J. Chem. Eng. Data 1991, 36, 1–4

Sorption and Diffusion of Light Hydrocarbons on Na–Y Zeolites

Simona Palmas,* Anna M. Polcaro, Renzo Carta, and Giuseppe Tola

Department of Chemical Engineering and Materials, University of Cagliari, Piazza d'Armi, 09123 Cagliari, Italy

The adsorption isotherms were determined on zeolite Na–Y at 298, 313, and 333 K for propane and propylene and at 298 K for butane, *trans*-butene, 1-butene, and *cis*-butene. The pressure of the experiments ranged from 5×10^{-2} to 30 kPa. The weight of adsorbed hydrocarbons was determined by a gravimetric method with a vacuum microbalance. The Henry constants were evaluated from the equilibrium measurements in the low-concentration range, and their sequence propane < butane < *trans*-butene < propylene < 1-butene < *cis*-butene, was discussed in terms of the different adsorbate–adsorbent interactions. Equilibrium data, over the whole pressure range, were correlated by using the simplified model by Ruthven, based on statistical thermodynamics, and the appropriate parameters are reported. For C4 hydrocarbons, the intracrystalline diffusion process was also investigated and the Darken equation was used to correlate the uptake curves at the higher pressures. The diffusion coefficients were found in the order butane > *trans*-butene > 1-butene > *cis*-butene and were compared to the available values in literature.

Introduction

Adsorption of hydrocarbons on molecular-sieve zeolites has been widely studied because of its theoretical and technological importance, and several models have been proposed (*1*) to describe single-component isotherms and to predict multicomponent equilibria from single-component isotherms. Numerous experimental data are required to obtain reliable values for the correlation parameters, but only a limited number of papers present tabulated data in the literature.

Adsorption kinetics has also been the topic of a great number of both experimental and theoretical works. Molecular migration in zeolitic adsorbate–adsorbent systems has been studied by both nuclear magnetic resonance spectroscopy and sorption experiments (*2–3*). Although more recent research has agreed satisfactorily with the data provided by these two techniques (*4–6*), some discrepancies, which cannot be attributed only to the different origins and preparation of the samples, still exist (*7–8*). Collecting further experimental data over a larger spectrum of zeolite samples and sorbate molecules would be useful in order to clarify these discrepancies.

In this work the adsorption equilibrium and kinetics for hydrocarbons on zeolite Na–Y have been examined. Adsorption isotherms were obtained for propane, propylene, butane, *trans*-butene, 1-butene, and *cis*-butene, starting with measurements from sufficiently low pressure so that the linear region could be well-defined. The intracrystalline diffusion process of C4 hydrocarbons has also been investigated by analyzing the trend in time of the uptake curves.

Experimental Section

The hydrocarbon gases were supplied by Fluka (purity greater than 99.9%); the adsorbent used was Na–Y zeolite (composition of the unit cell $Na_{57}(AlO_2)_{57}(SiO_2)_{135}$) supplied by Union Carbide. Optical and electron spectroscopic examination of the sample revealed a mean diameter of 28.6 μm and a narrow size distribution.

Adsorption measurements were carried out gravimetrically by using a high-vacuum electrobalance (Cahn RG sensitivity = 10^{-7} g) connected to a large reservoir of gas to ensure that the system pressure remained essentially constant during the adsorption runs. Temperature was controlled to within ±0.5 K, and the accuracy of the pressure readings was to within $\pm 10^{-8}$ kPa, during the preliminary outgassing of the apparatus, and within $\pm 5 \times 10^{-3}$ kPa, during the adsorption measurements.

To perform equilibrium measurements, the sample of adsorbent was accurately weighed and then activated in the balance at 773 K and 10^{-7} kPa. Data were obtained from both sorption and desorption runs; repeated measurements were carried out to verify the reproducibility of measured data. The amount of hydrocarbon adsorbed at equilibrium were expressed as molecules per cavity by assuming 3.77×10^{20} large cavities/g of dehydrated zeolite (8 supercages/unit cell (*9*)). The accuracy of the data was of ±0.002 molecules/cavity. All the isotherms are fully reversible since the sorption and desorption branches appear to coincide. In order to obtain kinetic data, samples of weights ranging between 3 and 6 mg were employed and thinly spread over the balance pan. Experimental fractional uptake curves were essentially the same for samples of different weight under the same pressure step change. A microcomputer (IBM PC), interfaced with the balance, was employed to monitor and store experimental uptake data (with a sampling frequency of 1 datum/s until equilibrium was achieved. Temperature and pressure were also monitored by computer, and their values were observed to remain constant during the entire adsorption run.

