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Concentration–Thermal Swing Adsorption Process for Separation of Bulk Liquid Mixtures

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ABSTRACT

A novel concentration–thermal swing adsorption process is described for separation of bulk binary liquid mixtures. The process is designed to produce essentially two pure products with high recoveries of both components. It is particularly suited for separation of azeotropic or close-boiling liquid mixtures which are difficult to separate by distillation. An example of the performance of the new process for separation of an azeotropic water–methyl acetate mixture is given. Experimental binary surface excess equilibrium isotherms, adsorptive mass transfer coefficients, and column dynamics for adsorption of water–methyl acetate mixtures on NaX zeolite are reported.

INTRODUCTION

Thermal swing adsorption (TSA) processes are traditionally used for removal of trace impurities from a contaminated liquid stream. A typical process scheme using fixed-bed adsorbers may consist of the following five sequential steps (1):

(a) The contaminated liquid stream is passed through a packed column of solid adsorbent for selective adsorption of the impurities while withdrawing a purified stream of the feed liquid. One or more impurity mass transfer zones is formed at the feed end of the column during this process, and the zone progressively moves toward the product end as more feed liquid is passed. The step is continued until one or more impurities breaks through the product end at some pre-set design level.

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(b) The column is then drained to remove a portion of the intra- and interadsorbent particle void liquid which has the composition of the feed liquid mixture. The drained liquid can be recycled to another adsorber as feed.

(c) The adsorber is then heated by flowing a stream of hot inert gas through the bed in a direction countercurrent to that of feed liquid flow in Step (a) to: (1) vaporize the remaining void liquid and (2) thermally desorb the adsorbed components. The vaporized and desorbed components are then removed from the effluent gas by condensation.

(d) After adequate thermal regeneration, the adsorber is cooled down to the ambient temperature by countercurrently flowing a stream of inert gas at the ambient temperature. Any components of the feed mixture coming out of the column during this step are also removed by condensation.

(e) Finally, the adsorber is refilled with a portion of the purified liquid stream produced during Step (a) and a new cycle starts.

The cycle time for the TSA process is generally governed by the durations of Steps (c) and (d). Heating and cooling the adsorber by direct flow of a gas is a slow process due to (1) low heat capacity of the gas and (2) limited gas flow rates controlled by column pressure drop. A typical practical time period for these two steps is one to several hours. Consequently, the design time for the adsorption step is long, so that at least one adsorber undergoes Step (a) of the TSA process while others undergo the regeneration steps. This, in turn, restricts the use of a TSA process to removal of trace or dilute impurities from a feed liquid mixture, because the amount of adsorbate to be removed per cycle in Step (a) is relatively small even when the cycle time for that step is long. This permits a large volume of feed to be treated per unit volume of the adsorber in Step (a) and minimizes the loss of the less strongly adsorbed component of the feed mixture (which is left in the column at the end of Step b) during the subsequent regeneration Steps (c) and (d). The amount of the less strongly adsorbed component of the feed mixture in the column at the end of Step (a) can be large due to coadsorption of that component and the large concentration of that component in the liquid-filled voids. The drain Step (b) only removes 40–50% of the void liquid from the column (2) while leaving behind the balance of the void liquid in the macropores of the adsorbent.

The key requirements for efficient operation of a TSA process are that (a) the adsorption capacities and selectivities of the impurities be very large at the conditions of the adsorption step, (b) the adsorptive mass transfer rates for the impurities be high, and (c) the heats of adsorption of the impurities be relatively low. This reduces the adsorber sizes, the

loss of the less strongly adsorbed component per cycle, and the heat energy required for thermal regeneration.

Separation of bulk liquid mixtures by the TSA process is often not practical because the amount of adsorbate to be removed per cycle in Step (a) of the process is very large. Consequently, the size of the adsorber and the loss of the less strongly adsorbed components during the regeneration steps become prohibitively high.

The present paper describes a novel concentration–thermal swing adsorption (CTSA) process which circumvents the problems for separation of bulk liquid mixtures described above. The process is patented by Air Products and Chemicals, Inc. (3).

