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Separation of Binary Liquid Systems by Sorption—A Comparison with Pervaporation

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Abstract

Studies were carried out on the separation of the ethanol–water and the methanol–acetone systems by sorption using different commercially available molecular sieves (m.s.) as adsorbents. The separation factor (α) is found to be around 100 for m.s. 3A/ethanol–water system and is around 85 for m.s. 4A/methanol–acetone system at respective azeotropic compositions. These separation factors appear to be better than the results reported by many workers using membrane process "pervaporation." A comparison is made between the selectivity of pervaporation and sorption with respect to the systems studied.

INTRODUCTION

Synthetic molecular sieve (m.s.) zeolites are extensively used in a number of separations including gases from gases, liquids from liquids, and solutes from solutions. Molecular sieves are high capacity selective adsorbents. They can separate molecules based upon the size and configuration of the molecules relative to the size and geometry of the main appertures of the structure. They adsorb molecules, particularly those with a permanent dipole moment, with a selectivity that is not found in other solid adsorbents. By taking advantage of this high selectivity, separation of many complicated binary systems of closely related compounds, isomers, and isotopes has been studied (*1–12*).

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During the last few years a number of papers have appeared on the separation of binary liquid systems (particularly ethanol–water and other azeotropic mixtures) by "pervaporation," a recently developed membrane technique (*13–25*).

In the present paper an attempt is made to compare separations performed by adsorption using molecular sieves with the reported separations by pervaporation for two azeotropes forming binary systems, ethanol–water and methanol–acetone.

MATERIALS AND METHOD

Material

Four types of molecular sieves (3A, 4A, 5A, and 13X) were obtained from Associated Chemical Corporation (ACC), Bombay. They were reactivated at about 350°C and 10^{-2} torr. Methanol with ^{14}C tracer was obtained from the Isotope Division of the Bhabha Atomic Research Centre. Karl Fischer reagent was supplied by E. Merck, Bombay, and the dioxane-based liquid scintillator was prepared in our laboratory using scintillation grade chemicals.

Method

Batch experiments were conducted in 50 mL Erlenmeyer flasks in a constant temperature bath at 27 ± 0.1°C. About 2 g of molecular sieves of each type were equilibrated with about 10 mL of ethanol–water solution with 0.92, 2.08, 2.78, 3.7, 5.22, and 8.09 wt% water, and methanol–acetone solution with 0.534, 1.99, 12.01, 19.99, 40.09, 60.14, and 79.96 wt% methanol. The methanol–acetone system contained a trace amount of $^{14}CH_3OH$. Samples were drawn from these equilibrated mixtures and the methanol–acetone solution was analyzed for the methanol concentration with the help of the $^{14}CH_3OH$ tracer whose β^- activity was measured using a Beckmann liquid scintillation counter. The ethanol–water system was analyzed for the water concentration by using a IEC-84-Automatic Karl Fischer titration apparatus following the standard procedure (*24*).

Column experiments were conducted in a glass column of 70 cm height and 12 mm diameter. A known amount of molecular sieve 4A (size 20–80 mesh) was packed in two separate columns (packing density = 0.78 g/cm^3) and solutions of azeotropic composition of methanol–acetone and ethanol–water were passed through at flow rates of about 0.25 and 0.75 mL/min, respectively.

Percolate from both columns was collected as fractions, and the composition of each fraction was determined as described in the batch experimental procedure.

Mass balance studies were also carried out by thermal desorption (at 300°C and 10^{-2} torr) of the exhausted molecular sieves from these column experiments.

RESULTS AND DISCUSSION

Ethanol–Water System

The results of the experiments were expressed in terms of separation factor α, defined as

$$\alpha = \frac{[H_2O/C_2H_5OH]_{\text{sorbed phase}}}{[H_2O/C_2H_5OH]_{\text{equilibrated solution}}}$$

The amounts of water and ethanol adsorbed by the molecular sieves were calculated by using the mass balance equations:

$$[W_{H_2O}]_{\text{sorbed}} = \frac{C_iV_i - C_e(V_i - V_am)}{V_a \times m}\ \text{g/g} \tag{1}$$

$$[W_{C_2H_5OH}]_{\text{sorbed}} = 1 - [W_{H_2O}]_{\text{sorbed}}\ \text{g/g} \tag{2}$$

where C_i = original H_2O concentration (g/g)
V_i = original weight of experimental solution
C_e = H_2O concentration in equilibrated solution
V_a = pore volume per gram of molecular sieve
m = weight of molecular sieve used for an experiment

V_a for each type of molecular sieve was determined by saturating it with water followed by thermogravimetric analysis.