Results and Discussion

Adsorption Equilibrium. The adsorption isotherms for C3 and C4 hydrocarbons on zeolite Na–Y were correlated by using the simplified equation derived by Ruthven (*10*) on principles of statistical thermodynamics

$$q = \frac{\sum_{s=1}^{m} \frac{sA_s(KP)^s}{s!}}{1 + \sum_{s=1}^{m} \frac{(KP)^s}{s!} A_s} \qquad (1)$$

where P is the pressure (kPa), q is the adsorbate concentration (molecules/cavity), K is the Henry constant [(molecules/cavity)/kPa], m is the maximum number of molecules that can be contained within the subsystem, and A_s represents the empirical parameters of intermolecular interaction ($A_1 = 1$).

In order to obtain reliable values for the correlation parameters of eq 1, the Henry constants were, at first, accurately determined, starting from the equilibrium measurements at pressures as low as possible and extrapolating to zero the ln (q/P) vs q curves (*11*). The interaction coefficients A_s were then evaluated by means of the expression for the spreading pressure given by Ruthven (*10*):

$$\pi = RT \ln \left(1 + \sum_{s=1}^{m} \frac{A_s(KP)^s}{s!}\right) \qquad (2)$$

π was calculated by numerical integration of the experimental data using Gibbs' equation, and the values of A_s were determined by optimizing the fit of exp(π/RT) vs KP curves. The

0021-9568/91/1736-0001$02.50/0

Table I. Parameters and Correlation Coefficients for Equation 1

sorbate	T^a	m	K^b	A_2	A_3	A_4	A_5	ρ
propylene	298	5	15.00	1.00	1.08	0.72	0.086	0.98
	313	5	7.31	1.00	1.62	0.24	0.066	0.99
	333	5	2.47	0.98	1.14	1.20	0.420	0.99
propane	298	4	0.82	1.00	0.72	2.00		0.97
	313	4	0.48	0.96	0.24	0.97		0.98
	333	4	0.26	1.40	0.30	2.40		0.96
butane	298	4	7.00	1.20	0.60	0.75		0.95
trans-butene	298	5	13.00	0.80	1.00	0.70	0.07	0.99
1-butene	298	5	19.00	0.90	1.20	0.80	0.50	0.96
cis-butene	298	5	33.70	0.90	1.50	0.50	2.00	0.90

[a] In K. [b] In (molecules/cavity)/kPa.

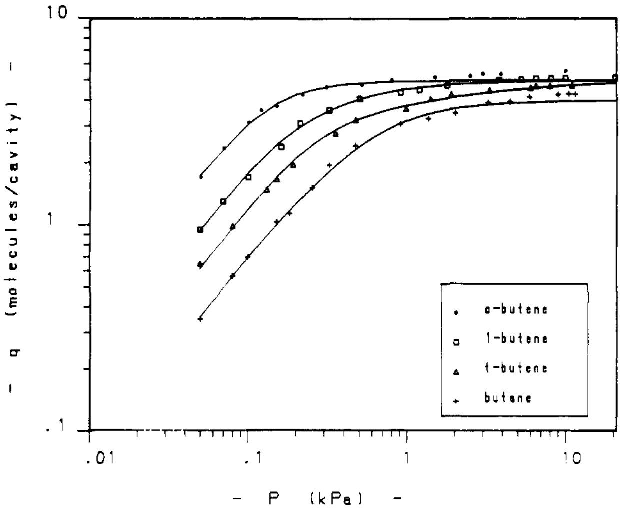

Figure 1. Experimental and calculated isotherms of C4 hydrocarbons at 298 K.

