

**ADSORPTION OF ETHYL ACETATE FROM ALIPHATIC
ALCOHOLS ON ACTIVATED CHARCOAL**

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ABSTRACT

The adsorption equilibria of binary mixtures of ethyl acetate and aliphatic alcohols on activated charcoal were studied at 298 K. It was found that activated charcoal adsorbed ethyl acetate preferentially from all mixtures with aliphatic alcohols. Influence of the alkyl chain length of aliphatic alcohols on the adsorption of ethyl acetate were compared by means of composite and individual isotherms. The adsorption equilibrium data were analysed on the basis of the Schay & Nagy Model.

Key Words - Activated charcoal, adsorption, aliphatic alcohols, binary mixtures.

RESUMO

A adsorção de misturas binárias de etil acetato e alcoóis alifáticos sobre carvão ativado foi estudada a 298 K. Foi constatado que o acetato de etila é adsorvido preferencialmente de todas as misturas contendo alcoóis alifáticos. O efeito do comprimento da cadeia dos alcoóis alifáticos sobre a adsorção do acetato de etila foi analisado em termos de istoermas individuais. Os dados obtidos para o equilíbrio da adsorção foram analisados usando o Modelo de Schay e Nagy.

1. INTRODUCTION

Adsorption from liquid mixtures on solids involves a number of very important processes and plays a significant role in many fields of the natural sciences.

The mechanism of the adsorption process from a binary liquid mixture onto a solid adsorbent has been studied by many investigators [1-6]. Various factors have been found to influence adsorption; such as nature of the adsorbents, chemical nature of the solute molecules, molecular size and shape [7], volatility [4], interfacial tension of components at the liquid / solid interface [6,8].

When a binary mixture is involved, the adsorbed layer has in general, a different composition from that of the bulk phase in equilibrium with it. Adsorption from a binary liquid mixture is expressed in terms of composite isotherms which is the functional relation between the surface excess of a component and its concentration in the equilibrium bulk phase [9]. The state of adsorbate may be judged directly from experimentally determined composite isotherms. The type of composite isotherm has been widely used for comparison the adsorption behavior of binary mixtures [11-13].

The purpose of the present work is to find a correlation between the hydrophobicity and adsorption tendency of the aliphatic alcohols from their mixtures with ethyl acetate on activated charcoal. Adsorption experiments were performed using binary mixtures of homologous series of alcohols ($C_3 - C_{10}$) and ethyl acetate. A simple model assuming ideal behaviour in both bulk and adsorbed phases was applied [14].

The adsorption equilibrium data were analysed on the basis of the Schay & Nagy Model. The thickness of surface layer formed in the adsorption process was determined by means of monolayer test [15,16]. Influence of chain length on adsorption was compared by means of composite and individual isotherms and the results were discussed.

2. EXPERIMENTAL

2.1 Chemicals

Ethyl acetate (99.5% pure), Propanol (99.5 % pure), Butanol (99.4 % pure), Pentanol (98 % pure), Hexanol (98% pure), Decanol (98% pure) were obtained from Sigma. The activated charcoal was microporous E. Merck (No.2184) sample and was further purified by extracting (Soxhlet) for several hours with benzene and acetone then evacuated at 423 K for 6 hours in vacuum. The specific surface area of the sample was 800 m²/g. The ratio of liquid to adsorbent was kept as low as possible to obtain maximum readings (5 milliliters per gram were chosen for all of the systems).

2.2 Procedure

A binary mixture was prepared for each experimental point ; its concentration was analyzed refractometrically using a Carl Zeiss Jena Refractometer. A weighed amount of adsorbent was then added to the binary mixture. The system consisting of the binary mixture and the adsorbent was shaken for 17-19 hr in a screw - capped Erlenmeyer flask, using a reciprocating shaker. Measurements were made over the whole range of concentrations lying between pure components. The temperature was thermostatically controlled to 298 K. The equilibrium composition of the bulk liquid , X_1 , was then analyzed refractometrically ; the calibration curves needed for the refractometric analyses were prepared by us. The refractive index composition curves of each of the binary mixtures were almost straight lines over the entire range of concentration.

3. RESULTS AND DISCUSSION

The surface excess n_1^e is related to the concentration of each component at the surface by the Eqn (1) :

$$n_1^e = n^0 \frac{\Delta X_1}{m} = n_1^s(1 - X_1) - n_2^s X_1 \quad (1)$$

where ΔX_1 is the change in the mole fraction of component 1, when n^0 moles of original solution are brought into contact with m grams of adsorbent; X_1 is the equilibrium mole fraction and n_1^s and n_2^s are the number of the moles of components 1 and 2 adsorbed from the binary mixture per gram of adsorbent respectively. The quantity $n_1^0 \Delta X_1 / m$; n_1^e is the experimentally determined specific surface excess concentration of component 1 and when plotted against X_1 gives composite isotherms.

