TRACER DIFFUSION OF CARBON DIOXIDE AND METHANOL IN ZEOLITE Y AND ZSM-5 USING ^{14}C LABELLED SORBATES

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ABSTRACT

This paper presents measurement of tracer diffusion coefficients of methanol and carbon dioxide in zeolite NaY and ZSM-5 using ^{14}C-labelled sorbates. Sorption equilibria for the above systems have also been measured. Isosteric heats of adsorption and activation energies of diffusion have been reported. A significant finding is that the tracer diffusion data could not be correlated by a single value of diffusivity. The diffusivity was observed to decrease with the extent of tracer diffusion. In many experiments the tracer diffusion process terminated before reaching the expected equilibrium. The data are extensively scrutinized for possibility of falsification by extraneous factors. A possibility of considerable discrepancy between the values of diffusivities determined by NMR and tracer diffusion technique is emphasized.

INTRODUCTION

DIFFUSIVITIES in zeolites are measured by a variety of experimental techniques which include gravimetry, volumetry, pulse field gradient NMR, gas chromatography and tracer diffusion. Gravimetry and the relatively recent NMR method have been most extensively employed. The tracer technique offers some advantages over the other methods. Unlike gravimetry, it does not involve any net adsorption and hence is free from heat effects. Further the physical process in the experiment involves countersorption which is more akin to that involved in the practical applications of zeolites as catalyst or adsorbent. Hence the values of diffusivity obtained by this technique may be expected to be relevant to practice. This is particularly important in view of the wide differences in the values of diffusivities obtained by different techniques[1-5]. Despite these advantages the reported tracer diffusion studies are rather limited[6-10].

In the present work tracer diffusion of carbon dioxide and methanol in zeolites NaY and ZSM-5 is investigated using ^{14}C labelled sorbates. The diffusivities have been measured at different sorbate concentration and temperatures. Sorption isotherms have also been measured at various temperatures. The heat of adsorption and activation energies of diffusion are reported. One of the significant findings is that tracer diffusion cannot be described by a constant value of diffusivity.

EXPERIMENTAL

The experimental assembly, shown in figure 1a, consists of sample cell C, bulb B equipped with a Geiger-Muller (GM) tube (LND INC make, tube no. 712) to measure the amount of radioactivity in the bulb. The GM tube was connected to an appropriate counting system which permitted measurement of count rate as well as total number of counts in a given time interval. Variations in pressure were recorded using a manometer.

The ^{14}C labelled compounds viz. methanol and aqueous solution of sodium carbonate were supplied by Bhabha Atomic Research Centre, Bombay. Labelled CO_2 was generated using aqueous solution of labelled sodium carbonate as follows. Phosphoric acid (guaranteed reagent) was added dropwise to the aqueous solution of labelled sodium carbonate.
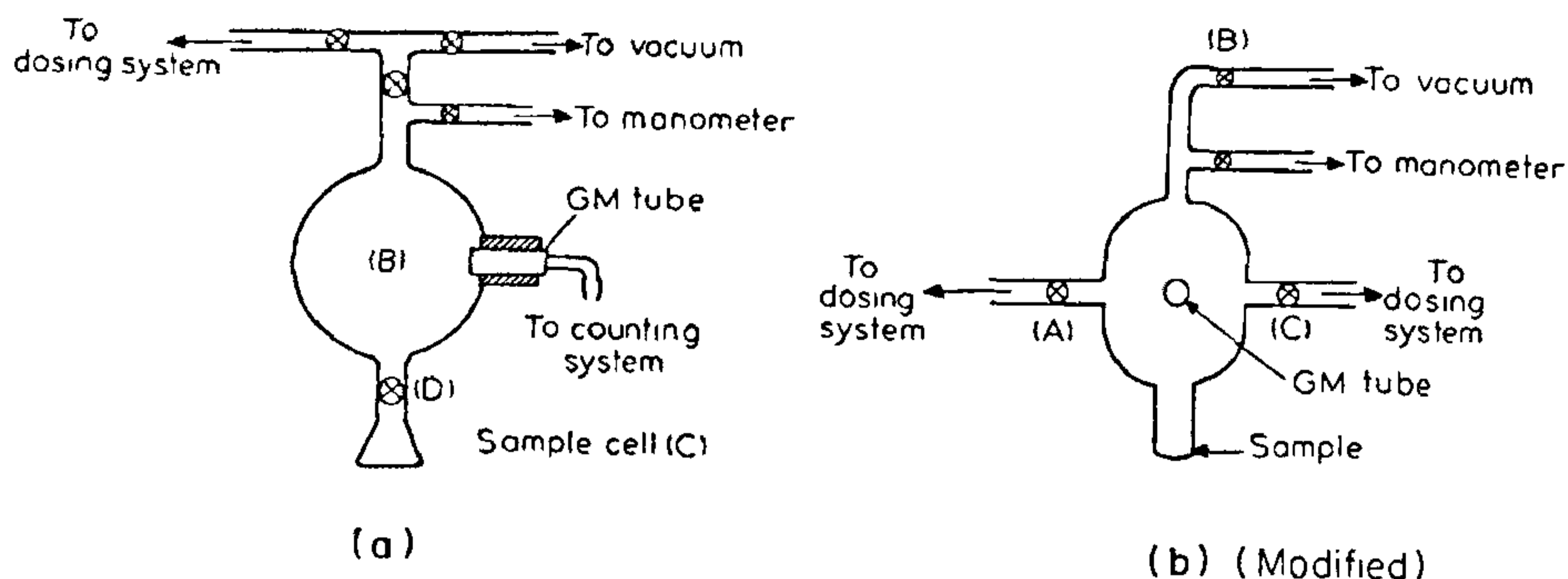
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(a)

(b) (Modified)

Figure 1. Experimental assembly.

Water generated during the reaction was condensed using liquid nitrogen-acetone trap ($T = 253$ K) and CO_2 was subsequently condensed in a bulb using liquid nitrogen trap. The labelled CO_2 was again expanded and passed over liquid nitrogen-acetone trap to remove traces of water. This procedure was repeated several times till no traces of water were found to condense in liquid nitrogen-acetone trap. Unlabelled CO_2 was similarly generated using aqueous solution of sodium carbonate and was stored in another bulb. Unlabelled methanol used was extra pure (acetone free).

