Adsorption Separation of Binary Gas Mixtures III. Effect of carrier gas

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The adsorption separations of binary gas mixtures (N_2-CO_2, N_2-C_2H_4, CO-CO_2, CO-C_2H_4, CO_2-C_2H_4 and CO_2-C_3H_6) by means of active carbon in flow method were studied in the fixed bed at 0°C and 1 atm. The over-all capacity coefficients $K_f a_v$ obtained by analysing the observed break-through curves were varied by a sort of carrier gas at the same flow rate. Considering the adsorption of the carrier gas, fluid film capacity coefficients $k_f a_v$ and solid film capacity coefficients $\beta k_s a_v$ were estimated from the values of the observed mixed gas adsorption isotherm and the observed diffusivity of the adsorbate in the adsorption of the pure adsorbate. Over-all capacity coefficients calculated from the values of $k_f a_v$ and $\beta k_s a_v$ were compared with the observed ones. The calculated $K_f a_v$ agreed fairly well with observed ones.

1. Introduction

In the previous paper[4] we reported the separation of the adsorbates such as CO_2, C_2H_4 from various binary gas mixtures by the adsorber of the fixed bed and the rate-controlling step was interdiffision through active carbon. In general, on the separation and refining of the contaminated gas in the chemical industry by the method of adsorption separation, it is often encountered that carrier gas is fairly adsorbable. Consequently, in practise, adsorption separation of such contaminated gas as above mentioned is important.

Now, we carried out the investigation of the adsorption separation of the various kinds of binary gas mixture in flow method which have adsorbable gases only and analysed the observed break-through curves. The capacity coefficients of mass transfer were obtained, and the influence of the flow rates and of the sort of carrier gase upon the capacity coefficients were examined.

2. Experimental

N_2 was obtained from cylinders and washed with water, and then CO, CO_2, C_2H_4, C_3H_6 and active carbon were prepared by the same way as mentioned in the previous paper[4]. The experimental apparatus used in this investigation was also the same one in the previous study, therefore in this paper the figure of the apparatus and the description of the experimental procedure were omitted.

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2.1. Results

The binary gas mixtures were N_2-CO_2, N_2-C_2H_4, CO-CO_2, CO-C_2H_4, CO_2-C_2H_4 and CO_2-C_3H_6. The experiments were operated by using the following six kinds of gas mixtures: 1) CO_2 5%, N_2 95%, 2) C_2H_4 5%, N_2 95%, 3) CO_2 5%, CO 95%, 4) C_2H_4 5%, CO 95%, 5) C_2H_4 5%, CO_2 95%, 6) C_3H_6 5%, CO_2 95%.

The separation experiment was carried out at 0°C and 1 atm. The packed bed and active carbon were the same in our previous study.

The flow rates of the gas mixture were arranged on the range of 100 to 800 ml/min.

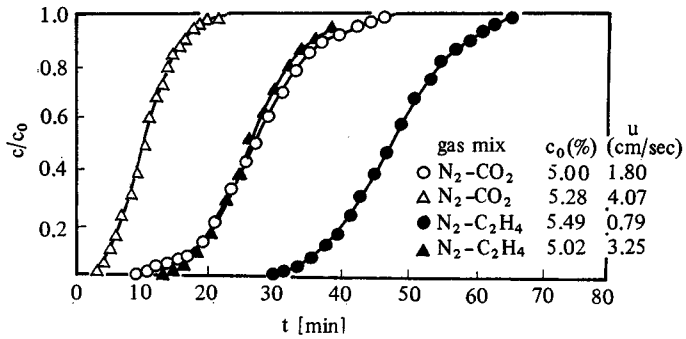

Fig. 1 Break-through curves of CO_2 & C_2H_4 (carrier-gas : N_2)

