

STUDY OF POROUS ADSORBENTS BY ISOTOPIC MOLECULAR EXCHANGE METHOD. I. SILICA*

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Introduction

The equilibrium isotopic molecular exchange is an exchange of identical molecules between phases in which the isotope ratio of one or more elements is different (e.g. benzene in inactive and ^{14}C labelled form) and there is neither intermolecular nor intramolecular isotopic exchange. The system is an equilibrium one except for the isotope ratio and this difference makes the exchange reaction heteroentropic, so the Gibbs free energy also changes at a given temperature:

$$\Delta G = -T\Delta S \quad (1)$$

(ignoring the isotope effect).

According to experience, conclusions can be drawn from the exchange rate on the accessibility and characteristics of the immobile liquid phase (1, 2, 3, 4).

The aim of the present investigation is 1. to determine the half time and total time of the adsorption/desorption process, 2. to determine the effect of a) the structure of a given solid (both chemical and physical), b) the nature of the liquid, c) in case of solutions the concentration, d) the solid/liquid ratio, and e) the temperature on the half time.

The solids under investigation are porous and nonporous silicas. The liquids used are benzene, heptane and ethanol.

Experimental procedure

The experimental procedure consists of three consecutive steps.

- (1) Equilibration of the system.
- (2) Change of the liquid phase.
- (3) Determination of the change in isotope ratio in the bulk liquid phase as a function of time.

* Dedicated to Prof. G. Schay on the occasion of his 75th birthday.

Equilibration of the system

Two types of procedures can be utilized for studying molecular isotopic exchange. The first procedure entails to use two identical systems under identical conditions differing only by isotope ratio. In the second technique only one system, which is labelled, is used. In both cases it is important to allow sufficient time for adsorption equilibrium to be complete. Although obvious, it is stressed that both the purity of the liquid phase and the history of the adsorbent must be identical and reasonable.

Change of the liquid phase

Theoretically, several techniques could be used for separating the labelled liquid from the adsorbent. However, not all of these methods are suitable for use with volatile organic liquids and solutions. The separated adsorbent contains two parts of liquid; the "adsorbed" phase and the free liquid. It is essential not to disturb the adsorption equilibrium while the adsorbent is removed from bulk liquid.

In the case of granular adsorbents of large particle size, it is convenient to remove the liquid phase by decantation or pipetting. For small nonporous adsorbents, centrifugation followed by pipetting is convenient.

Care must be taken to replace the same volume of liquid at the same concentration as was removed.

Determination of the change in isotope ratio in the bulk liquid as a function of time

In the present study, only radioactive isotopes were used as labelled adsorbate, although stable isotopes could also be used. Hence, the isotope ratio is determined in the same way as the activity of the liquid phase.

There are two basic possibilities for the determination of the activity of the liquid phase as a function of time. The first is a sampling technique in which small aliquots of liquid are removed from the system and analyzed separately. This sampling can be accomplished by removing liquid from a continuously circulating system or by removing the sample from a non-circulating stirred liquid. In the second possibility, the circulating liquid is analyzed continuously without its removal from the system. In the present study, only the sampling technique is used.

The organic liquids are labelled with Carbon-14. The radioactivity was measured with a Packard-TriCarb liquid scintillation counter (3000 series) and the liquid scintillator was liquiflou (New England Nuclear) diluted with scintillation grade toluene as per manufacturer's specifications. All samples were weighed and the measured intensity was expressed on a per gram basis. The volume of the sample was about 0.5 ml.

The background intensity, using 5 to 15 ml of liquid scintillator, was about 20 cpm. The counting efficiency was determined as a function of liquid scintillator. The maximum was at 10 ml scintillator, but the difference between 5 and 10 ml was less than 10% and 5 ml of scintillator was used.

Materials

Adsorbents

Silica was chosen since it can be obtained commercially in both porous and nonporous forms and its surface properties can be varied by pretreatment. The types of silica used are shown in Table I.