The zeolites ZSM-5 with silica to alumina ratio of 32 and NaY (SK – 40) with silica to alumina ratio of 5.5 were obtained from Associated Cement Companies, Thane and Union Carbide, USA respectively. The particle size distribution was measured by optical microscopy. The particles of both the zeolites were spherical. Average diameters for ZSM-5 and NaY were 1.79 and 2.8 μm respectively. Prior to each experiment, the zeolite was heated in a stream of air at 823 K for 4 h followed by *in situ* heating under vacuum at 623 K for 3 h. All experiments were carried out using 0.2 g of zeolite sample.

Sorption isotherms of CO_2 and methanol were determined on ZSM-5 and NaY zeolite at 303, 323 and 343 K by following the usual volumetric procedure[11].

Prior to tracer diffusion experiments the characteristic curve of GM tube was determined. Calibration curve (count rate vs press-

ure of labelled sorbate) was obtained by measuring the pressure of the labelled sorbate on the manometer and the corresponding count rate. The calibration was carried out before every experiment. Each time the background count rate was substracted to get the net count rate due to labelled sorbate only. The count rate in all the experiments carried out was < 500 counts/s, well below the saturation count rate of the GM tube (which was about 2000 counts/s). The background count rate was about 1.7 counts/s.

Diffusion of the labelled sorbate in the sample cell can be expected to take finite time to reach the GM tube and get it registered. The magnitude of this time delay was estimated by carrying out simple mixing experiment. The sample bulb C (without zeolite) was filled with labelled sorbate at the desired pressure, while bulb B was filled with the corresponding unlabelled sorbate at the same pressure and temperature. The sample valve D was opened and the time for complete homogenization of the activity was determined. This time was substracted as zero time correction in tracer diffusion experiment carried out under identical conditions. The time as determined by the above procedure increased with increase in pressure. The correction times of 15 to 115 min were observed in the pressure range of 50 and 250 mm of Hg at 303 K. This procedure, though approximate, can be acceptable since this correction was always small as compared to the half-life of the experiment.

To measure the tracer diffusion rates, the pre-treated zeolite was saturated with labelled sorbate at the desired pressure and temperature, noting down the exact amount of sorbate adsorbed. The sample valve D was closed and the labelled sorbate in bulb B was recondensed. Unlabelled sorbate was then introduced in bulb B up to the same pressure at which the zeolite was saturated with labelled sorbate. Tracer diffusion was initiated by opening the valve D. The count rate increased due to desorbed labelled sorbate and was noted down as a function of time.

The fractional exchange was then evaluated as

$$\frac{Q_t - Q_0}{Q_\infty - Q_0} = $$

$$\frac{\text{Count rate at time } t \text{—initial rate}}{\text{Count rate at equilibrium—initial rate}} \quad (1)$$

where Q_0, Q_t and Q_∞ are the amounts of sorbate desorbed at time zero, t and infinity respectively and the initial count rate was estimated due to the unadsorbed labelled sorbate present in the sample cell at the beginning of the experiment. The count rate at equilibrium was estimated assuming uniform distribution of labelled and unlabelled sorbate in the sorbed and the gas phase.

RESULTS

Sorption equilibria

Figure 2 shows sorption isotherms of CO_2 and methanol on ZSM-5 at three different temperatures of 303, 323 and 343 K. The sorption data could not be fitted with Langmuir isotherm, however, the fit was reasonably good with the following isotherm

$$q = K_1 p / (1 + K_2 p).$$

Table 1 gives the values of constants K_1 and K_2 for sorption of methanol and CO_2 in NaY and ZSM-5 at different temperatures. Isosteric heats of adsorption were determined by the usual procedure[12]. Figure 3 shows the variation of isosteric heat of sorption with fractional
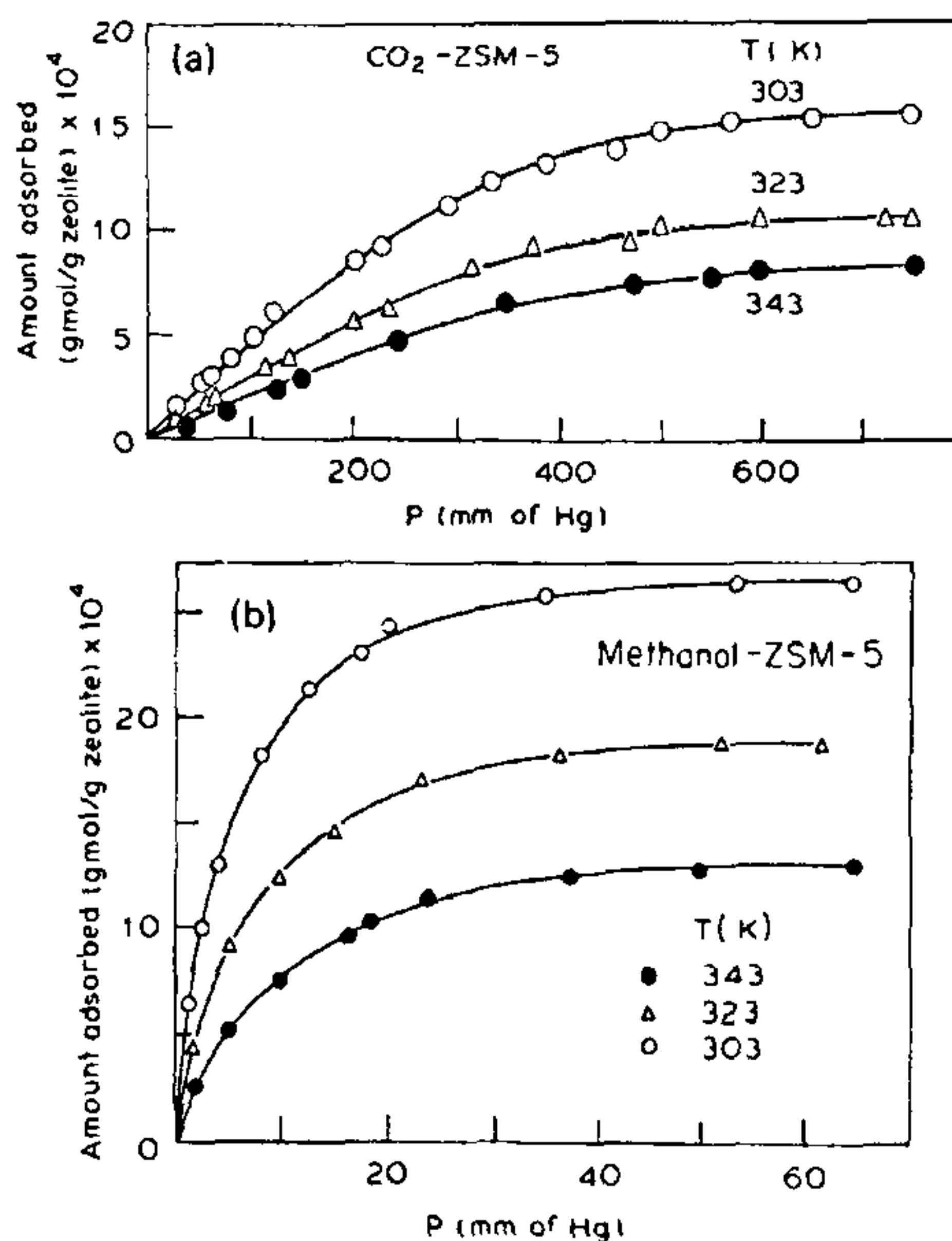

Figure 2. Sorption isotherms of CO_2 and methanol on ZSM-5.

occupancy θ_t, which was defined as the ratio of the amount of sorbate adsorbed to that adsorbed at saturation at the same temperature.

