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Short communication

Effect of heat of adsorption on the adsorptive drying of solvents at equilibrium in a packed bed of zeolite

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Abstract

A packed bed of 3 Å zeolite is used to dry ethanol solutions initially at 24°C and containing up to 6.6 wt.% water. In view of the highly exothermic nature of the process, the progress of the thermal wave through the bed is followed and its effect on product dryness identified. The thermal wave is found to leave the bed around the time at which breakthrough of water begins to occur. For a given flow rate, the water concentration in the initial effluent and the peak temperature rise are found to be directly proportional to the water concentration in the feed. For a given feed concentration, both the initial effluent water concentration and the peak temperature rise can be reduced by decreasing the feed velocity. However, very low water concentrations should be achievable by removing the exotherm. In addition, equilibrium isotherms are reported for the adsorption of water on 3 Å molecular sieve zeolite, and the individual isotherms conform closely to Langmuir and Freundlich models. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Zeolite; Adsorption; Heat effects; Liquid phase; Drying; Solvents

1. Introduction

Molecular sieve zeolites are suitable adsorbents for the removal of low levels of water from organic solvents. Water, because of its small molecular diameter, 28 nm, can easily enter zeolite channel structures, whilst most organic molecules, such as ethanol, 44 nm, are essentially excluded. For water in zeolites, the electrostatic interaction forces can be very high and can give rise to heats of adsorption comparable to heats of chemical reaction [1,2]. Hence the exotherm which occurs when water is adsorbed can become appreciable for high water concentrations in the feedstock [2,3]. For example, in the vapour phase adsorptive process, to break the ethanol–water azeotrope (4.4 wt.% water at 1 bar) temperature rises as high as 120°C can occur and have deleterious effects on the adsorption isotherm and product dryness [4]. Depending on the process conditions and the system under consideration, the thermal wave created by the exotherm can travel through a packed bed of adsorbent at a speed greater than or equal to the mass transfer wave of water. Garg and Ausikaitis [5] have indicated how control over the thermal wave can be used to advantage in the vapour-phase drying of the ethanol–water azeotrope. The empirical criterion which is used to determine the relative speeds of the thermal and the mass transfer waves [5] is the magnitude of the cross-over ratio (COR), as defined by

$$\mathrm{COR} = \frac{C_{\mathrm{pf}}/(Y_{\mathrm{i}} - Y_{\mathrm{o}})}{C_{\mathrm{ps}}/(X_{\mathrm{i}} - X_{\mathrm{o}})} \tag{1}$$

where COR is the cross-over ratio, X_{i} is the adsorbent loading in equilibrium with the concentration of adsorbate behind the mass transfer front ($g_{\mathrm{adsorbate}}/g_{\mathrm{adsorbent}}$), X_{o} the adsorbent residual loading ahead of mass transfer front which is a result of a previous regeneration step ($g_{\mathrm{adsorbate}}/g_{\mathrm{adsorbent}}$), Y_{i} the inlet adsorbate concentration ($g_{\mathrm{adsorbate}}/g_{\mathrm{carrier\ fluid}}$) Y_{o} the outlet adsorbate concentration in equilibrium with X_{o} ($g_{\mathrm{adsorbate}}/g_{\mathrm{carrier\ fluid}}$), C_{pf} the heat capacity of the carrier fluid (kJ/kg$_{\mathrm{fluid}}$ K) and C_{ps} the heat capacity of the adsorbent (kJ/kg$_{\mathrm{adsorbent}}$ K).

If COR $\ll 1$, the thermal front is likely to lag behind the mass transfer wave, and hence a good dryness can be achieved, whilst preserving the heat of adsorption inside the bed [5]. The specific heat of ethanol liquid is about twice that of the vapour [6], and thus COR is likely to be higher for a liquid phase separation. When COR approaches unity, it can be expected that the thermal and the mass transfer waves will exit the bed simultaneously [3]. Adsorption is almost always an exothermic process, and for high purity to be achieved, the heat of adsorption must be removed. Sowerby

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[7] reported that heat exchange with the surroundings for a feed of 5 wt.% water is likely to affect the performance of the adsorption process, and should, therefore, be taken into account when using experimental data from small diameter laboratory scale equipment for the scale-up of adsorption columns. However, little attention has been paid to the effect of the thermal wave on the dryness in the liquid phase applications. The main purpose of the present work was to determine how the thermal dynamics of adsorption can affect the dryness of the product in liquid phase adsorptive drying. As an exemplifying process, the recovery of dry ethanol from aqueous solution using a 3 Å molecular sieve was used. Therefore, a number of factors were taken into consideration when designing the column. Empirical quid lines published in the literature were used. The factors reported in [8–10] are conflicting, and hence a compromise was required in order to optimize the design parameters practically.