The composite isotherms for adsorption from binary mixtures of ethyl acetate (1) + propanol (2), ethyl acetate (1) + butanol (2), ethyl acetate (1) + pentanol (2), ethyl acetate (1) + hexanol (2), ethyl acetate (1) + decanol (2) on activated charcoal surfaces at 298 (± 0.1) K were shown in Fig.1. Any isotherm point reported in Fig.1 was the mean of four or five parallel determinations.

As seen in Fig.1 the composite adsorption isotherms for all of the binary mixtures studied were U shaped with a maximum at relatively low concentrations of component 1. It is observed that the composite isotherms were almost of Type II curves as classified by Schay & Nagy's Model and reflect strong adsorption of ethyl acetate [7].

Activated charcoal is known to have dual character and in the case of alcohols and ethyl acetate mixtures the surface phase was of a mixed character, i.e., it contained the molecules of both solution components. The composition isotherms showed that there was preferential adsorption of ethyl acetate from all of the alcohol solutions throughout the whole concentration range. The composition of the adsorbed layer changed with the alkyl chain length. The amount of ethyl acetate molecules on the adsorbed layer decreased from propanol to decanol. This indicated that some ethyl acetate molecules were displaced from the surface by the longer chain alcohols.

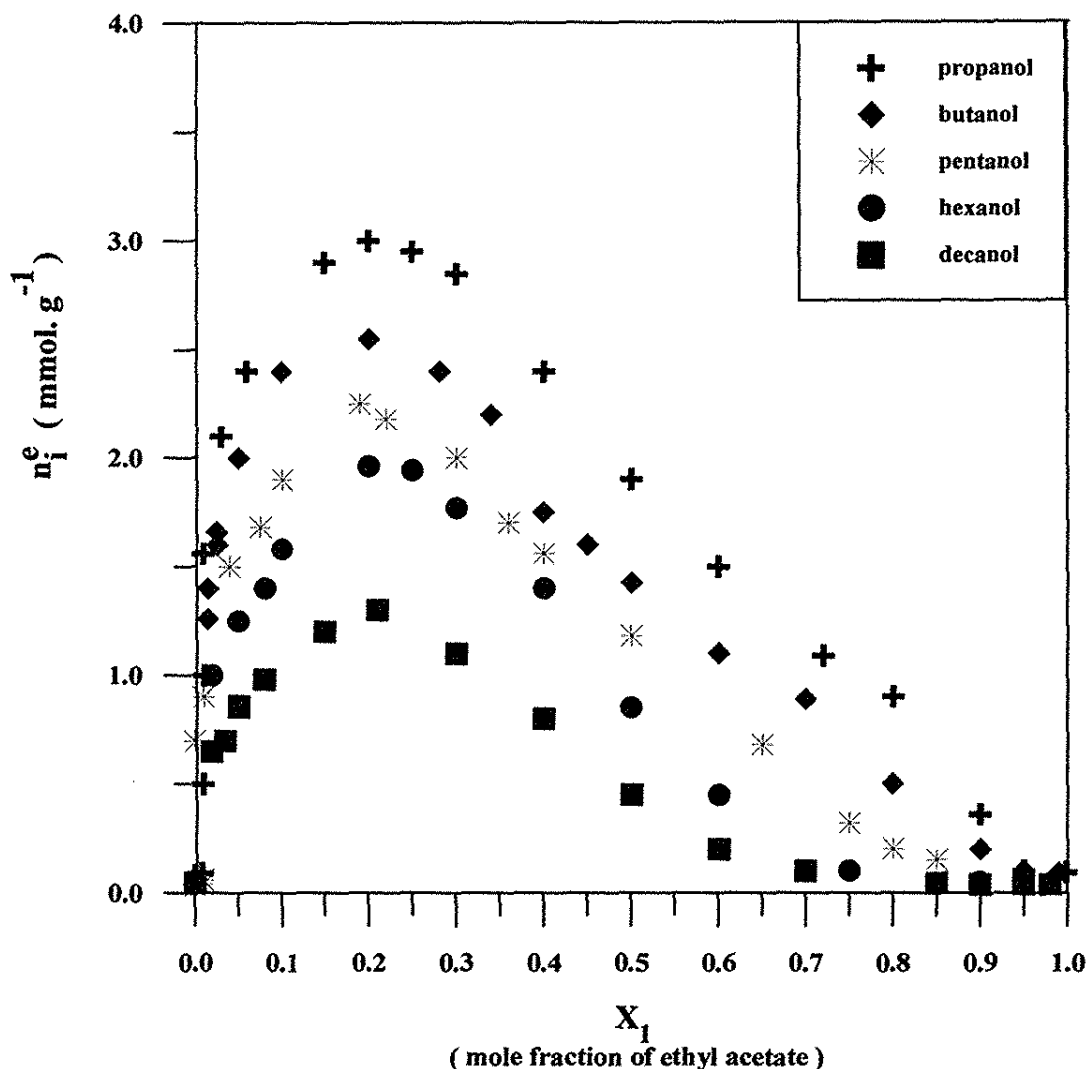


Fig.1. Specific surface excess isotherms of ethyl acetate (1) from alcohol solutions at 298 K on activated charcoal.