Tracer diffusion

When tracer diffusion of CO_2 was studied at 303 K and 250 mm of Hg pressure

Table 1 *Constants in sorption isotherms*

System	$T(K)$	$K_1 \times 10^6$	$K_2 \times 10^3$
Carbon dioxide—ZSM-5	303	6.0	1.8
	323	3.4	1.2
	343	2.35	0.6
Methanol—ZSM-5	303	980.0	239.0
	323	456.0	137.0
	343	230.0	94.0
Carbon dioxide—NaY	303	37.3	12.2
	323	11.5	3.7
	343	4.35	0.548
Methanol—NaY	303	879.5	71.0
	323	426.0	19.0
	343	224.0	7.5
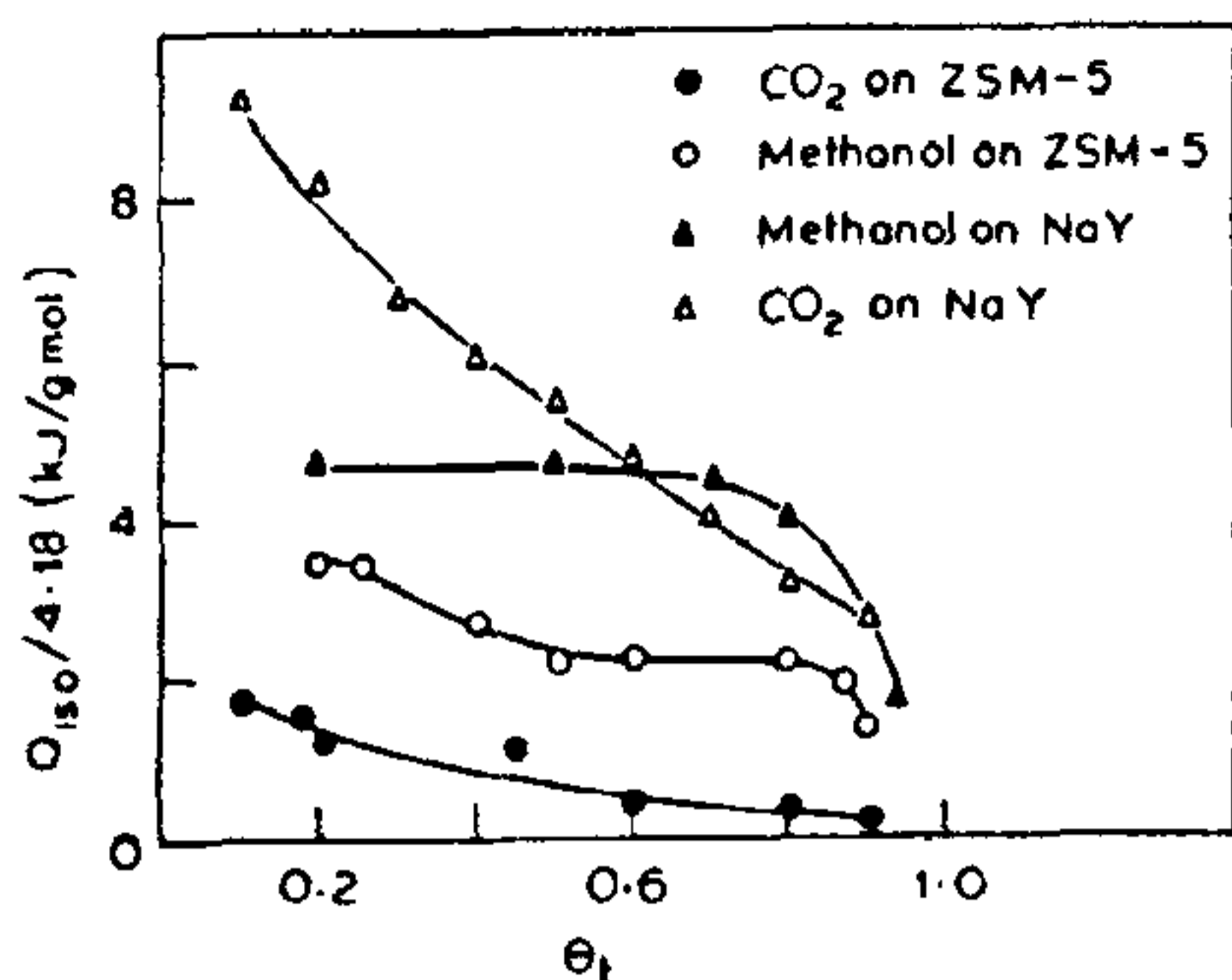
Figure 3. Variation of isosteric heat of adsorption with θ_t.

Figure 4. The percentage of exchange vs $\sqrt{t}$ plots for tracer diffusion of CO_2 in ZSM-5; tests for the validity of data.

($\theta_t = 0.645$), a dead time was observed at the beginning. Figure 4a (upper curve) shows the results after applying the zero time correction as discussed in the earlier section. A dead time was observed even after applying the correction. To investigate the origin of the dead time, another experimental assembly was constructed. A schematic diagram of the assembly (figure 1b) shows the valve separating the sample cell and that the bulb containing the GM counter is eliminated in this apparatus. To measure tracer diffusion rate, the zeolite was first degassed as described earlier and equilibrated with 250 mm of Hg pressure of labelled CO_2. To replace the gas phase by unlabelled CO_2 valves A and B were simultaneously opened in a controlled manner so that the pressure in the cell was held constant. The replacement was continued till the radioactivity decreased to 20% of the original value. This operation could be completed in 10 min which is a small time interval as compared to the time scale of the experiment. The end of the above operation was taken as the zero time of the experiment.