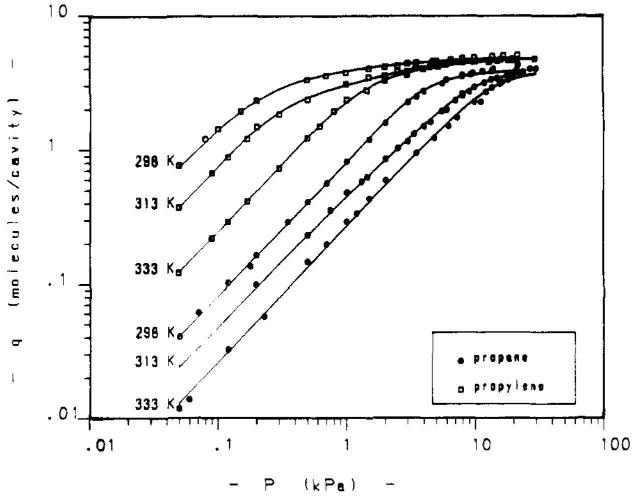

Figure 2. Experimental and calculated isotherms of C3 hydrocarbons at 298, 313, and 333 K.

values of the Henry constants and the intermolecular interaction coefficients are shown in Table I. By introducing these parameters into eq 1, the experimental isotherms fit well with those calculated, as can be seen from the correlation coefficients ρ also reported in Table I. Figures 1 and 2 give the comparison between experimental and calculated isotherms: some deviations can be observed only at high concentrations because eq 1 always considers an integer of molecules the limiting amount for adsorption, but this is not true for all the experimental systems.

The values of the Henry constants determined for the examined hydrocarbons are found in the sequences

propane < butane < *trans*-butene < propylene < 1-butene < *cis*-butene

This behavior is attributable to the extent of the interaction between the adsorbed molecules, which differ in electronic and geometric structures, and the cations of the zeolite network. So, for propane and butane, which are capable of taking part in only nonspecific interactions with the adsorbent, the values of K are considerably lower than for alkenes, because in this case a specific interaction between the π bond and the adsorption centers is established.

The trend of K with temperature obtained for propane and propylene also reflects the stronger adsorbate-adsorbent interactions for alkene as compared to alkane. Indeed, with use of the van't Hoff equation, a limiting adsorption heat for propane equal to -27 ± 1 kJ/mol, which agrees exactly with that given by Dzhigit et al. (*12*) on Na-Y zeolite in the same temperature range, is found. In the case of propylene the value for ΔH° is considerably larger ($\Delta H^\circ = 43 \pm 1$ kJ/mol). A similar behavior was noticed (*13*) also for 1-butene and butane: in fact a difference between the sorption heats in Na-Y zeolite at zero coverage (ΔH°(butene) − ΔH°(butane) = −15.1 kJ/mol) was found and attributed to different adsorbate-adsorbent interactions.

The influence of the molecule geometry on adsorption is made clear by the different behavior of the isomeric butenes. In fact because of the different arrangements of the two terminal methyl groups, the interactions with the adsorption centers could be hindered in the case of *trans*-butene and instead could be favored for *cis*-butene. This steric effect could contribute to determining the observed sequence of K. The same order was also found for the isotherms of these compounds on Na-X (*14*): however the Henry constants on Na-Y are lower than on Na-X due to (*12*) the minor extent of the adsorbate-adsorbent interactions as the number of Na^+ cations per unit cell changes from zeolite Na-X to zeolite Na-Y.

If a well-defined physical significance can be kept for the calculated interaction coefficients, the values of A_s, always rather close to unity, suggest that the mutual interactions of molecules are of minor importance for these systems (*15*). In particular, they are insignificant when the cage contains no more than two molecules ($A_2 \approx 1$); at higher concentrations repulsive interactions or restrictions of rotation take place since the values of A_4 and A_5 are less than unity in most systems.

Adsorption Kinetics. By following the time response of the adsorbate-absorbent system after changing the pressure, the diffusion process at 298 K of C4 hydrocarbons in the Na-Y zeolite has been also investigated. This traditional technique may involve a series of difficulties mainly arising from the finite rate of sorption heat release and external transport resistance (*2*). Extracrystalline resistances have been minimized by using a sufficiently small adsorbent sample spread out as thinly as possible over the balance pan. The weight and the configuration of the adsorbent have also been varied to confirm the absence of significant extracrystalline resistance to heat or mass transfer (*3*).

