

ADSORPTION OF POLAR ORGANIC  
AQUEOUS SOLUTIONS ONTO ACTIVATED CARBON

By

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical and Petroleum-Refining Engineering.

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ABSTRACT

The objective of this research is a Thermodynamic study of adsorption onto activated carbon of compounds of varying polarity from nonelectrolyte solution. Experimental data are reported for the adsorption at 30 °C and 45 °C of the homologous series of alcohols in aqueous solutions for single-solutes from ethanol to 1-pentanol, and for 2-propanol.

The data are also reported for two bi-solute systems (ethanol - 1-propanol, and ethanol - 2-propanol) at 30 °C. The study is largely concerned with adsorption isotherms over the entire composition range and does not deal exclusively with highly dilute solutions.

In this study we introduce, the pseudo-solution model which is an extension of the so-called pore filling model. Such a model is ideally suited for microporous adsorbents such as activated carbon. Here we assume that both the solutes as well as the solvent will fill the pores, and the concentration of the solutes will be increased, while that of the solvent will be decreased.

This differs from coverage (the amount of adsorbent surface covered by adsorbate) in that multilayer adsorption is also treated by this method. In this model, the adsorption equilibrium is treated as an osmotic equilibrium between two solutions having different compositions. One

solution represents the bulk phase and the other the adsorbed phase. The adsorbed phase is composed of adsorbates and the adsorbent. The nonideality in both phases is accounted for in terms of an activity coefficient whose composition dependence is described by a modification of UNIFAC (Universal Functional Group Activity Coefficient) where additional parameters to account for adsorbent-adsorbate interactions are considered. UNIFAC, together with the Gibbs adsorption equation was used to predict a priori single solute and bi-solute equilibria.

The parameters used for prediction are obtained from one system of single solute which contains the same functional group as the other single solute and bi-solute mixtures to be predicted.

Agreement with experimental data is good. Prediction of single solute adsorption is within about 2-4%, and for bi-solute the prediction is about 4-6%.

The method was also used to fit experimental data of single-solutes for acetone, acetic acid, and 2-propanol at 25 °C. It was found that the method represent the single-solute data well. The agreement with the experiment is within 5-7%.

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NOMENCLATURE

A	surface area ( $\text{m}^2/\text{g}$ )
$A_k$	Van der Waals group surface area
a	interaction parameter
$C_o$	concentration ( $\text{moles}/\text{cm}^3$ )
$f_i$	standard state fugacity of pure i
$f_i^L$	fugacity of component i in the bulk liquid phase
$f_i^l$	fugacity of component i in the adsorbed phase
$f_i^V$	fugacity of component i in the vapor phase
$g^E$	excess Gibbs energy per mole of the mixture
k	number of groups
m	capacity of the pores for pure ith liquid
n	number of moles
$n_T'$	total number of moles adsorbed
N	number of molecules
p	total pressure
$p^S$	vapor pressure of saturated liquid
$Q_k, q_k$	group surface area parameters
$R_k, r_k$	group volume parameters
R	universal gas constant
T	absolute temperature
u	energy of interaction
V	volume of solution
$V_p$	pore volume

$v_k$	number of the group of type k
$V_k$	Van der Waals group volume
$W_I$	initial weight of the mixture
$W_F$	final weight of the mixture
$X_I$	initial weight fraction
$X_F$	equilibrium weight fraction
$X_i$	mole fraction of component i in the bulk phase
$X_i'$	mole fraction of component i in the adsorbed phase
$X_m$	group fraction
$Y_i$	mole fraction of component i in the gas phase
Z	lattice coordination number

#### Greek Letters

$\gamma_i$	activity coefficient of ith component in bulk liquid
$\gamma_i'$	activity coefficient of ith component in adsorbed phase
$\gamma_i^C$	combinatorial activity coefficient
$\gamma_i^R$	residual activity coefficient
$\gamma_{ip}^*$	activity coefficient of pure ith component
$\tau$	interaction parameter
$\theta_i$	molecular surface area fraction for the ith group
$\theta_s$	area fraction for the adsorbent
$\phi_i$	molecular volume fraction for the ith group
$\bar{\phi}$	molar free energy of immersion of adsorbent in liquid solution
$\bar{\phi}_i$	molar free energy of immersion of adsorbent in the pure ith liquid

- $\mu$  chemical potential
- $\rho$  density of the mixture ( $\text{cm}^3/\text{g}$ )
- $\sigma$  surface tension at the solid-liquid interface

Subscript and Superscript

- i ith component
- ' adsorbed phase
- 1 solute one
- 2 solute two
- k number of the groups
- c combinatorial
- R residual
- s stand for the adsorbent

ACKNOWLEDGEMENT

The author wishes to express his gratitude to Dr. V. F. Yesavage for his guidance and helpful discussions during the course of this work.

Appreciation is also extended to Dr. Kidnay, Dr. Sloan, Dr. Hines, Dr. Lienert and Professor Dickinson for acting as committee members.

I also acknowledge with thanks, the financial support I received from the Libyan People throughout my study and research at CSM.

Finally, I would like to acknowledge my wife and my friends whose support make this work possible.

"Thanks, God"

## INTRODUCTION

Adsorption equilibria for mixtures of organic pollutants are required for design of purification processes. Recent studies (1) indicate the economic feasibility of purifying industrial and municipal waste waters by adsorption onto activated carbon.

Removal of these pollutants is a difficult task because of the diverse number of compounds typically present and extremely low concentrations normally encountered. To reduce experimental work, it is desirable to predict the adsorption of single solutes in aqueous solution over a wide range of concentration.

Although it has long been recognized that various adsorbents, notably activated carbons, greatly improve water quality, few systematic studies are available for adsorption from aqueous solution over a wide range of concentration (2, 3), "This lack of extensive and accurate data impedes progress toward establishing useful engineering correlations for prediction of adsorption equilibria." A considerable number of correlations prior to (1965), have been reviewed by Kipling (4). However, these correlations are not general, and applied either to the adsorptions of partially or completely miscible binary organic liquids.

Ideal adsorbed solution theory (5-7), and the potential

theory (8-14), have proved to provide an accurate prediction of multicomponent adsorption equilibria for gaseous mixtures. Unfortunately, their application to the case of liquids is confined to a very low concentration range, and the non-ideality in the adsorbed phase has to be introduced before reliable prediction is obtained.

The nature of the adsorbed phase has to be given a high priority, as mentioned by Wohleber (12). The greatest uncertainty in predicting adsorption is not due to a lack of knowledge of adsorption phenomena, but rather it is due to a lack of understanding of the solution properties of the adsorbed phase.

The concept of activity coefficient which has proved to be useful in correlating and interpreting other types of equilibria, has not been applied widely to the case of liquid mixture adsorption, especially in the case of aqueous solutions.

The UNIFAC group contribution method has proven to be a reliable and fast method for predicting liquid phase activity coefficients in nonelectrolyte mixtures at low to moderate pressures, and temperatures between 30-145 °C (15-17). The UNIFAC method is based on the solution of groups concept. The groups are structural units such as CH<sub>3</sub>, OH, and others, which when added form the parent molecules. Instead of considering a liquid mixture as a solution of molecules, the

mixture is considered as a solution of groups. The activity coefficients are then determined by the properties of the group rather than by those of the molecules.

The activity coefficients are calculated from two terms: a combinatorial part essentially due to differences in size and shapes of the molecules and a residual part due to energetic interactions between the groups.