2. Apparatus and procedures

The apparatus consisted of a 1.76 cm inside diameter stainless steel column mounted vertically inside a thermostatically controlled oven, and packed to a height of 40 cm with commercially available spherical beads of 3 Å zeolite (1.6–2.5 mm in diameter) manufactured by the Davison Chemical Division. Water from W.R. Grace and Co. was used. A 10 cm long bed of similarly sized glass beads was placed at each end of the zeolite to provide good flow distribution. Five thermocouples protruding through the column wall into the adsorbent bed were used to monitor the progress of the thermal wave. A constant flow rate (2.15–5.78 cm/min) of the feed of known composition (2.46–6.55 wt.% water) was provided by a positive displacement metering pump. Flow was upwards and the liquid effluent passed into a fraction collector for water analysis by Karl Fischer titration. All adsorption experiments were carried out at feed and oven temperatures of 24°C. The experimental conditions are summarized in Table 1. Each experiment was preceded by a thorough desorption of water from the zeolite.

Separate batch experiments were carried out to determine the equilibrium isotherms. An ethanol–water solution of known concentration was shaken with a known weight of freshly regenerated adsorbent for at least 8 h in a flask placed in a thermostatically controlled environment. The final concentration of water in the solution was obtained by Karl Fischer analysis. By assuming that no ethanol was adsorbed by the zeolite, for the reasons given above, the uptake of water on the adsorbent was obtained by simple mass balance:

$$q^* = \frac{v(c_0 - c^*)}{w} \tag{2}$$

3. Results

3.1. Equilibrium and heat of adsorption

The equilibrium water loading as a function of solution concentration is shown in Fig. 1 for temperatures of 24, 29 and 34°C. Full lines indicate fits obtained with the Langmuir isotherm equation

$$q^* = \frac{K_L Q c^*}{(1 + K_L c^*)} \tag{3}$$

the constants for which are given in Table 2. The Freundlich equation

$$q^* = K_F (c^*)^{1/n} \tag{4}$$

also fitted the data, although somewhat more poorly at low concentrations. The Freundlich constants are given in Table 2. As expected, both K_L and K_F decrease steadily

Table 2
Isotherm parameters

Temperature (°C)	Langmuir		Freundlich	
	K_L (g_{soln}/g_{water})	Q (g_{solid}/g_{water})	K_F (g_{soln}/g_{water})	$1/n$
24	0.325	0.255	0.065	0.548
29	0.185	0.245	0.040	0.682
34	0.092	0.254	0.023	0.772

Table 1
Experimental conditions

Interstitial velocity (cm/min)	Modified bed Re	Feed conc. (wt.% water)	Initial effluent conc. (wt.% water)	Average bed loading (g_{water}/g_{solid})
3.570	0.082	2.68	0.068	0.109
3.570	0.082	3.45	0.069	0.121
3.570	0.082	4.38	0.097	0.134
3.570	0.082	6.55	0.129	0.151
2.320	0.053	2.660	0.049	0.096
3.570	0.082	2.680	0.068	0.109
4.710	0.108	2.670	0.101	0.111
6.250	0.144	2.670	0.141	0.131

