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ADSORPTION OF n-BUTANE AND 1,3-BUTADIENE ON CROSS-LINKED POLYSTYRENE

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SUMMARY

   Adsorption isotherms of n-butane and 1,3-butadiene and their mixtures on cross-linked polystyrene at 25°C were measured by the frontal analysis method. Single-component isotherms appear to be of the Freundlich type. A binary Freundlich isotherm is adopted for discussing binary data and a method for calculating binary parameters is presented. Another binary Freundlich isotherm, which fails to agree with our data, was examined also.

INTRODUCTION

   Porous polymer beads are used as a stationary phase in chromatographic analysis because of their good separation power. The polymer adsorbents can be tailored to have suitable pore size and surface area. Water, alcohols and other polar compounds can be separated by gas–solid chromatography[1] (GSC) in a short time with a sharp, symmetrical peak. The selectivity of polymer adsorbents is noticeable in that it is possible to separate methane from its isotopic compound, tetradeuterated methane[2]. A linear isotherm is a necessary prerequisite for a symmetrical peak in GSC. For adsorbents such as activated carbon, the adsorption isotherm was observed to be significantly non-linear even for very low concentrations[3]. The study of adsorption isotherms on polymers has not been extensive[4–6]. Burke and Ackerman[4] obtained nitrogen adsorption isotherms for Porapaks N, P, Q, R, S and T. Houriet *et al.*[5] studied the physical adsorption of nitrogen, argon, sulfur dioxide and neopentane on poly(vinylidene fluoride). Gray and Guillet[6] used the pulse-flow method to measure the adsorption isotherm of n-decane and n-hexanol on poly(methyl methacrylate) and polystyrene for temperatures between 25°C and 60°C. Their results show anti-Langmuir type isotherms for solutes at very low partial pressures.
   Measurements of adsorption isotherms using GSC are usually conducted through the "frontal analysis by characteristic points" (FACP) method or through the pulse flow method[7]. When adsorbent particles have large diffusional resistance,

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the use of these two methods generally leads to adsorption isotherms with a larger curvature than the true isotherm[8]. The frontal analysis (FA) method[9], introduced in the early stage of the development of GSC, gives a better result because it is based on the mass-balance relation. The aim of this study is to report adsorption isotherms for two hydrocarbon gases, *viz.*, *n*-butane and 1,3-butadiene on crosslinked polystyrene measured by the FA method. The same method is applied also to measure the binary adsorption isotherm of these two gases.

EXPERIMENTAL

Measurements were conducted by a gas chromatographic method using a finite input concentration. Since the flow system used in the present study was described elsewhere[10,11], only a brief description is given here. The flow system was constructed of stainless-steel tubing and valves with PTFE seats and gaskets. Calibrated hydrocarbon–helium mixtures (with a nominal concentration of 1%) were prepared by Matheson Gas Co. (East Rurtherford, NJ, U.S.A.). The calibrated gases were mixed with pure helium in different proportions. Gas flow-rates were measured with an accuracy of $\pm 0.5\%$ by flowmeters. The concentration of the hydrocarbon at the downstream side of the column was measured at regular time intervals by a Varian 3700 gas chromatograph.

Cross-linked polystyrene beads (20–40 mesh), purchased from Applied Science Labs. (State College, PA, U.S.A.), have a free-fall density of 0.34 g/cm^3, a surface area of 650 m^2/g and an average pore diameter of 50 Å. A stainless-steel adsorption column (10 $\times$ 1.08 cm I.D.) was packed with 3.23 g of polystyrene beads. The adsorption column was immersed in a water-bath; the temperature was controlled to within $\pm 0.02°$C.

RESULTS AND DISCUSSION

Experiments were conducted first to measure the adsorption isotherm of each single-component gas. Different inlet concentrations were prepared by diluting calibrated hydrocarbon–helium mixtures by pure helium. The solid-phase concentration, q_0, corresponding to a gas-phase concentration, C_0, is calculated from the mass-balance equation[10,11]:

$$(1 - \varepsilon)q_0 + \varepsilon C_0 = uC_0 \int_0^{\infty} [1 - C(t)/C_0]dt \tag{1}$$

Here ε is the void fraction of the column, u is the superficial flow velocity and $C(t)$ is the outlet concentration measured at the column exit.