In order to show the relation between preference of activated charcoal for ethyl acetate and polarity of the competing solvent, the relation between surface excess amount of ethyl acetate at mole fraction of 0.4 and the number of carbons of alcohols and the relation between dielectric constants of alcohols and the number of carbons of alcohols were plotted in the same figure (Fig.2). As can be seen in Fig. 2 there is a striking similarity between the two relations. As the difference between the dielectric constants of ethyl acetate and competing alcohol decreased , the amount of ethyl acetate at the interface decreased.

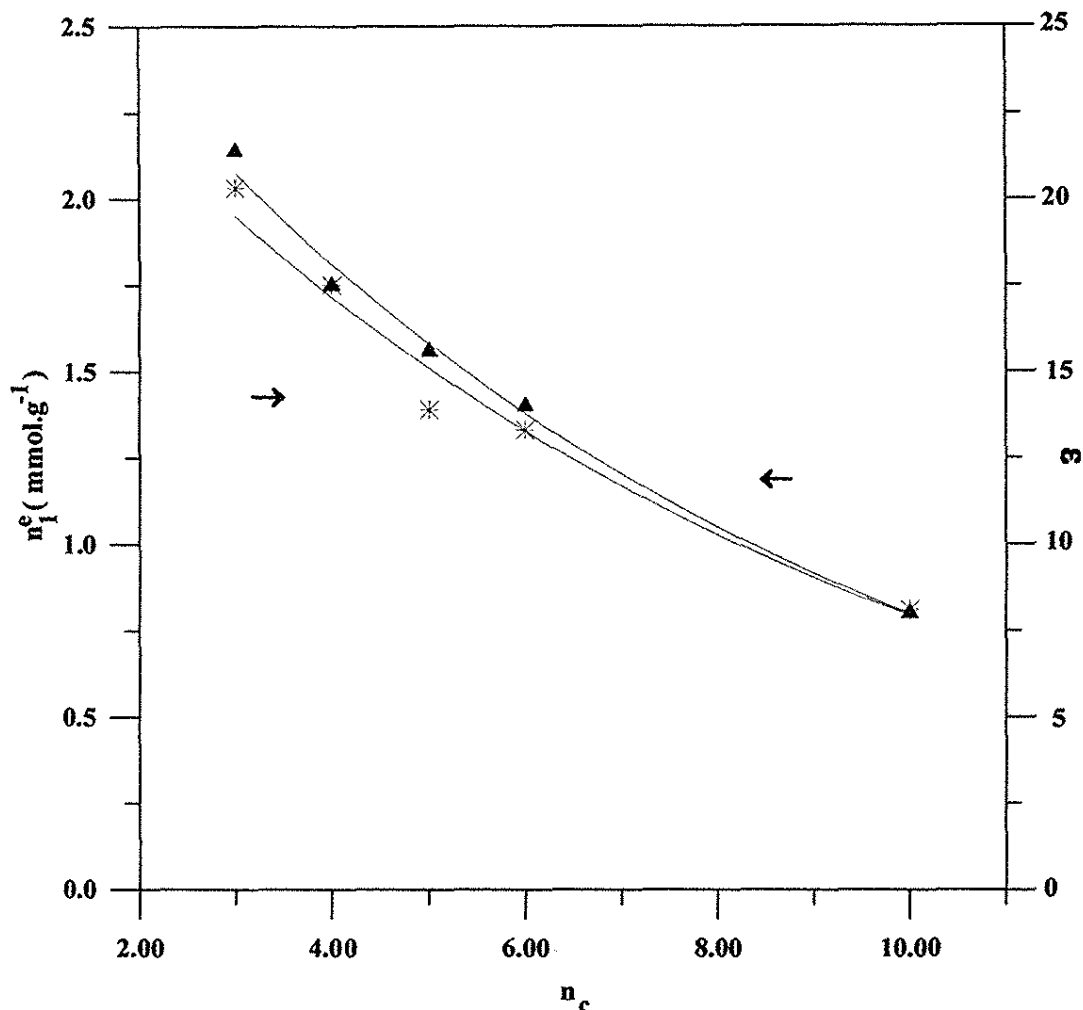


Fig.2. Dielectric constant of alcohols (ϵ) and surface excess of ethyl acetate (n_1^e) as a function of the alkyl chain length (n_c).

A simpler model assuming ideal behaviour in both phases (IBP Model) was applied to the experimental data using Eqn (2) [14] :

$$\frac{x_1 x_2}{n_1^e} = \left(\frac{1}{n^s} \right) x_1 + \frac{K}{(1-K)n^s} \quad (2)$$

where n^s is the total number of moles in the adsorbed phase that is surface layer capacity and K is the constant associated with the difference of the adsorption energies of both component of the liquid mixture. The K and n^s values derived from the linear plots according to this expression are given in Table 1. Since ethyl acetate (component 1) was preferentially adsorbed K was smaller than unity for each case.