For the methanol–acetone system:

$$\alpha = \frac{[CH_3OH/CH_3COCH_3]_{\text{sorbed phase}}}{[CH_3OH/CH_3COCH_3]_{\text{equilibrated solution}}}$$

TABLE 1
Separation Factor for the Ethanol–Water System on Molecular Sieve Adsorbents

Sample	Original concentration of water (wt%)	m.s. 3A	m.s. 4A	m.s. 5A	m.s. 13X
1	0.92	130	129	66	55
2	2.08	—	93	52	45
3	2.78	142	86	45	31
4[a]	3.70	111	83	38	31
5	5.22	67	70	28	24
6	8.09	35	55	28	18

[a] Azeotropic composition.

and the methanol and acetone contents in the molecular sieves were determined using Eqs. (1) and (2).

Results of batch experiments with the ethanol–water system are given in Table 1. Table 2 contains the results for the methanol–acetone system. From these results it is clear that selectivity decreases with increasing concentration of water or methanol for both systems. For the ethanol–water system, selectivity follows the m.s. order 3A > 4A > 5A > 13X, i.e., α decreases with increasing pore size of the molecular sieves. Similar observations were also obtained for the methanol–acetone system. The separation factor by pervaporation at an azeotropic composition of ethanol–water are tabulated in Table 3. For this system m.s. 3A has the best separation factor ($\alpha = 111$) followed by m.s. 4A ($\alpha = 83$). By comparing the α of these two techniques, it is clear that only PAN and PSF membranes give a relatively good separation factor for this system, but the permeation rates reported are too slow to be of any importance (0.15×10^{-2} and 0.04×10^{-2} cm/h, respectively). For the methanol–acetone system the best selectivity is obtained from m.s. 4A ($\alpha = 84$), which is much higher than the reported value of $\alpha = 2.9$ by pervaporation for PTFE–PVP membranes (*16*).

Column Experiments

Results of column experiments with an azeotropic composition of ethanol–water and methanol–acetone are presented in the form of

TABLE 2
Separation Factors for the Methanol-Acetone System on Molecular Sieve Adsorbents

Sample	Original wt% of CH_3OH	m.s. 4A	m.s. 5A	m.s. 13X
1	0.534	954	894	118
2	1.99	1125	—	32.3
3[a]	12.01	84	28.9	7.1
4	19.99	45.5	12.7	4.1
5	40.09	11.7	15.7	5.3
6	60.14	4.0	3.8	1.5
7	79.96	3.1	0.8	1.0

*Azeotropic composition

breakthrough curves in Figs. 1 and 2, respectively. Breakthrough points in both cases are very sharp. For the ethanol-water system, until the breakthrough point was achieved, a percolate stream of ethanol with 0.35% water by weight was generated from a feed of about 3.7% water.

The major use of pure, water-free ethanol is expected to be as a fuel extender of gasoline (gasohol mixture) (*25, 26*). Normally the water tolerance limit is 0.5% by volume in gasohol (90% gasoline-10% ethanol) (*27*) at 30°C. Thus the column results indicate the potential of the sorption technique for the production of gasohol-grade ethanol. The breakthrough curves for the methanol-acetone system also show a very high selectivity for methanol adsorption. From a feed of about 12% by weight of methanol, a percolate stream was generated with only about 0.1% methanol concentration until the column reached the saturation or breakthrough point.

Selectivity of molecular sieves for water or methanol from their systems is attributed to the sieve effect and the specific interaction effect. In the case of the ethanol-water system, because water is more polar than ethanol (their dipole moments are 1.85 and 1.69 debyes, respectively), water is adsorbed preferentially due to the higher electrostatic interaction of water molecules with the cations present in the cavities of molecular sieves.

Different selectivity with respect to different molecular sieves appears to be due to the sieve effect. Because of ethanol's larger dimensions compared to water, its diffusion in the matrix decreases with decreasing pore size of the adsorbent, i.e., m.s. 3A < m.s. 4A < m.s. 5A < m.s. 13X.