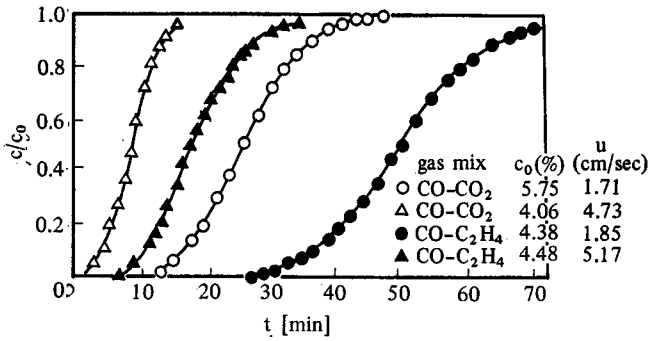

Fig. 2 Break-through curves CO_2 & C_2H_4 (carrier gas : CO)

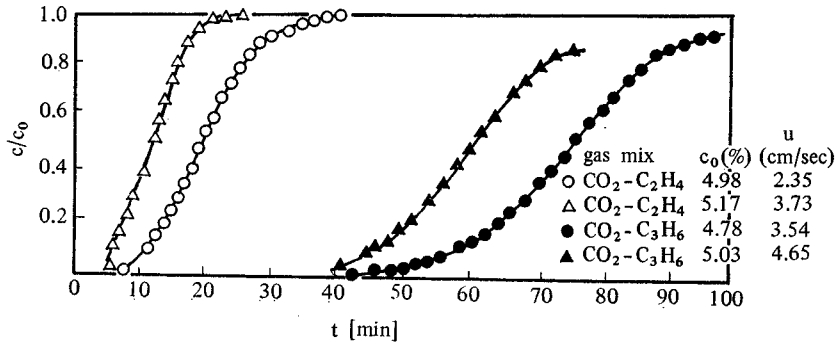

Fig. 3. Break-through curves of C_2H_4 & C_3H_6 (carrier gas : CO_2)

Some of the observed break-through curves are shown in Fig. 1, 2 and 3. As shown in the break-through curves of these figures the larger the adsorbability of the carrier gas was, the more the adsorption separation capacity of adsorber was decreased at the same adsorbate.

3. Discussion

Over-all capacity coefficients $K_f a_v$ of mass transfer were obtained by applying the modified Beaton's method[4] to the observed break-through curves. These values of $K_f a_v$ are plotted against the flow rates in Fig. 4. As shown in Fig. 4, the larger the adsorbability of the carrier gas was, the more $K_f a_v$ was decreased, and effects of the flow rate on $K_f a_v$ were different by the sort of carrier gas.

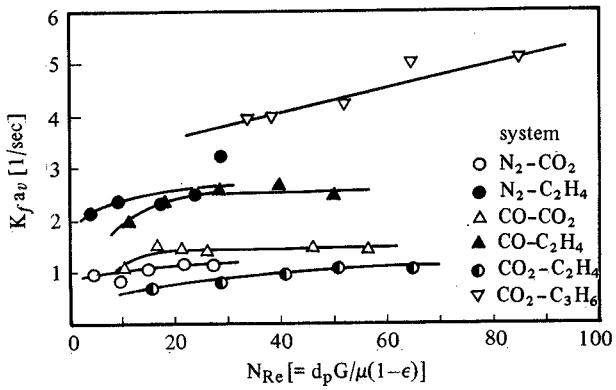

Fig. 4 N_{Re} vs $K_f a_v$

Over-all fluid film capacity coefficient $K_f a_v$ is given by the following equation.

$$\frac{1}{K_f a_v} = \frac{1}{k_f a_v} + \frac{1}{\beta k_s a_v} \tag{1}$$

or

$$R_{0v} = R_f + R_s \tag{2}$$

where $k_f a_v$ is fluid film capacity coefficient, $\beta k_s a_v$ is solid film capacity coefficient, R_{0v} is over-all mass transfer resistance, R_f is fluid film mass transfer resistance, R_s is solid film mass transfer resistance.

Accordingly, $K_f a_v$ is calculated from $k_f a_v$ and $\beta k_s a_v$ by the equation (1).