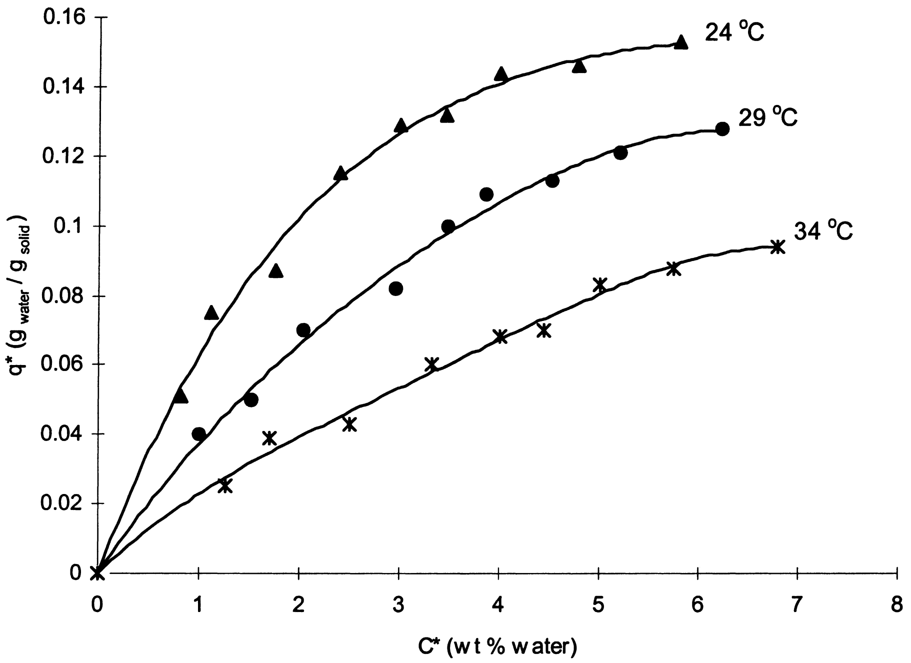

Fig. 1. Equilibrium isotherms at 24°C, 29°C and 34°C (asterisks indicate experimental data, full lines represent Langmuir fits).

with increasing temperature, whilst the monolayer loading Q is largely unaffected. The coefficient $(1/n)$ is directly proportional to temperature. Fig. 2 shows the dependence of K_L on temperature written in the form of the van Hoff equation

$$K_L = K_L' \exp\left(\frac{\Delta H}{RT}\right) \tag{5}$$

The average heat of adsorption at equilibrium conditions is calculated to be 96 kJ/mol, i.e. within the region normally expected for exothermic chemical reactions.

3.2. Breakthrough curves and thermal waves

An example breakthrough curve and the progress of its associated thermal wave through the bed are shown

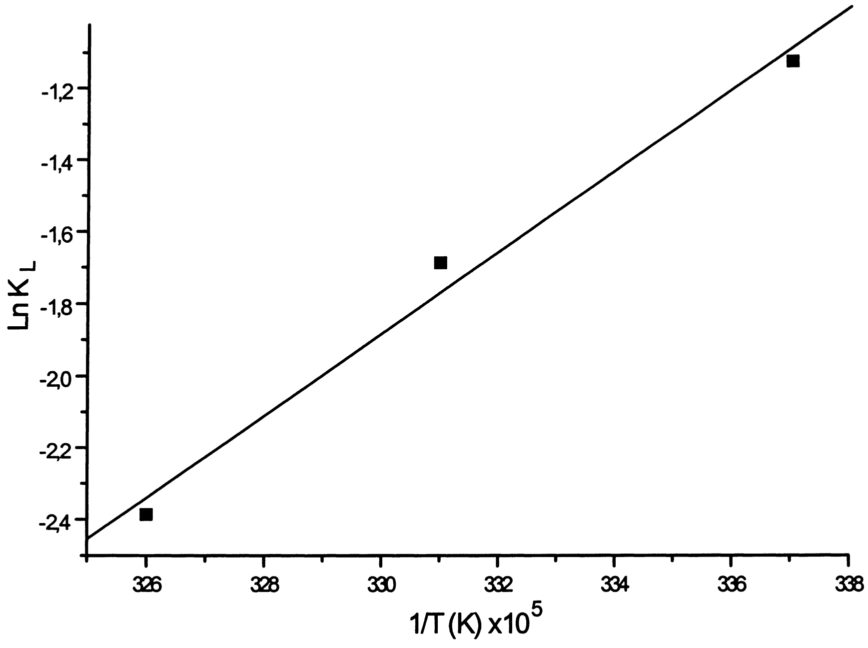

Fig. 2. Effect of temperature on Langmuir constant K_L.