Curve II in figure 4a shows the observations of this experiment. The results again exhibit a dead time and are very close to the results obtained from the other experimental assembly after applying the zero time correction. The above experiment indicates that the dead time is probably intrinsic to the tracer diffusion phenomenon and is not due to the resistance posed by the valve separating the sample cell
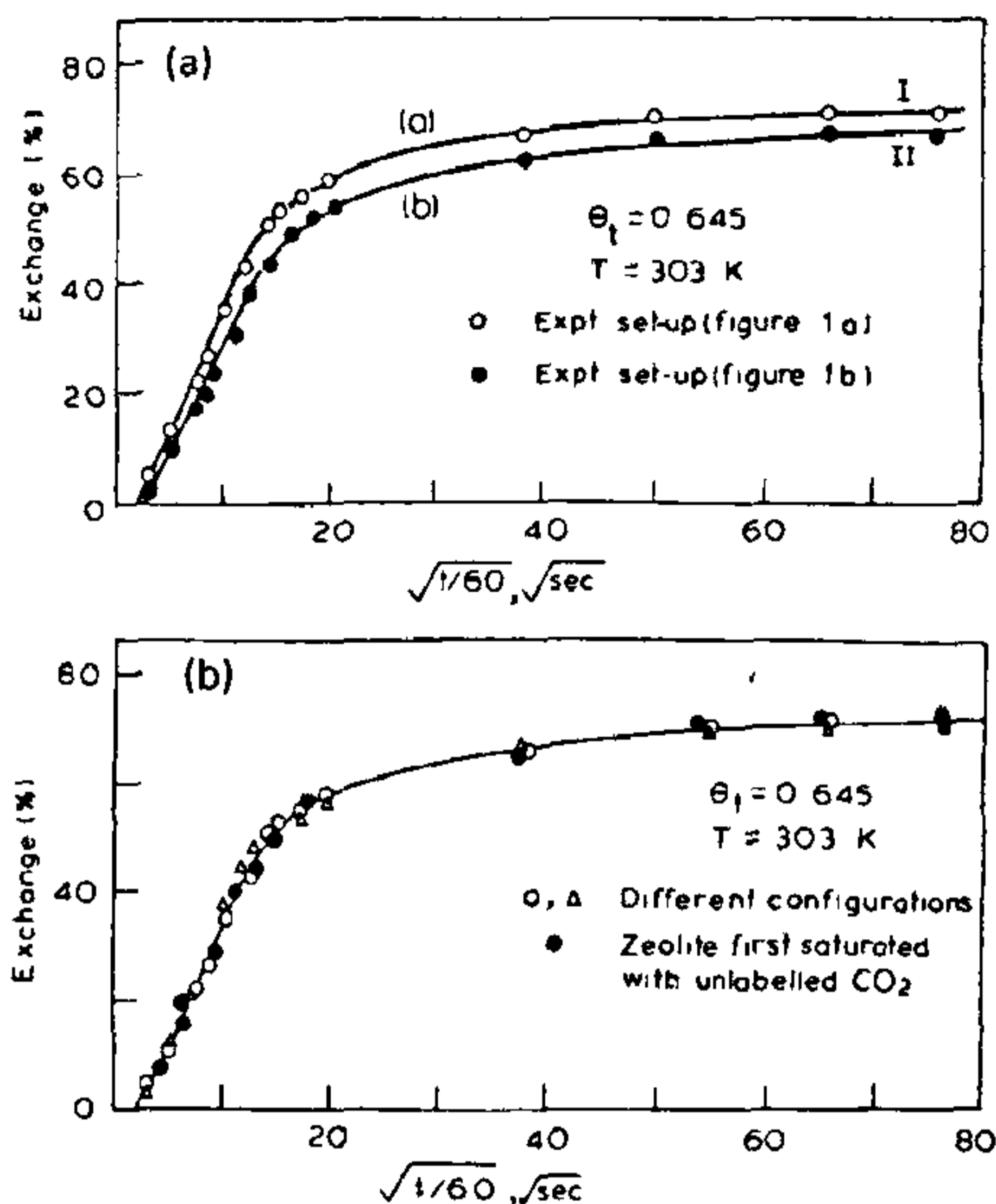
from the GM counter. Dead time has also been observed in earlier studies[8,13,14]. The subsequent experiments were carried out in the assembly shown in figure 1 since the other assembly involves significant loss of the labelled compounds.

To investigate the possible role of interparticle transport, an experiment was carried out using different physical configuration of the sample under otherwise similar conditions (303 K and 250 mm of Hg). Figure 4b gives the comparison of the results obtained with two different configurations of the zeolite sample. The results of two experiments are identical which implies absence of intercrystalline diffusional effects. To test the validity of the results further, an experiment was conducted by initially adsorbing unlabelled CO_2 and replacing the gas phase by labelled sorbate under otherwise similar conditions (temperature $= 303$ K and $P = 250$ mm of Hg). The results of this experiment are also compared in figure 4b.

A significant observation is that the extent of exchange which reached a value of 71% after

48 h registered no increase up to 96 h. This implies that the tracer diffusion came to a halt before reaching the equilibrium exchange of 100%. The pressure in the system remained constant during the experiment indicating no possibility of the loss of either labelled or unlabelled sorbate at any stage during the experiment. To ensure that the initially adsorbed labelled sorbate was indeed in the adsorbed state, the zeolite sample was heated to 623 K to desorb the adsorbed gas at the end of experiment 1. The count rate increased as a result of desorption and ultimately showed radioactivity corresponding to the labelled sorbate present in the system at zero time.

After establishing the validity of the observations of the initial experiments, tracer diffusion of CO_2 was investigated at various sorbate concentrations. The results are shown in figure 5(a). The effect of temperature was studied by carrying out experiments at three different temperatures of 303, and 323 and 343 K. Tracer diffusion of CO_2 was also studied in NaY zeolite at different occupancies

and temperatures. Figure 5b shows the findings of these experiments.

Tracer diffusion of methanol was also studied in ZSM-5 and NaY zeolite. Experiments at lower occupancies were very difficult since very low pressures had to be employed to achieve low sorbate concentration. Experiments were therefore conducted at fractional occupation of 0.69, 0.83 and 1. Figure 6 gives the observations of these experiments.

The principal observations from these results are summarized below.

(i) In all the experiments with CO_2 as sorbate a dead time was observed while no dead time was observed in the experiments with methanol except the experiments at $\theta_t \approx 1$.