TABLE 3
Highest Separation of the Ethanol–Water System at Azeotropic Composition by Pervaporation

Sample	Type of membrane	α	Ref.
1	AMV-SO_4^{2-} (anion exchange)	50	*13*
2	AMV-OH^- (anion exchange)	40	*13*
3	AMV-SCN^- (anion exchange)	33	*13*
4	AMV-Cl^- (anion exchange)	12	*13*
5	Cellulose triacetate (CTA)	8	*13*
6	PTFE–PVP	2.9	*16*
7	PTFE–PVP	6.6	*17*
8	Cellulose	6.2	*17*
9	Cellulose acetate	5.9	*17*
10	Cellulose acetate	11	*22*
11	Polyacrylonitrile (PAN)	70	*14*
12	Polysulfone (PSF)	332	*14*
13	CMV (cation exchange)	<2	*13*
14	RC-100	8.8	*29*

Thus the selectivity for separation of the ethanol–water system increases in the order 3A > 4A > 5A > 13X. This is also evident from the Freundlich isotherms at 27°C (Fig. 3), where the *n* value follows the order 3A < 4A < 5A < 13X. In the methanol–acetone system, it is the sieve effect that plays the decisive role. Even though acetone is more polar than methanol (their dipole moments are 2.86 and 1.7 debyes, respectively), methanol is adsorbed preferentially on molecular sieves because of the large difference in the molecular dimensions of the two species (Table 4) (*28*). Because of methanol's small dimensions, it can diffuse in all the matrices in all possible orientations. Acetone, due to its large dimensions, can enter the matrices only in some orientations. This is evident from the fact that as we go from m.s. 4A to 5A to 13X (pore sizes 4.2, 5, and 8 Å,

TABLE 4
Dimensions of Acetone and Methanol

	Height (thickness) (Å)	Width (Å)	Length (Å)	Dipole moment (debye)
Methanol	3.7	3.8	4.2	1.7
Acetone	3.7	4.7	6.5	2.86