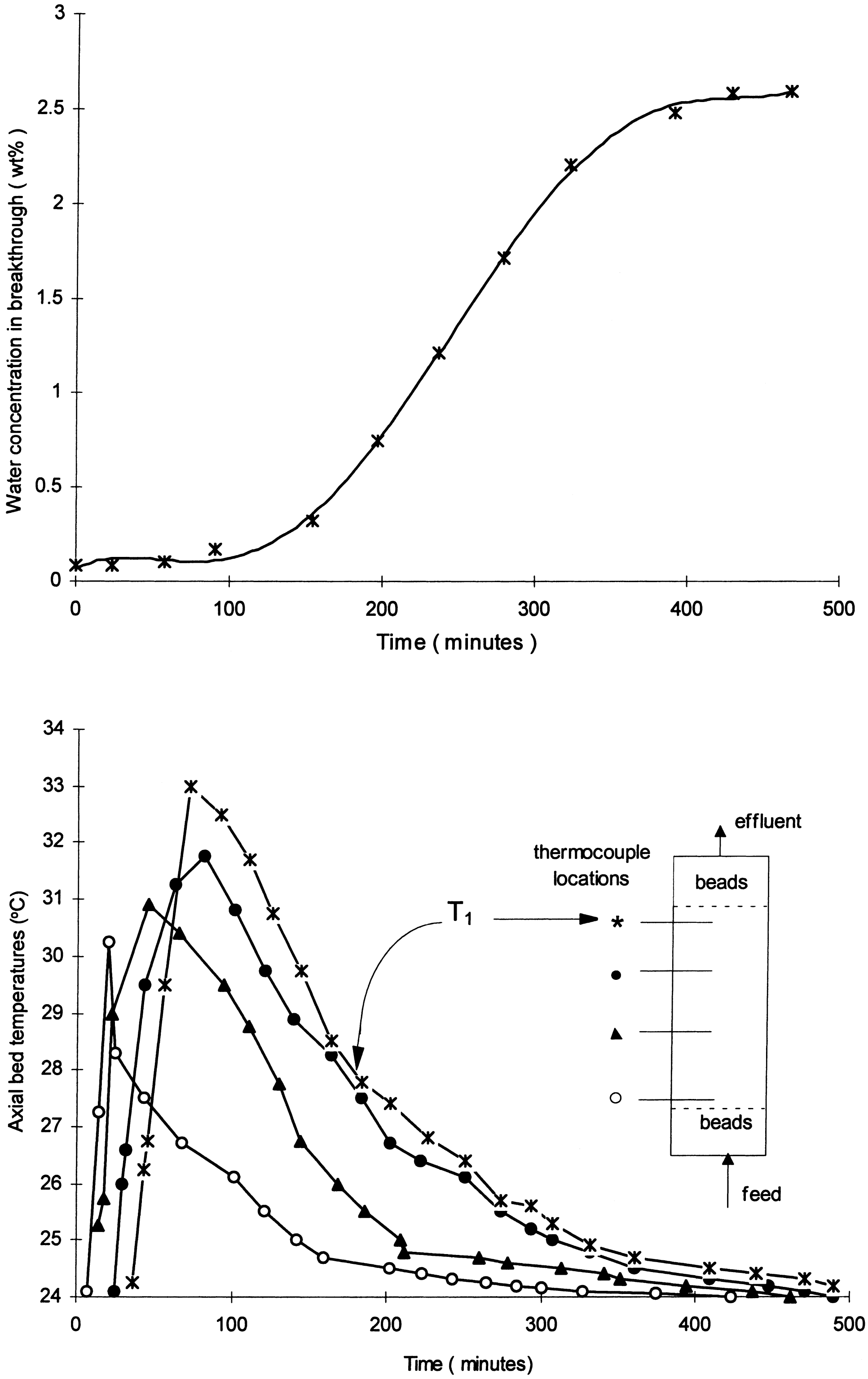

Fig. 3. Example of breakthrough curve and temperature profiles.

in Fig. 3 for a feed flow rate of 3.3 cm/min and a feed water concentration of 2.67 wt.%. The thermal wave passed out from the bed (indicated roughly by temperature T_1) at about the same time as the concentration of water began to increase in the breakthrough curve. A temperature rise coincident with breakthrough is not desirable from an equilibrium point of view (Fig. 1), although some marginal advantage could be gained from improved kinetics [11]. For this run, the maximum axial temperature rise was about 8°C, and the radial temperature gradient was found to be

