



CHAPTER I

INTRODUCTION

Adsorption is a separation process in which component in the fluid phase, gas or liquid, are transferred into pores of a solid adsorbent and accumulate on the pore surface. Adsorption separation processes are in widespread industrial use, particularly in the petroleum refining and petrochemical industries. A familiar example is the use of an adsorber packed with a suitable hydrophilic adsorbent which acts as a drier for removal of traces or moisture from either gas and liquid stream. Similar processes are the removal of undesirable impurities such as hydrogen sulfide and mercaptans from natural gas or the removal of organic pollutants from water.

Liquid-solid adsorption has become an important separation process in modern technology. Adsorption at the liquid-solid interface involves the preferential accumulation of one or more component of a liquid mixture at the surface of the solid. The application of liquid phase adsorption as a means of separating mixtures into two or more streams, each enriched in a valuable component which is to be recovered, is a more recent development. Although distillation has assumed a dominant role in separation technology and is the standard process compared to other potential processes. However distillation is not an energy efficient process and with rising costs of energy, alternative separation processes have attracted increasing attention.

In liquid phase adsorption , highly porous solids are packed in the fixed bed column and liquid may be percolated continuously through the bed until saturation. Separation occurs due to preferential accumulation of a component A on the surface of the adsorbent (the pore surface), leaving less adsorbed component B to pass through the adsorption column.

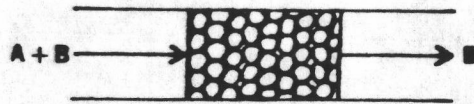


Figure 1.1 Adsorption column where A is preferentially adsorbed .

1.1 Previous studies of naphthene-paraffin binary mixture adsorption.

The use of liquid phase bulk separation of hydrocarbon is currently not often reported in the literature. There are however old references relating to the use of adsorbents as silica gel and activated carbon for the liquid phase separation of hydrocarbons of different chemical types. In a previous study published in 1935(2) it was shown that for hydrocarbons of similar molecular weights the existence of a double bond influenced adsorbability. In that study olefins or aromatics were removed from saturated hydrocarbon mixtures by percolation through silica gel. In the same study it was shown that paraffins and naphthenes could be separated with silica gel.

In 1947 , Hirscher and Amon (2) reported the separation

of a number of mixtures of paraffin isomers, naphthene isomers and paraffin-naphthene mixtures through adsorption (as presented in appendix H for the case of n-hexane and cyclohexane separation on activated carbon). They also presented the effect of concentration on relative adsorbability and concluded that the adsorption isotherms are of two possible types, an S-type isotherm and a U-type isotherm as shown in figure 1.2. Both types of isotherms represent the adsorption behavior of binary liquid mixtures. When an excess solution is poured through a column of adsorbent, the first portion of percolate will be richer in the component less easily adsorbed. The volume of solute preferentially adsorbed can be calculated through a summation over all percolate fractions which differ in concentrations from the charge to the column according to the following equation.

$$V = \frac{v(C_0 - C)}{100} \quad (1.1)$$

where V = volume adsorbed

v = volume of given cut

C_0 = initial concentration of solute

C = solute concentration in a given cut

The amount of preferential adsorption as calculated by equation 1.1 is only an apparent value and not the true adsorption, as it neglects the volume change due to adsorption of the solute. The isotherms which are obtained therefore depend on the adsorbent and the adsorbability. If two liquids in a binary mixture have nearly equal adsorbabilities the adsorption isotherm should exhibit an

S-type isotherm, and each component will be preferentially adsorbed in the region of low concentration.