CONCENTRATION–THERMAL SWING ADSORPTION PROCESS

The new process is designed for separation of a binary bulk liquid mixture which retains all the steps of the conventional TSA process described earlier. However, it introduces a new rinse step, (a'), at the end of Step (a) in which the adsorber is rinsed with a stream of essentially pure, more strongly adsorbed component (A) of the feed liquid mixture in a cocurrent direction (same as feed flow). A new MTZ is formed at the feed end of the column during this step, and it moves progressively toward the product end as more rinse liquid is passed. The column ahead of this MTZ remains saturated with the feed liquid mixture (A + B) while the column behind the MTZ remains saturated with pure component A. The step is continued until the MTZ completely exits the column. The effluent liquid stream during this step has essentially a feed-liquid-like composition when the length of the MTZ for the rinse step is small, and it is recycled as feed to another column by mixing it with fresh feed.

The purpose of the new rinse step is to remove and recycle all of the less strongly adsorbed component (B) of the feed-liquid mixture left behind in the column (void space and coadsorbed) at the end of Step (a). Consequently, essentially pure component (A) can be recovered from the column during Steps (b), (c), and (d) of the process while essentially pure component (B) is produced during Step (a). Thus, the process produces two essentially pure products from a binary bulk liquid feed with very high recoveries of both components while using a thermal swing regeneration scheme.

Figure 1 shows a schematic flow sheet for the CTSA process. It consists of four parallel adsorbers, liquid pumps, switch valves, gas heaters, and a source of dry air. The process is so designed that one adsorber is always

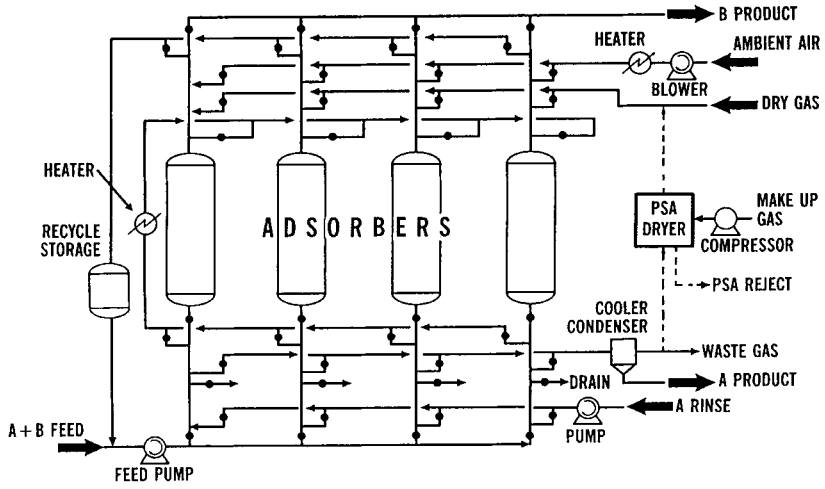

FIG. 1 Schematic diagram of CTSA process.

receiving the feed-liquid mixture and the recycled effluent from Step (a'). The heating Step (c) of the process is divided into two parts for economic reasons. First, the adsorber is heated to an intermediate temperature by flowing hot ambient air through the column (Step c1). Then the adsorber is heated to the final regeneration temperature using a dry gas stream (Step c2). The cooling is also done using the dry gas. The dry cooling gas is countercurrently introduced to an adsorber which has completed Step (c2), and the effluent from that column is reheated and used to heat another adsorber countercurrently which is undergoing Step (c2). The hot effluent from this second adsorber is cooled down to the ambient temperature in order to remove the desorbed and void Component A from that stream by condensation.