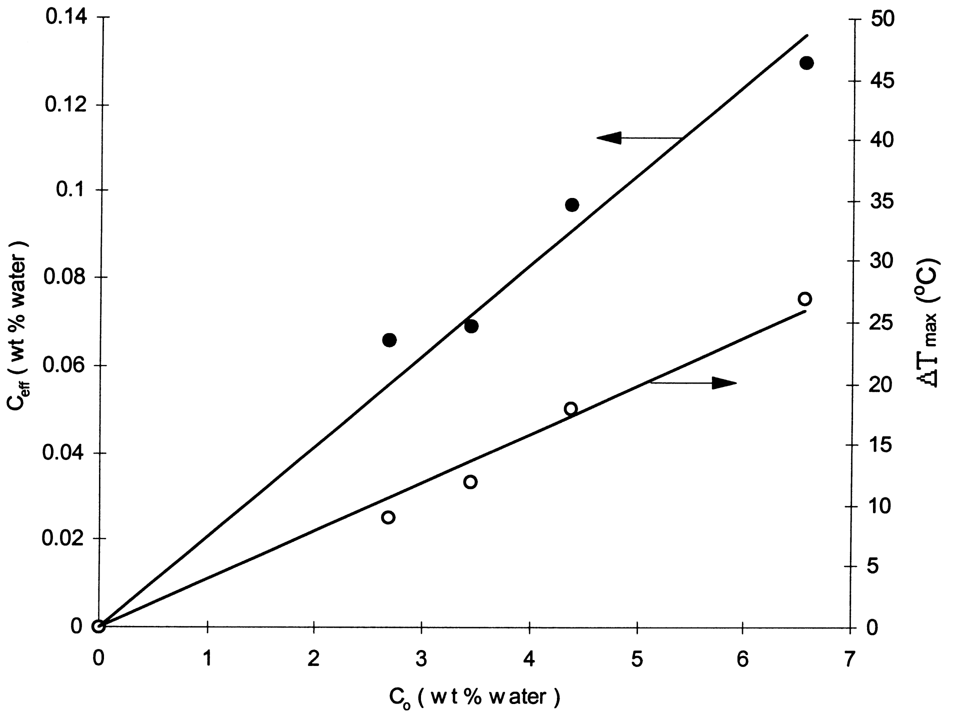

Fig. 4. Effect of feed concentration on initial product water concentration and maximum rise in end bed temperature (constant feed flow rate).

really small. For small water concentrations, the heat generated in the mass transfer front is generally carried ahead of the front by the carrier fluid, which is moving at a much higher velocity than the water adsorption front in the bed. This may cause the product fluid to be slightly warmer than the feed fluid, but does not affect the adsorption dynamics within the mass transfer front which will remain isothermal. For high water concentrations, the heat generated can remain within or behind the front, and the adsorbent temperature rises significantly. In this case, the rate of heat generated by adsorption is greater than the rate at which it is carried out of the mass transfer front by the carrier fluid. For these situations, adsorption is occurring at a temperature higher than that of the feed. This reduces the efficiency of the adsorbent for water removal by both lowering the effective water equilibrium capacity and elongating the mass transfer front. This can cause early breakthrough of water into the product, and a shallow breakthrough curve. Although the column to particle diameter ratio is quite small (=8.6), the radial temperature gradient is small and has a negligible effect on the efficiency of the bed since the other design ratios, e.g. column length to particle diameter ratio (=195) were appropriately chosen, as discussed in the literature [8–10].

3.3. *Effects of feed flow rate and concentration*

The breakthrough curve and its associated thermal wave sharpen, and hence the maximum temperature rise is increased as the feed concentration is increased. The effect of the feed concentration on the initial product water concentration and maximum temperature rise in the end bed temperature is shown in Fig. 4. For the range of conditions studied, both parameters increase linearly with the feed concentration. The origin is a valid data point for both lines in Fig. 4. The average bed loading (ABL) is defined as follows:

$$\mathrm{ABL} = \frac{(m_f - m_p - m_e)}{w} \tag{6}$$

Since ABL is calculated for conditions immediately after the breakthrough has been completed, its value would be expected to be around that given by the equilibrium isotherms. As seen in Fig. 5, ABL compares well with q^* obtained at the feed temperature. Thus, despite the thermal transient passing through the bed, adsorptive loadings in equilibrium with the feed composition are re-established at a temperature very close to that of the feed.

