m^2}$$
$$\left. \times \left\{\frac{\partial(N^2\eta_m)}{\partial N_1} - \frac{N\eta_m}{\delta_m^2}\frac{\partial(N\delta_m^2)}{\partial N_1}\ln\frac{1+(2+2\sqrt{2})\theta}{1+(2-2\sqrt{2})\theta}\right\}\right]$$
$$\quad (7)$$

where

$$\xi_1 = \frac{A}{kT}\left(\frac{h^2}{2\pi m_1 kT}\right)^{1/2}\exp\left(\frac{\phi_1}{kT}\right) \quad (8)$$

$$\delta_m = \left(\frac{\pi}{2A}\right)^{1/2} d_m \quad (9)$$

$$\eta_m = \frac{\alpha_m}{kTA} \quad (10)$$

and P is total pressure and y_i the mole fraction of component i in gas phase. Detailed analytical forms of the appropriate partial derivatives in Eq. (7) are given in **Appendix**. The adsorption isotherm for each individual component can be found from Eq. (7).

The isotherm for pure gas adsorption of component i is easily derived from Eq. (7) and is given by the following expression:

$$P = \frac{N_i}{\xi_i}\exp\left[R(\theta) + \frac{N_i}{2}\delta_i\frac{\partial R(\theta)}{\partial\theta} - \eta_i\frac{2\theta}{1+4\theta-4\theta^2} \right.$$
$$\left. - \frac{\eta_i}{\sqrt{2}\,\delta_i^2}\left\{1 - \frac{1}{2}\ln\frac{1+(2+2\sqrt{2})\theta}{1+(2-2\sqrt{2})\theta}\right\}\right] \quad (11)$$
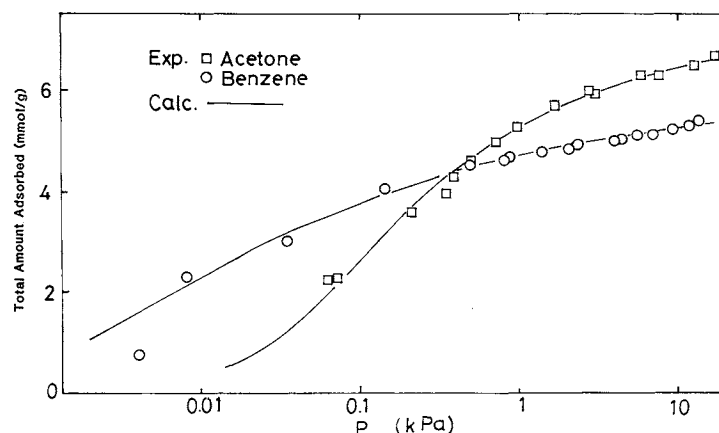
where

Fig. 2. Correlation of pure gas component adsorption on G-2X by the two-dimensional fluid model.

Table 2. Determined values of parameters for each component.

Adsorbate	Adsorbent	$\xi \times 10^{-20}$ [Pa·g]	$\eta \times 10^{20}$ [g]	$\delta \times 10^{10}$ [g$^{1/2}$]	ΔP^* [kPa]
Methanol		12.5	0.133	0.214	0.01–12
Acetone	MS-13X	221	0.123	0.287	0.01–17
Benzene		33.3	0.132	0.314	0.02–11
n-Hexane		20.0	0.120	0.371	0.02–17
Methanol		0.0130	0.0482	0.121	0.15–18
Acetone	G-2X	0.154	0.0581	0.167	0.01–17
Benzene		5.53	0.0378	0.199	0.05–14
n-Hexane		48.1	0.0310	0.248	0.05–16
Methanol		0.0292	0.0951	0.194	0.1 –15
Acetone	MSC-5A	1.63	0.0912	0.289	0.01–10
Benzene		10.2	0.0631	0.322	0.02–12
n-Hexane		19.5	0.0606	0.396	0.01–15

Average absolute deviation in the correlations of pure gas adsorption by the model is within 2.5%.

* ΔP: pressure range in the experiments of pure gas adsorption.

$$\delta_i = \left(\frac{\pi}{2A}\right)^{1/2} d_i \qquad (12)$$

$$\eta_i = \frac{\alpha_i}{kTA} \qquad (13)$$

The parameters ξ_i, δ_i and η_i for each component were determined by fitting Eq. (11) to the experimental data of pure gas adsorption. The calculated results for the pure gas adsorption of acetone and benzene on G-2X are shown in **Fig. 2**. It was confirmed that the adsorption equilibria for the other systems are also fitted well with the two-dimensional fluid model. The optimum values of the parameters are summarized in **Table 2**.

In utilizing the predictive model for mixture systems, one of the most important factors is the choice of mixing rules. Firstly, under the assumption of the random distribution of adsorbed molecules on adsorbent surface, the following simple mixing rules
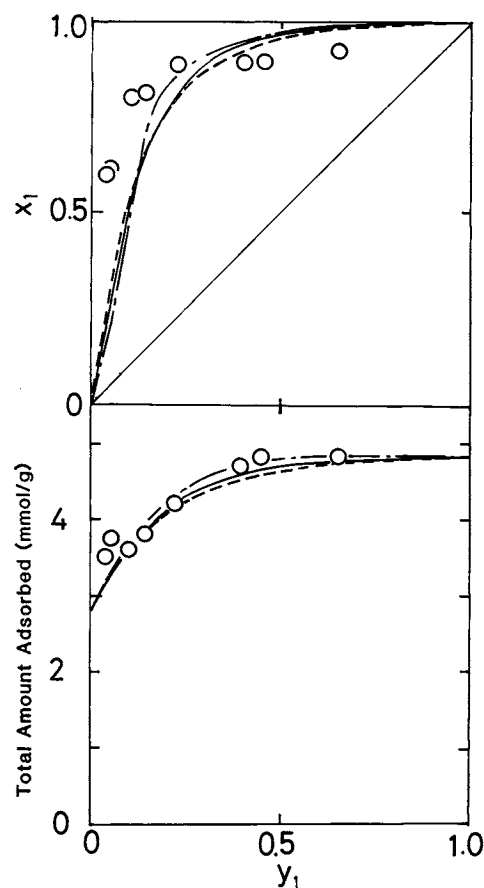