Table I

Type	Name	Specific surface area m ² /g	Particle size (mesh)	Pore volume ml/g	Notice
Porous	Grade 59	340	3—8	1.15	Davison Chemical Div. W. R. Grace Activated at 300 °C for 12 hrs.
Porous	Grade 40	800	6—12	0.43	Davison Chemical Div. W. R. Grace Activated at 300 °C for 12 hrs.
Porous	Grade 62	340	60—200	1.15	Davison Chemical Div. W. R. Grace Activated at 300 °C for 12 hrs.
Nonporous	HiSil	127		—	Pittsburgh Plate Glass Co. Activated at 110 °C for 12 hrs. (completely hydrophilic)
Nonporous	CabOSil	187			Cabot Corp. Activated at 110 °C for 12 hrs. (partially hydrophilic)

Notes: The surface area of the porous silica was determined by the manufacturer

The surface area of HiSil and CabOSil was obtained from the literature (4)

All silicas were extracted with pure benzene and porous solids were activated at 300 °C in vacuo

Liquids

(1) Benzene — Spectrographic grade obtained from Fisher Scientific Co.

(2) Benzene labelled by Carbon-14 — obtained from New England

Nuclear.

(3) Heptane — Spectrographic grade obtained from Fisher Scientific Co.

Results

All measured data were selected on the basis of the Chauvenet criterion after the experimental error was determined (5).

Presentation of data

The specific measured intensity (cpm/g) was calculated from the average measured intensity (cpm). All data are presented as

$$\ln \left[1 - \frac{i(t)}{i_{\infty}} \right] \text{ vs } t \quad \ln(1 - i(t)/i_{\infty}) \text{ vs } t$$

where $i(t)$ is the specific measured intensity at time t , and i_{∞} is the specific measured intensity after the exchange equilibrium (for $\frac{di}{dt} = 0$). The ratio $F = i(t)/i_{\infty}$ is called the exchange ratio.

Sources of error and reproducibility of the measured data

After preliminary investigations, it became obvious that the source of systematic error could be determined and methods for reducing or eliminating these systematic errors developed. Furthermore, random errors had to be determined.

Sources of systematic errors

(1) Heterogeneity of materials — It is readily possible to control the heterogeneity of the liquid part of the system. This is however, not true for the adsorbent since a different sample of solid must be used for each measurement. Although the heterogeneity of the adsorbent can be reduced by careful pretreatment procedure, the error caused by heterogeneity cannot be completely eliminated.

(2) Equilibration of the system.

(3) Change of the liquid phase — There are two major sources of error likely to arise in this stage of the experiment:

(a) The liquids to be exchanged are not identical. This error is controllable and can be eliminated.

(b) Disruption of the solid/liquid equilibrium during the separation procedure. This effect is not completely controllable. The possibility of this error can be reduced but not eliminated.

(4) Determination of the radioactivity as a function of time using a sampling technique. Four major sources of error arise in this step:

(a) Inhomogeneity of the liquid phase as a function of distance from the exchange phase boundary due to insufficient stirring of the liquid phase.

(b) Timing — The time required for sampling is about 1 second.

(c) Weighing the sample.

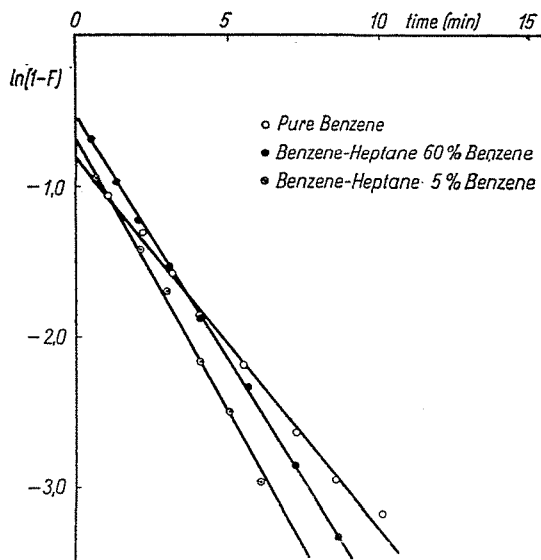


Fig. 1. Equilibrium exchange curves for silica gel / benzene-heptane systems (4 g silica : 35 ml solution)