In addition, the breakthrough curve and its associated thermal wave sharpen, and hence the maximum temperature rise is increased as the flow rate is increased for a given feed concentration. The effect of the flow rate on the initial product water concentration, maximum temperature rise and ABL is shown in Fig. 6. For the range of conditions studied, linear relationships between the three parameters and the feed water concentration are observed. Fig. 7 shows that the ABL becomes closer to q^* at the feed temperature of 24°C when the feed velocity is the highest. This is probably

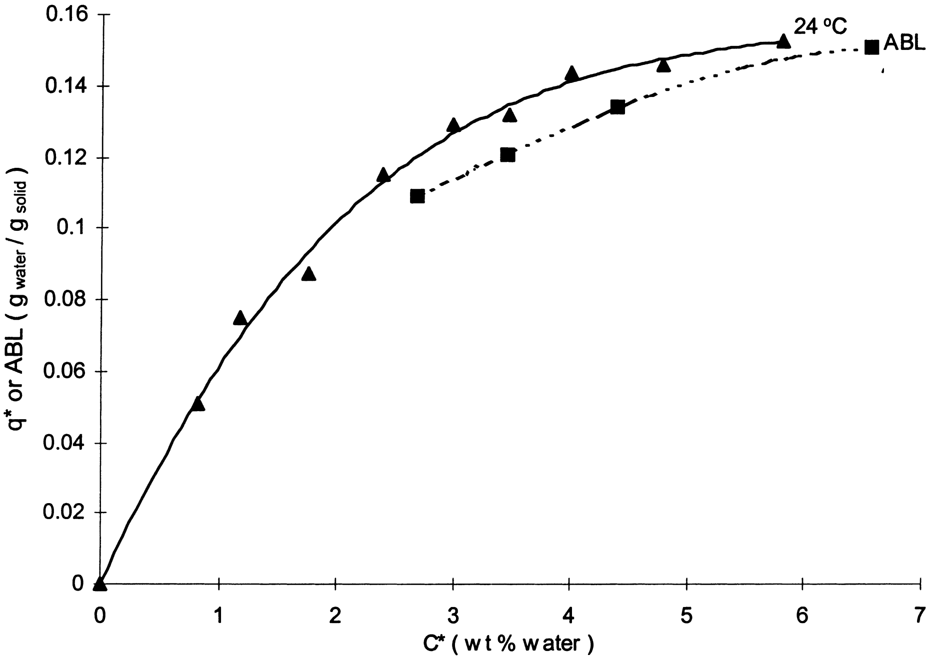

Fig. 5. Equilibrium isotherm at 24°C (points indicate experimental data, full line represent the Langmuir fit) and the effects of feed concentration on ABL.

the result of improved interparticle heat transfer at higher velocities allowing a faster return of the bed to the feed temperature. Despite the effect of channelling, ABL becomes higher with increased feed flow rate.

4. Discussion

Teo and Ruthven [12] studied the adsorption of water from aqueous ethanol using 3 Å zeolite (1.6 mm cylindrical