Fig. 3. Comparison of experimental and calculated results of methanol(1)–acetone(2) system for MS-13X. Exp.: ○. Calc.: ——, two-dimensional fluid model (random distribution); ————, ideal adsorbed solution model; —·—, two-dimensional fluid model (local distribution).

were selected.

$$\eta_m = x_1^2 \eta_1 + 2x_1 x_2 \sqrt{\eta_1 \eta_2} + x_2^2 \eta_2 \qquad (14)$$

$$\delta_m^2 = x_1^2 \delta_1^2 + 2x_1 x_2 \left(\frac{\delta_1 + \delta_2}{2}\right)^2 + x_2^2 \delta_2^2 \qquad (15)$$
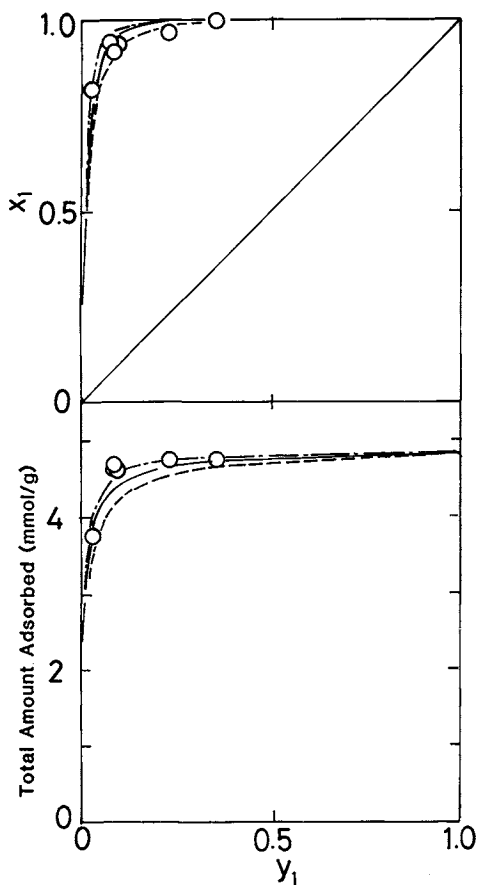
The results predicted by the two-dimensional fluid

Fig. 4. Comparison of experimental and calculated results of methanol(1)–benzene(2) system for MS-13X. Exp.: O. Calc.: ———, two-dimensional fluid model (random distribution); ————, ideal adsorbed solution model; ———, two-dimensional fluid model (local distribution).

Fig. 5. Comparison of experimental and calculated results of acetone(1)–benzene(2) system for MS-13X. Exp.: O. Calc.: ———, two-dimensional fluid model (random distribution); ————, ideal adsorbed solution model; ———, two-dimensional fluid model (local distribution).

model with these mixing rules are presented in **Figs. 3–14**, together with the results predicted by the ideal adsorbed solution model.

From Figs. 3, 7 and 12 it can be seen that the calculated values using both the two-dimensional fluid model and the ideal adsorbed solution model compare well with the experimental data for the methanol–acetone system for each adsorbent. Except for this binary system the experimental results obtained with MSC-5A do not agree with those predicted by either of the models, while those of MS-13X are consistent with the results calculated with both the models. On the other hand, for the adsorbent G-2X the two-dimensional fluid model allows estimation closer to the measured values than the ideal adsorbed solution model, although estimations made with the two-dimensional fluid model are not always satisfactory. It is, however, noted that good results tend to be derived more frequently from the two-dimensional model than from the other model.

As shown in Table 2, the ξ value of each component for the adsorption on G-2X and MSC-5A appears to be small compared with that on MS-13X.
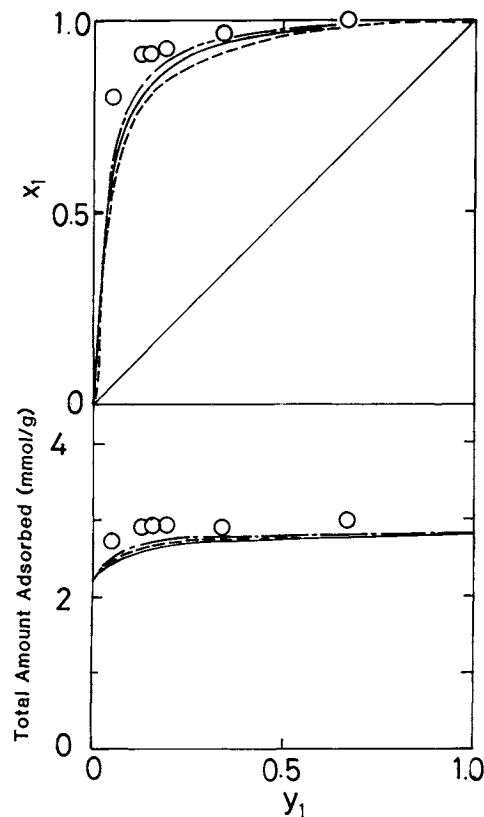
The parameter ξ is the measure of the adsorption energy role in the adsorption. Therefore, the results in Table 2 may allow the inference that the adsorption equilibria of G-2X and MSC-5A can be easily affected by the adsorbate-adsorbate interaction, making it difficult to apply the ideal adsorbed solution model except for the case of the methanol–acetone system. The good estimation for this polar–polar mixture system may be due to the similarity in their polarities.