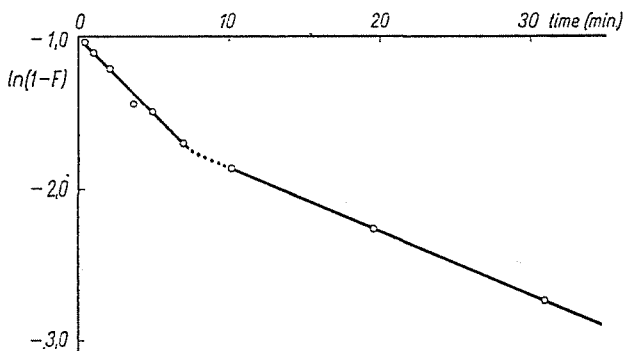


Fig. 2. Equilibrium exchange curve for silica gel 40 / benzene system (4 g silica : 35 ml benzene)

- (d) Radioactivity determination.
- (e) Decrease in the volume of the system during the investigation.
This source of error will be important if the exchange rate depends considerably on the volume of the liquid phase. This dependence is negligible for the systems investigated.

Fig. 1 represents $\ln(1 - F)$ as a function of time for silica gel 59 in equilibrium with three different solutions with the same solid/liquid ratio (4/70). Curve 1 is for pure benzene; curve 2 is for benzene-heptane solution with 60% by wt. of benzene and curve 3 is for benzene-heptane solution with 5% by wt. of benzene. Fig. 2 shows the exchange curve for silica gel 40/pure

benzene. Within experimental error the three curves of Fig. 1 are linear. The slope of each is the measured exchange constant k_m .

Table II summarizes the values of the measured exchange constant for silica gel 59, benzene and benzene/heptane systems at 25 °C. This table gives only a partial list of the results of the experiments carried out and represents data obtained after solving experimental problems as sampling, stirring rate, etc.

Table II
 k_m values for silica gel 59 systems at 25 °C

Concentration Benzene % by wt.	$\frac{g}{g}$ Silica	$\frac{cm^3}{g}$ Solution	k_m
100	4	35	0.26
100	4	35	0.27
100	2	35	0.25
100	4	70	0.25
100	4	70	0.24
100	4	70	0.26
100	2	105	0.29
60	4	35	0.34
60	4	35	0.34
60	2	35	0.34
60	2	35	0.36
60	4	70	0.37
60	4	70	0.42
60	2	70	0.42
60	2	105	0.38
5	4	35	0.36
5	2	35	0.41
5	4	70	0.38
5	2	70	0.31
5	4	105	0.36
5	2	105	0.31

Table II shows significant differences in the measured exchange constants k_m among pure benzene and benzene/heptane solutions. No significant differences in k_m could be found among the various solid/liquid ratios from 4 g solid/35 ml liquid to 2 g solid/105 ml liquid. The results do not show significant differences in the exchange constants in 5% and 60% benzene/heptane mixtures.

The half times of the exchange process on silica 59 from pure benzene

and benzene/heptane mixtures are 2.67 and 1.92 min. respectively, calculated from the averages of the measured k_m values.

The time to reach equilibrium is stated to be 10 times the half time.

Table III summarizes the results for silica gel 40 using pure benzene and benzene-heptane mixtures at 25 °C; the calculated half times from k_{m_1} and k_{m_2} being 6.9 min. and 17.3 min, respectively.

The half times of non-porous silicas are less than 2 sec.

Table III
 k_m values for silica gel 40 systems at 25 °C

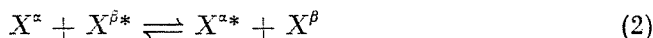
Concentration Benzene % by wt.	g Silica	ml Solution	k_{m_1}	k_{m_2}
100	4	35	0.11	0.042
100	4	70	0.12	0.042
100	2	35	0.096	0.041
100	2	70	0.11	0.043
60	4	35	0.13	0.045

Discussion

Tentative formalkinetic interpretation of the linear molecular exchange curves

The exchange curves of the pure benzene and benzene-*n*-heptane mixtures are linear in the case of silica gel grade 59.

The supposed exchange process is as follows:



where X is the symbol of the actual component (e.g. in the case of benzene-*n*-heptane solution if labelled benzene is used, X is the symbol of the unlabelled benzene and X^* is that of labelled benzene), α and β are the symbols of the liquid and the "exchange" phase, respectively.