Figs. 1 and 2 are log log plots of the adsorption isotherm of *n*-butane and 1,3-butadiene. Both isotherms appear to follow the Freundlich equation and are very close to each other; in fact, the adsorption data are so close that a separate plot is necessary for each gas. The coefficient K_i and the exponent α for the Freundlich isotherm

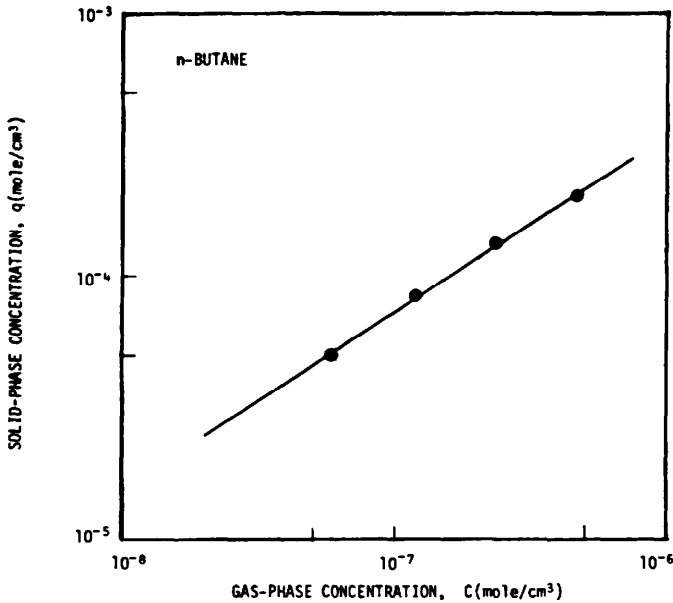$$q_i = K_i C_i^{\alpha} \tag{2}$$

are calculated and given in Table I.

Fig. 1. Adsorption isotherm of n-butane on cross-linked polystyrene at 25°C.

In the experiments to measure the binary adsorption isotherm, nine input concentrations were prepared by mixing butane–helium, 1,3-butadiene–helium and pure helium in different ratios. The solid-phase concentration for each gas is still calculated through eqn. 1; however, the solid-phase concentration of each gas is a
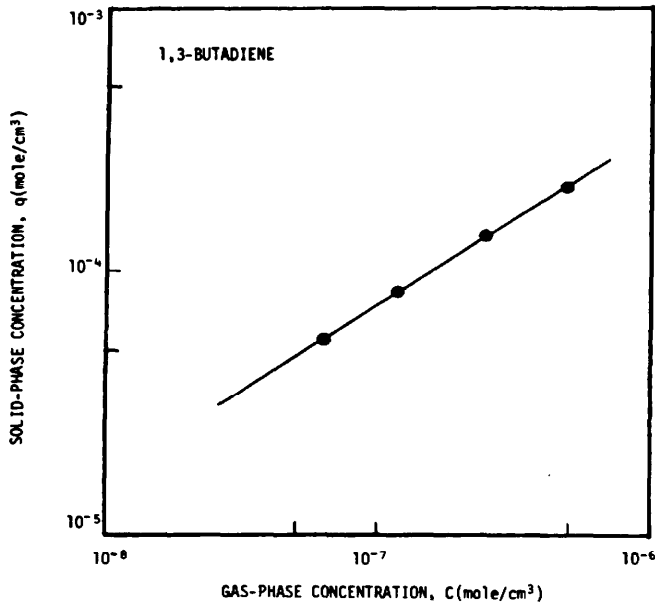

Fig. 2. Adsorption isotherm of 1,3-butadiene on cross-linked polystyrene at 25 C.

TABLE I

PARAMETERS OF ISOTHERMS FOR n-BUTANE, 1,3-BUTADIENE AND BINARY MIXTURES
OF THESE TWO GASES

Gas	α	K_i	K_{ij}	β	γ
n-Butane	0.669	3.55_6	1046	0.591	1.140
1,3-Butadiene	0.652	2.77_3	11.0_4	0.650	0.890

function of the gas-phase concentrations of both gases. A binary adsorption isotherm
was proposed to be of the following form[12]:

$$q_i = \frac{K_i C_i^{\gamma + \beta}}{C_i^{\beta} + K_{ij} C_j^{\gamma}} \tag{3}$$

When the concentration C_j is zero, eqn. 3 becomes

$$q_i^* = K_i C_i^{\gamma} \tag{4}$$

which is exactly the same as eqn. 2. Note that the representation of the binary iso-
therm by eqn. 3 requires three more parameters than does eqn. 2 for the isotherm of a
single-component gas. It is also of interest to know, based on the results discussed
later, that the parameter K_{ij} takes on different values for n-butane and 1,3-butadiene
and that these values are not related; in fact, they will have different units if the
parameter γ is different for different gases. At this stage, we treat them only as
empirical parameters because eqn. 3 satisfies some system[12].