3.2 Effect of adsorbate interaction on adsorption

There may be a number of reasons for the disagreement between experimental and estimated results. One may be simplicity of assumption for the mixing rules of random distribution. In a mixture system with large differences in molecular affinities, the distribution of local molecular concentration should not be ignored and may have a considerable effect on the adsorption.

Wilson's well-known equation[10] considers the effect of local molecular concentration and is widely applicable to vapor-liquid equilibrium. The present work attempts to apply Wilson's equation to adsorption equilibrium.

The following equations, which are based on the concept of local concentration, can be assumed for
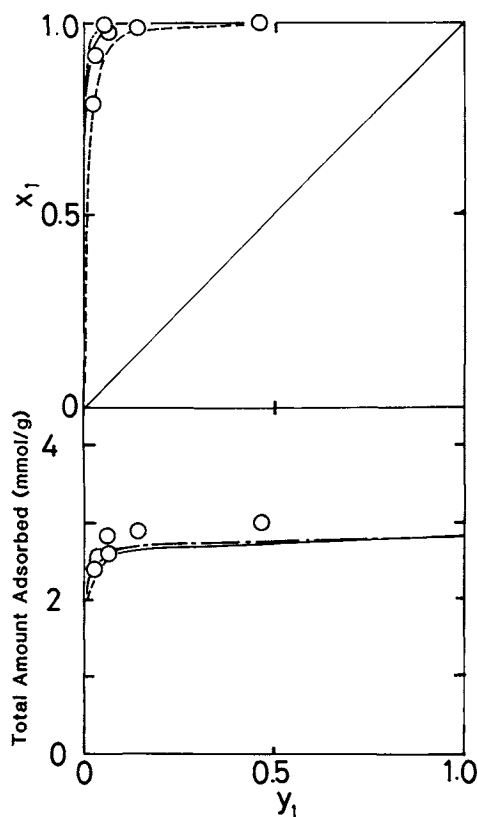
Fig. 6. Comparison of experimental and calculated results of acetone(1)–n-hexane(2) system for MS-13X. Exp.: $\bigcirc$. Calc.: ———, two-dimensional fluid model (random distribution); – – – –, ideal adsorbed solution model; —·—, two-dimensional fluid model (local distribution).

the mixing rules:

$$\eta_m = (1/kTA)\{x_1(x_{11}\alpha_1 + x_{21}\alpha_{21}) + x_2(x_{12}\alpha_{12} + x_{22}\alpha_2)\}$$

$$= x_1(x_{11}\eta_1 + x_{21}\eta_{21}) + x_2(x_{12}\eta_{12} + x_{22}\eta_2) \qquad (16)$$

$$\delta_m = (\pi/2A)^{1/2}\{x_1(x_{11}d_1^2 + x_{21}d_{21}^2)$$

$$+ x_2(x_{12}d_{12}^2 + x_{22}d_2^2)\}$$

$$= x_1(x_{11}\delta_1^2 + x_{21}\delta_{21}^2) + x_2(x_{12}\delta_{12}^2 + x_{22}\delta_2^2) \qquad (17)$$

where

$$\eta_{12} = \eta_{21} = \sqrt{\eta_1\eta_2} \qquad (18)$$

$$\delta_{12} = \delta_{21} = \frac{d_1 + d_2}{2} \qquad (19)$$

and x_{ij} is the local mole fraction of i around j. The ratio of the mole fractions x_{ij}/x_{jj} is given by the following equations.[10]

$$\frac{x_{21}}{x_{11}} = \frac{\tau_2 \exp(\lambda_{21}/kT)}{\tau_1 \exp(\lambda_{11}/kT)} \qquad (20)$$

$$\frac{x_{12}}{x_{22}} = \frac{\tau_1 \exp(\lambda_{12}/kT)}{\tau_2 \exp(\lambda_{22}/kT)} \qquad (21)$$

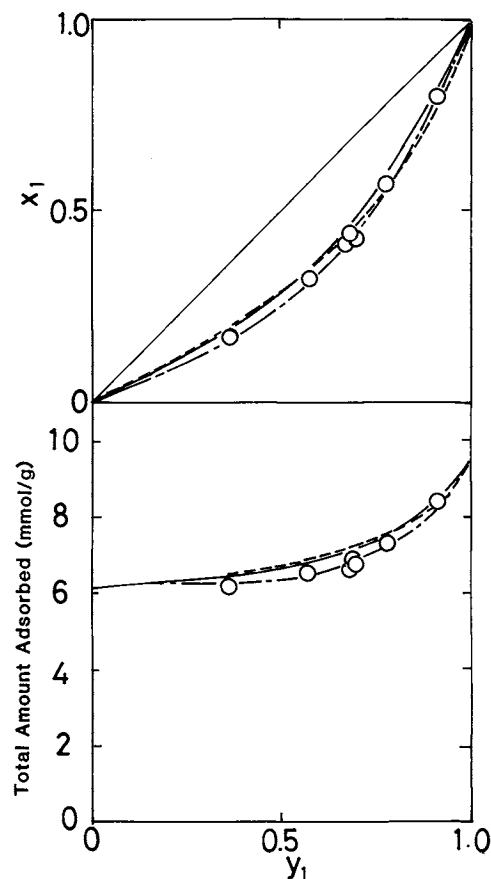where τ_i is the fraction of surface area defined by