These results are in agreement with previous studies [9,16,17]. The relation between the values of K and carbon number of alcohols were plotted in Fig.3. As seen in Fig.3 , K linearly increased with increasing chain length of alcohols.

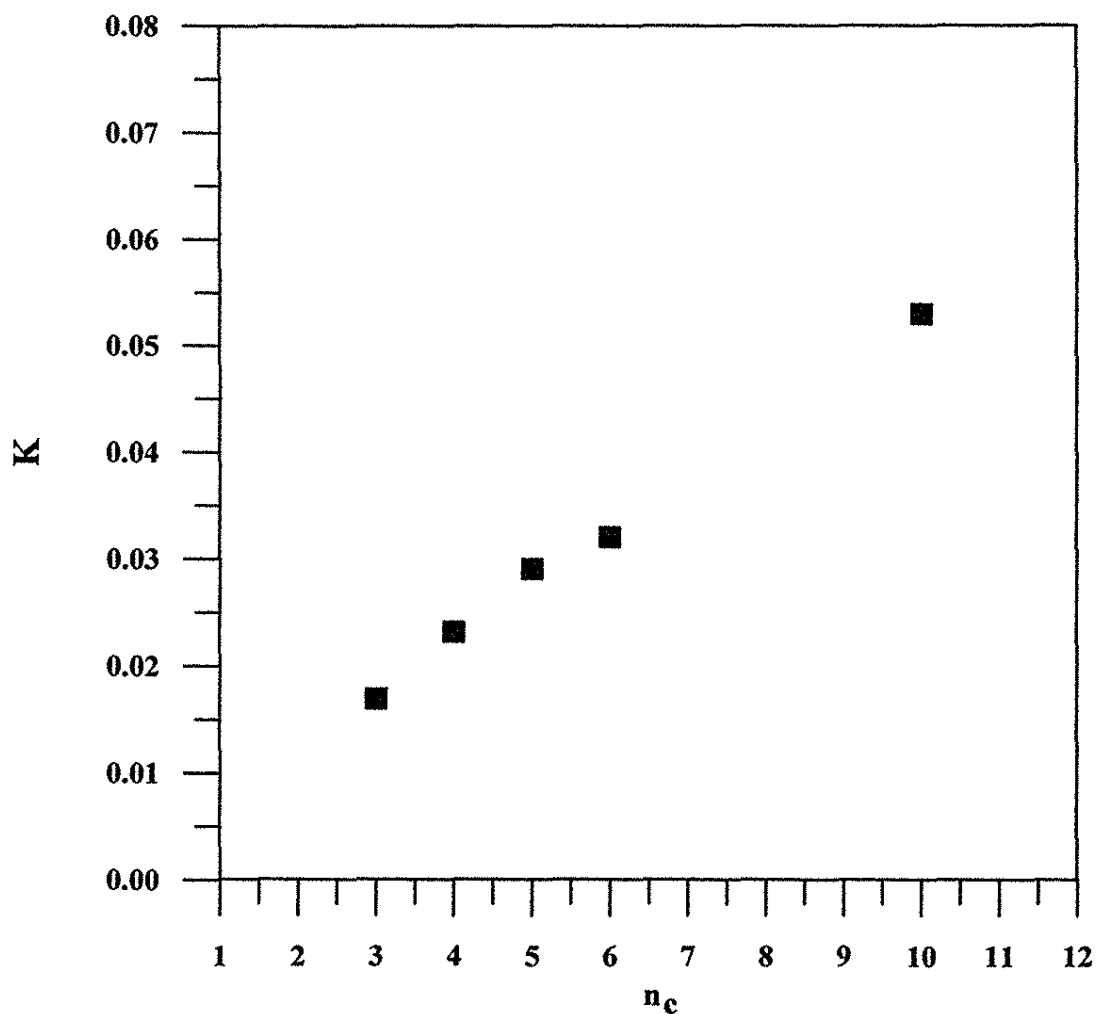


Fig.3. Adsorption equilibrium constant (K) as a function of the alkyl chain length n_c .

Taking into account the surface layer capacities n^s , the number of moles of component 1 in the surface phase is given by [18] :

$$n_1^s = n_1^e + n^s X_1 \quad (3)$$

The number of moles in the surface phase can also be calculated using the expression below [11]

$$n_1^s = \frac{Sx_1 + n_1^e A_2}{A_2 + (A_1 - A_2)x_1} \quad n_2^s = \frac{Sx_2 - n_1^e A_1}{A_2 + (A_1 - A_2)x_1} \quad (4)$$

where 'S' the specific surface area of the adsorbent ; and A_1 and A_2 the cross-sectional areas of the adsorbed molecule (1) and (2) at the interface respectively. The cross sectional areas determined from the empirical equation of Mc Lellan and Harnsberger were 31.46, 26.26, 30.05, 33.66, 36.98 and 48.80 \AA^2 /molecule for ethyl acetate, propanol , butanol , pentanol , hexanol and decanol respectively . The two sets of n_1^s values calculated by Eqn (3) and Eqn (4) were compared. It was observed that the values of n_1^s calculated from Eqn (4) were almost similar to the ones calculated from Eqn (3) but a slight deviation of n_1^s values calculated by Eqn (3) occurred at higher concentrations of alcohols for all the systems. Therefore n_1^s values calculated by Eqn (4) were used preferentially for obtaining individual isotherms.