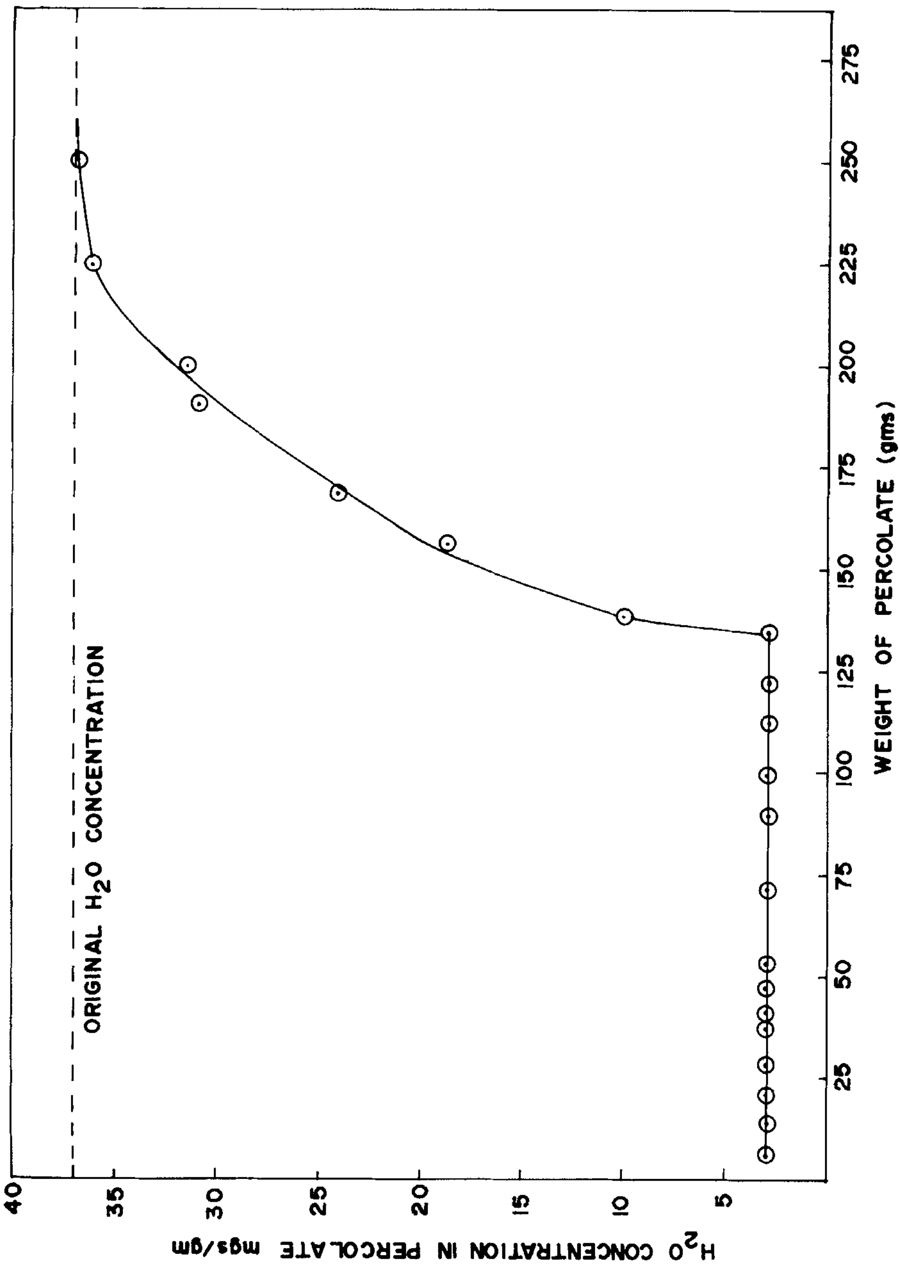

FIG. 1. Breakthrough curve for the C_2H_5OH/H_2O system on molecular sieve 4A.

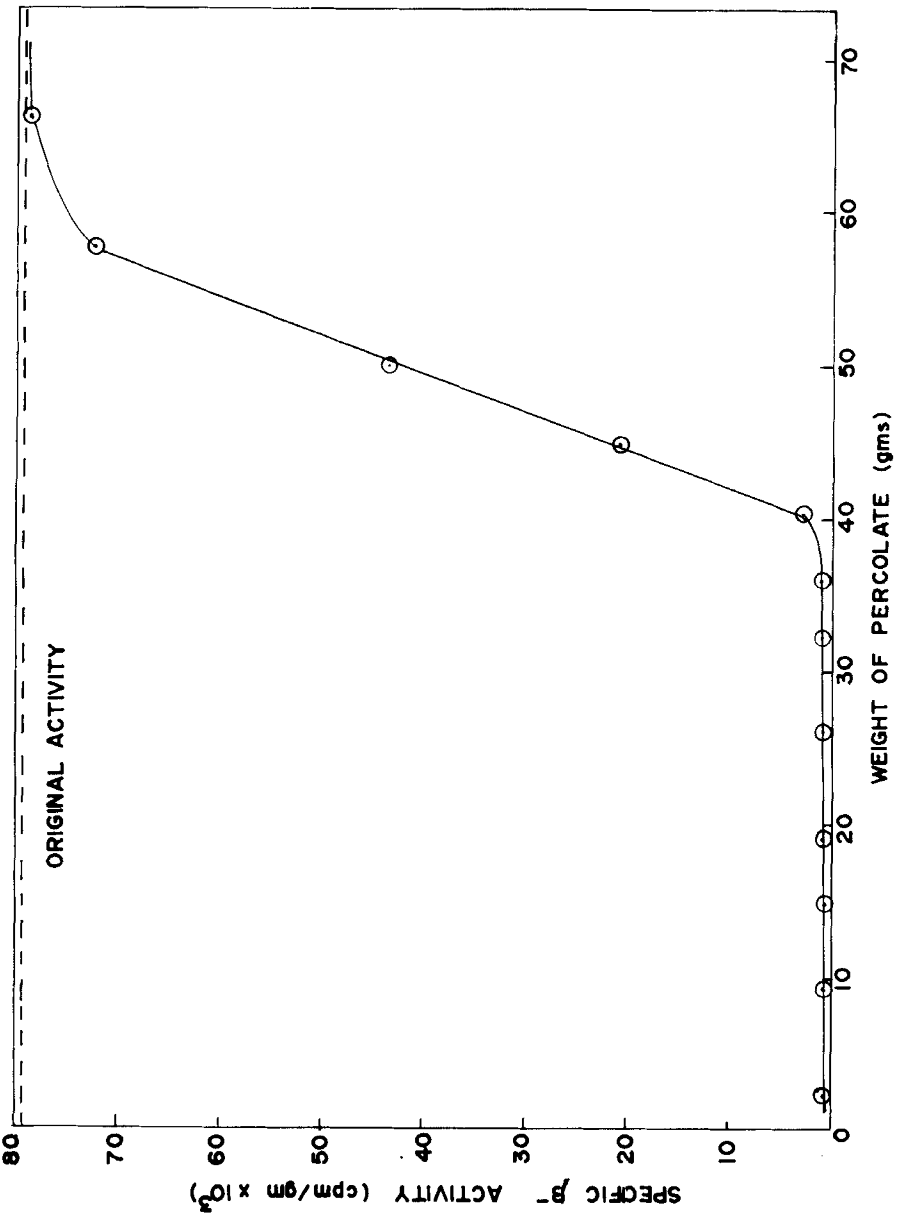

FIG. 2. Breakthrough curve for the CH_3OH/CH_3COCH_3 system on molecular sieve 4A.