Fig. 7. Comparison of experimental and calculated results of methanol(1)–acetone(2) system for G-2X. Exp.: $\bigcirc$. Calc.: ———, two-dimensional fluid model (random distribution); – – – –, ideal adsorbed solution model; —·—, two-dimensional fluid model (local distribution).

$$\tau_i = \frac{x_i d_i^2}{\sum_j x_j d_j^2} \qquad (22)$$

and λ_{ij} is the interaction energy between i and j, which is given by

$$\lambda_{ij} = \sqrt{\lambda_{ii}\lambda_{jj}} \qquad (23)$$

The value of λ_{ii} is determined on the assumption that the total interaction energy of adsorbed molecules can be approximated by nearest-neighbour interaction energy. According to this assumption, the total interaction energy under the close-packing condition of the adsorbed molecules in pure gas adsorption is expressed as follows:

$$U = \frac{1}{2} NZ\lambda_{ii} \qquad (24)$$

where Z is the number of nearest-neighbour molecules around a core molecule. Assuming $Z = 3$, which leads to $\theta = 0.6046$ under the close-packing condition, the following equation is derived from Eqs. (24) and (2).

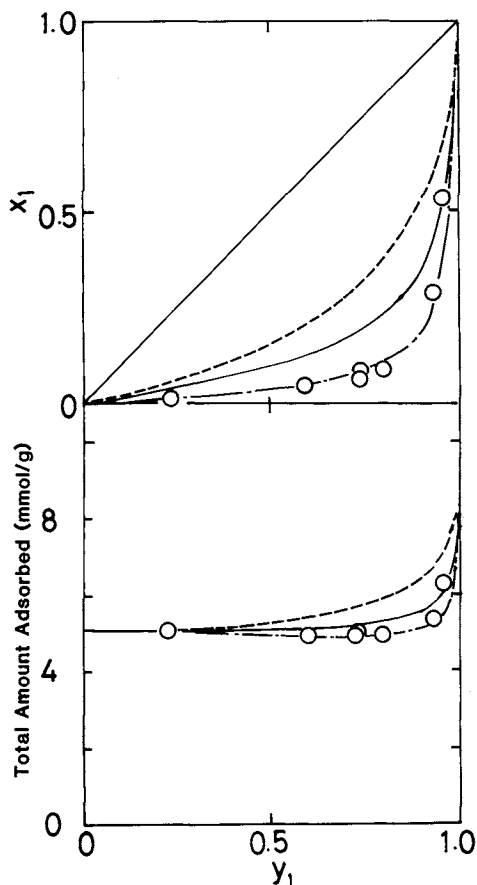$$\lambda_{ii} = 0.3092\alpha_i/d_i^2 = 0.3902(\pi kT/2)\eta_i/\delta_i^2 . \qquad (25)$$

Fig. 8. Comparison of experimental and calculated results of methanol(1)–benzene(2) system for G-2X. Exp.: ◯. Calc.: ——, two-dimensional fluid model (random distribution); ————, ideal adsorbed solution model; —·—, two-dimensional fluid model (local distribution).
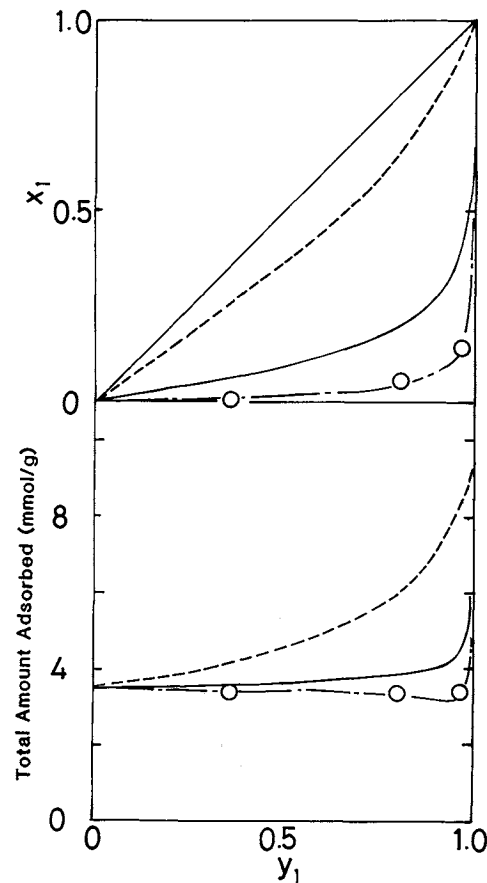

Fig. 9. Comparison of experimental and calculated results of methanol(1)–n-hexane(2) system for G-2X. Exp.: ◯. Calc.: ——, two-dimensional fluid model (random distribution); ————, ideal adsorbed solution model; —·—, two-dimensional fluid model (local distribution).

Thus all the parameters for the mixing rules of Eqs. (16) and (17) are determined from those in Table 2 for pure component adsorption.

The adsorption equilibria calculated by use of Eqs. (16) and (17) for adsorbents MS-13X and G-2X are plotted in Figs. 3–11. Obviously the calculated results for G-2X are improved by the introduction of the new mixing rules. For adsorbent MS-13X the new mixing rules scarcely change the calculated results, which are close to the experimental results. However, for adsorbent MSC-5A the introduction of the new mixing rules showed no improvement, as shown in Figs. 12 and 13 where the results of methanol–acetone and acetone–n-hexane systems are plotted.

It is interesting to note a tendency in the experimental data for the adsorbent MSC-5A in Figs. 12–14, where each set of data shows azeotropic characteristics. It also seems important that in the low mole fraction range of y_1 the adsorbed phase is rich in component 1, which has a smaller molecular size than component 2.