The individual adsorption isotherms $n_1^s = f(x_1)$ and $n_2^s = f(x_2)$ are shown in Figure 4 (a-e). Their shape confirmed the presence of both components on the activated charcoal phase within the whole concentration range. It was observed that n_1^s did not change significantly with X_1 at relatively high concentration. Therefore the adsorbed layer was assumed to have constant composition.

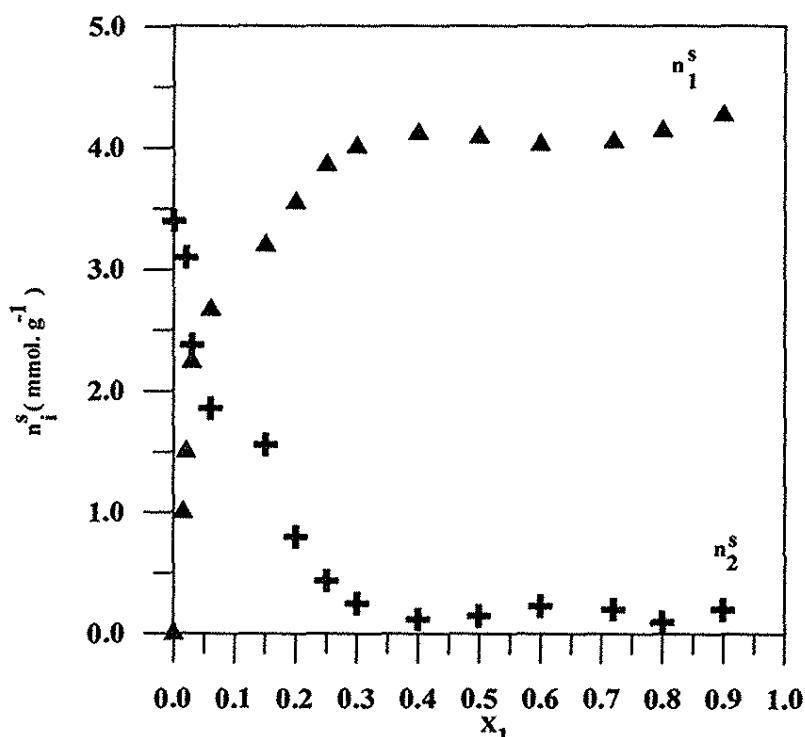


Fig.4a. Individual isotherms for adsorption on activated charcoal from ethyl acetate (1) + propanol (2) solutions at 298 K. (X_1 : mole fraction of ethyl acetate)

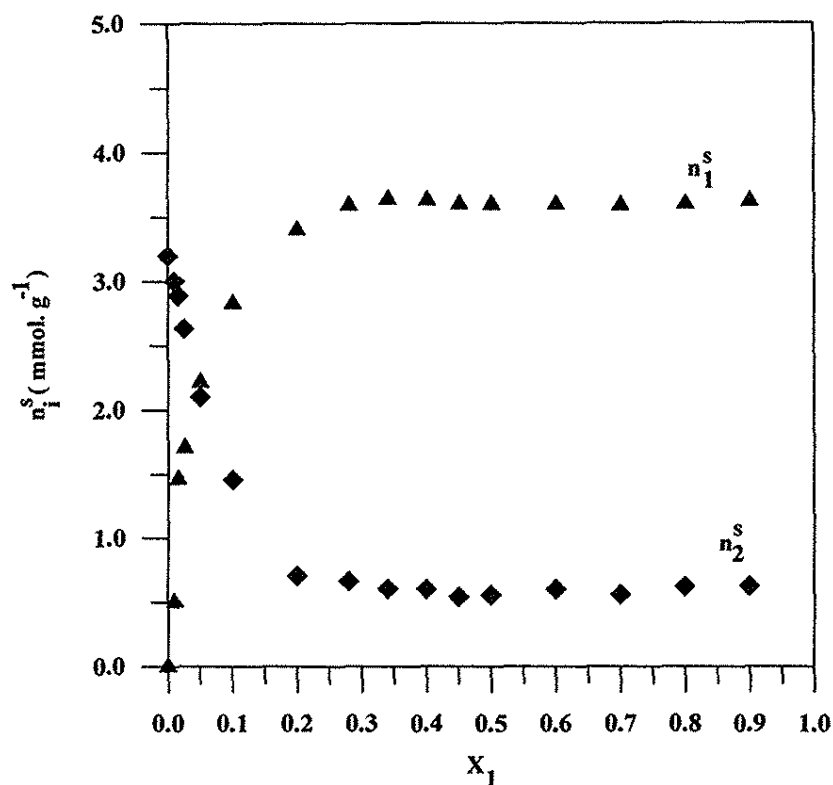


Fig.4b. Individual isotherms for adsorption on activated charcoal from ethyl acetate (1) + butanol (2) solutions at 298 K.(X_1 : mole fraction of ethyl acetate)