The "exchange" phase is that part of the system which does not mix immediately with the bulk liquid, i.e. which remains heteroentropic relative to the bulk liquid phase. The exchange phase could be equal to the adsorbed phase but could be much greater in the case of porous materials.

The rate of appearance of isotope molecules in the liquid phase α is

$$\frac{dA^{\alpha*}}{dt} = R_1 a^\beta (1 - a^\alpha) - R_2 a^\alpha (1 - a^\beta) \quad (3)$$

but since the system is in equilibrium

$$R_1 = R_2 = R \quad (4)$$

where R is the constant exchange rate, a is the specific activity $\left(a = \frac{A^*}{A}\right)$, A is the total amount in moles) of the component X in phase α or β and A^* is the amount of isotope molecules in phase α or β .

$Ra^\beta(1 - a^\alpha)$ is the rate of the appearance of isotope molecules in the phase α from the phase β . The meaning of $Ra^\alpha(1 - a^\beta)$ is the same only the direction is reversed.

From Eq. (3):

$$\frac{dA^{\alpha*}}{dt} = R(a^\beta - a^\alpha) \quad (5)$$

The boundary conditions are:

$$\text{for } t = 0, \quad a^\alpha = a_{(0)}^\alpha \quad \text{and} \quad a^\beta = a_{(0)}^\beta.$$

Since the system is closed:

$$A_{(0)}^{\alpha*} + A_{(0)}^{\beta*} = A^{\alpha*} + A^{\beta*} + A_\infty^{\alpha*} + A_\infty^{\beta*} \quad (6)$$

where $A_{(0)}^*$ is the number of the isotope molecules in phase α or β for $t = 0$; A^* is the number of the isotope molecules in phase α or β at a time t and A_∞^* is the number of isotope molecules in phases α or β if the system is in total equilibrium, i.e. not heteroentropic, or for $\frac{dA^*}{dt} = 0$.

If the system is in total equilibrium

$$a_{(\infty)}^\alpha = a_{(\infty)}^\beta \quad (7a)$$

or

$$\frac{a_{(\infty)}^{\alpha*}}{A^\alpha} = \frac{A_{(\infty)}^{\beta*}}{A^\beta} \quad (7b)$$

From Eqs 5 and 6 the indefinite integral:

$$-\ln(A_{\infty 1}^{\alpha*} - A^{\alpha*}) = R \frac{A^\alpha + A^\beta}{A^\alpha A^\beta} t + b \quad (8)$$

$$b = -\ln(A_\infty^{\alpha*} - A_{(0)}^{\alpha*}) = -\ln A_\infty^{\alpha*} \quad (9)$$

and Eq. 8 can be rewritten as:

$$\ln \left(1 - \frac{A^{z*}}{A_{\infty}^{z*}} \right) = -R \frac{A^z + A^\beta}{A^z A^\beta} t \quad (10a)$$

or

$$\ln(1 - F) = -R \frac{A^z + A^\beta}{A^z A^\beta} t \quad (10b)$$

where

$$F = \frac{A^{z*}}{A_{\infty}^{z*}} \quad (11)$$

is defined as the exchange ratio.

If $A_{(0)}^{z*} \neq 0$, Eq. 10 becomes:

$$\ln(1 - F) = -R \frac{A^z + A^\beta}{A^z A^\beta} t + C \quad (12)$$

where

$$C = \ln \left(1 - \frac{A_{(0)}^{z*}}{A_{\infty}^{z*}} \right) \quad (13)$$

Eqs 10 are formally identical with the McKay equation describing the simple homogeneous exchange processes.

The measured rate constant k_m can be described as:

$$k_m = R \frac{A^z + A^\beta}{A^z A^\beta} = k(A^z)^a (A^\beta)^b \dots \frac{A^z + A^\beta}{A^z A^\beta} \quad (14)$$

where (A) is the concentration, i.e. $(A) = \frac{A}{V}$, V is the volume.

For $A^z \gg A^\beta$

$$k_m = R \frac{1}{A^\beta} = k(A^z)^a (A^\beta)^b \dots \frac{1}{A^\beta} \quad (15)$$

From Eqs 14 and 15, k appears to be a constant under isotherm conditions. But it is known that k might contain many parameters and to guess a and b values some ideas must be supposed about the physical meaning of k .