Three types of group parameters are needed: group volume parameters ( $R_k$ ), group surface area parameters ( $Q_k$ ), and group interaction parameters ( $a_{mn}$  and  $a_{nm}$ ).

Therefore, the objective of this work is to investigate the dependence of adsorption on activity over more extensive homologous series of alcohols (single-solute and bi-solute systems) on activated carbon. Five single solutes from ethanol to 1-pentanol and 2-propanol have been studied at 30 and 45 °C. Also bi-solutes of (ethanol - 1-propanol and ethanol 2-propanol) have been studied at 30 °C. The non-ideality in the bulk phase and in the adsorbed phase is accounted for in terms of activity coefficients whose composition dependence are described by UNIFAC. The parameters of UNIFAC in the bulk phase are those found in the literature (15-17). The parameters in the adsorbed phase are the same as in the bulk phase for adsorbate-adsorbate interactions. The parameters of adsorbate-adsorbent, and adsorbent-adsorbate interactions were developed in this study.

The adsorbate-adsorbent and adsorbent-adsorbate interactions contain either implicitly or explicitly, information on the system being investigated. The direct measurement of the amount and composition of solute by activated carbon is virtually impossible for adsorption from liquids. Therefore, by using component material balances on the bulk phase liquid we calculate the amount adsorbed, and by introducing the pseudo-solution model, we calculate the adsorbed phase composition. The pseudo-solution model is an extension of the so-called pore filling model. This model is based on the development by Dubinin (18), which in principle is based on Polanyi's Potential Theory (19-20). This differs from coverage in that multilayer adsorption is also treated by this method. This model was also used to modify the group surface area in the adsorbed phase to account for the adsorbent.

The developed parameters combined with the Gibbs adsorption equation were used to predict a priori single-solute and multi-solute equilibria. The developed parameters were assumed to be temperature independent, and only single-solutes at one temperature were used in the development. None of the data of single-solute or bi-solutes were needed in the prediction of the amount adsorbed. The prediction agrees with the experimental data within 2-4% for single-solutes, and 4-6% for the bi-solutes systems. The model was tested on other experimental data for acetone, acetic

acid and 2-propanol in aqueous solution at 25 °C, adsorbed on different activated carbon. It was found that the model represents the data well, the agreement with the experimental is within 6-7%.

Unlike other correlations, our model can be extended to multi-solute systems without any mathematical difficulties, nor is there any limitation on whether or not the solutes are miscible in all proportions with the solvent. Finally, unlike some models which are useful only in predicting multi-solute equilibrium from single solute data, this method can also be used to predict single-solute equilibrium for compounds not studied, provided that the group interaction parameters are known.

SECTION I  
LITERATURE REVIEW

A better understanding of the role of adsorption phenomena in chemical processes and methods of physical separation has become increasingly important in recent years. In spite of its importance, there have been few attempts to generalize the correlations for prediction of adsorption equilibrium.

Problems incident to the formulation of such theories have been extensively reviewed by Kipling (4). The following section gives the summary of the main correlations and their assumptions when applied to the adsorption of liquid mixtures via activated carbon.

1. Empirical Adsorption Isotherms

Langmuir and Freundlich equations have been widely used (21,22) to represent adsorption isotherms for solutes from liquid solution over small ranges of concentration. A Langmuir type model does not provide an adequate fit for many single-solute isotherms, and it is thermodynamically inconsistent (3) when applied to multi-solute mixtures. Although the Freundlich equation is suitable for highly heterogeneous surfaces, it does not approach Henry's law at vanishing concentrations. It is often found that when Freundlich's equation is fit to adsorption data at high and

intermediate concentrations, it provides a poor fit for adsorption data at low concentrations.

Recently (23-24) attention is given to the use of three-parameter isotherms, Toth equation (25), Redlich-Peterson equation (24), and three-parameter Newman equation. Each of these reduces to Henry's law at very low concentration. Unfortunately, no general procedure is available to make a priori estimates of these parameters.

## 2. Polanyi Potential Theory

Manes and Hofer (10), Wohleber (12), Wohleber and Manes (13), Chiou and Manes (9), Rosene and Manes (26), and Rosene, Ozcon and Manes (27), have applied Polanyi Potential theory to adsorption of solids, completely miscible and partially miscible solutes from solution on activated carbon. Since Polanyi theory for adsorption from solution is valid only for those solutes that undergo separation into nearly pure solute phase, completely miscible liquids, and partially miscible liquids cannot be treated by this theory. In addition, Hansen and Fackler (8) point out, Polanyi theory is not symmetric with respect to solute and solvent and therefore cannot be general. Thus if a solute adsorbs positively from dilute solution, the solvent must in turn adsorb negatively when dilute in the same solute.

To account for this discrepancy, Hansen and Fackler

modified the Polanyi theory. Although their modification is applicable to partially and completely miscible liquids the thermodynamic origin is questionable and the agreement with experiment was not satisfactory without an additional arbitrary assumption.

Wohleber and Manes (13), employed with greater success the Hansen and Fackler modification of the Polanyi theory for correlating the adsorption of completely miscible organic liquids from dilute liquid solutions. The arbitrary division of solutes into solid, partially miscible and completely miscible does not provide a uniform account of the adsorption process which must ultimately depend on molecular forces, and it prevents prediction of solute mixture adsorption for those solutes that lie in different divisions. Also, as Wohleber (12) mentioned, both the miscible and partially miscible models are necessary in the case of solutions far from their critical temperature.

Therefore, the question has not been answered as to whether miscible adsorbates could be treated by the partially miscible model for solutions near their critical solution temperature. Although the prediction for the binary mixtures of partially miscible solutes, is within a factor of about two for the mole fraction in the adsorbed phase, however, for more dilute adsorbate solutions, the difference

between predicted and observed adsorbate composition may be as high as a factor of ten.

These deviations from theory are explained if one assumes that the adsorbed phase is not an ideal solution.

### 3. Corresponding States Theory of Adsorption

Radke and Prausnitz (2, 3) applied the corresponding states theory. The basis of their correlation follows from statistical mechanical treatment of adsorption from dilute liquid solution which leads to an adsorption "virial" equation. In this equation they assume the infinitely dilute potential of the mean force interactions for each solute molecule and the adsorbent can be divided into a vertical potential of the mean force interactions for each solute molecule with the surface and lateral potential of the mean force interactions between the molecules confined to a plane parallel to the adsorbent surface.

Direct use of the adsorption virial equation is not practical since the higher coefficients are difficult to calculate and a large number of coefficients are required except at extremely low concentrations.

In addition, their result does not confirm to the generalized adsorption isotherm; also they conclude that a priori estimation of the vertical interaction energies of solute molecules with activated carbon in dilute aqueous

solution is a difficult task.

#### 4. Ideal Adsorbed Solution Theory (IAS)

Radke and Prausnitz (2, 3) presented a thermodynamic method for predicting aqueous multi-solute adsorption from single solute adsorption data. This method which utilizes the concept of an ideal solution, proposed by Myers and Prausnitz (6), is useful for engineering design because the experimental effort required to obtain multi-solute adsorption data is much larger than that required to obtain single solute adsorption data. The thermodynamic method is based on a minimum of assumptions; it is not derived from a specific molecular model but follows from thermodynamic arguments appropriate to dilute solutions.

Ideal dilute solution theory appears to provide a satisfactory agreement with experimental only at very low concentration, and for small organic molecules, which do not exhibit extensive loadings.