(ii) The percentage exchange vs $\sqrt{t}$ plots were linear at lower time scale (up to 50% exchange at $\theta_t = 0.645$ and up to 80% exchange at $\theta_t = 0.177$ for CO_2—ZSM-5 system).

(iii) The rate of tracer diffusion decreased with increase in sorbate concentration at a given temperature.
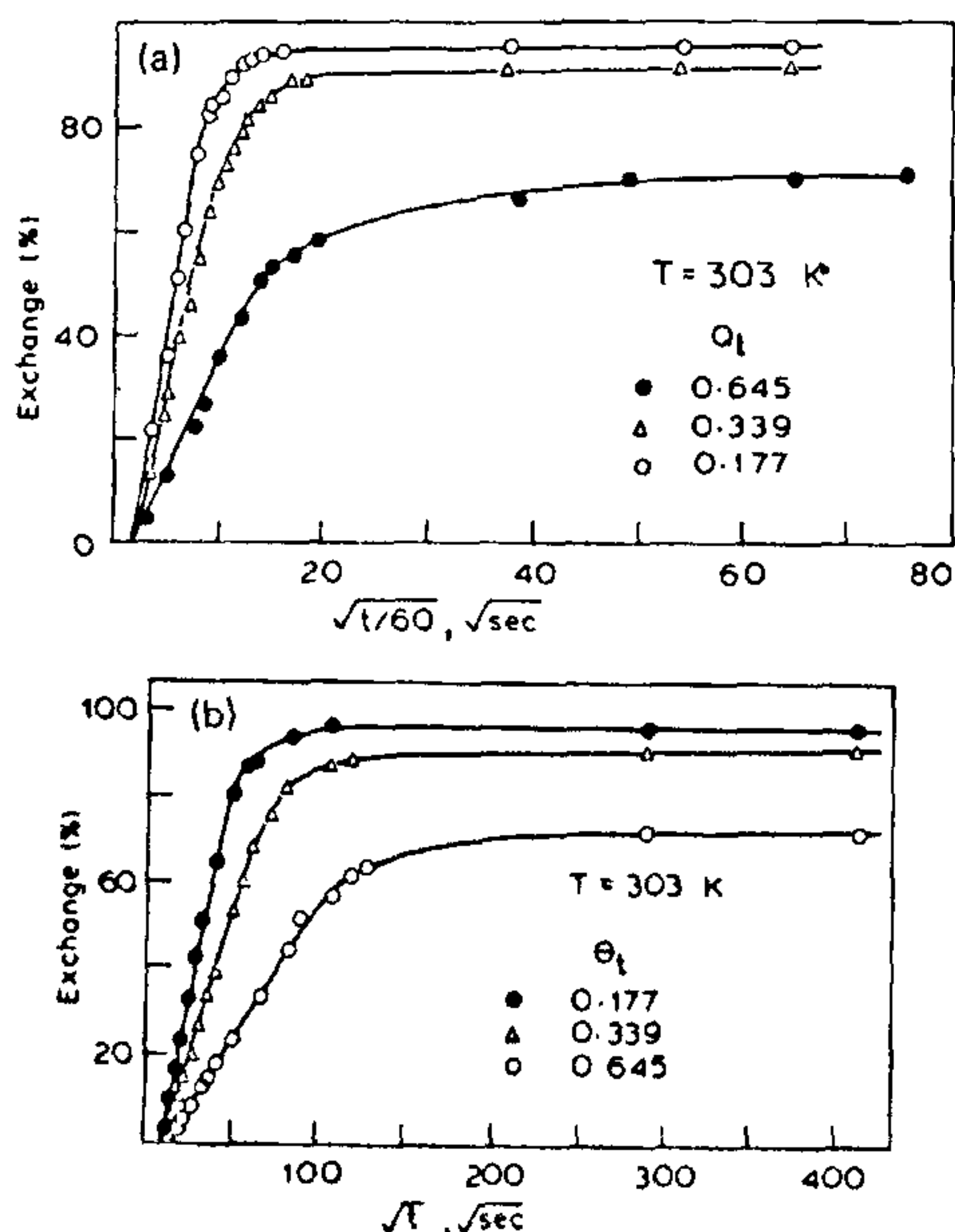
Figure 5. Tracer diffusion of CO_2 in (a) ZSM-5, and (b) NaY.
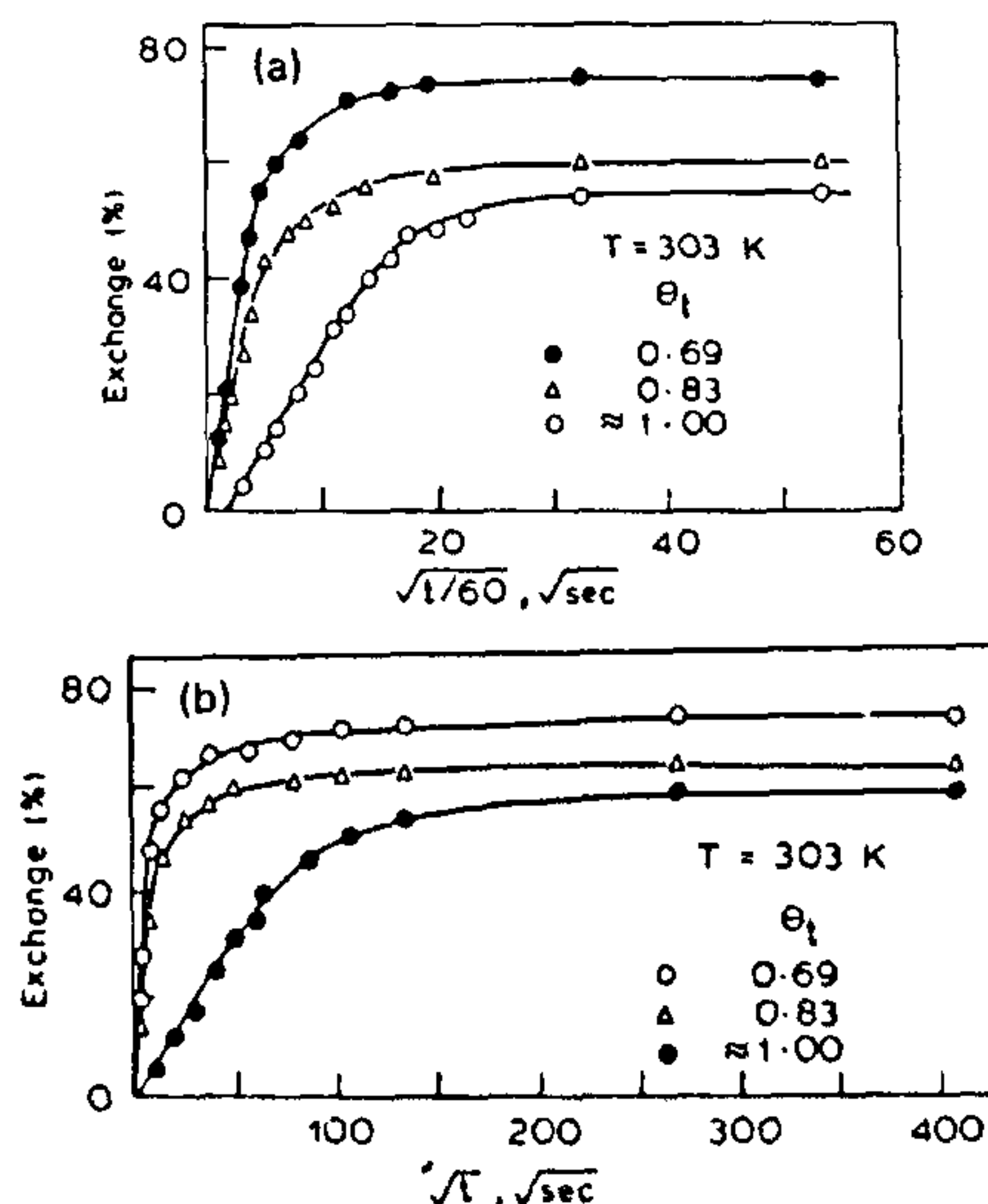
Figure 6. Tracer diffusion of methanol in (a) ZSM-5, and (b) NaY.