According to the film theory, fluid film mass transfer coefficient k_f is given by the following equation, when adsorption of a carrier gas is negligible and only adsorbate is adsorbed.

$$k_f = \frac{D_g P}{TR\delta p_{BM}} \tag{3}$$

where δ is film shickness, D_g is diffusion coefficient of adsorbate in gas phase, p_{BM} is

logarithmic mean value of partial pressure of carrier gas at the bothsides of the fluid film, P is total pressure.

When a carrier gas is adsorbable, fluid film coefficient k_f is not given by equation (3).

In the general case, when the total molal flow is N_A+N_B, the rate of transfer of A is[3]

$$N_A = (N_A+N_B)\frac{p_A}{P}-\frac{D_g dp_A}{RTdx} \tag{4}$$

Integration gives

$$N_A-N_B = \frac{D_g P}{RT}\ln\left(1-\left(1+\frac{N_B}{N_A}\right)\frac{p_{A2}}{P}\Big/1-\left(1+\frac{N_B}{N_A}\right)\frac{p_{A1}}{P}\right) \tag{5}$$

If there is such simple relation between desorbed moles of carrier gas B and adsorbed moles of adsorbate A as is given by next equation (6),

$$n_B = sn_A \tag{6}$$

substituting equation (6) into equation (5), N_A may be given by equation (7)

$$N_A = \frac{1}{1-s}\frac{D_g P}{RT}\ln\left(\frac{p_{B2}+s(P-p_{B2})}{p_{B1}+s(P-p_{B1})}\right) \tag{7}$$

where p_A is partial pressure of adsorbate A, p_B is partial pressure of carrier gas B, subscript 1 & 2 denotes inlet and outlet of film.

If logarithmic mean of $p_{B1}+s(P-p_{B1})$ and $p_{B2}+s(P-p_{B2})$ is expressed in p'_{BM}, equation (7) becomes equation (8).

$$N_A = \frac{D_g}{RT}\left(\frac{P}{p'_{BM}}\right)(p_{A1}-p_{A2}) = k_f^0\left(\frac{P}{P'_{BM}}\right)(p_{A1}-p_{A2}) \tag{8}$$

where k_f^0 is fluid film mass transfer coefficient for equimolecular counterdiffusion. Hence, we get k_f' given by equation (9).

$$k_f' = k_f^0\left(\frac{P}{p'_{BM}}\right) \tag{9}$$

From the adsorption isotherm s is given by following equation[6]

$$s = V_m^c/V_m^a+\eta \tag{10}$$

where V_m^a and V_m^c are saturated adsorbed amount of pure adsorbate and pure carrier gas respectively. η is correction term on interaction between adsorbate and carrier gas, and in this experimental condition η is nearly constant.

The numerical values of s calculated by the equation (10) were as follows: For CO_2-C_2H_4, $s=1.02$, for CO_2-C_3H_6, $s=0.81$, for CO-CO_2, $s=0.62$, for CO-C_2H_4, $s=0.82$. For N_2-CO_2 & N_2-C_2H_4, s was unknown because mixed adsorption equilibria of N_2-CO_2 & N_2-C_2H_4 were not measured. Adsorbed amount of N_2, however, was less than half of the

one of CO, so s might be less than 0.5.

k_f^0 was calculated at various experimental conditions by the equation of Chu et al.[1], and $k'_f a_v$ for various systems was determined by the equation (9) and contact area a_v for the packed bed. The $k_f' a_v$ for various systems is tabulated in Table 1.

Average pore radius of active carbon was less than mean free path of all gases used in this experiment at 1 atm. so it was considered that molecules of the carrier gas had no effect on the diffusion of the adsorbate molecules in the pores of the active carbon and that the carrier gas molecules were not accumulated in the pores of the active carbon for the following reasons: 1) diffusivity of the carrier gas was larger than the one of the adsorbate[6], 2) when one mole of adsorbate was adsorbed desorbed moles of the carrier gas were less than unity.