However, for more strongly adsorbing solutes the non-ideality in the adsorbed phase should be expected, and therefore the predicted results are far from the experimental. A maximum deviation of 25 percent occurs even at low concentrations.

When the concentration dependence of activity coefficient in the adsorbed phase is expressed by a one parameter Margules equation it reduces the error to within 4 percent.

An additional problem, is the lack of adsorption data in the very low concentration range, which is required in the IAS model. Perhaps most important, regardless of the single solute isotherm equation, the IAS model becomes increasingly more difficult to use as the number of solutes increases.

To alleviate the mathematical complexity in using the IAS model, Digiano et al. (28) introduce the simplified IAS model which is a special case of the IAS. The simplified IAS is based on the argument that if all competing solutes have identical isotherms, the total loading in the mixture is the same as that in each respective, single solute system, provided that the spreading pressure is also the same. Under this condition, the single-solute concentrations are equal to the total concentration of the mixture. Modelling of competitive adsorption can also be simplified for the more realistic case in which solutes have different isotherms. Hypothetical solutes must be defined in a way that all have the same isotherm equation and thus also the same spreading pressure dependence.

If each single-solute can be expressed by a simple form of Freundlich equation, the integral form of spreading pressure can be evaluated explicitly. Then the simplified model can be readily extended to include any number of competing solutes. However, it is often found that when Freundlich's

equation is fit to adsorption data at high and intermediate concentrations, it provides a poor fit for adsorption data at low concentrations.

Therefore, the simplified IAS model has some limitation in that it can be applied only if the single solute data can be expressed by some simple form of equation.

#### 5. Sircar and Myers Model (29-32)

Sircar and Myers propose a model of the solution/solid interface based on statistical thermodynamics, which assumes that only the bulk phase behaves nonideally. An additional feature of the model is that  $m$ , the amount of material in the adsorbed phase, need not be that for an integral number of layers as in more recent theories (33-34). The latter feature could explain the apparent development of multilayer islands on heterogeneous surfaces consisting of different crystallite faces (33).

Sircar and Myers found quantitative fit with experimental isotherms of near ideal solutions and near quantitative fit for two very non-ideal associated (ethanol) solutions on highly heterogeneous activated carbon.

This agreement is especially surprising (33) since the model assumes a lattice liquid on a homogeneous surface. In this test, they did not determine whether the amount of material in the adsorbed phase was physically realistic.

Coltharp (33), tested Sircar and Myers model in two cases: The ideal adsorbed phase model (IAP) and ideality in both phases (IBP).

He concluded that the IAP model generally gave a poorer fit with experimental data. The amount of the adsorbed phase was compatible with possible island multilayers of one solution system although physically unlikely amounts were indicated for the other system.

The IBP model fit experimental data better than the IAP model, where both were applicable even though the amount in the adsorbed phase was unreasonable in one case.

These results suggest that adsorbed phase activity coefficients cannot be neglected for solutions with a substantially non-ideal bulk phase.

## 6. The Adsorbed Phase Model

Larinov and Myers (35), and Minka and Myers (36) have recently proposed a model to predict multicomponent adsorption from binary adsorption. The basic assumption is that the original liquid solution consisting of a total  $n^0$  moles may be divided after the establishment of equilibrium into two phases: an adsorbed phase containing  $n'$  moles and a bulk phase containing  $n$  moles so that

$$n^0 = n + n' \quad (1)$$

This assumption applies only for microporous adsorbent,

$n'$  may be estimated by

$$\frac{1}{n'} = \sum \frac{x'}{m} \quad (2)$$

where  $x'$  is the composition in the adsorbed phase, and  $m$  is the capacity of pores for pure  $i$ 'th liquid, given by the amount adsorbed from the vapor of that liquid at saturation.

The advantage of the adsorbed-phase model is that the multilayer structure of the liquid may be ignored. The multilayer character of the interface is explained by the decay, with distance, of the potential energy for interactions of the adsorbate molecules with the adsorbent. Using the above assumption, Minka and Myers derive 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 adsorbed phase to predict multicomponent liquid mixture in terms of adsorption from pairs of liquid.

However, aqueous solution was not tested, where hydrogen bonding and high non-ideality would be expected. The calculated activity coefficient was fitted in the form of Redlich-Kister equation with four parameters in the case of the binary system. This form of equation cannot be general and applied only for the system under consideration. The activity coefficient in the adsorbed phase is related to the capacity of the adsorbent, which cannot be calculated unless

isotherms for the pure vapors are available. The application of this model is limited by the difficulty in the numerical integration of the free energy of immersion in the case of multicomponent prediction.

#### 7. The Double-Layer Model

J. Toth (25) applied the general mass balance of Ostwald de Izaguirre form of monolayer and double layer, which is based on Kipling's and Schay's analysis.

According to their analysis in the linear section of composite isotherms for nonideal binary liquid mixtures one possible condition for linearity is that the composition of the monolayer adsorbed phase changes only slightly. This condition can be interpreted thermodynamically within relatively well definable limits. The limits of interpretation can be widened by supposing that there is a double-layer adsorbed phase in which the mole fractions of components attain gradually the mole fraction values characteristic of the bulk phase.

The monomolecular-layer or double-layer assumption is not essential. For example, the adsorbed phase might correspond more closely to  $1\frac{1}{2}$  molecular layers (35). In addition, only non-ideality in the bulk phase has been taken into account and no attempt was made to investigate the nonideality in the adsorbed phase.

SECTION II  
THEORETICAL STUDY

The concept of activity coefficient which has proved to be useful in correlating and interpreting other types of equilibria, has not been applied widely to the case of liquid mixture adsorption, especially in the case of aqueous solutions. It will be shown later how the concept of activity can be readily introduced for the case of the mixture adsorption equilibria.

Therefore, our intention in this work is to introduce the pseudo-solution model, and to use it along with UNIFAC to predict single and multi-solute isotherms. A number of developments reported in the literature were used. The concept of the adsorbed phase model (35-36), was adopted. The basic assumption of the adsorbed phase model is that the original liquid solution may be divided after establishment of equilibrium into two phase an adsorbed phase and a bulk phase equations, (1) and (2).

The advantage of using the adsorbed-phase model of adsorption is that the multilayer structure of the liquid may be ignored.

Proposed Theoretical Analysis

In this work we introduce the pseudo-solution model in which the solutes and solvent will fill the pores of the

adsorbent. It is the extension of the so-called pore-filling model (19,20). Here we assume the pores will be filled by the solvent and the solutes after the immersion of the adsorbent. The adsorbed phase will have the same composition as the bulk phase before starting adsorption, then the composition of the solute will be increased (i.e., the solute adsorbed and consequently the solvent will desorb) until the equilibrium is reached. At any time, the composition in the adsorbed phase will follow this relation:

$$\sum x_i' = 1 \quad (3)$$

In equation (3) the solvent mole fraction is included, and is treated as one of the components. According to the adsorbed phase model we can write:

$$\begin{aligned} V_o C_i^o &= n_i^o = n + n' \\ &= C_i (V_o - V_p) + C_i' V_p \end{aligned} \quad (4)$$

$$\text{and} \quad n_i' = C_i' V_p = V_o C_i^o - C_i (V_o - V_p) \quad (5)$$

where  $V_o$  = original volume of solution added to  
(m) quantity of adsorbent ( $\text{cm}^3/\text{g}$ )

$C_i^o$  = concentration of component i in the  
original solution ( $\text{moles}/\text{cm}^3$ )

$C_i$  = equilibrium concentration in the bulk  
phase ( $\text{moles}/\text{cm}^3$ )

$V_p$  = pore volume of adsorbent ( $\text{cm}^3/\text{g}$ ).