Taking the ratio q_i^*/q_i, we have

$$\frac{q_i^*}{q_i} - 1 = K_{ij} \cdot \frac{C_j^{\gamma}}{C_i^{\beta}} \tag{5}$$

or

$$\log (q_i^*/q_i - 1) = \log K_{ij} + \gamma \log C_j - \beta \log C_i \tag{6}$$

The left side of eqn. 6 is a measurable quantity. By considering $\log C_j$ and $\log C_i$ as
independent variables, the parameters K_{ij}, β and γ can be determined from a multi-
variable regression method. Calculated results for each sample gas in binary mixtures
are listed in Table I. A test of eqn. 6 is made in Figs. 3 and 4 where the left-hand side is
plotted versus the right-hand side. Except for two individual cases (run 4 for butane
and run 8 for 1,3-butadiene), the correlation based on eqn. 5 is very good. Calculated
solid-phase concentrations are listed also in Table II for comparison with the experi-
mental results.

Another binary Freundlich isotherm was suggested by Sheindorf et al.[13]. Their
equation is given as:

$$q_1 = K_1 C_1 (C_1 + a_{12} C_2)^{n_1 - 1} \tag{7}$$

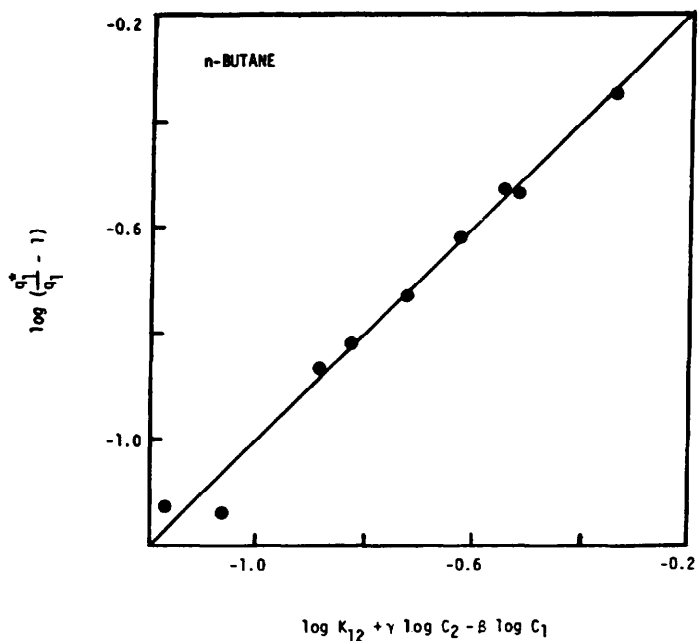$$\log K_{12} + \gamma \log C_2 - \beta \log C_1$$

Fig. 3. The experimental values of the left-hand side of eqn. 6 *versus* the calculated values of the right-hand side of eqn. 6 for *n*-butane in binary mixtures of *n*-butane and 1,3-butadiene on cross-linked polystyrene at 25°C. A line of unit slope is shown for comparison.
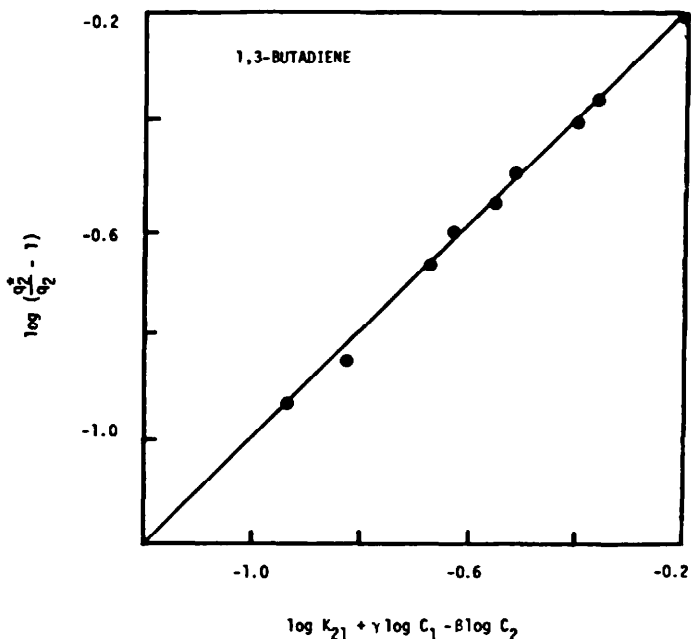

$$\log K_{21} + \gamma \log C_1 - \beta \log C_2$$

Fig. 4. The experimental values of the left-hand side of eqn. 6 *versus* the calculated values of the right-hand side of eqn. 6 for 1,3-butadiene in binary mixtures of *n*-butane and 1,3-butadiene on cross-linked poly-styrene at 25°C. A line of unit slope is shown for comparison.