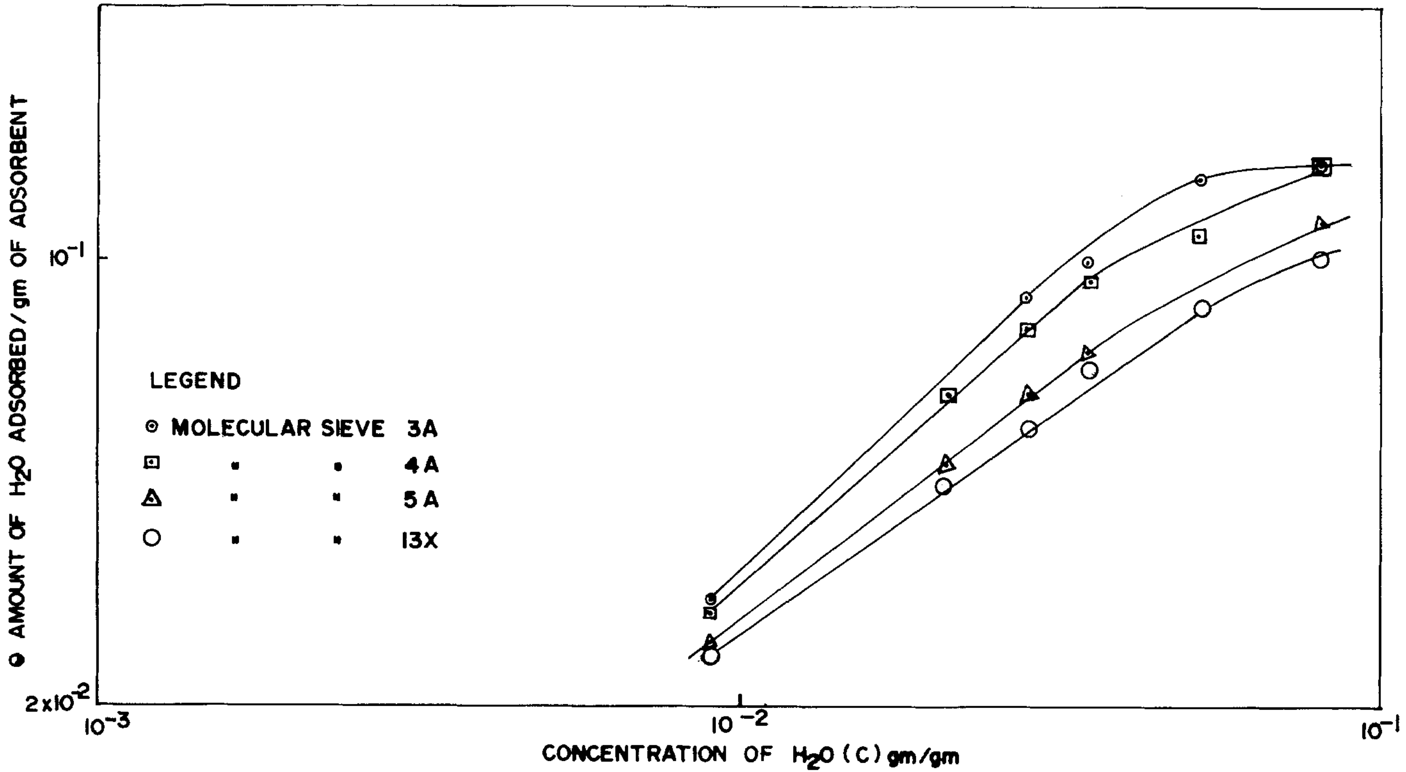

FIG. 3. Adsorption isotherms for H_2O from the H_2O/C_2H_5OH system on molecular sieves at 27°C.