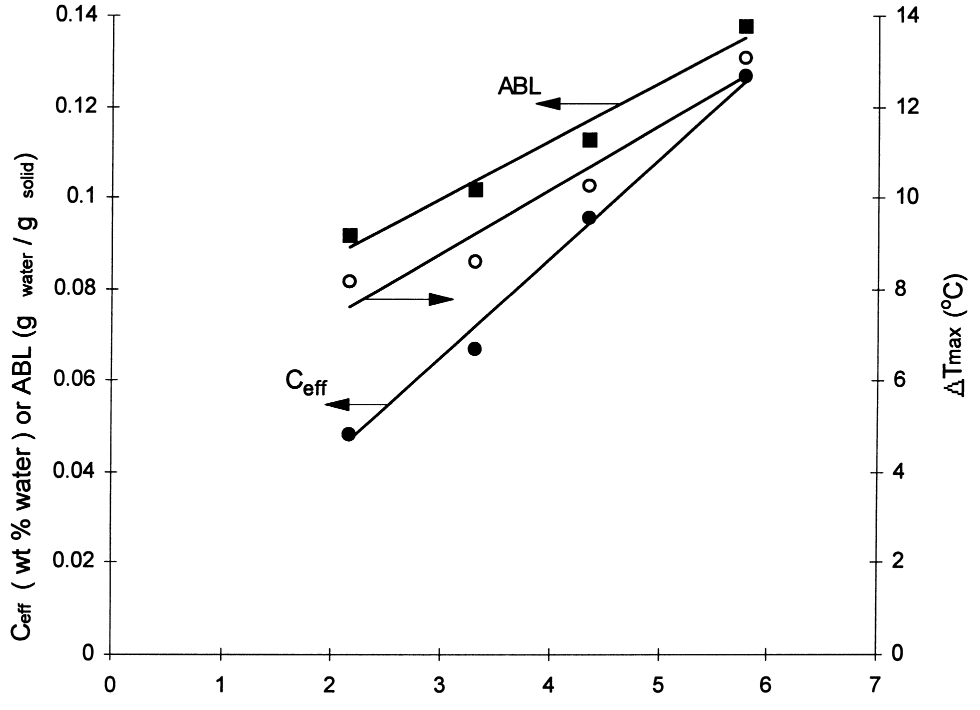

Fig. 6. Effect of feed flow rate on initial product water concentration, average bed loading and maximum rise in end bed temperature (constant feed concentration).

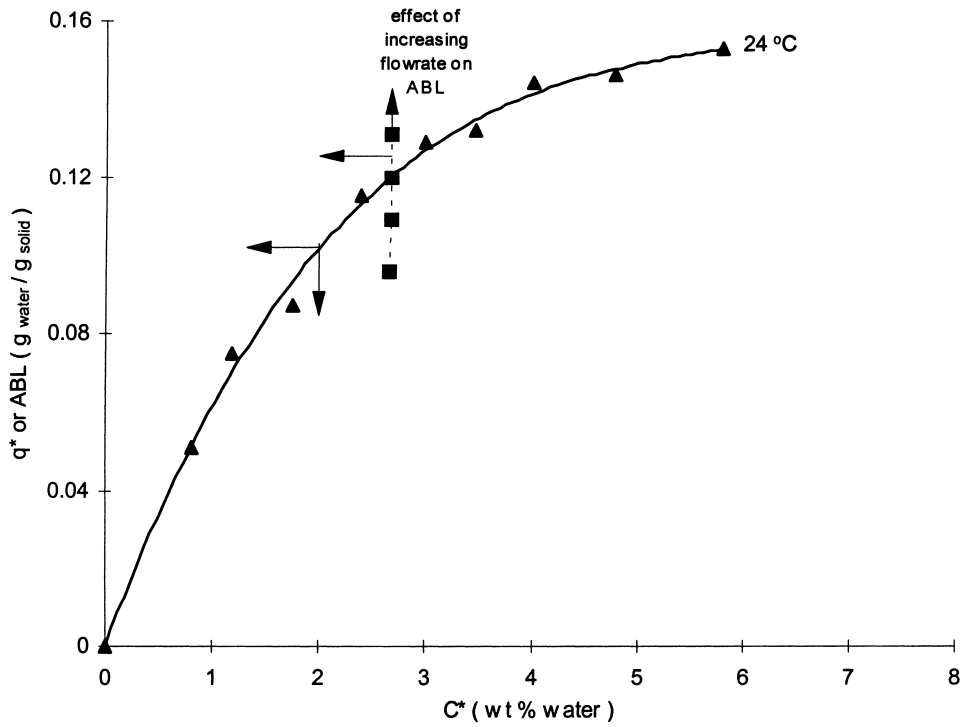

Fig. 7. Equilibrium isotherm at 24°C (points indicate experimental data, full line represents Langmuir fit) and the effects of feed flowrate on ABL.

pellets supplied by Sigma). Breakthrough experiments were carried out in a 2.5 cm diameter × 76 cm length jacketed glass column maintained at 24°C. The feedstock contained 4.7 wt.% water, and flow velocities were in the range 0.789–1.654 cm/min. Product dryness prior to breakthrough were not reported by Teo and Ruthven [12] and in-column temperatures were not measured. Moreover, the feed concentration of 4.7% water used by Teo and Ruthven [12] would have created a peak temperature rise to around 18°C, which would have been difficult to dissipate radially in a bed of zeolite contained in a 2.54 cm diameter glass column.