The amount of solvent adsorbed can be calculated using this relation (3):

$$\sum n_i' V_i + n_s' V_s = V_p \quad (6)$$

where  $V_i$  and  $V_s$  are the partial molar volumes of solute  $i$  and solvent in the bulk phase, respectively.

The composition in the adsorbed phase can be calculated using the relation:

$$x_i' = \frac{n_i'}{\sum n_i' + n_s'} \quad (7)$$

### Thermodynamic Framework

The application of solution thermodynamics to the adsorbed phase requires the definition of a standard state. In this study, the standard state of UNIFAC is used, since in this study, UNIFAC is used to predict the bulk phase liquid and adsorbed phase activity coefficients. The standard state is defined as the state of the pure bulk liquid, which at a temperature  $T$ , is in equilibrium with its saturated vapor at a total pressure  $P$ .

This standard state leads us directly to a consideration of adsorption from the gas phase where at equilibrium, the partial molar fugacity of component  $i$  is equal to the partial molar fugacity in the adsorbed phase. The fugacity of component  $i$  in the gas phase is given by (37-38):

$$f_i^V = y_i \phi_i P \quad (8)$$

$y_i$  is the mole fraction of component  $i$  in the gas phase,  $\phi_i$  is the fugacity coefficient, and  $P$  is the total pressure. For most adsorption systems the pressure is subatmospheric and  $\phi_i$  may be set equal to unity.

The partial molar fugacity when the adsorbed phase is in equilibrium with a gas is given by

$$f_i = f_i^V = \gamma_i^{*'} x_i' f_i^O \quad (9)$$

Where  $\gamma_i^{*'}$  is the activity coefficient in the adsorbed phase ( $\gamma_i^{*'}$   $\neq$  1 as  $x_i' \rightarrow$  1), and  $x_i'$  is the mole fraction in the adsorbed phase.

$f_i^O$  is the standard state fugacity of pure  $i$  at vapor pressure ( $P_i^O$ ).

Now, if we consider a liquid mixture being adsorbed, it can be assumed that the bulk liquid is obtained by increasing the gas phase pressure (fugacity) to form the bulk liquid. Therefore the thermodynamic system is the gas phase in equilibrium with the bulk liquid which is in equilibrium with the adsorbed phase. At equilibrium the fugacity of component  $i$  in the gas phase, in the bulk phase, and in the adsorbed phase are equal.

The differential change in Gibbs free energy in going from the gas phase to the condensed phase which is in equilibrium with adsorbed phase can be obtained from the isothermal Gibbs-Duhem equation (35):

$$\begin{aligned}
 A d\sigma &= - \sum n_i' d\mu_i' \\
 &= - \sum n_i' R T d \ln f_i' \quad (10)
 \end{aligned}$$

where  $A$  is the specific surface area of the adsorbent, and  $\sigma$  is the surface tension or spreading pressure at the solid-liquid interface. The total change in the free energy is given by integrating equation (10) at constant composition as the total system pressure increases.

$$\begin{aligned}
 \int_{\text{vap}}^{\text{Liq}} A d\sigma &= - \int_{f_i}^{f_i'} n_i' R T d \ln f_i' \\
 \sigma A &= - \sum n_i' R T \ln \frac{f_i'}{f_i} \quad (11)
 \end{aligned}$$

where  $f_i'$  is the fugacity of component  $i$  in the adsorbed phase and  $f_i$  is the fugacity of component  $i$  when the adsorbed phase is in equilibrium with a gas. The product  $\sigma A$ , or surface tension  $\times$  specific surface area of the adsorbent is equal to  $\phi$  (the free energy of immersion of adsorbent in the mixture).

$$\phi = - \sum n_i' R T \ln \frac{f_i'}{f_i} \quad (12)$$

The liquid adsorbed is always in equilibrium with a gas which is increased in total pressure. If the gas is ideal, since we are at low vapor pressures in our adsorption system,  $f_i'/f_i = f_j'/f_j$  and from equation (12)

$$\phi = - R T \ln \frac{f_i'}{f_i} \Sigma n_i'$$

$$\text{or } f_i' = f_i \exp^{-\frac{\phi}{n_T RT}} \quad (13)$$

where  $n_T'$  is the total number of moles adsorbed.

The bulk phase fugacity of component  $i$  is given by

$$f_i^L = \gamma_i x_i f_i^O \exp \frac{v_i^S (P - P_i^S)}{R T} \quad (14)$$

For subatmospheric pressure the exponential in equation (13) may be set equal to unity.  $\gamma_i$  is the activity coefficient in the bulk phase, and  $x_i'$  is the mole fraction.

If a mixture of solutes is in equilibrium with an adsorbed phase, then fugacity of solute  $i$  in the bulk phase is equal to that in the adsorbed phase:

$$f_i^L = f_i' \quad (15)$$

Therefore equations (12) through (14) give:

$$\gamma_i x_i f_i^O = \gamma_i^{*'} x_i' f_i^O \exp^{-\frac{\phi}{n_T' RT}} \quad (16)$$

Note that because of the assumption in using the standard state as that of the bulk phase  $\gamma_i^{*'} \neq 1$  as  $x_i' \rightarrow 1$

Therefore, from equation (16), as  $x_i' \rightarrow 1$

$$\gamma_{ip}^{*'} = \exp \frac{\phi_i}{n_T RT} \quad (17)$$

where  $\gamma_{ip}^{*'}$  is the activity coefficient of pure  $i$ 'th component, which does not equal one. Obviously as defined  $\gamma_{ip}^{*'}$  is related to the free energy change of adsorption

of a pure liquid,  $\phi_i$  resulting from the adsorbate-adsorbent interactions. Now we redefine  $\gamma_i^{*}$ , so that

$$\gamma_i' \longrightarrow 1, \text{ as } x_i' \longrightarrow 1$$

Let 
$$\gamma_i' = \gamma_i^{*'} \exp \frac{-\phi_i}{n_T RT} \quad (18)$$

Equation (15), now becomes:

$$\gamma_i x_i = \gamma_i' x_i' \exp \left( \frac{\bar{\phi} - \bar{\phi}_i}{RT} \right) \quad (19)$$

where  $\phi_i$  is the molar free energy of immersion of the adsorbent in the pure i'th liquid.

Equation (19) is the main equation in this analysis,  $\gamma_i$  and  $\gamma_i'$  are the activity coefficient in the bulk phase and in the adsorbed phase respectively, and could be calculated by using UNIFAC if  $x_i$  and  $x_i'$  with the interaction parameters are known.

#### Activity Coefficient in Both Phases

The group-contribution method was used (15-17) to predict the activity coefficients in binary and multicomponent mixtures, often with good accuracy for mixtures containing water, hydrocarbons, alcohols, chlorides, nitrites, ketones, amines, acids, and other organic fluids in the temperature range 30 to 140°C.

In this work we use the UNIFAC (Universal Functional Group Activity Coefficient) method. The logarithm of the activity coefficient is assumed to be the sum of two contributions: a combinatorial part, essentially due to differ-

ences in size and shape of the molecules in the mixture, and a residual part, essentially due to energy interactions. The functional group sizes and interaction surface areas are introduced from independently obtained pure-component, molecular structure data. UNIFAC (15-17, 39-50) gives a good representation of both vapor - liquid and liquid - liquid equilibria. In multicomponent mixtures the UNIFAC equation for activity coefficient of (molecular) component  $i$  is

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R \quad (20)$$

#### Combinatorial Residual

The combinatorial activity coefficients are calculated using Staverman's potential (51). This combinatorial part takes into account contributions from differences in both molecular size and molecular shape. These are in turn obtained from the well defined group volume and area constants  $R_k$  and  $Q_k$ .