Let us see now how the measured exchange constant k_m varies with the change of concentration and of the solid/liquid ratio for a first-order exchange reaction.

First-order molecular exchange reaction

There are two possibilities of the concentration dependency:

$$R = k_1^{\alpha} \frac{A^{\alpha}}{V^{\alpha}} \quad (16)$$

$$R = k_1^{\beta} \frac{A^{\beta}}{V^{\beta}} \quad (17)$$

$$k_m = k_1^{\alpha} \frac{A^{\alpha} + A^{\beta}}{V^{\alpha} A^{\beta}} \quad (18)$$

for $A^{\beta} \ll A^{\alpha}$

$$k_m = k_1^{\alpha} \frac{A^{\alpha}}{V^{\alpha} A^{\beta}} \quad (19)$$

or

$$k_m = k_1^{\beta} \frac{A^{\alpha} + A^{\beta}}{V^{\beta} A^{\alpha}} \quad (20)$$

for $A^{\beta} \ll A^{\alpha}$

$$k_m = k_1^{\beta} \frac{1}{V^{\beta}} \quad (21)$$

According to Lieser⁽⁷⁾ in the case of non-porous solid phase the k_1 value of a first-order heterogeneous isotopic exchange process is

$$k_1 = D \frac{A_s}{\bar{r}} \frac{1}{V^{\alpha}} \quad (22)$$

where D is the diffusion constant (cm^2/sec), A_s is the surface area (cm^2), V^{α} is the volume of the liquid phase (cm^3) and \bar{r} is the average diameter of the particles (cm). Taking into account that in the present case the dimension of R is mole time and the "exchange" volume is generally not equal to the surface phase the Lieser constant must be transformed to

$$k_1 = D \frac{V^{\beta}}{\bar{l}^2} \quad (23)$$

where \bar{l} is an average distance characteristic for the adsorbent and may be for the type of the liquid molecules.

Combining systematically Eqs (23) with (18), (19), (20) and (21), results

in:

$$k_m = k_1^* V^\beta \frac{A^\alpha + A^\beta}{V^\alpha A^\beta} \quad (24)$$

$$k_m = k_1^* \frac{V^\beta A^\alpha}{A^\beta V^\alpha} \quad (25)$$

$$k_m = k_1^* \left(1 + \frac{A^\beta}{A^\alpha} \right) \quad (26)$$

and

$$k_m = k_1'' \quad (27)$$

where

$$k_1^* = \frac{D}{l^2} \quad (28)$$

In the case of a pure liquid:

$$A^\alpha = k V^\alpha \quad (29)$$

and

$$A^\beta = k V^\beta \quad (30)$$

From (24) and (26):

$$k_m = k_1^* \left(1 + \frac{V^\beta}{V^\alpha} \right) \quad (31)$$

and from Eq. (25):

$$k_m = k_1^* \quad (32)$$

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Summary

The kinetics of isotope molecular exchange in the interface of porous silica and benzene or benzene-*n*-heptane mixtures labelled ^{14}C was studied. Two types of the so-called exchange curves have been obtained. The first type is a linear one in the $\ln\left(1 - \frac{i}{i_\infty}\right)$ vs. time representation, but the second type contains two lines of different slopes. The results were discussed by formalkinetic method.

References

1. KIPLING, J. J.: Adsorption from Solutions of Non-Electrolytes, pp. 231—232 (Academic Pr. London 1965)
2. SMITH, R. N., GEIGER, C. F., PIERCE, C.: J. Phys. Chem. **57**, 382 (1953)
3. NAGY, L. Gy.: Dr. Sci. Thesis (Budapest 1970)
4. NAGY, L. Gy., ARONSON, M., LEIDHEISER, H.: Lehigh report (Lehigh University, Betlehem Pa., USA 1971)
5. OVERMAN, R. T., CLARK, H. M.: Radioisotope Techniques (McGraw-Hill B. C., New York 1960)
6. HAISSINSKY, M.: Nuclear Chemistry (Publishing House of the Hungarian Academy of Sciences, Budapest 1963)
7. LIESER, K. H., GUTLICH, P., ROSENBAUM, I.: Exchange Reaction (IAEA, Vienna 1965)

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