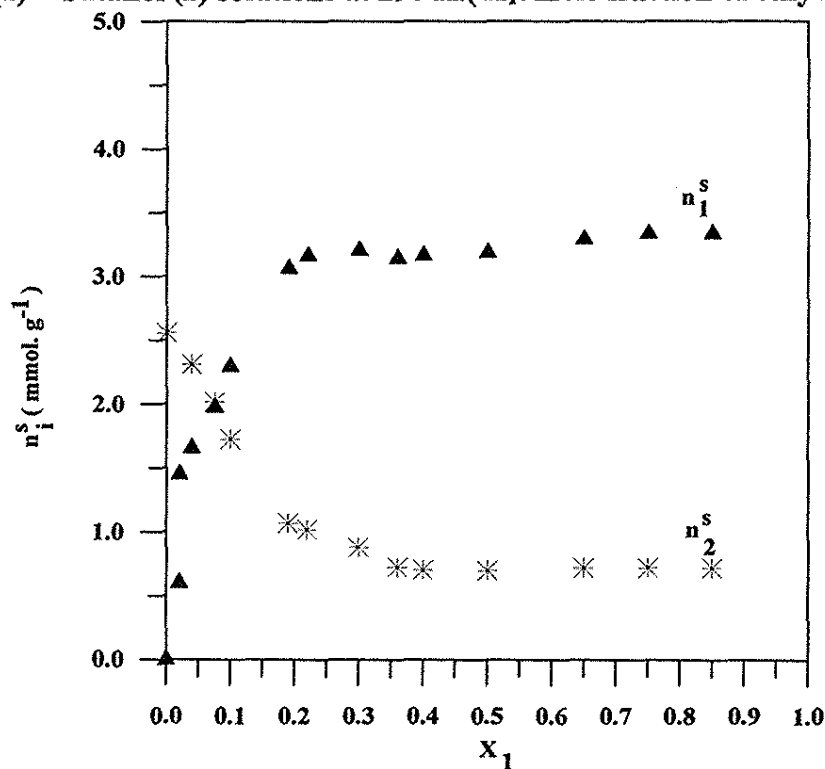


Fig.4c. Individual isotherms for adsorption on activated charcoal from ethyl acetate (1) + pentanol (2) solutions at 298 K. (X_1 : mole fraction of ethyl acetate)

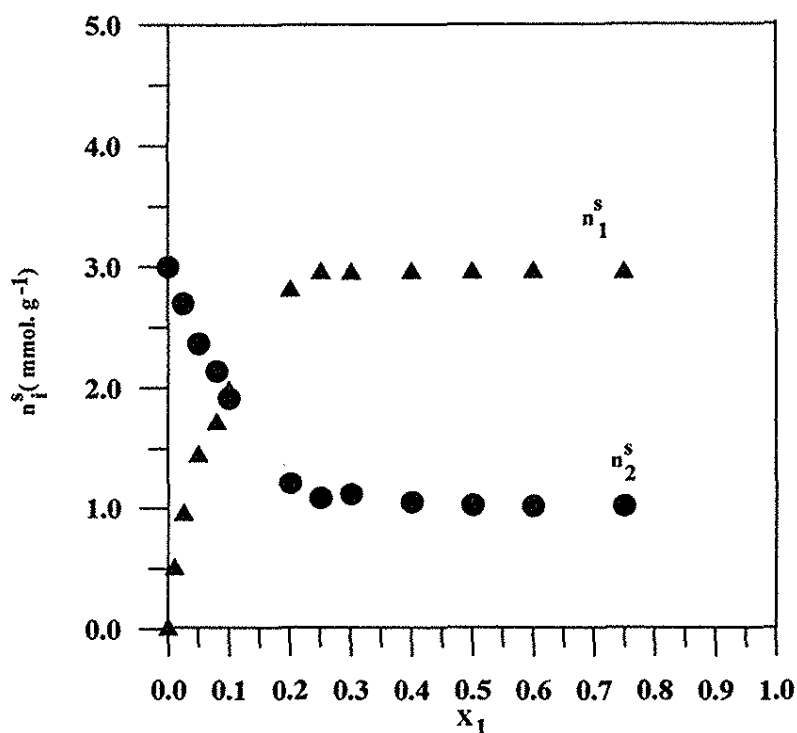


Fig.4d. Individual isotherms for adsorption on activated charcoal from ethyl acetate (1) + hexanol (2) solutions at 298 K. (X_1 : mole fraction of ethyl acetate)