In mixtures of polar and nonpolar components, the polar components have large intermolecular forces

compared to the nonpolar components. Therefore, if the interaction of the adsorbate had a significant effect on adsorption, the adsorbed phase should have been rich in the polar component in the higher concentration range of the polar component in the gas phase. This expectation is contrary to the result obtained in the experiments and, therefore, it is difficult to attribute the azeotropic tendency to the interaction effect of the adsorbate.[*1]

The adsorbent MSC-5A has a surface structure of micropores which form slits with an average width of 0.5 nm. This width is narrow compared to that of the other adsorbents and is close to the size of the adsorbed molecules. It can, therefore, be inferred that the molecules adsorbed on MSC-5A were able to have interactions with both sides of the slit walls. Accordingly, there is a possibility that the strong dependency of adsorption energy on slit width makes the assumption of uniform adsorption energy un-

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[*1] It is helpful to consider the nature of vapor-liquid equilibria. In methanol–n-hexane and acetone–n-hexane systems, the tendency of azeotrope in the vapor-liquid equilibria[4] is contrary to that observed in the adsorption equilibria.
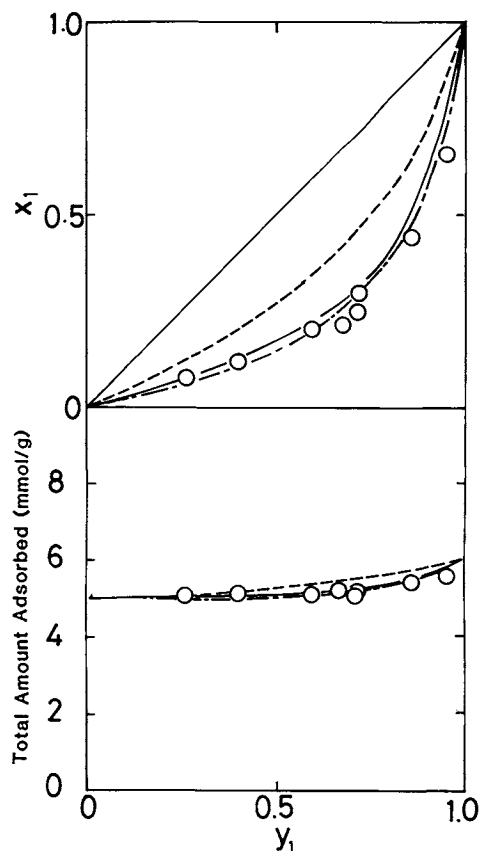
Fig. 10. Comparison of experimental and calculated results of acetone(1)–benzene(2) system for G-2X. Exp.: ○. Calc.: ———, two-dimensional fluid model (random distribution); — — —, ideal adsorbed solution model; — · —, two-dimensional fluid model (local distribution).
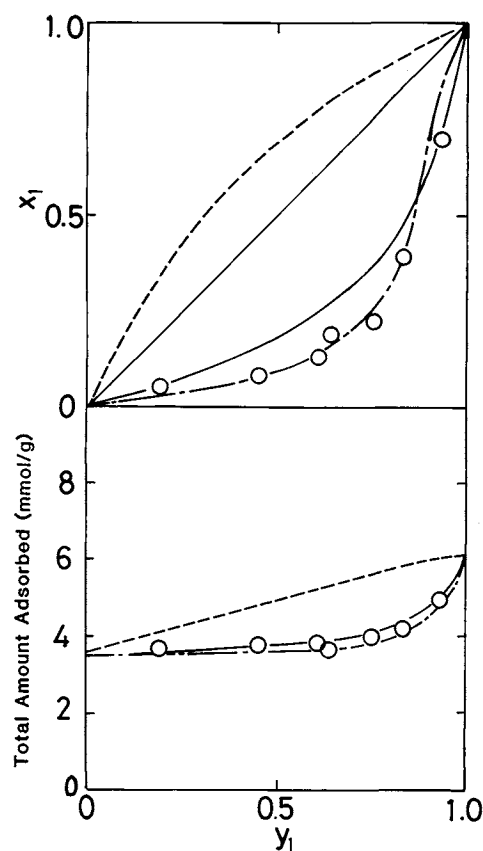

Fig. 11. Comparison of experimental and calculated results of acetone(1)–n-hexane(2) system for G-2X. Exp.: ○. Calc.: ———, two-dimensional fluid model (random distribution); — — —, ideal adsorbed solution model; — · —, two-dimensional fluid model (local distribution).

satisfactory even if there is no wide distribution in slit width. On the other hand, in the case of G-2X and MS-13X the size distribution of micropores does not seem to be important since adsorbed molecules have interaction only with one side of a slit wall or the other. This peculiarity of the MSC-5A surface structure may be related to the result of hysteresis in adsorption.

3.3 Effect of nonuniformity of adsorption energy

The poor estimation for the adsorbent MSC-5A may be due to the nonuniformity of adsorption energy. To examine this possibility the following model is proposed.

1. The surface of the adsorbent is composed of two kinds of surface areas, with adsorption energies ϕ_a and ϕ_b, and to each surface area Eq. (7) is applicable.

2. The fraction of the surface area with adsorption energy ϕ_b to total surface area, r, is constant and independent of the adsorbate.