(iv) In most experiments 100% exchange could not be achieved and the tracer diffusion process apparently came to a halt at an intermediate stage. Only exceptions were the experiments with CO_2 at low occupancies and higher temperatures where equilibrium tracer diffusion was observed.

The tracer diffusivities were computed from the slope of the initial linear portion of the percentage exchange vs $\sqrt{t}$ plots using the equation on page 9 of Ref. 15. The values of diffusivities obtained at various temperatures and sorbate concentrations, given in tables 2 and 3, also indicate the values of activation energies for diffusion.

DISCUSSION

One of the significant observation of the study is that the rate of tracer diffusion was found to decrease markedly with the extent of tracer diffusion and in several experiments the tracer diffusion process came to a halt before reaching the equilibrium. This implies that the process cannot be described by a single value of diffusivity. The variation of diffusivity with the extent of tracer diffusion can be examined through τ-t plots which are based on the complete solution of the diffusion equation. For spherical particles the following solution has been given by Carman and Haul[16].

$$\frac{Q_t - Q_0}{Q_\infty - Q_0} = (1 - \alpha)$$

$$\left[1 - \frac{\gamma_1}{\gamma_1 + \gamma_2} e. \; \mathrm{erfc} \left(\frac{3\gamma_1}{\alpha} \tau^{1/2} \right) \right]$$

$$- \frac{\gamma_2}{\gamma_1 + \gamma_2} e. \; \mathrm{erfc} \left(\frac{-3\gamma_2}{\alpha} \tau^{1/2} \right) \quad (3)$$

where $\alpha =$

$$\left[\frac{\text{amount of labelled sorbate in gas phase}}{\text{amount of labelled sorbate in adsorbed phase}} \right]_{t \to \infty}$$

$\gamma_1 = \frac{1}{2}[(1 + 4/3\alpha)^{1/2} + 1]$ and $\gamma_2 = \gamma_1 - 1$

$\tau = Dt/r^2$, and r is the radius of spherical particle.

Table 2 *Tracer diffusion of carbon dioxide and methanol in ZSM-5*

θ, CO_2 in ZSM-5	T(K)	$D \times 10^{18}$ (m²/s)	E(kJ/gmol)
0.177	303	16.42	
	323	38.91	33.82
	343	78.48	
0.339	303	6.59	
	323	14.26	30.6
	343	27.16	
0.645	303	2.01	
	323	4.39	29.85
	343	7.99	
Methanol in ZSM-5			
0.69	303	0.6	
	323	2.9	60.94
	343	10.16	
0.83	303	0.47	
	323	2.28	61.2
	343	7.99	
≈ 1.0	303	0.34	
	323	0.89	38.83
	343	2.03	

Table 3 *Tracer diffusion of carbon dioxide and methanol in NaY*

θ, CO_2 in NaY	T(K)	$D \times 10^{17}$ (m²/s)	E(kJ/gmol)
0.177	303	4.25	
	323	10.83	34.94
	343	21.41	
0.339	303	1.88	
	323	4.18	31.06
	343	7.9	
0.645	303	0.48	
	323	0.91	25.46
	343	1.56	
Methanol in NaY			
0.69	303	0.3	
	323	0.6	27.63
	343	1.08	
0.83	303	0.2	
	323	0.45	32.94
	343	0.92	
≈ 1.0	303	0.13	
	323	0.27	31.48
	343	0.55	