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED SOLID-PHASE CONCENTRATIONS OF n-BUTANE AND 1,3-BUTADIENE ON CROSSLINKED POLYSTYRENE AT 25°C FROM NINE BINARY MIXTURES OF THESE GASES

Run	Gas-phase concentration, C $(10^{-7}\ mole/cm^3)$		Solid-phase concentration, q $(10^{-4}\ mole/cm^3)$			
	n-Butane	1,3-Butadiene	n-Butane		1,3-Butadiene	
			Exptl.	Calc.	Exptl.	Calc.
1	2.633	2.459	1.130	1.136	1.029	1.036
2	2.631	1.644	1.215	1.221	0.7470	0.7451
3	2.636	0.8218	1.304	1.316	0.4094	0.4078
4	1.759	0.8271	0.9972	0.9863	0.4643	0.4638
5	1.762	1.640	0.9022	0.9027	0.8123	0.8128
6	1.773	2.480	0.8337	0.8281	1.119	1.121
7	0.8808	2.472	0.4644	0.4641	1.214	1.217
8	0.8823	1.644	0.5198	0.5257	0.9117	0.9045
9	0.8785	0.8246	0.5911	0.5959	0.5318	0.5375

According to the derivation, $a_{12} = 1/a_{21}$; therefore, only five parameters are needed for a binary mixture and four of the parameters can be determined through a single-component isotherm. When we tested the method of Sheindorf $et\ al.$ (eqn. 18 of ref. 13) with our data, we did not obtain agreement; in fact, the system chosen by these authors in their theoretical discussion did not agree also. When they fit the parameter a_{12} using binary data, they obtained a linear plot; however, when they compared the solid-phase concentration with experimental values, there was a systematic error. A more adequate approach for determining the parameters would be to obtain those parameters first that can be determined uniquely from the single-component isotherm and then to add the binary parameters later. Another difficulty with eqn. 7 is that the mathematical derivation indicates that K_1 is proportional to the temperature. Since the equation becomes a linear isotherm, when $n_1 = 1$, the adsorption constant K_1 should depend on temperature in accord with the Arrhenius relation, $viz.$, $K_1 = A \exp(-\Delta H_{ads}/RT)$.

The agreement of our data neither indicates the correctness of eqn. 3 nor does it invalidate the use of eqn. 7 because ten parameters were used in a binary system. Since we observed that the Freundlich isotherm holds very well for a gas–polystyrene system over a wide concentration range, it is worthwhile to compare further eqns. 3 and 7 using more than two adsorbates and at different temperatures.

CONCLUSION

We studied the adsorption isotherms of n-butane and 1,3-butadiene on polystyrene at 25°C. Both gases follow the Freundlich isotherm and their mixtures follow a generalization on the Freundlich isotherm. Since two generalization methods exist in the literature, it is necessary to examine their difference more closely by using three adsorbates and by measuring data at different temperatures.

REFERENCES

1 O. L. Hollis, *Anal. Chem.*, 38 (1966) 309.
2 J. J. Czubryt and H. D. Gesser, *J. Gas Chromatogr.*, 6 (1968) 41.
3 A. V. Kiselev and Y. Z. Yashin, *Gas-Adsorption Chromatography*, Plenum, New York, 1969.
4 M. F. Burke and D. G. Ackerman, Jr., *Anal. Chem.*, 43 (1971) 573.
5 J. P. Houriet, P. Ghiste and H. I. Stoecki, *Helv. Chim. Acta*, 57 (1974) 851.
6 D. G. Gray and J. E. Guillet, *Macromolecules*, 5 (1972) 316.
7 R. J. Laub and R. L. Pecsok, *Physicochemical Applications of Gas Chromatography*, Wiley, New York, 1978.
8 J. C. Huang, D. Rothstein, B.-G. Wu and R. Madey, *J. Chromatogr.*, 244 (1982) 15.
9 D. H. James and C. S. G. Phillips, *J. Chem. Soc., London*, (1954) 1066.
10 J. C. Huang, R. Forsythe and R. Madey, *Sep. Sci. Technol.*, 16 (1981) 475.
11 J. C. Huang, R. Forsythe and R. Madey, *J. Chromatogr.*, 214 (1981) 269.
12 W. Fritz and E. U. Schlunder, *Chem. Eng. Sci.*, 36 (1981) 721.
13 C. Sheindorf, M. Rebhun and M. Sheintuch, *J. Colloid Interface Sci.*, 79 (1981) 136.