3. The ratio of the adsorption energies, ϕ_b/ϕ_a, equals 2 independent of the absorbate.

4. The mixing rules are expressed by Eqs. (14) and (15).

Assumption 3 takes into account the maximum and minimum adsorption energies at which an adsorbed molecule interacts with both sides of the slit wall or with one side or the other. Assumption 4 is made from the viewpoint of simplicity and also from the consideration that the interaction of the adsorbate is not a very important factor in the adsorption for this particular adsorbent. Although this model may be regarded as too simple to predict the experimental results accurately, the purpose of this analysis is primarily to investigate whether the model can explain the azeotropic phenomenon.

The parameters of the model were determined by fitting the data of pure component adsorption. Adsorption equilibria were calculated for mixtures using $r = 1/5$, $1/10$ and $1/20$ and are presented in **Figs. 15–17**. The calculated results for the methanol–acetone and methanol–n-hexane systems reveal azeotropic behaviour and the values calculated with $r = 1/20$ are close to the measurements. However, for the acetone–n-hexane system the model does not show azeotropic characteristics. This discrepancy may be thought to be caused by the simplified assumption of the model. It can also be attributed to a failure to
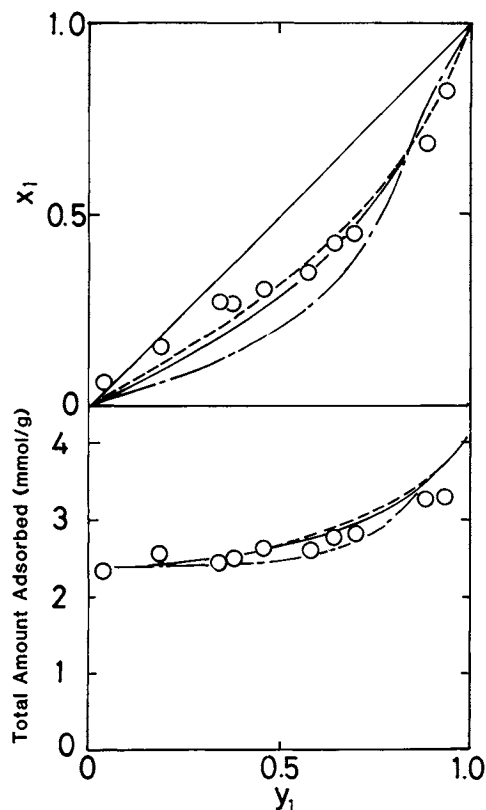
Fig. 12. Comparison of experimental and calculated results of methanol(1)–acetone(2) system for MSC-5A. Exp.: ○. Calc.: ——, two-dimensional fluid model (random distribution); –––––, ideal adsorbed solution model; —·—, two-dimensional fluid model (local distribution).
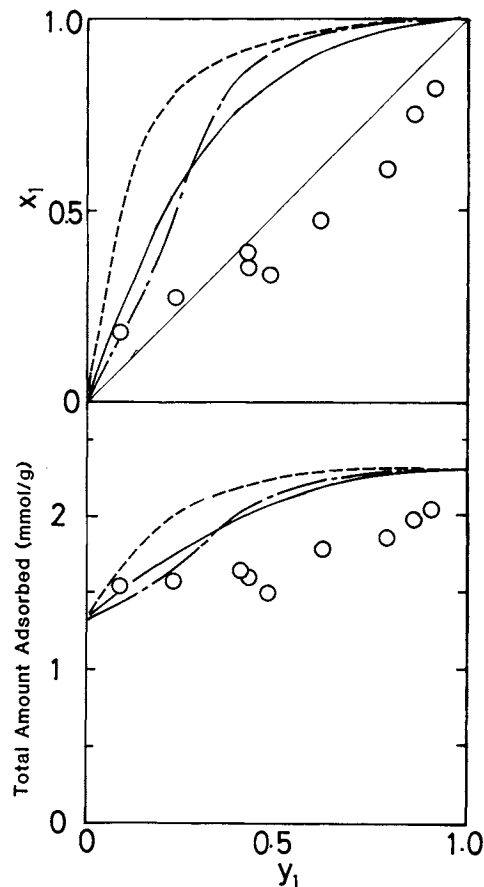

Fig. 13. Comparison of experimental and calculated results of acetone(1)–n-hexane(2) system for MSC-5A. Exp.: ○. Calc.: ——, two-dimensional fluid model (random distribution); –––––, ideal adsorbed solution model; —––, two-dimensional fluid model (local distribution).

determine the parameter values accurately owing to experimental error. Accordingly, in this work an attempt was made to find the optimum values of the parameters for all the adsorption data of mixture adsorption and pure component adsorption. Finally, the adsorption equilibria obtained by this method are plotted in Figs. 15–17. As seen in these figures, the model reveals an azeotropic tendency in each mixture system. It should also be noted that the model gives results for pure gas adsorption very close to those obtained experimentally, as can be seen in **Fig. 18** where the adsorption equilibria for acetone and n-hexane are presented.

Figure 19 shows the adsorption equilibria calculated for each adsorption area, a and b, for the methanol–acetone system. Since the molecular size of methanol is smaller than that of acetone, the concentration of methanol in the adsorbed phase on the surface area with the higher adsorption energy ϕ_b is greater than that on the surface area with the lower adsorption energy ϕ_a. This difference in concentration accounts for the azeotropic behaviour.

Conclusions

Binary adsorption-equilibrium data were obtained

under constant total pressure using as adsorbents molecular sieve 13-X, activated carbon G-2X and molecular sieving carbon MSC-5A, for hydrocarbon gaseous mixtures containing polar components. The experimental results were compared with results calculated from two different types of predictive models: the ideal adsorbed solution model and the two-dimensional fluid model.

It was found that the two-dimensional fluid model gave a better fit than the ideal adsorbed solution model. However, results estimated from the two-dimensional fluid model were, except with MS-13X, not always satisfactory.