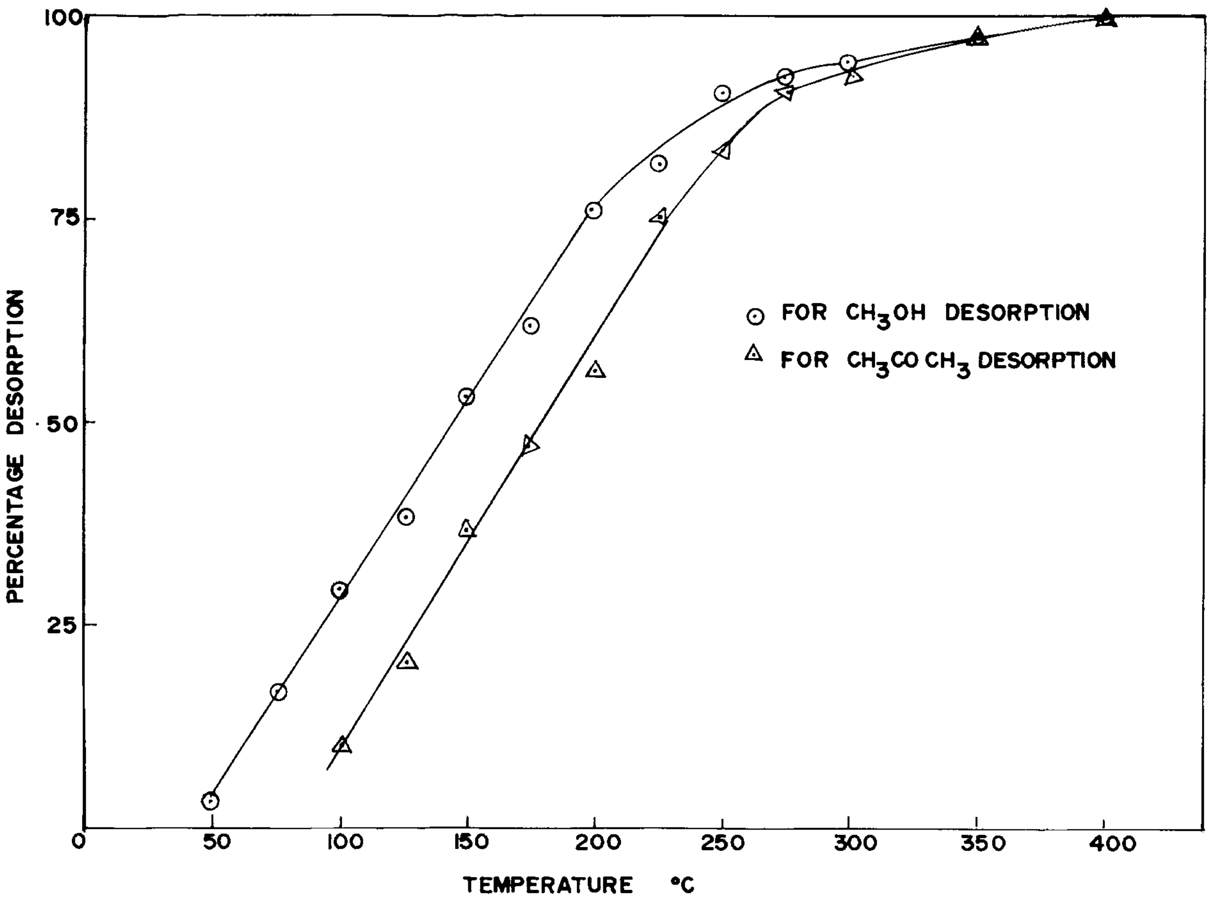

FIG. 4. TGA curves for molecular sieve 4A saturated with CH_3OH and CH_3COCH_3.

respectively), selectivity decreases as the number of orientations of acetone which allow diffusion into the matrix increases.

This fact is further confirmed by thermogravimetric analysis of molecular sieve 4A, saturated with methanol and acetone separately. These results are given in Fig. 4. It is evident from the figure that the rate of desorption of acetone with respect to temperature is low compared to the corresponding desorption of methanol under identical conditions. This can be attributed to the fact that due to its larger dimensions, acetone molecules can come out of pores only in certain orientations during desorption whereas methanol can come out easily due to its smaller dimensions and hence under all possible orientations.

CONCLUSION

The selectivity by absorbency of commercially available molecular sieves for the separation of the binary liquid systems studied is better than the reported separation by pervaporation. Even though better separation factors have been reported for the ethanol–water system by pervaporation in a few cases, very slow permeation rates make this process unattractive compared to the sorption technique with synthetic molecular sieves as the adsorbent. Molecular sieves have been successfully used for the commercial separation of many species whereas commercial utilization of pervaporation is difficult.

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