$R_k$  and  $Q_k$  are obtained from atomic and molecular structure data, the Van der Waals group volumes and surface areas  $V_k$  and  $A_k$  are tabulated for some important groups (15-17).

$$R_k = V_k / 15.17 \quad (21)$$

$$Q_k = A_k \cdot 25 \cdot 10^9 \quad (22)$$

Both the combinatorial and residual parts of the UNIFAC derivation are presented in Appendix A, and only the main working equations are presented in this section.

The combinatorial part is given by (51):

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (23)$$

$$l_i = \frac{Z}{2} (r_i - q_i) - (r_i - 1)$$

$$Z \text{ (coordination number)} = 10$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad ; \quad \phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (24)$$

Molecular surface area fraction                      Molecular volume fraction

$$j = 1, 2, \dots, M \text{ (number of components)}$$

The Van der Waals volume,  $r_i = \sum_k V_k^i R_k$  and Van der Waals surface area  $q_i = \sum_k V_k^i Q_k$

$$K = 1, 2, \dots, N \text{ (number of groups in molecule } i).$$

In these equations,  $x_i$  is the mole fraction of component  $i$ , and  $V_k^i$ , always an interger is the number of groups of type  $k$  in molecule  $i$ .

The contribution from group interactions, the residual part, is assumed to be the sum of the individual contributions of each solute group in the solution less the sum of the individual contributions in the pure component environment (15-17):

$$\ln \gamma_i^R = \sum_k V_k^i \left[ \ln \Gamma_k - \ln \Gamma_k^i \right] \quad (25)$$

$K = 1, 2, \dots, N$  (number of different groups in the mixture).

$\Gamma_k$  is the residual activity coefficient of group  $k$  in a solution,  $\Gamma_k^i$  is necessary to attain the normalization that activity coefficient  $\gamma_i$  becomes unity as  $x_i \rightarrow 1$ .

The individual group contributions in any environment containing groups of kinds 1, 2, ...,  $N$  are assumed to be only a function of group concentration and temperature.

The residual activity coefficient for group  $k$  is given by (17):

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \sum_m \theta_m \tau_{mk} \right) - \sum_m \left( \theta_m \tau_{km} / \sum_n \theta_n \tau_{nm} \right) \right] \quad (26)$$

$m$  and  $n = 1, 2, \dots, n$  (all groups)

equation (26) also holds for  $\Gamma_k^i$ .

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad X_m = \frac{\sum_j V_m^j X_j}{\sum_n \sum_j V_n^j X_j} \quad (27)$$

Group surface area

Group fraction

fraction

In equation (26)  $\tau_{nm}$  is given by:

$$\tau_{nm} = \exp(-a_{nm}/T) \quad (28)$$

$$a_{nm} = (u_{nm} - u_{mm})/R \quad (29)$$

Where  $a_{nm}$  represent the group-interaction parameter.

It is a measure of the difference in the energy of interaction

( $U_{nm}$  and  $U_{mn}$ ) between group n and group m, and between two groups m:

Note that  $a_{nm} \neq a_{mn}$  and that the group interaction parameters are assumed independent of temperature, and are tabulated for some important groups (15-17). The adsorbate-adsorbate group interactions both in the bulk phase and in the adsorbed phase are shown in Table (III).

Equations (20) through (29) were applied directly in the bulk phase. Since the combinatorial part is very small compared to the residual part (i.e.  $\ln \gamma^C \ll \ln \gamma^R$ ) which is the case for the highly polar systems, with slight difference in molecular size, it was applied directly in the adsorbed phase without any further modification

Since in a microporous adsorbent an appreciable fraction of the adsorbate surface area is in proximity with adsorbents, the residual part was modified to account for the effect of the adsorbent. This modification was done on the group surface area fraction equation (24) by applying the pseudo-solution model as follows:

$$\bar{V} = \sum \bar{V}_i x_i \quad (30)$$

where  $\bar{V}_i$  = molar volume occupied by pure species

$$\left( \frac{\text{volume of } i}{\text{mole of sol.}} \right) \text{ and } \bar{V} = \frac{\text{total volume of adsorbate}}{\text{mole of solution}}$$

Therefore equation (27) for the surface area fraction becomes

$$\theta_i = \frac{(V_p / \sum_j V_j x_j) x_i A_i}{\frac{V_p \sum_j A_j x_j}{\sum_j V_j x_j} + A} \quad (31)$$

Where  $A_i$  ( $\text{cm}^2/\text{mole}$ ), and  $V_j$  ( $\text{cm}^3/\text{mole}$ ) are the Van der Waals areas and volumes of the molecules given by Bondi (5), therefore from equations (21) and (22).

$$A_i = (2.5 \times 10^9) q_i \quad (32)$$

$$V_i = (15.17) r_i \quad (33)$$

Where  $q_i$  and  $r_i$  (are the same as  $Q_k$  and  $R_k$ ), are the surface area and volume structure parameters of a molecule which are tabulated (15,17) for some important groups.

$A$  is the specific area of the adsorbent ( $614 \times 10^4 \text{cm}^2/\text{g}$ ) and  $V_p$  ( $.68 \text{cm}^3/\text{g}$ ) is the pore volume of the adsorbent.

Equations (30) through (34) give

$$\theta_i = \frac{(1.648 V_p) x_i q_i}{\frac{1.648 V_p \sum_j x_j q_j}{\sum_j r_j x_j} + A} \quad (34)$$

$$\theta_s = 1. - \theta_i \quad (35)$$

Where  $\theta_s$  is the area fraction of activated carbon.

In equation (35) only the surface area  $A$  ( $\text{cm}^2/\text{g}$ ) and pore volume  $V_p$  ( $\text{cm}^3/\text{g}$ ) are needed to account for the effect of the adsorbent. The basic assumption in using the pseudo-solution model is that, the adsorbed phase is contained within

the pores. This assumption applies for microporous adsorbents only. For nonporous adsorbents upon which molecules adsorb in multiple layers, the assumption is weak unless additional assumptions, such as the validity of the B.E.T. theory (Brunauer, Emmett, and Teller), are introduced.

If the adsorbate-adsorbate and adsorbate-adsorbent interactions are known, the prediction of single solute or multi-solute is straightforward. The complete procedure is illustrated as follows:

1. Equation (19) for a two-component system becomes:

$$x_1 \gamma_1 \exp \frac{-(\bar{\phi} - \bar{\phi}_1)}{RT} = x_1 \gamma_1 \quad (36)$$

$$x_2 \gamma_2 \exp \frac{-(\bar{\phi} - \bar{\phi}_2)}{RT} = x_2 \gamma_2 \quad (37)$$

where subscript (1) represents the solute and (2) represents water.

2. Divide equation (36) by equation (37):

$$\frac{x_1 \gamma_1 \exp \frac{-(\bar{\phi} - \bar{\phi}_2)}{RT}}{x_2 \gamma_2 \exp \frac{-(\bar{\phi} - \bar{\phi}_1)}{RT}} = \frac{x_1 \gamma_1 \gamma_2 \exp \left( \frac{\bar{\phi}_2}{RT} \right)}{x_2 \gamma_2 \gamma_1 \exp \left( \frac{\bar{\phi}_1}{RT} \right)} \quad (38)$$

3. The exponentials in equation (38) are equal to the pure component activity coefficient equation (17). The pure component activity coefficient is the combination of the activity coefficient of the compound and the adsorbent less the activity coefficient of the compound in its solution.