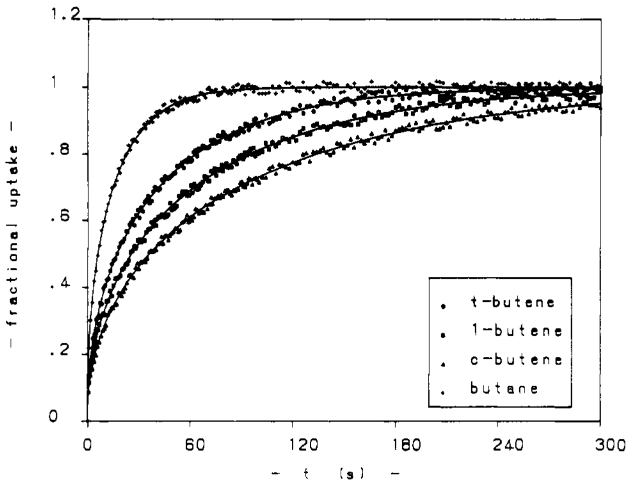

Figure 3. Uptake curves for C4 hydrocarbons in the region of Henry's law, correlated by eq 3.

Table II. Intracrystalline Diffusivities for C4 in Na-X and Na-Y Zeolites at 298 K

sorbate	sorbent	D_0, cm^2/s	method	ref
cis-butene	Na-Y	0.17×10^{-8}	gravimetry	this work
cis-butene	Na-X	0.60×10^{-8}	NMR spectroscopy	19
1-butene	Na-Y	0.25×10^{-8}	gravimetry	this work
1-butene	Na-X	20×10^{-7}	NMR spectroscopy	19
1-butene	Na-X	20×10^{-7}	NMR spectroscopy	17
trans-butene	Na-Y	0.37×10^{-8}	gravimetry	this work
trans-butene	Na-X	20×10^{-7}	NMR spectroscopy	19
butane	Na-Y	1.0×10^{-8}	gravimetry	this work
butane	Na-X	4×10^{-5}	NMR spectroscopy	17
butane	Na-X	2.3×10^{-7}	chromatography (zlc)	20
butane	Na-Y	4.5×10^{-14}	chromatography	23

When the pressure of adsorbate in the bulk phase was sufficiently low that a linear dependence of adsorbate concentration on the pressure could be assumed, the uptake curve was interpreted according to the well-known equation (*16*) that describes the diffusion process for an assemblage of isothermal spherical particles with instant equilibration at the surface

$$M_t/M_\infty = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-Dn^2\pi^2 t/r_0^2) \tag{3}$$

where M_t = total amount of adsorbed substance at time t, M_∞ = total amount of adsorbed substance after infinite time, and D = diffusion coefficient.

In Figure 3, experimental transients are compared with the curves calculated with eq 3. The values of diffusion coefficients obtained by matching the experimental uptake to eq 3, with r_0 = 28.6 μm, are given in Table II.

Outside the domain of Henry's law, the gradient of chemical potential has to be considered the driving force of diffusion fluxes. Therefore, the uptake curves have been interpreted in terms of "corrected" diffusivity D_0 by using the Darken equation (*1*):

$$D(C) = D_0\,\frac{\partial \ln P}{\partial \ln C} \tag{4}$$

Thus, to correlate kinetic data at higher pressure, Fick's law was numerically integrated by expressing $D(C)$ with use of eq 4: the corrected diffusivities D_0 were assumed equal to the diffusion coefficients derived from the analysis of the uptake curves in Henry's law region (see Table II), and the "thermodynamic factor" $\partial \ln P/\partial \ln C$ was numerically obtained from the equilibrium isotherms. Details of calculation are reported in the appendix. The fractional uptake evaluated by means of this numerical procedure is compared to the experimental transients in Figure 4. The agreement between the experimental and calculated curves may indicate that the heat-transfer resistance is of minor importance for the examined systems and the kinetic data may be represented by an isothermal model. Moreover the corrected diffusivities D_0 do not appear concentration-dependent, at least up to medium pore filling: a similar trend is shown by the NMR self-diffusivities for unsaturated hydrocarbons in zeolite Na-X, whereas a small decrease was noticed for butane (*17*). Table II also gives the diffusion coefficients obtained by means of different experimental techniques at the same temperature. The value of diffusivity for butane in this work has been found in acceptable agreement with the value obtained by chromatography zlc (zero length column) (*18*). Table II shows also the value of diffusivity obtained from chromatography (*23*) that results several orders of magnitude smaller. It is important to realize that this value can be subject to uncertainty because it is calculated by extrapolation at 298 K from data obtained in a temperature range much higher (398-495 K). The diffusivities obtained by the NMR data decrease in the same sequence observed in this work

n-butane - *trans*-butene - 1-butene - *cis*-butene

but show much larger values (*17*, *19*). Nevertheless it should be emphasized that large discrepancies between the NMR self-diffusivities and the corrected diffusivities obtained by sorption experiments have been widely observed, especially for large-port zeolites (*8*). Various causes, such as intrusion of heat or mass extracrystalline transfer resistance or the existence of surface barriers, have been proposed to interpret this behavior (*20*-*23*).