Comparison of the experimental and calculated results for the adsorbent G-2X suggested that the interaction of the adsorbate has a significant effect on the adsorption equilibria, and it was shown that the estimated results can be improved by introducing new mixing rules which consider the distribution effect of local molecular concentration.

On the other hand, for the adsorbent MSC-5A it was suggested that the failure to consider the effect of the distribution of adsorption energy can lead to poor
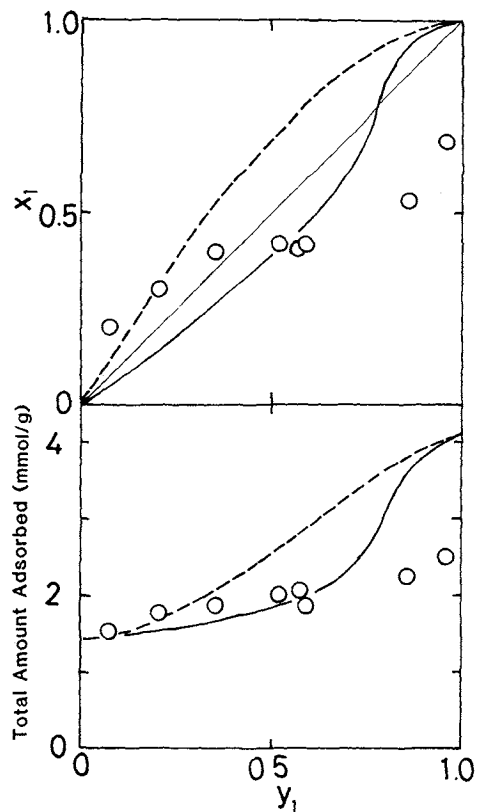
Fig. 14. Comparison of experimental and calculated results of methanol(1)–n-hexane(2) system for MSC-5A. Exp.: O. Calc.: ———, two-dimensional fluid model (random distribution); —–—–, ideal adsorbed solution model.
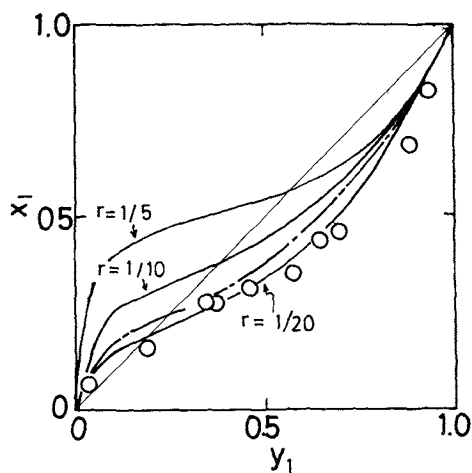

Fig. 15. Effect of nonuniformity of adsorption energy on adsorption equilibrium of methanol(1)-acetone(2) system for MSC-5A. Exp.: O. Calc.: ———, determined from pure data; —–—–, determined from pure data and mixture data ($r = 1/20$).

estimates which do not express the azeotropic tendency commonly observed in the adsorption data. The experimental results were explained by means of a model which takes into account the nonuniformity of adsorption energy.
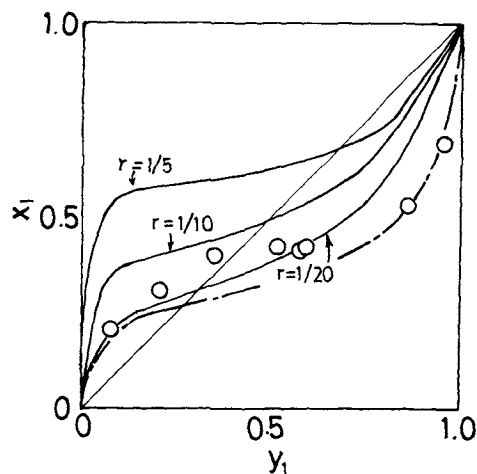
Fig. 16. Effect of nonuniformity of adsorption energy on adsorption equilibrium of methanol(1)-n-hexane(2) system for MSC-5A. Exp.: O. Calc.: ———, determined from pure data; —–—–, determined from pure data and mixture data ($r = 1/20$).
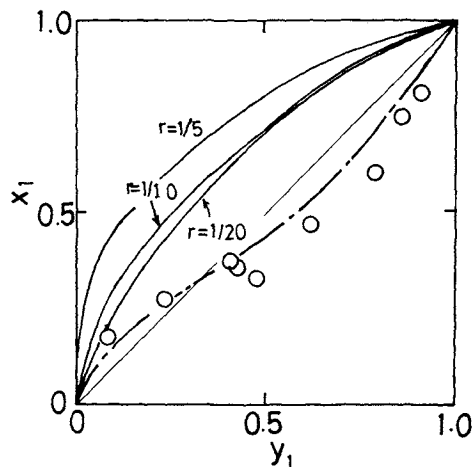

Fig. 17. Effect of nonuniformity of adsorption energy on adsorption equilibrium of acetone(1)-n-hexane(2) system for MSC-5A. Exp.: O. Calc.: ———, determined from pure data; —–—–, determined from pure data and mixture data ($r = 1/20$).