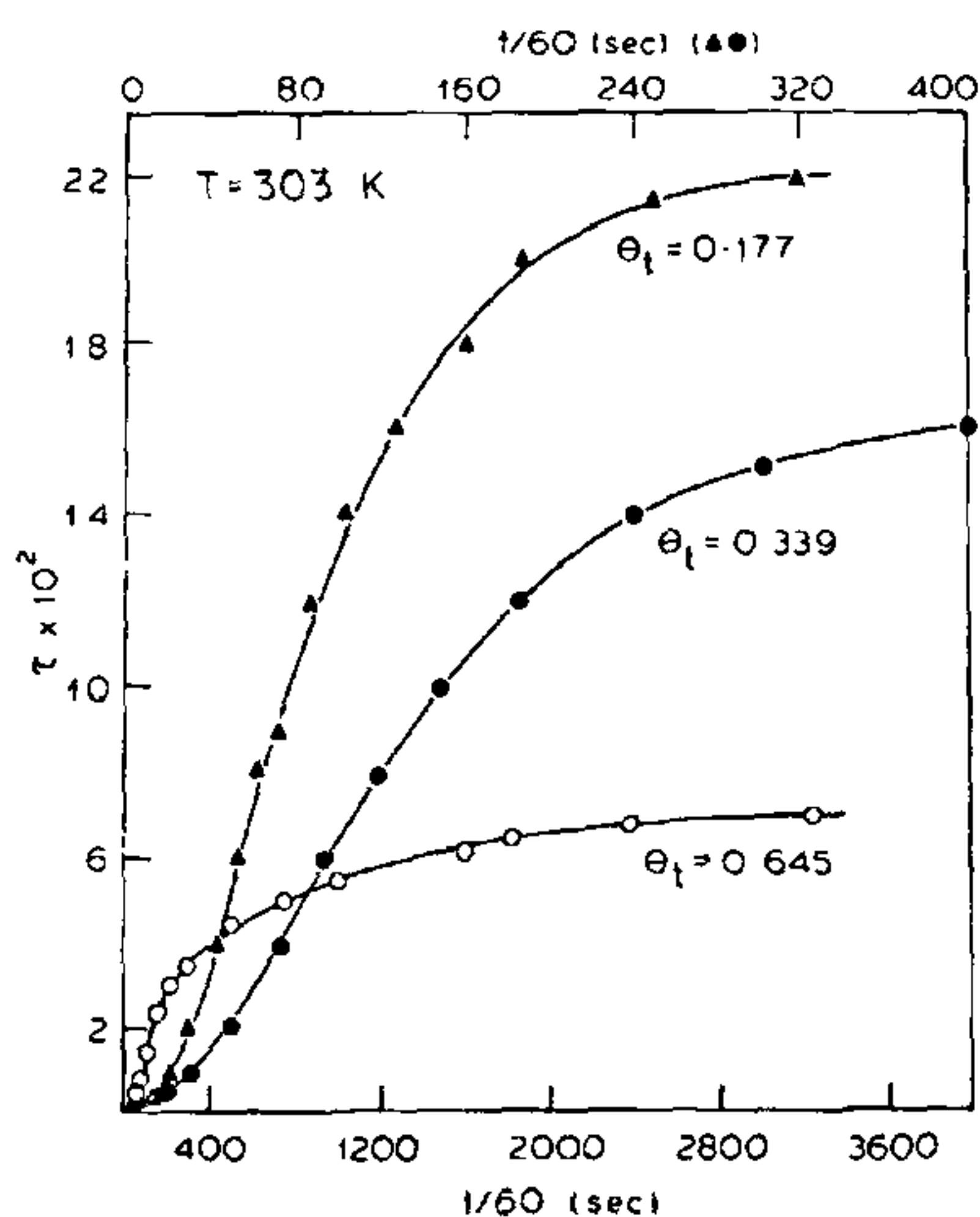Figure 7. τ-t plots for tracer diffusion of CO_2 in ZSM-5.

Figure 8. τ-t plots for tracer diffusion of methanol in ZSM-5.

To plot τ vs t, the values of the fractional exchange (LHS of the above equation) are evaluated at various values of τ. The corresponding values of time can be obtained from the experimental data. Since τ is Dt/r^2, τ vs t plots are expected to be straight lines if the diffusivity has a constant value. The shortcoming of the above procedure is that it employs a mean value of zeolite crystallite size and this assumption is valid only approximately at the higher extent of diffusion[17].

The $\tau - t$ plots for tracer diffusion of CO_2 and methanol in ZSM-5 (figures 7 and 8). Clearly indicate that the results cannot be explained with a single value of diffusivity. These figures show results for only 6 experiments; however, the above finding is valid for all the experiments conducted in the present study.

These observations contradict the common belief that tracer diffusion in zeolites can be described by a single value of diffusivity. The experimental data were therefore very elabor-ately scrutinized for the possibility of falsification by some of the associated processes. The experiments carried out to examine the role of intercrystalline diffusion and diffusion in the gas phase were already described. Identical
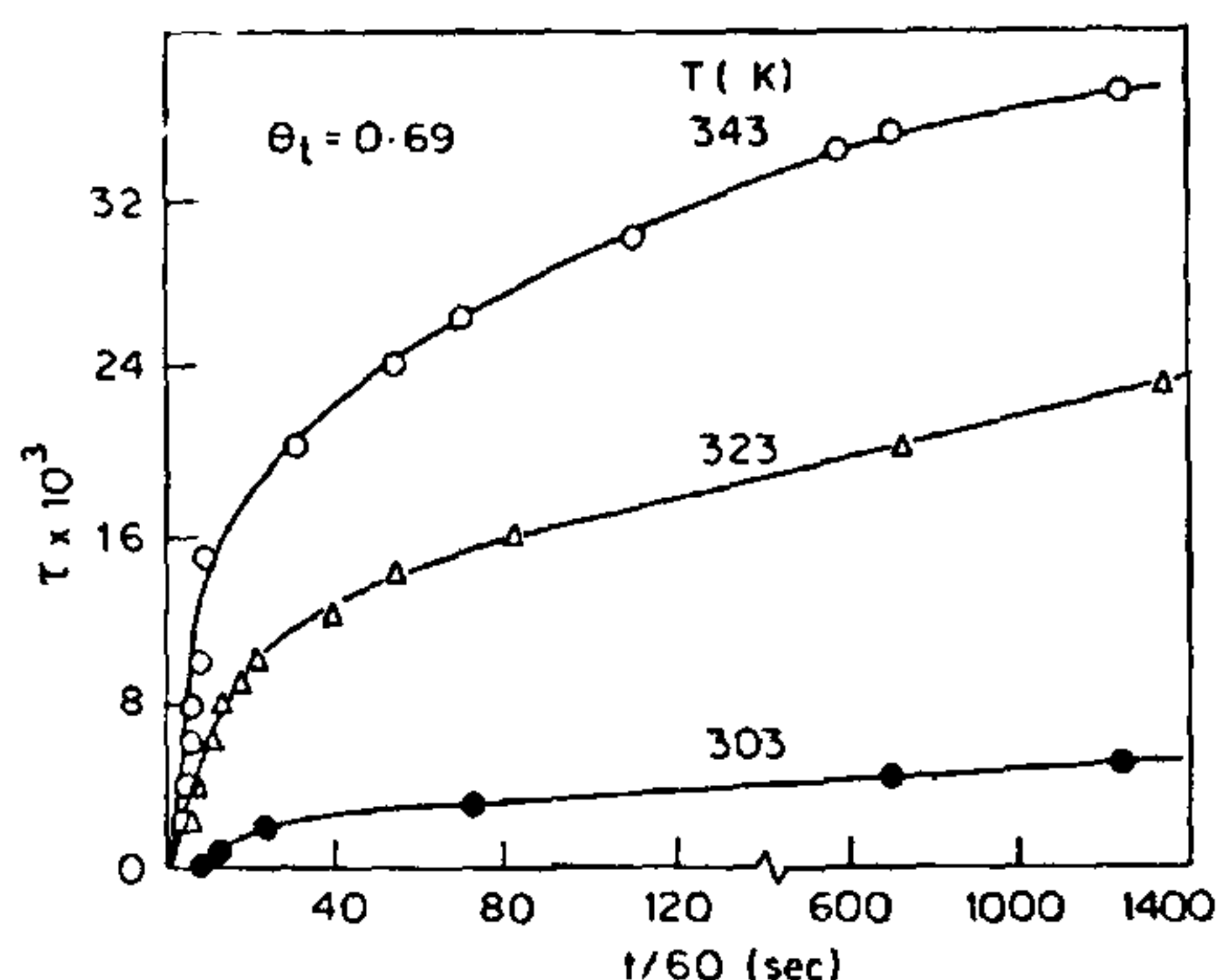
rates were observed using zeolite samples with different physical configurations and two different experimental assemblies. The time required for homogenization of gas phase in the equipment was determined in the absence of zeolite was found to be small as compared to the time scale of the experiment. Sorbates employed were of high purity and absence of leaks in the system was carefully ensured. The counting system was calibrated before every experiment and it was shown that identical results could be obtained by reversing the role of labelled and unlabelled sorbates. Since tracer diffusion involves counter-diffusion of similar sorbates the experiments are free from heat effects. The fact that similar trends are observed with two different zeolites obtained from two different sources indicates that defects in zeolite structure are not likely to be the cause of the behaviour. Further the sorption capacities of the zeolite samples were found to be comparable to that reported earlier[18-20] and initial sorption in the evacuated zeolite was observed to be rapid and continuous. A variable diffusivity can also be observed as a result of the crystallite size distribution[17]. However, in the present work variation of diffusivity up to a zero value is observed which cannot be explained on the basis of this factor. Another possible artifact is the role of a surface barrier. The plots of percentage exchange vs $\sqrt{t}$ based on present results showed linearity over a wide