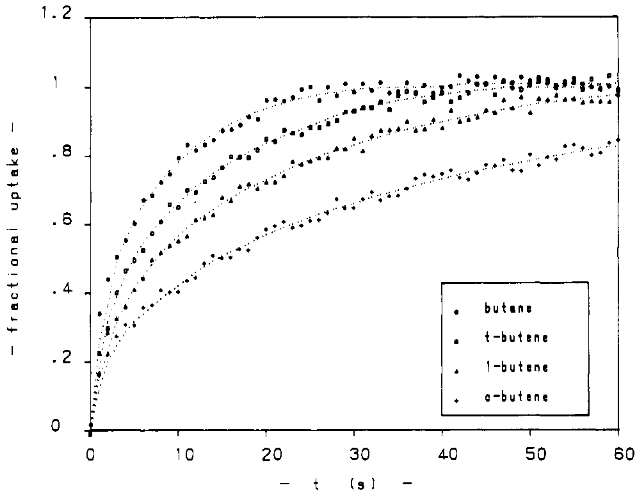

Figure 4. Comparison of uptake curves evaluated by the numerical procedure reported in the appendix, with experimental data outside the region of Henry's law.

Appendix

The diffusion process for an assemblage of isothermal spherical particles with instant equilibration at the surface can be described by

$$\frac{\partial C(r,t)}{\partial t} = \frac{1}{r^2}\,\frac{\partial}{\partial r}\left[D(C)\,\frac{\partial C(r,t)}{\partial r}\right] \tag{I}$$

with the following conditions

$$t \geq 0 \qquad \partial C/\partial r = 0 \qquad r = 0 \tag{II}$$

$$t \geq 0 \qquad C = C_0 \qquad r = r_0 \tag{III}$$

$$t = 0 \qquad C = 0 \qquad 0 < r < r_0 \tag{IV}$$

C_0 being the adsorbate concentration at equilibrium with the gaseous phase.

By introducing the following dimensionless variables

$$Y = C/C_0 \qquad X = r/r_0 \qquad \tau = tr_0^2/D$$

and considering eq 4, eq I becomes

$$\frac{\partial Y(X,\tau)}{\partial \tau} = \frac{1}{X^2}\left[2Xf(Y)\frac{\partial Y(X,\tau)}{\partial X} + X^2f'(Y)\left[\frac{\partial Y(X,\tau)}{\partial X}\right]^2 + X^2f(Y)\frac{\partial^2 Y}{\partial X^2}\right]$$

The function $Y(X,\tau)$ is then substituted by $\tilde{Y}(X,\tau)$ defined by a Lagrange interpolation formula

$$\tilde{Y}(X_k,\tau) = \sum_{I=1}^{N+2} l_I(X_k)Y_I(\tau)$$

where the Lagrangian coefficient functions are polinomials of n grade such as

$$l_I(X_k) = \prod_{\substack{I=1 \\ I\neq k}}^{N+2} \frac{X - X_I}{K_k - X_I}$$

$-Y_I(\tau)$ are the values of $Y(X,\tau)$ at the $N+2$ collocation points: N points are evaluted as zeros of the Jacobi polynomial with $\alpha = 1$ and $\beta = 1$; $N = 10$ proved to be adequate to obtain sufficient accuracy. The extreme points can be evaluated from the boundary conditions (II, III):

$$Y(0,\tau) = \frac{-l_{N+2}(0) + \sum_{I=2}^{N+1} l'_I(0)\ \tilde{Y}(\tau)}{l'_I(0)}, \qquad Y(1,\tau) = 1$$

In this way the examined system is transformed into a system of ordinary differential equations, which with the further condition (IV)

$$Y(X,0) = 0$$

was solved by numerical integration using a Gear method implemented in a routine of the IMSL collection.