Consequently, in this experimental condition, solid film capacity coefficient $\beta k_s a_v$ of adsorbate may be expressed by the same equation for nonadsorbable carrier gas-adsorbate systems. $\beta k_s a_v$ is given by the following equation[2].

$$\beta k_s a_v = \frac{60 D_e \beta}{d_p^2} \tag{11}$$

where D_e is effective diffusion coefficient of adsorbate in pores of a adsorbent, β is gradient of a adsorption isotherm (adsorption coefficient), d_p is diameter of a adsorbent particle.

D_e was estimated with following assumptions from the observed diffusion coefficient of adsorbate in the adsorption of the pure adsorbate. The assumptions were 1) average pore radius of the active carbon was less than mean free path of all gases used in this experiment at 1 atm, so it was considered that the molecules of the carrier gas had no effect on diffusion of adsorbate molecules in the pores of the active carbon, and 2) diffusion coefficient of a adsorbate increased with adsorbed amount of adsorbate[5], therefore diffusivity of a adsorbate might increase with the adsorbed amounts of the adsorbate and the carrier gas, because the life times of the adsorbate molecules on a inside wall of a pore might be decreased with the adsorption of the carrier gas and the adsorbate[5].

According to the assumption that the diffusion coefficient was equal to the one of the pure adsorbate (adsorbate only existing) at adsorbed amount V', the diffusion coefficient D_e of the adsorbate in the presence of the adsorbable carrier gas was estimated.
V' is given by equation (12)

$$V' = V + \frac{\tau_c}{\tau} V_c \tag{12}$$

where V is adsorbed amount of adsorbate, τ is mean life time of adsorbate molecule, τ_c is mean life time of the carrier gas molecule, V_c is adsorbed amount of the carrier gas.

τ and τ_c can be calculated from the adsorption isotherms.

It was considered that the pores of the adsorbent would be narrowed by adsorption of a

carrier gas on the inside wall and therefore the adsorption of the carrier gas might interfere the diffusion of the adsorbate in the pores. However, it was considered that the influence might be insignificant, because the total adsorbed amount of the carrier gas was slight and the adsorbed molecules did not form even monolayer on the wall of the pores, hence the influence was ignored.

Being based on the above assumptions, D_e was calculated from the observed diffusivity of the pure adsorbate[5], and β was determined from the observed mixed gas adsorption isotherm and further solid film capacity coefficients were calculated.

Table 1

Gas Mixture		Concentration (mol fraction)	Flow Rate (based on empty column) (cm/sec.)	N_{Re} $\frac{d_p}{\mu(1-\epsilon)}$	$k'_f a_v$ (1/sec.)	$\beta k_s a_v$ (1/sec.)	$K_f a_v$ (1/sec.)	
Carrier gas	Adsorbate						Calculated	Observed
N_2	CO_2	0.0437	0.921	4.92	9.02	2.74*	2.10	0.98
		0.0500	1.80	9.65	10.2	"	2.16	0.85
		0.0484	2.80	15.0	11.3	"	2.21	1.04
		0.0528	4.07	21.9	12.2	"	2.24	1.13
		0.0467	5.09	27.2	12.9	"	2.26	1.12
N_2	C_2H_4	0.0546	0.788	4.20	8.88	3.60**	2.56	2.12
		0.0549	1.77	9.44	10.60	"	2.69	2.38
		0.0490	3.23	17.1	12.17	"	2.78	1.72
		0.0502	3.25	17.3	12.14	"	2.78	2.31
		0.0508	4.47	23.8	13.03	"	2.82	2.48
		0.0542	5.42	28.9	13.52	"	2.84	3.20
CO	CO_2	0.0550	1.04	10.16	6.14	2.47	1.76	1.09
		0.0575	1.71	16.77	6.84	"	1.81	1.50
		0.0403	2.19	21.2	6.67	"	1.80	1.46
		0.0433	2.71	26.2	7.65	"	1.86	1.39
		0.0406	4.73	45.8	9.86	"	1.98	1.47
		0.0440	5.82	56.4	11.04	"	2.02	1.40
CO	C_2H_4	0.0454	1.21	11.56	6.84	2.94	2.06	1.99
		0.0439	1.85	17.8	7.47	"	2.11	2.34
		0.0462	2.97	28.55	8.31	"	2.18	2.56
		0.0457	4.10	39.4	9.65	"	2.26	2.66
		0.0448	5.17	49.6	10.77	"	2.31	2.42
CO_2	C_2H_4	0.0477	0.89	15.5	4.63	1.89	1.34	0.73
		0.0495	1.65	28.8	5.43	"	1.40	0.77
		0.0498	2.35	41.0	6.44	"	1.46	0.95
		0.0466	2.91	50.8	7.27	"	1.50	1.08
		0.0517	3.73	64.9	8.35	"	1.54	1.08
CO_2	C_3H_6	0.0491	1.56	33.4	4.29	6.66***	2.65	3.90
		0.0474	2.09	38.15	5.43	"	3.04	3.94
		0.0376	2.88	52.0	6.52	"	3.36	4.20
		0.0478	3.54	64.6	7.28	"	3.55	5.00
		0.0503	4.65	85.0	8.49	"	3.80	5.10