In one embodiment shown in Fig. 1 by the dashed lines, a conventional pressure swing adsorption (PSA) system is used to produce the dry gas, which can be air. The PSA process operates at an elevated feed pressure and the dry gas is produced at about the same pressure. The heating Step (c2) and the cooling Step (d) of the CTSA process are also run at the same pressure so that the Component A-laden effluent gas from the adsorber is recycled to the PSA system following condensation and removal of Component A from that gas. A slight recompression is needed to overcome the pressure drops in the column and condenser. This significantly reduces the compression energy required to operate the PSA system for producing the dry gas. Only a very small gas stream (20–30% of total dry

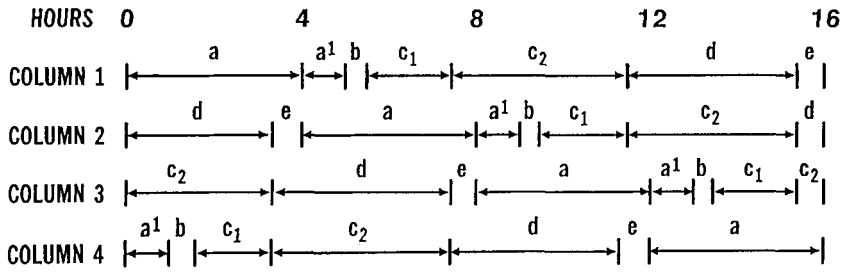

FIG. 2 *Cycle times of CTSA process.*

gas) needs to be compressed to the PSA feed pressure in order to make up for the loss of the processed gas (required for regeneration of the PSA system).

Figure 2 shows an example of the cycle steps of the CTSA process using a 16-hour total cycle time. The durations of individual Steps (a), (a′), (b), (c1), (c2), (d), and (e) are, respectively, 4.0, 1.0, 0.5, 2.0, 4.0, 4.0, and 0.5 hours. One column is always undergoing Step (a), another Step (c2) and a third Step (d) so that the feed liquid is continuously processed and the PSA drier is continuously operated. Furthermore, when one column is carrying out Step (d), another one is undergoing Step (c2) so that they can be operated in series.

SEPARATION OF BINARY WATER–METHYL ACETATE MIXTURE BY THE CTSA PROCESS

We evaluated the performance of the CTSA process for separation of a bulk binary mixture of water (1) and methyl acetate (2). The mixture is immiscible between water compositions of 28.2 and 92.9 mol% and forms an azeotrope at 18 mol% water. Figure 3 shows the isobaric vapor–liquid equilibrium data for the system at 1 atmosphere (4). Consequently, the separation of this mixture by distillation is extremely capital- and energy-intensive. An alternative separation concept for this mixture would be beneficial.

It was found that NaX zeolite can be used to selectively adsorb water (1) from mixtures with methyl acetate (2). Figure 4 shows the experimental binary surface excess isotherm for adsorption of water at 30°C, which

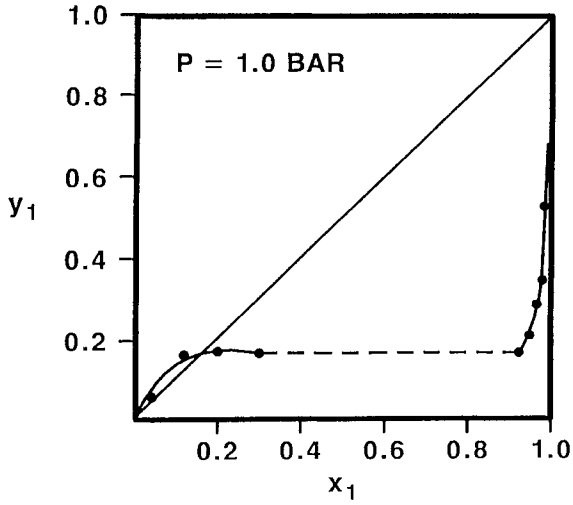

FIG. 3 Vapor–liquid equilibrium data for water (1)–methyl acetate (2) mixtures.