Registry No. Propane, 74-98-6; propene, 115-07-1; butane, 106-97-8; *trans*-2-butene, 624-64-6; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1.

Literature Cited

(1) Ruthven, D. M. *Principles of adsorption and adsorption processes*; Wiley: New York, 1984.
(2) Karger, J.; Pfeifer, H. *Zeolites* **1987**, *7*, 90.
(3) Ruthven, D. M. *AIChE Symp. Ser.* **1984**, *80*, 21.
(4) Karger, J.; Caro, J. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1363.
(5) Karger, J.; Rutven, D. M. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1485.
(6) Bulow, M.; Lorenz, P.; et al. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1099.
(7) Caro, J.; Bulow, M.; Karger, J. *J. Chem. Eng. Sci.* **1985**, *40*, 2169.
(8) Goddard, M.; Ruthven, D. M. *Zeolites* **1988**, *6*, 283.
(9) Meyer, W. In *Atlas of zeolites structure types*, 2nd revised ed.; Olson, D. H., Ed.; Butterworth: London, 1988.
(10) Ruthven, D. M.; Goddard, M. In *Fundamentals of Adsorption*; Myers, A. L., Belford, G., Eds.; American Institute of Chemical Engineers: New York, 1984.
(11) Barrer, R. M.; Davies, J. A. *Proc. R. Soc. London* **1970**, *A320*, 289.
(12) Dzhigit, O. M.; Kiselev, A. V.; Rachmanova, T. A. *Zeolites* **1984**, *4*, 389.
(13) Thamm, H.; Stach, H.; Fiebig, W. *Zeolites* **1983**, *3*, 95.
(14) Harlfinger, R.; Hoppach, D.; et al. *Zeolites* **1983**, *3*, 123.
(15) Ruthven, D. M.; Goddard, M. *Zeolites* **1986**, *6*, 275.
(16) Crank, J. *The mathematics of diffusion*; Clarendon Press: Oxford, U.K. 1967.
(17) Germanus, A.; Karger, J.; Pfeifer, H. *Zeolites* **1984**, *4*, 188.
(18) Eic, M.; Ruthven, D. M. *Zeolites* **1988**, *8*, 472.
(19) Karger, J.; Michel, D. *Z. Phys. Chem.* (*Leipzig*) **1976**, *257*, 983.
(20) Lee, L. K.; Ruthven, D. M. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 2406.
(21) Struve, P.; Kocirik, M.; et al. *Z. Phys. Chem.* (*Leipzig*) **1982**, *263*, 49.
(22) Bulow, M. *Z. Chem.* **1985**, *25*, 81.
(23) Fu, C.; Ramesh, M. S. P.; Haynes, H. W. *AIChE J.* **1986**, *32*, 1848.

Received for review June 2, 1989. Revised February 8, 1990. Accepted June 27, 1990.

Vapor-Liquid Equilibria in the Systems Methyl Acetate-Methyl Methacrylate and Methyl Acetate-Propyl Bromide-Methyl Methacrylate

Jaime Wisniak* and Abraham Tamir

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105

The vapor-liquid equilibrium at 760 mmHg has been determined for the title systems. The binary system behaves ideally. The data were correlated by various equations, and the appropriate parameters are reported. No azeotrope is present.

The present work was undertaken to measure VLE data for the title systems for which no isobaric data are available. Data for the two other binaries have already been measured (*1*, *2*).

Experimental Section

Purity of Materials. Methyl acetate, analytical grade (99.5%+), and propyl bromide (99.4%) were purchased from Merck; methyl methacrylate (99.4%+) was purchased from Fluka. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties of the pure components appear in Table I.

Table I. Physical Constants of Pure Components

index	compound	refractive index (25 °C)	bp(760 mmHg), °C	purity, GLC (min) %
1	methyl acetate	1.3588[a] 1.3589[b]	56.9[a] 56.94[b]	99.5
2	propyl bromide	1.4320[a] 1.4317[b]	70.55[a] 71.00[b]	99.4
3	methyl methacrylate	1.4118[a] 1.4120[c]	100.4[a] 100.3[c]	99.4

[a] Measured value. [b] Reference 11. [c] Reference 12.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*3*) was used in the equilibrium determination. The experimental features have been described

0021-9568/91/1736-0004$02.50/0