4. Since the exponentials in equation (38) are fixed over the whole concentration range, the prediction of the composition in the adsorbed phase is a trial and error procedure.

- a. At a given  $x_1$  and  $x_2$  calculate  $\gamma_1$  and  $\gamma_2$
- b. Assume a value of  $x_1'$  ( $x_2' = 1 - x_1'$ ).
- c. Use equations (20) through (35) to calculate  $\gamma_1'$  and  $\gamma_2'$ .
- d. In equation (38) all the terms on the R.H.S. are now known, the L.H.S. can be calculated directly.
- e. Repeat step (c) using the new calculated  $x_1'$  until a reasonable value of  $x_1'$  and  $x_2'$  are obtained.
- f. The predicted amount adsorbed can be calculated using equation (7).

The equilibrium criteria, equations (36) and (37) can be used to calculate,  $\bar{\phi}$  if other terms are known.

The correlation can also be extended to predict multi-solute adsorption without any complication by adding additional equations equating the partial molar fugacities such as equations (36) and (37). A computer program was developed to predict single-solute and multi-solute adsorption equilibria using the above mentioned procedure. A complete explanation is given within the program which is presented in Appendix B. A sample of calculation is shown in Appendix C.

SECTION III  
EXPERIMENTAL SECTION

Materials - The adsorbent used was a commercial 20x40 mesh size activated carbon obtained from Darco Company, Denver, Colorado. Its pore volume,  $V_p$ , was determined by mercury porosimetry to be ( $.68 \text{ cm}^3/\text{g}$ ). The specific total surface area is  $614 \text{ m}^2/\text{g}$  as determined by  $\text{N}_2$ -BET method. All the above analyses were done by Micromeritics Instrument Co. of Atlanta, Georgia. The analysis indicated that the pore volume was distributed over a wide range of pore sizes, as is the case of many activated carbons. According to the manufacturer's information, the activated carbon was washed by a strong acid to leach out all the undesirable inorganics such as iron, aluminum, magnesium and calcium.

Prior to use the activated carbon was washed with distilled water and dried at  $125^\circ\text{C}$  for 24 hours.

All of the organic compounds, except ethanol were purchased from J. T. Baker Chemical Company. Gas chromatographic analysis of these organics revealed less than .5% impurities. Ethanol was obtained from the Chemistry Department at CSM with approximately 99% purity.

Procedure - A single-solute, and bi-solute mixture was prepared for each experimental point; Its mass and its weight fraction were determined gravimetrically. Adsorption

isotherms were determined by contacting a volume  $V$  (50 to 100 ml) of solution with a known mass of adsorbent in 125 ml Erlenmeyer flasks sealed with Teflon. The flasks were then continually shaken for 48 hours in a wristshaker thermostated to within  $\pm 1$  °C at 30, 45 °C for single solute mixtures, and at 30 °C for bi-solute mixtures. Preliminary tests indicated that equilibrium was closely approached after 36 hours.

After equilibrium was established the carbon was allowed to settle and then a portion of the sample was withdrawn for analysis after filtration. The analysis to determine the equilibrium composition was accomplished by GLC (HP 5750 series) using hydrogen flame ionization detector. The chromatograph column is a 2 ft x 1/4 in. o.d. packed with porapak Q (80-100 mesh size) as stationary phase.

The experimental conditions of the chromatograph are presented in Table I. The amount of each solute adsorbed on the carbon at equilibrium was calculated from the mass balance equation on the bulk phase.

Since the alcohol-water mixture is a highly non-ideal solution, the following equations were used rather than equation (5):

$$W_I = V_I \rho_I X_I \quad (39)$$

$$W_F = (V_I - V_P) \rho_F X_F \quad (40)$$

$$\Delta W = W_I - W_F \quad (41)$$

Where  $W_I$  = Initial wt. of the mixture before adding the adsorbent (g)

$V_I$  = Actual initial volume of the mixture ( $\text{cm}^3$ )

$\rho_I$  = Initial density of the mixture ( $\text{g}/\text{cm}^3$ )

$X_I$  = Initial wt fraction of the solute

$W_F$  = Final wt of the mixture (g)

$V_P$  = Pore volume of the adsorbent ( $\text{cm}^3/\text{g}$ )

$X_F$  = Equilibrium wt fraction of the solute in the bulk phase

$\rho_F$  = Final density of the mixture ( $\text{g}/\text{cm}^3$ )

$\Delta W$  = Amount adsorbed (g/g of adsorbent)

The composition in the adsorbed phase was calculated according to equation (7).

To increase the accuracy of gas chromatography to determine the equilibrium composition analysis, the external standard technique (EST) (52) was employed. EST involved the preparation of standard mixtures of the components of interest. The chromatograph was run over the range of interest of %i (w) (wt fraction).

For each component, a calibration curve was plotted of %i (w) vs A (i) (peak area generated during the run using an HP digital integrator). A mixture of the same components in a sample of unknown composition was run under the identical conditions as the calibration runs. Then %i (w) in the sample was read off directly from the curve corresponding to

A (i) in the sample run.

The advantage of using this techniques is that response need not be linear since the calibration curve itself embodies the exact relationship between %i (w) and A (i) at all levels of %i (w) in the calibration range. Another advantage is that, only peaks of interest need be calibrated.

When using equations (39) to (41) and equation (7) the molar volume in the adsorbed phase was taken to be equal to the molar volume of the bulk phase. Standard solutions were prepared to check the accuracy of the analysis; The error in the measurement of the equilibrium composition in the bulk phase was estimated to be 3% for single solutes, and about 4% for the bi-solute systems.

TABLE - I  
CHROMATOGRAPH OPERATION CONDITIONS

Column dimension:	2'x ½' O.D.
Column temperature:	120 - 140 °C
Carrier gas flow rate:	30 ml/min
Hydrogen flow rate:	36 ml/min
Air flow rate:	500 ml/min
Detector temperature:	180 °C
Injector temperature:	160 °C
Detector signal attenuation:	256
Sample size:	1 µl

SECTION IV  
RESULTS AND DISCUSSION

This section presents only the best and final approach for predicting the amount of adsorption using UNIFAC. Other approaches have been tested, but they failed to represent the experimental data obtained in this study.

For example the main additional method which was tested is that of Minka et al. (36). In this method the standard state of the pure adsorbate was used. The adsorbed phase activity coefficient was calculated, and UNIFAC was used to fit the experimental activity coefficient. Although a reasonable fit was found for the individual completely soluble-solutes isotherms at 30°C, prediction of these solutes at another temperature could not be made because other assumptions, such as the temperature dependence for the difference in the free energy of immersion has to be introduced. Also the prediction of partially soluble-solutes could not be made because an expression for predicting the free energy of immersion which covers the low concentration range for these systems is needed. No attempt was made to use this method for the bi-solute system, because of the mathematical difficulties in the numerical integration to calculate the difference in the free energy of immersion, and the experimental data

for the bi-solute system are needed in the integration. Therefore, only the results obtained using the approach developed in this study will be discussed.