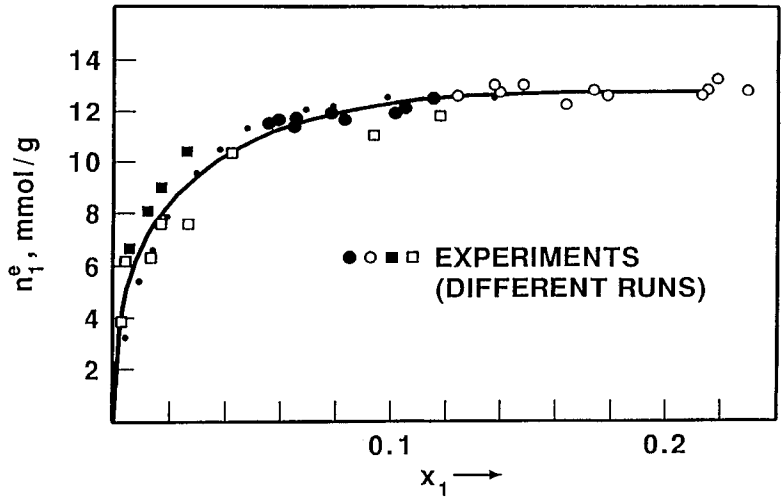

FIG. 4 Equilibrium adsorption of water (1) + methyl acetate (2) liquid mixtures on NaX zeolite.

was measured by using the conventional technique (5). n_1^e (mol/kg) is the surface excess of water in equilibrium with a bulk liquid phase water mole fraction of x_1. A gas chromatograph was used to analyze the liquid mixture compositions before and after contact with the adsorbent. The adsorbent was regenerated at 300°C under N_2 before use.

It may be seen from Fig. 4 that the isotherm is U-shaped with a very high slope at the limit of $x_1 \rightarrow 0$. This indicates that water is very selectively adsorbed from methyl acetate by NaX zeolite (6). The surface excess for water approaches a value of 13.0 mol/kg as the bulk liquid phase mole fraction of water approaches its lower miscibility limit in methyl acetate. This represents a very large apparent adsorption capacity for water.

The liquid phase mass transfer coefficients for adsorption of water from mixtures with methyl acetate on NaX zeolite were measured using a differential kinetic test described elsewhere (7, 8). A closed loop recirculating adsorption apparatus was used. Again, a gas chromatograph was used to determine the compositions of the liquid mixture in the apparatus as a function of time. Figure 5 shows a typical result of the kinetic test at 30°C. It plots the logarithm of the quantity $|(x_1 - x_1^\infty)|$ against time (t) measured during the course of the kinetic experiment. x_1 is the mole fraction of water in the bulk liquid phase of the system at time t. x_1^∞ is the mole fraction of water in the bulk liquid phase of the system after equilibrium is established. The data of Fig. 5 were generated by contacting a liquid

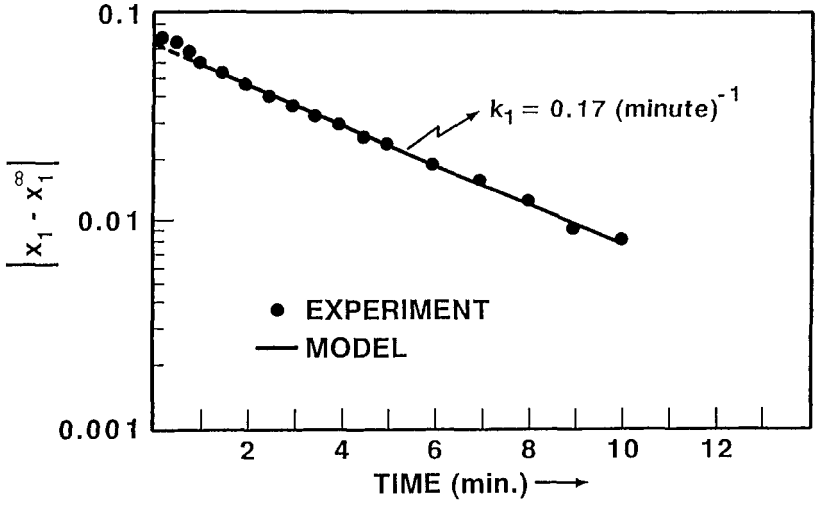

FIG. 5 Adsorption kinetics of water (1)–methyl acetate (2) mixtures on NaX zeolite.

mixture containing 20.0 mol% water and 80.0 mol% methyl acetate with a sample of NaX zeolite which had been initially saturated with pure methyl acetate, and monitoring the change in concentration of water in the bulk liquid phase with time. Thus, the data represent a case of adsorption of water from methyl acetate on the zeolite. The adsorbent particles were zeolite crystals bonded by a clay in bead form (1900 μm diameter).