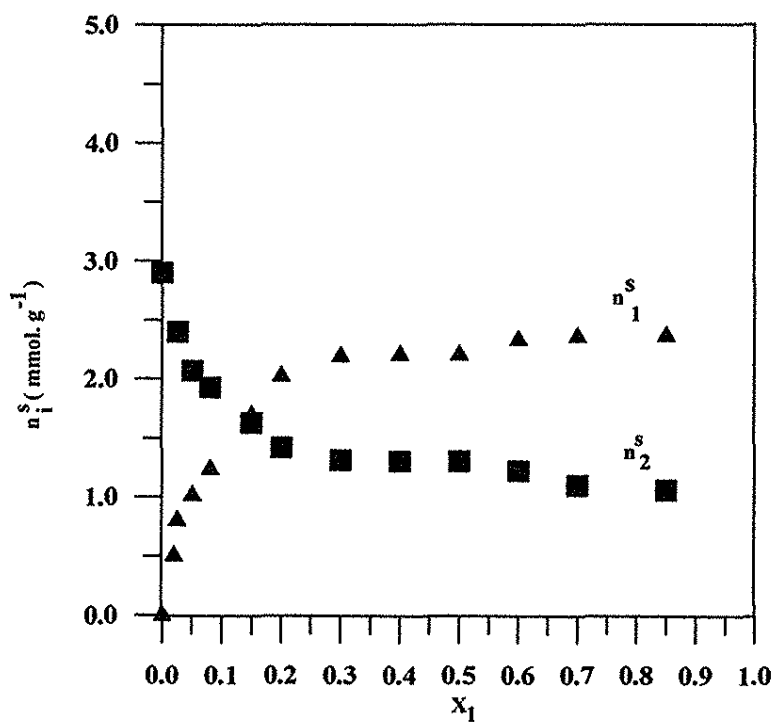


Fig.4e. Individual isotherms for adsorption on activated charcoal from ethyl acetate (1) + decanol (2) solutions at 298 K. (X_1 : mole fraction of ethyl acetate)

The composition of the adsorbed layer was determined by Schay & Nagy's Model [7] in which the composition of adsorbed layer was calculated from the expression below.

$$x_1^s = \frac{Sx_1 + n_1^e A_2}{S + (A_2 - A_1)n_1^e} \quad (5)$$

The x_1^s values were plotted as a function of x_1 in Fig.5 for all of the binary mixtures studied. As seen in Fig. 5 , x_1^s values were higher than x_1 for all systems.

The determination of the thickness of surface layers formed in the adsorption process was done by means of the monolayer test. The adsorbed layer was assumed to have a constant composition at relatively high X_1 (Fig.4a-e) which leads to a molecular thickness t of adsorbed layer defined by

$$\frac{n_1^s}{(n_1^s)m} + \frac{n_2^s}{(n_2^s)m} = t \quad (6)$$

where $(n_i^s)m$ is the number of moles of component i required to cover the surface of 1g of adsorbent completely. Values of t were found to be sufficiently close to unity for all the systems and confirmed monolayer adsorption [18]. The monolayer data was found to be compatible with experimental data.

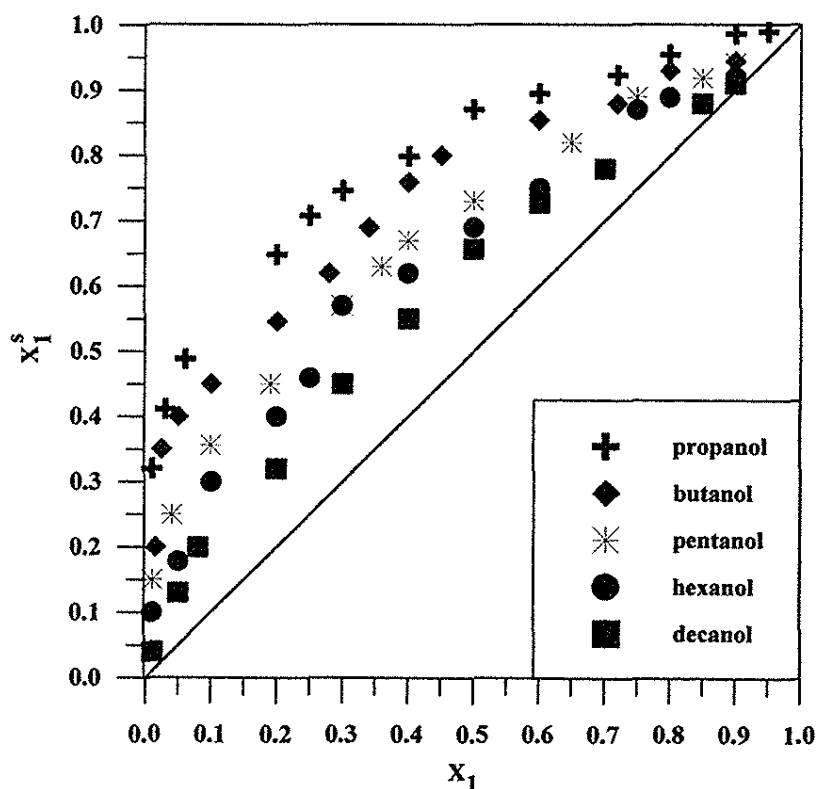


Fig.5. Composition of adsorbed layer X_1^s (composition of adsorbed layer) versus X_1 (mole fraction of ethyl acetate) at 298 K.