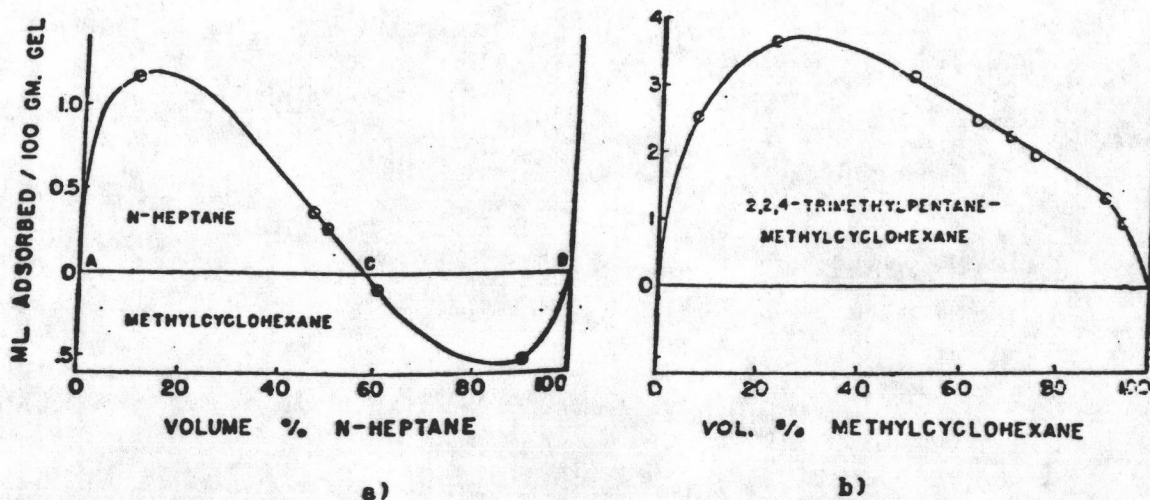


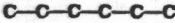



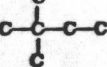
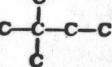


Figure 1.2 Adsorption isotherms neglecting volume in the liquid mixture as a result of solute adsorption, a) S-type isotherm. b) U-type isotherm.

If one component is more strongly adsorbed than the other the isotherm will be an U-type isotherm and each component can be separated to high purity depending on column separation efficiency. Mair(1945) used this technique to separate mixtures of naphthenes ,paraffins , olefins and aromatics. However for a binary system which exhibits an S-type isotherm, it is not possible to obtain pure components from a given mixture.

The relative adsorbability on silica gel and activated carbon is also shown in table I for selected types of hydrocarbon.

Table 1 (2)

RELATIVE ADSORBABILITY AS A FUNCTION OF STRUCTURE IN ORDER OF DECREASING ADSORBABILITY		
	Silica Gel	Activated Carbon
C ₆ and C ₇	C ₆ and above	
	Alkylcyclopentane	
	Alkylcyclohexane	
	n-Paraffin	
	Isoparaffin	

In 1971, Sircar and Myers studied the thermodynamic for adsorption from binary liquid mixtures of hydrocarbons on activated carbon using the Gibbs equation for adsorption, and found that a pertinent experimental variable was the surface excess, (n_s^m). In 1973(16), Sircar and Myers derived an equation for the surface excess in terms of the free energy of immersion of the adsorbent, the capacity of the adsorbent at saturation, and activity coefficients in the bulk and the adsorbed phases.

A theoretical analysis of adsorption from solution leading to a suitable equation of the adsorption isotherm is more difficult to perform than an analysis for gaseous phase adsorption for two reasons; first the thermal motion of molecules in the liquid phase, as their mutual interactions and phase behaviors of liquids are theoretically less well understood than the corresponding properties of gases, and secondly for adsorption from solutions at least two components compete to adsorb onto the surface of the adsorbents.

The primary requirement for an adsorption process is a suitable adsorbent with sufficiently high selectivity, capacity and life. During design and calculation of fixed bed adsorption

columns, the major problem is the calculation of the concentration-time relationships or breakthrough curves which involves the influence of both external mass transfer and intraparticle diffusion. Although the mechanism of intraparticle mass transfer in liquid phase adsorption has yet to be clarified, pore diffusion and surface diffusion are considered to be possible mechanisms. One method for determining intraparticle diffusion coefficients was presented by K.Hashimoto and K.Miura (3). The external mass transfer coefficients as well as the axial dispersion coefficients were estimated from some published correlation (4,5) as shown in appendix C.

1.2 The objectives of this study.

1. To study adsorption isotherms of a binary mixture of n-hexane and cyclohexane on a suitable adsorbent at 15°C.
2. To measure the breakthrough curves of binary mixtures of n-hexane and cyclohexane when percolated through an adsorption column.
3. To calculate breakthrough curves for a binary liquid mixture from the basic mathematical equations through numerical methods for comparison with the experimental data.

1.2 The scope of this study.

1. To measure the adsorption isotherms of a paraffin-naphthene binary mixture on activated carbon.
2. To measure a set of breakthrough curves for the

n-hexane-cyclohexane binary mixture using a laboratory scale column packed with coconut shell based activated carbon at 15°C.

3. To compare experimental breakthrough curves with those calculated from the mathematics.