* For N_2-CO_2, $\beta k_s a_v$ was estimated as being in the middle of H_2-CO_2 and CO-CO_2.

** For N_2-C_2H_4, $\beta k_s a_v$ was estimated as being in the middle of H_2-C_2H_4 and CO-C_2H_4.

*** For CO_2-C_3H_6, $\beta k_s a_v$ was estimated as ideal mixed adsorption.

Over-all capacity coefficient $K_f a_v$ was calculated by the equation (1) and tabulated in Table 1 with the observed capacity coefficient.

The agreement between the observed capacity coefficients and calculated ones was fairly satisfactory. Accordingly, the over-all capacity coefficient can be calculated from the diffusion coefficient of the pure adsorbate and the mixed adsorption isotherm by means of the above method.

4. Summary

1) To known the effect of a carrier gas on over-all capacity coefficient for a adsorbate, adsorption separation of various binary gas mixtures was investigated at 0°C & 1 atm.

Over-all capacity coefficients obtained by analysing the observed break-through curves were varied by the sort of carrier gas at the same flow rate.

2) Fluid film capacity coefficient $k_f a_v$ was calculated by using the Chu's equation, and solid film capacity coefficient $\beta k_s a_v$ was calculated from the values of the observed mixed adsorption isotherm and observed diffusion coefficient of the pure adsorbate in the pores of the active carbon. And further over-all capacity coefficient $K_f a_v$ was calculated by the equation (1).

The calculated over-all capacity coefficients were compared with the observed ones. Agreement between calculated $K_f a_v$ and observed one was fairly good.

3) Over-all mass transfer coefficient for any gas mixture can be calculated from the values of the observed mixed gas adsorption isotherm of the gas mixture and the observed diffusion coefficient of the pure adsorbate in the pores of the active carbon.

5. Notation

a_v	:	effective contact area for mass transfer
D_e	:	diffusion coefficient of adsorbate in pores of a active carbon
D_g	:	diffusion coefficient in gas phase
d_p	:	diameter of a adsorbent particle
K_f	:	over-all mass transfer coefficient
k_f	:	fluid film mass transfer coefficient
k_f^0	:	fluid film mass transfer coefficient for equimolecular counter-diffusion
k_s	:	solid film mass transfer coefficient
n_A & n_B	:	number of moles of gas A & B
N_A & N_B	:	molal flow of gas A & B
P	:	total pressure
p_{BM}	:	logarithmic mean of partial pressure of gas B
R_{0v}	:	over-all mass transfer resistance
R_f	:	fluid film mass transfer resistance
R_s	:	solid film mass transfer resistance
s	:	constant in equation (6)

V & V_c : adsorbed amount of adsorbate and carrier gas

V_m^a & V_m^c: saturated adsorbed amount of pure adsorbate and pure carrier gas

β : adsorption coefficient

δ : film shickness

η : correction term on interaction at mixed adsorption

τ & τ_c ; mean life time of adsorbate molecule and carrier gas molecule

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