A previously reported surface excess linear driving force (SELDF) model was used to obtain the overall mass transfer coefficient (k) for adsorption of water from methyl acetate on the zeolite (8). According to this model, the plot of Fig. 5 should be linear with a slope of k (time^{-1}), which is, indeed, the case presented here. A further analysis of the overall adsorptive mass transfer coefficient indicated that the primary resistance to transfer of water from the bulk liquid phase to the zeolitic adsorption sites was controlled by diffusion of water through the liquid-filled macropores of the clay binder. Details of the procedure for this analysis are given elsewhere (8). Therefore, we concluded that the effective mass transfer coefficient for adsorption of water from methyl acetate on NaX zeolite beads can be significantly increased by using smaller bead sizes; consequently, the lengths of the mass transfer zones for Steps (a) and (a′) of the CTSA process can be decreased to acceptable sizes.

A column dynamics test was then carried out to simulate Step (a) of the CTSA process by displacing pure methyl acetate (2) from a column packed with NaX zeolite beads (580 μm diameter, d_p) with a feed liquid mixture containing 13.7 mol% water (1) in methyl acetate (2) at 25.0°C. A particle Reynolds number (d_pG/μ) of 5.1 was used at the feed conditions. G and μ are, respectively, the mass flow rate and the viscosity of the feed mixture at the conditions of the experiment. The column was 0.011 m in diameter and 0.68 m long.

Figure 6 shows the results of the dynamics test. It plots the dimensionless quantity $[(x_1 - x_1^S)/(x_1^F - x_1^S)]$ as a function of dimensionless time $[t/t_m]$. x_1 is the mole fraction of water in the effluent liquid at time t. x_1^F (= 0.137) and x_1^S (= 0.0) are, respectively, the mole fraction of water in the feed liquid and the mole fraction of water in the saturating liquid mixture present in the column at the beginning of the experiment. t_m is the stoichiometric time (6) for the vertical mass transfer zone to travel the column length under local equilibrium conditions (no adsorptive mass transfer resistance). The circles represent the experimental points. The solid line in Fig. 6 gives the calculated breakthrough curve for the test case under the condition of constant pattern zone formation (8). It was calculated using the water surface excess isotherm of Fig. 3 and an overall water adsorption mass transfer coefficient (k) of 1.8 (minute)$^{-1}$. This value of k would be predicted for the adsorbent particle size of 580 μm

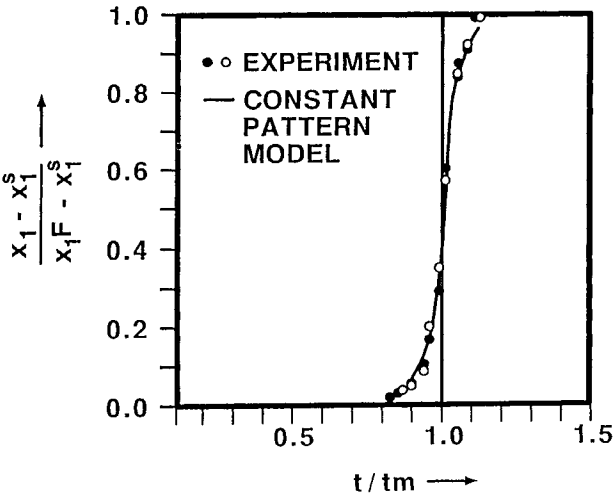

FIG. 6 Breakthrough curve for 13.7 mol% water (1)–methyl acetate (2) mixture displacing methyl acetate on NaX zeolite.

from the data of Fig. 5 if liquid-phase macropore diffusion were the controlling mass transfer resistance for adsorption of water [$k \propto (d_p)^{-2}$].