For a feed of given water content, the product dryness can be improved somewhat by keeping the feed velocity low. The adsorbent vendor [13] recommends that the liquid velocity of ethanol should not exceed 7.62 cm/min, and should not be below 3.05 cm/min in order to avoid extremely large beds. The velocities used in this study and in that of Teo and Ruthven [14] were mainly within this range. Carton et al. [15] studied the use of 3 Å zeolite in a 1.5 cm diameter × 48 cm length column to dry ethanol at 22°C from a feed concentration of 6 wt.% water. Purities were not reported, but the treatment capacity (cm^3 ethanol per 100 g zeolite) was found to be inversely proportional to the velocity in the range 0.5–2 cm/min. Reducing the velocity allows a greater contact time, but unfortunately, it increases the external film resistance, which has a major impact on the shape of the early portion of the breakthrough curve [16,17].

Since the product dryness, which is determined by the shape of the leading edge of the breakthrough curve, determines whether the specification can be met, it is clearly necessary to adopt a more rigorous non-isothermal model for design and analysis, similar in concept to that reported by Ruthven et al. [18] for gas phase adsorption.

However, a simple expedient for producing very dry ethanol from a feed of high water concentration would be to use a series network of adsorption beds with interstage cooling. For the conditions studied in this work, the ratio of the final water concentration in the effluent before breakthrough to the uptake water concentration for j such beds is given by

$$\frac{c_{\mathrm{eff}}}{(c_0 - c_{\mathrm{eff}})} = (0.02)^j \tag{7}$$

Thus a product containing less than 0.01% water should be obtainable from the azeotrope in two beds with interstage cooling back to 24°C.

5. Conclusions

The product dryness which is obtained when aqueous ethanol solutions are dried in a packed column of 3 Å zeolite is found to be directly proportional to the water concentration in the feedstock. The strongly exothermic nature of the adsorption process creates a thermal wave which begins to leave the column at around the same time as the breakthrough of water begins to occur. The exotherm at the end of the bed is directly proportional to the feed water concentration, and thus creates unfavourable equilibrium conditions. The dryness obtained from a feed of a given concentration can, however, be improved by reducing the linear velocity through the column. The behaviour of the individual isotherms is straightforward and conforms to Langmuir and Freundlich models, and the parameters calculated from these models agree well with independently measured values such as the limiting heat of adsorption. In the practical application of zeolite desiccants, the choice of regeneration temperature depends critically on the desired humidity level. If this is relatively high, a relatively low regeneration temperature will suffice as it is neither necessary nor desirable to remove the adsorbed water. On the other hand, if a very low humidity level is required, this can only be achieved within the sorption region, and a much higher regeneration temperature is needed.

6. Nomenclature

ABL	average bed loading defined by Eq. (6) $(g_{water}/g_{adsorbent})$
c^*	water concentration in solution at equilibrium (wt.% or g/cm)
c_{eff}	water concentration in effluent before breakthrough (wt.% or g/cm)
c_0	water concentration in initial or feed solution (wt.% or g/cm)
ΔH	heat of adsorption (kJ/mol)
j	exponent in Eq. (6)
K_F	Freundlich constant (g_{soln}/g_{water})
K_L	Langmuir constant (g_{soln}/g_{water})
K_L'	van Hoff constant $(g_{solution}/g_{water})$
m_e	mass of water in bed voidage (g)
m_f	mass of water fed into bed (g)
m_p	mass of water collected in product (g)
n	exponent in Freundlich equation
Q	monolayer loading – Langmuir equation $(g_{water}/g_{adsorbent})$
q^*	water loading on adsorbent at equilibrium $(g_{water}/g_{adsorbent})$
R	universal gas constant (kJ/kmol K)
Re	Reynolds number
T	temperature (K)
v	volume of solution in batch equilibrium experiment (cm^3)
w	mass of adsorbent (g)

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