range (at least up to 40% exchange) which suggest that the diffusion rate was probably governed by intracrystalline process. Further failure to reach thermodynamic equilibrium cannot be explained on the basis of surface barriers. These considerations preclude the possibility of the present data being falsified by any of the known source of error. It thus appears that decreasing and non-constant diffusivity can be an intrinsic feature of tracer diffusion.

The earlier studies give an inconclusive picture in this regard. Satterfield and Katzer[21,22], and Moore and Katzer[23] studied countersorption of aromatic hydrocarbon in zeolite Y and mordenite and observed a variable diffusivity. In some experiments the countersorption was observed to terminate before reaching the equilibrium as observed in the present study. Another study[24] reported countersorption of hydrocarbons in NaY and also observed variable diffusivity. However, Quig and Rees[8], and Sargent and Whitford[7] studied tracer diffusion of *n*-alkanes and CO_2 respectively in zeolite 5A and observed that tracer diffusion could progress up to thermodynamic equilibrium and could be described with a constant value of diffusivity. More experimental work is necessary to resolve this aspect.

Another important aspect that can be discussed in the light of the present results is the relative magnitudes of diffusivities obtained by the various techniques. Ruthven and Yucel[25] studied diffusion of CO_2 in 5A by gravimetry and observed a diffusivity of 1×10^{-12} m²/s. Sargent and Whitford[7] studied tracer diffusion of CO_2 in 5A at the same temperature and observed a diffusivity of 1.39×10^{-15} m²/s. The tracer diffusion coefficients of CO_2 observed in the present work are also several orders of magnitude lower than that observed by Ruthven and Yucel. Similar differences in the diffusivities for unidirectional diffusion (gravimetry or volumetry) and counterdiffusion have been reported[21,26,27] for a variety of systems. Barrer and Fender[6] also observed tracer diffusion coefficient of water in chabazite to be about 40 times lower than that for unidirectional diffusion. These results seem to indicate that tracer diffusion coefficients are perhaps significantly lower than those determined by gravimetry. Quig and Rees[8], however, observed comparable values of diffusivities by volumetry and tracer technique.

Comparison of the tracer diffusion coefficient and the NMR diffusivities can be more interesting in view of the similarity in the physical phenomena involved in the two techniques. (Both the techniques measure diffusion at constant total sorbate concentration). However measurement of diffusivities by these two techniques on identical systems is not reported. However, a very indirect comparison of the values can be made on the basis of the reported values for similar systems. Karger[4] observed the diffusivity of methane in 5A to be 1×10^{-9} m²/s by NMR technique. The diffusion coefficients of methane and CO_2 in 5A have been observed to be comparable[25,26]. The results of Sargent and Whitford[7] show the value of tracer diffusivity of CO_2 in 5A to be 1.39×10^{-15} m²/s. Thus a very wide discrepancy between the diffusivities obtained by NMR and tracer technique may be expected. More work on identical systems is necessary to make accurate comparison. However, such discrepancy may be expected on the basis of the Monte Carlo simulations presented in the preceeding paper. The simulations indicate that the value of diffusivity is likely to depend on the time scale of measurement. Higher values of diffusivities determined by the NMR technique can be due to its very low time scale as compared to the tracer diffusion experiments.

CONCLUSIONS

The paper reports measurements of sorption equilibria and tracer diffusivities of CO_2 and methanol in zeolites ZSM-5 and NaY at different temperatures. The values of isosteric heats of adsorption and activation energies for diffusion are reported.

The results show that tracer diffusion coefficient decreases with increase in sorbate con-

centration which is in agreement with the trend observed by the NMR measurements. A significant observation is that the tracer diffusion process could not be described by a single value of diffusivity. Diffusivity decreased with the extent of tracer diffusion and in most experiments tracer diffusion came to a halt before the equilibrium. The effect was more significant at higher sorbate concentration. These observations agree with the behaviour that may be expected on the basis of the Monte Carlo simulations reported in the previous paper.

Notation

D, diffusivity, m^2/s.

E, activation energy for diffusion ($kJ/gmol$).

K_1, constant in equation (2) gmol/g zeolite, (mm of Hg).

K_2, constant in equation (2) (1/mm of Hg).

q, amount of sorbate adsorbed, gmol/g zeolite.

q_{iso}, isosteric heat of adsorption ($kJ/gmol$).

Q_0, Q_t, Q_∞, amount of sorbate desorbed at time 0, t and infinity respectively.

r, radius of crystallite (m).

t, time (s).

T, temperature (K).

α, ratio of amount of sorbate in gas phase to that in adsorbed state at infinite time.

γ_1, γ_2, constants in equation (3).

θ_i, fractional occupancy.

τ, Dt/r^2.

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