The remarkable match between the experimental and the calculated breakthrough curves in Fig. 6 indicates that the constant pattern model can be used to describe the column dynamics for the Steps (a) and (a′) of the CTSA process for the separation of water (1) + methyl acetate (2) bulk liquid mixtures. Step (a) of the process would consist of selectively adsorbing water from methyl acetate by flowing the feed through a column of NaX zeolite saturated with methyl acetate. Step (a′) would consist of displacing all void and coadsorbed methyl acetate remaining in the column at the end of Step (a) by cocurrently flowing a stream of pure water through the column. The constant pattern mass transfer zone length for Step (a) of the process was calculated to be only 0.27 m.

The total stoichiometric feed (F) and effluent (E) liquid quantities (mol/kg) at $t = t_m$ for the breakthrough experiment can be calculated by (8):

$$F = [\{(n_1^{eF} - n_1^{eS})/(x_1^F - x_1^S)\} + \bar{n}^F] \quad (1)$$

$$E = [\{(n_1^{eF} - n_1^{eS})/(x_1^F - x_1^S)\} + \bar{n}^S] \quad (2)$$

where superscripts F and S represent, respectively, the feed liquid and the initial column saturation liquid compositions for the displacement test. $\bar{n}$ is the total specific liquid saturation capacity (mol/kg) of the packed

column at the corresponding conditions. $\bar{n}$ for pure water, pure methyl acetate, and 13.8 mol% water + methyl acetate mixture were measured to be, respectively, 59.9, 13.8, and 24.5 mol/kg. The values of F and E, calculated by using Eqs. (1) and (2), along with the surface excess isotherm of Fig. 3 and the $\bar{n}$ values given above were, respectively, 119.4 and 108.6 mol/kg. The experimentally measured values of F and E from the data of Fig. 6 at $t = t_m$ were, respectively, 115.0 and 118.0 mol/kg. These results show the consistency between the equilibrium and dynamic experiments for the system of interest.

LOCAL EQUILIBRIUM MODEL

The short mass transfer zone lengths for Steps (a) and (a′) of the CTSA process for separation of the water–methyl acetate liquid mixture, demonstrated by Fig. 6, can be further reduced by using lower particle Reynolds numbers at the feed conditions for these two steps. In fact, these two steps can be run essentially under local equilibrium conditions using 500 μm diameter NaX zeolite particles when the particle Reynolds number is less than 2. Consequently, Eqs. (1) and (2) can be used to calculate the specific quantities (mol/kg) of feed introduced and effluent removed from the column for Steps (a) and (a′) of the CTSA process. The effluent from Step (a′) is recycled as feed. Thus, it easily can be shown by using Eqs. (1) and (2) that the net specific feed quantity, F* (mol/kg), for the CTSA process is given by

$$F^* = n_1^{eF}/x_1^F(1 - x_1^F) \tag{3}$$

n_1^{eF} is the specific equilibrium surface excess for adsorption of water from the feed mixture having a water mole fraction of x_1^F. For a water composition of 15.7 mol% in the feed mixture, Eq. (3) shows that the net specific feed handling capacity of the NaX zeolite for the CTSA process is very large (F* = 98.2 mol/kg).

A design of the CTSA process under local equilibrium conditions for production of 40 million pounds of methyl acetate per year from a 15.7 mol% water in methyl acetate feed mixture using the cycle times of Fig. 2 shows that each adsorber would contain only 3000 lb NaX zeolite (3.0 ft diameter and 10.5 ft length). The particle Reynolds numbers at the feed conditions for Steps (a) and (a′) will be, respectively, 1.0 and 0.25. The energy costs for the separation by the CTSA process were estimated to be only about 60% of that for conventional azeotropic distillation. Thus, the CTSA process provides significant advantages for separation of water–methyl acetate mixtures.

CONCLUSIONS

The concentration–thermal swing adsorption process provides an energy-efficient means for separation of bulk liquid mixtures which are difficult to separate by distillation, such as azeotropic and close-boiling liquid mixtures. The process can be used to separate a bulk binary liquid mixture into two essentially pure products with high recoveries of both components. Further, the process does not require any additional distillation for the separation as needed by other adsorptive bulk liquid separation schemes.

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