### Single Solute Adsorption

#### 1. Completely soluble solutes:

The experimental adsorption isotherms for ethanol, 1-propanol, and 2-propanol in water were studied at 30 and 45 °C. Isotherms of these solutes are presented in Table V through Table X, and in Figures 1 through Figure 3.

The activity coefficient in the bulk phase was calculated using UNIFAC with the recently revised parameters (17). These parameters, representing the adsorbate-adsorbate interactions are assumed to be the same in both phases, and are shown in Table III. The calculated activity coefficient in the bulk phase agrees to within 1% of the experimental activity coefficient from the literature (53-55).

All homologous series members of alcohols with the exception of methanol can be represented by a combination of  $\text{CH}_3$ ,  $\text{CH}_2$  and OH groups; e.g., ethanol contains  $1\text{CH}_3$ ,  $1\text{CH}_2$  and  $1\text{OH}$  rather than by  $\text{CH}_3\text{CH}_2\text{OH}$  as previously assumed in the original articles on UNIFAC.

The group adsorbent interaction parameters were estimated by using the optimization search technique utilizing the following objective function:

$$F_{\text{opt}} = 100 \left[ \frac{\sum_i \sum_j \left( \frac{x'(\text{exp}) - x'(\text{cal.})}{x'(\text{exp})} \right)^2}{2 \cdot \text{DNP}} \right]^{\frac{1}{2}} \quad (42)$$

$F_{\text{opt}}$  = optimum standard deviation

$x'(\text{exp})$  = experimental adsorbed phase composition

$x'(\text{cal})$  = calculated adsorbed phase composition

using UNIFAC

DNP = number of data points

The summation is to be taken over all data points,  $j$ , and components,  $i$ . In using the search technique, starting values of the parameters to be estimated are assumed. The root mean square deviations will be calculated with each parameter incremented in both the positive and negative direction. The base values of the parameters will shift to the point which had the lowest root mean square deviation. The procedure will continue until the root deviation of the base value is lower than any of the points surrounding it. The estimated parameters are those corresponding to the optimum standard deviation.

Using equation (42), a comparison was made between the calculated and experimental adsorbed phase composition of ethanol, 1-propanol and 2-propanol in water at 30 °C. The estimated group-adsorbent interaction parameters are shown in Table IV. By assuming that these parameters are temperature independent and using the procedure for predicting the

composition in the adsorbed phase, and by using equation (7), the prediction of the amount adsorbed for ethanol, 1-propanol, and 2-propanol in water at 45 °C were predicted to within 3.4% as shown in Table V through Table X.

The interaction of  $-CH_2$  and  $-CH_3$  was assumed to be the same with activated carbon. This assumption has also been used (2,16,52) for interaction with other groups. Since the interaction of activated carbon with  $-OH$  and  $H_2O$  is expected to be weak interaction, these values were assumed to be zero.

A little improvement on the predicted amount adsorbed was found when using the individual optimum parameters obtained from fitting the experimental single-solute data to predict the same single-solute data at another temperature. Furthermore, the estimated parameters are slightly different from those obtained from the combined single-solutes data.

## 2. Partially soluble solutes

1-butanol, and 1-pentanol are partially soluble in water. The study of these two solutes is limited to a very low concentration (up to the saturated concentration). The experimental adsorption isotherms at 30 °C and 45 °C, are shown in Tables XI through XIV, and in Figures 4 and 5. The group-adsorbate interaction obtained from completely soluble solutes were used to predict the amount adsorbed at 30 °C and at 45 °C.

The predicted values are in good agreement with the experimental data. A standard deviation of 2.8% was obtained at 30 °C, and 3.6% at 45 °C. This proves the validity of using our correlations to predict completely soluble solutes as well as partially soluble solutes using the same parameters. None of the experimental values of partially soluble solutes were used in the prediction.

Figures 1 through 7, indicate that as the temperature increases, the amount adsorbed at a given composition (concentration) decreases. This effect is more pronounced at the lower concentrations. Thus, as in gas-phase adsorption, adsorption from aqueous solution is an exothermic process.

The result also shows that the amount adsorbed increases with increasing chain length. This result agrees with Traube's rule (4), which states that, the addition of a methyl group in homologous series of alcohols reduces its solubility in water, and therefore increases its ability to adsorb on the surface of the adsorbent.

Slightly different parameters were obtained by using the data of partially miscible solutes. However, little improvement of the calculated values was found. Since the predicted values are in good agreement with the experiment by using the parameters obtained from completely soluble solutes, no attempt was made to list different parameters.

### Tertiary System Adsorption (Bi-Solutes)

Two bi-solutes systems ethanol-1-propanol, and ethanol-2-propanol in water were studied at 30°C. The same parameters obtained from completely single solutes data were used to predict the data of these bi-solute systems. The experimental and predicted amount adsorbed are presented in Tables XV and XVI. As shown in Figures 6 and 7, the predicted amounts of each component adsorbed agreed well with experimental data, especially at lower concentrations. The deviation is higher at high concentration. This is probably due to steric hinderance or higher interaction with activated carbon (3, 12). The agreement is within 4.7% for the (ethanol-1-propanol-water) system and within 5.9% for the (ethanol-2-propanol-water) system. Again, none of the experimental data of the bi-solute system were used in the prediction.

### Comparison with the Work of Wohleber and Manes (13)

Single solute adsorption isotherms for 2-propanol, acetone, and acetic acid onto activated carbon at 25°C were reported by Wohleber (12). These systems were chosen to verify the applicability of our correlations to different groups. The model was used to fit the experimental adsorption isotherms for acetone and acetic acid, and to predict the 2-propanol-water system. The predicted amount of

2-propanol adsorbed agrees with the experimental to within 6.7%. This agreement is good, considering different activated carbon with different physical properties was used; i.e. different surface area and pore volume. Also the revised parameters were extrapolated beyond the range of application of UNIFAC which is above 25°C. The predicted values are far better than those obtained by Wohleber (12) using the modified potential theory. Both results were compared with the experimental shown in Table XVII and in Figure (8).

Acetone contains 1 CH<sub>3</sub> and 1 CH<sub>3</sub>CO, acetic acid contains 1 CH<sub>3</sub> and COOH. The interaction parameter of CH<sub>3</sub> with activated carbon was assumed to be the same as that obtained previously. However, the interaction parameters for CH<sub>3</sub>CO and COOH were obtained using the data of acetone and acetic acid in water. The model represent these data very well. The calculated results were compared with those obtained using the potential theory which are presented in Table XIII through XIV, and in Figure (9) through (10).

The result using our model agree with the experiment to within 6.8% for acetone and 6.1% for acetic acid. The result of acetic acid could not be represented by potential theory over the whole range of data reported because of non-ideality in both phases. However, when we used our correlations a better result was obtained compared to that of Wohleber (12).