The surface area S of the adsorbent by assuming a monolayer model of the surface phase is given by [19]

$$S = a_1 n_1^s + a_2 n_2^s \quad (7)$$

where a_i is the area occupied by one mole of component i in the surface phase. Using molecular areas given before and the values of n_i^s calculated by Eqn 4 corresponding to $X_i=0.5$ leads to values of S . (Table 1)

Table I. Adsorption Parameters
* Determined For the Adsorption of Ethyl Acetate on Activated Charcoal.

Mixture	K	n^s (mmol.g ⁻¹)	S (m ² /g)
Ethyl acetate + Propanol	0.017	4.0	799.0
Ethyl acetate + Butanol	0.0232	3.3	801.36
Ethyl acetate + Pentanol	0.0291	3.06	786.39
Ethyl acetate + Hexanol	0.0321	2.37	786.34
Ethyl acetate + Decanol	0.053	1.901	798.57

(Specific surface area of activated charcoal obtained from nitrogen adsorption by the BET method is 800 m²/g .)

* The parameters K, n^s and S are defined in the text.

4. CONCLUSION

The adsorption of liquids from binary mixtures (alcohol - ethyl acetate) was found to be sensitive to the polarity difference of the competing liquids.

Although ethyl acetate preferentially adsorbed on activated charcoal from all of the binary mixtures of alcohols studied the composition of the adsorbed layer changed with the alkyl chain length of the alcohols.

It was found that the number of ethyl acetate molecules in the adsorption layer decreased with an increase of the alkyl chain length of alcohols indicating that some ethyl acetate molecules were displaced from the surface by the longer chain alcohols.

The results may be interpreted in terms of polarity difference between ethyl acetate and the competing alcohols for adsorption on the activated charcoal.

5. REFERENCES

1. L.C. Lloyd, and B.L.Harris, *J.Chem.Soc.* 58, 899 (1954).
2. H.R.Chipalkatti, C.H.Giles and (the late) Vallance D.G.M., *J.Chem.Soc.*, 4375 (1954).
3. J.J. Kipling and D.B. Peakall, *J.Chem.Soc.*, 4828 (1956).
4. A.Blacburn, J.J.Kipling and D.A.Tester, *J.Chem.Soc.*, 2373 (1957).
5. G.I.Berezin, A.V.Kiselev, R.T.Sagatelyan and V.A.Sinitzyn, *Colloid Interface Sci.* 38,2, (1972).
6. G.S.Ash, R.Bown, and D.H.Everett, *J.C.S. Faraday Trans.*, 1,71,123 , (1975).
7. a) L.G.Nagy, , and G.Schay, *Acta Chim. Hung.*, 39,365 (1963).
b) Schay G., in " *Surface and Colloid Science*", E.Matijevic , Ed., Interscience, New York, USA, Vol.2, (1969), p.179 .
8. T. Elton, *J.Chem.Soc.* 3813, (1954).
9. S.Sircar, and A.L.Myers, *The J.Phys.Chem.*, 74 (14),2828, (1970).
10. L.G.Nagy, and G.Schay, *J.Chim.Phys.*, 140 (1961).
11. S.K.Suri, A.S.Brar and L.D.Ahuja, *J.Colloid Interface Sci.*, 69, 347, (1979).
12. H.D.Everett, and T.R.Podoll, *J.Colloid Interface Sci.*, 82,1,14, (1981).
13. S.K.Suri, and M.Patel, *Colloid Interface Sci.*, 84,1,36, (1981).
14. T.M.Cocharp, *J.Col.Interface.Sci.*, 54(2), 311, (1976).
15. J.Oscik, J.Goworek, and R.Kusak, *J.Col.Interface.Sci.* ,79 (2), 308, (1981).
16. I.Dèkány, D.F.Szàntò, W.Armin and G.Lagaly, *Ber.Bunsenges.Phys.Chem.*, 90,422, (1986).
17. M.Tunçay, S.Göktürk, A.Mardinli and M.Mahramanlioğlu, in " *Physical Adsorption : Experiment, Theory and Applications*", J.Fraissard, Ed., Kluwer Academic Publishers, Nice, France (1997), p. 553.
18. R.E.Day, and G.D.Parfitt, *J.Phys.Chem.*, 71, 3073, (1967)
19. B.Buczek, A.Swiatkowski, and J.Goworek, *Carbon*, 33(2), 129-134, (1995).
20. A.L.Mc.Clellan, and H.F.Harnsberger, *J.Colloid Interface Sci.*, 23, 577, (1967).