Appendix: Analytical forms of partial deviatives

$$\frac{\partial R(\theta)}{\partial \theta} = 0.043 + \frac{0.743}{1-\theta} + \frac{1.257}{(1-\theta)^2} + \frac{0.0215}{(1-\theta)^3} \qquad (A-1)$$

For the model of random distribution

$$\frac{\partial \eta_m}{\partial N_1} = \frac{2x_2}{N} \{ x_1 \eta_1 + (x_2 - x_1)\sqrt{\eta_1 \eta_2} - x_2 \eta_2 \} \qquad (A-2)$$

$$\frac{\partial (\delta_m^2)}{\partial N_1} = \frac{2x_2}{N} \left\{ x_1 \delta_1^2 + (x_2 - x_1)\left(\frac{\delta_1 + \delta_2}{2}\right)^2 - x_2 \delta_2^2 \right\} \qquad (A-3)$$
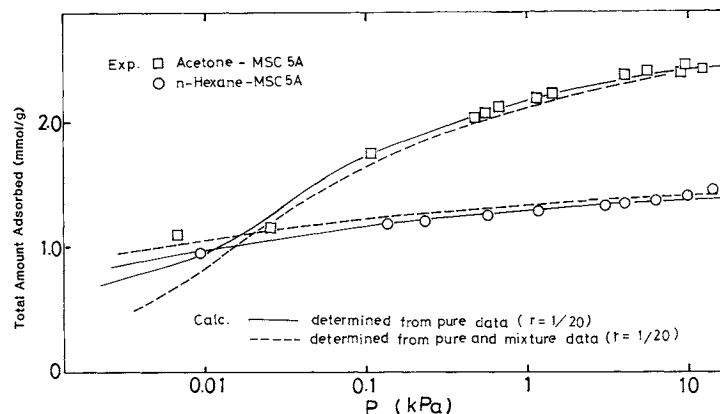
For the model of local distribution

Fig. 18. Correlation of pure component adsorption by a model considering nonuniformity of adsorption energy.
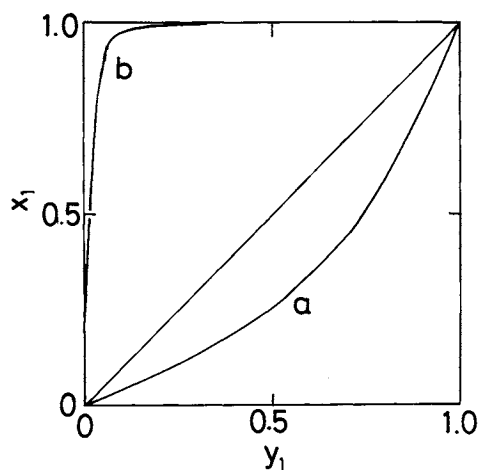

Fig. 19. Calculated compositions for each adsorption area for methanol(1)–acetone(2) system for MSC-5A.

$$\frac{\partial \eta_m}{\partial N_1} = \frac{x_2}{N}\{(x_{11}\eta_1 + x_{21}\eta_{21}) - (x_{12}\eta_{12} + x_{22}\eta_2)\}$$

$$+ x_1 \frac{\partial x_{11}}{\partial N_1}(\eta_1 - \eta_{21}) + x_2 \frac{\partial x_{12}}{\partial N_1}(\eta_{12} - \eta_2) \qquad \text{(A-4)}$$

$$\frac{\partial(\delta_m^2)}{\partial N_1} = \frac{x_2}{N}\{(x_{11}\delta_1^2 + x_{21}\delta_{21}^2) - (x_{12}\delta_{12}^2 + x_{22}\delta_2^2)\}$$

$$+ x_1 \frac{\partial x_{11}}{\partial N_1}(\delta_1^2 - \delta_{21}^2) + x_2 \frac{\partial x_{12}}{\partial N_1}(\delta_{12}^2 - \delta_2^2) \qquad \text{(A-5)}$$

$$\frac{\partial x_{11}}{\partial N_1} = \frac{\delta_1^2}{N}\frac{x_2 \exp(\lambda_{11}/kT)\exp(\lambda_{21}/kT)}{\{x_1\delta_1^2\exp(\lambda_{11}/kT) + x_2\delta_2^2\exp(\lambda_{21}/kT)\}^2} \qquad \text{(A-6)}$$

$$\frac{\partial x_{12}}{\partial N_1} = \frac{\delta_2^2}{N}\frac{x_2 \exp(\lambda_{12}/kT)\exp(\lambda_{22}/kT)}{\{x_1\delta_1^2\exp(\lambda_{12}/kT) + x_2\delta_2^2\exp(\lambda_{22}/kT)\}^2} \qquad \text{(A-7)}$$

Nomenclature

A	= surface area of adsorbent	$[\text{m}^2/\text{g}]$
A_f	= free surface area	$[\text{m}^2/\text{g}]$
d	= molecular size	$[\text{nm}]$

h	= Planck constant	$[\text{J}\cdot\text{s}]$
k	= Boltzmann constant	$[\text{J/K}]$
m	= molecular mass	$[\text{g}]$
N	= number of adsorbed molecules per unit mass of adsorbent	$[\text{g}^{-1}]$
P	= total pressure	$[\text{Pa}]$
r	= fraction of surface area with higher adsorption energy to total surface area	$[-]$
T	= absolute temperature	$[\text{K}]$
U	= total interaction energy of adsorbed molecules	$[\text{J}]$
x	= mole fraction in adsorbed phase	$[-]$
y	= mole fraction in gas phase	$[-]$
Z	= number of nearest-neighbour molecules	$[-]$
α	= interaction parameter of adsorbate	$[\text{K}\cdot\text{m}^2]$
δ	= model parameter defined by Eq. (9)	$[\text{Pa}^{-1}\text{g}^{-1}]$
η	= model parameter defined by Eq. (10)	$[\text{g}]$
ζ	= model parameter defined by Eq. (8)	$[\text{g}^{1/2}]$
θ	= surface coverage	$[-]$
ϕ	= adsorption energy	$[\text{J}]$

$\langle$Subscripts$\rangle$

i, m	= component
m	= mixture

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