TABLE II  
GROUP VOLUME AND SURFACE AREA PARAMETERS (16,52)

	<u>R<sub>k</sub></u>	<u>Q<sub>k</sub></u>
CH <sub>2</sub>	.6744	.540
CH <sub>3</sub>	.9011	.848
OH	1.	1.2
H <sub>2</sub> O	.92	1.4
CH <sub>3</sub> CO	1.6724	1.488
COOH	1.3013	1.224

TABLE IIIADSORBATE-ADSORBATE GROUP INTERACTIONS <sup>a</sup><sub>mn</sub> (15-17)

	<u>CH<sub>2</sub></u>	<u>OH</u>	<u>H<sub>2</sub>O</u>	<u>CH<sub>2</sub>CO</u>	<u>COOH</u>
CH <sub>2</sub>	0	986.5	1318	476.4	663.5
OH	156.4	0	353.5	84	199
H <sub>2</sub> O	300	-229.1	0	-195.4	-14.09
CH <sub>2</sub> CO	26.76	164.5	472.5	0	669.4
COOH	315.3	-151.0	-66.17	-297.8	0

TABLE IV  
ADSORBATE GROUP-ADSORBENT (C) INTERACTION

	<u>a<sub>mn</sub></u>
CH <sub>3</sub> -C	-335.11
OH-C	765.80
H <sub>2</sub> O-C	1209.76
CH <sub>3</sub> CO-C	-317.5
COOH-C	-405.08
C-CH <sub>3</sub>	-289.48
C-OH	0
C-H <sub>2</sub> O	0
C-CH <sub>3</sub> CO	-206.7
C-COOH	110.65
C-C	0

TABLE V

ADSORPTION OF ETHANOL FROM AQUEOUS SOLUTION AT 30 °C

<u>X<sub>1</sub></u> <u>(bulk)*</u>	<u>W<sub>1</sub> (exp.)</u> <u>(mm/g) **</u>	<u>W<sub>1</sub> (calc.)</u> <u>(mm/g)</u>
.0198	2.0768	2.0506
.0459	3.8541	3.5557
.0812	4.8828	4.8695
.1245	5.7263	5.9387
.1742	6.5774	6.7440
.2314	7.3652	7.4676
.3012	8.0241	8.1743
.3874	8.7348	8.8267
.4933	9.4189	9.4847
.6124	10.1113	10.0709

\*Subscript (1) represents the solute

\*\*mm/g (m mole/g)

TABLE VIADSORPTION OF ETHANOL FROM AQUEOUS SOLUTION AT 45 °C

<u>X<sub>1</sub></u> <u>(bulk)</u>	<u>W<sub>1</sub> (exp.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (calc.)</u> <u>(mm/g)</u>
.02	1.9528	1.9835
.0479	3.4902	3.3330
.0836	4.6128	4.4491
.1264	5.4939	5.4124
.1728	6.1657	6.2469
.2331	6.9615	7.0481
.2991	7.7167	7.7144
.3859	8.4091	8.5381
.4782	9.1602	9.1271
.6065	9.8622	9.9237

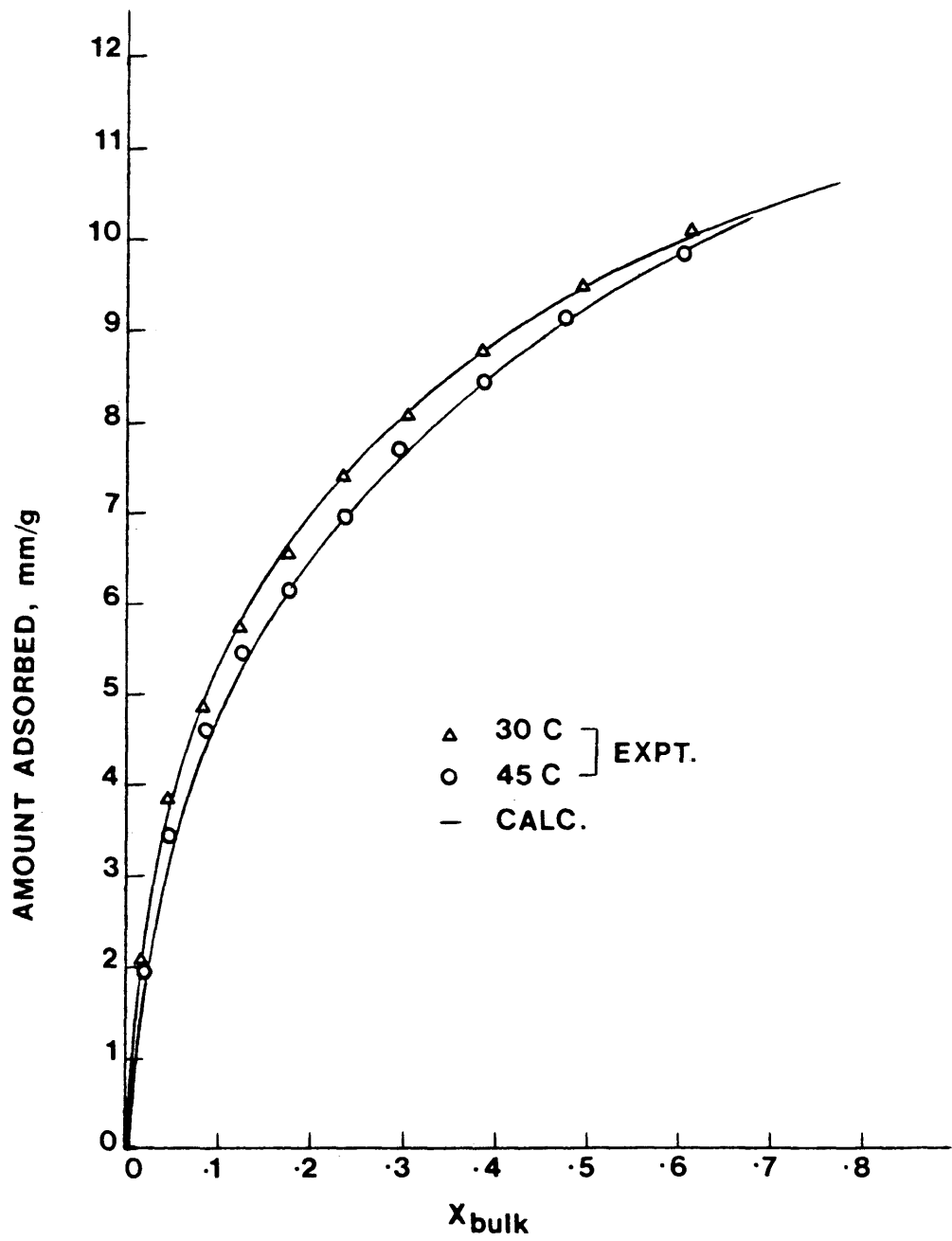


Fig-1- Adsorption of Ethanol from Aqueous Solution

TABLE VIIADSORPTION OF 1-PROPANOL FROM AQUEOUS SOLUTION AT 30 °C

<u>X<sub>1</sub></u> <u>(bulk)</u>	<u>W<sub>1</sub> (exp.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (calc.)</u> <u>(mm/g)</u>
.0119	2.0063	1.8738
.0327	3.601	3.313
.0587	4.3353	4.2581
.0917	5.0266	4.9110
.1334	5.4968	5.5049
.1813	5.9772	5.9294
.2414	6.46	6.3363
.3171	6.9725	6.7293
.4129	7.4428	7.1880
.5416	7.9342	7.7028

TABLE VIII  
ADSORPTION OF 1-PROPANOL FROM AQUEOUS SOLUTION AT 45 °C

<u><math>X_1</math></u> <u>(bulk)</u>	<u><math>W_1</math> (exp.)</u> <u>(mm/g)</u>	<u><math>W_1</math> (calc.)</u> <u>(mm/g)</u>
.012	1.8577	1.6798
.0323	3.1577	3.0233
.0592	3.730	3.7118
.0948	4.556	4.529
.1329	5.0845	5.0286
.1798	5.514	5.5056
.2362	6.1283	6.0287
.3131	6.6705	6.5182
.4065	7.0955	6.9283
.5353	7.535	7.484

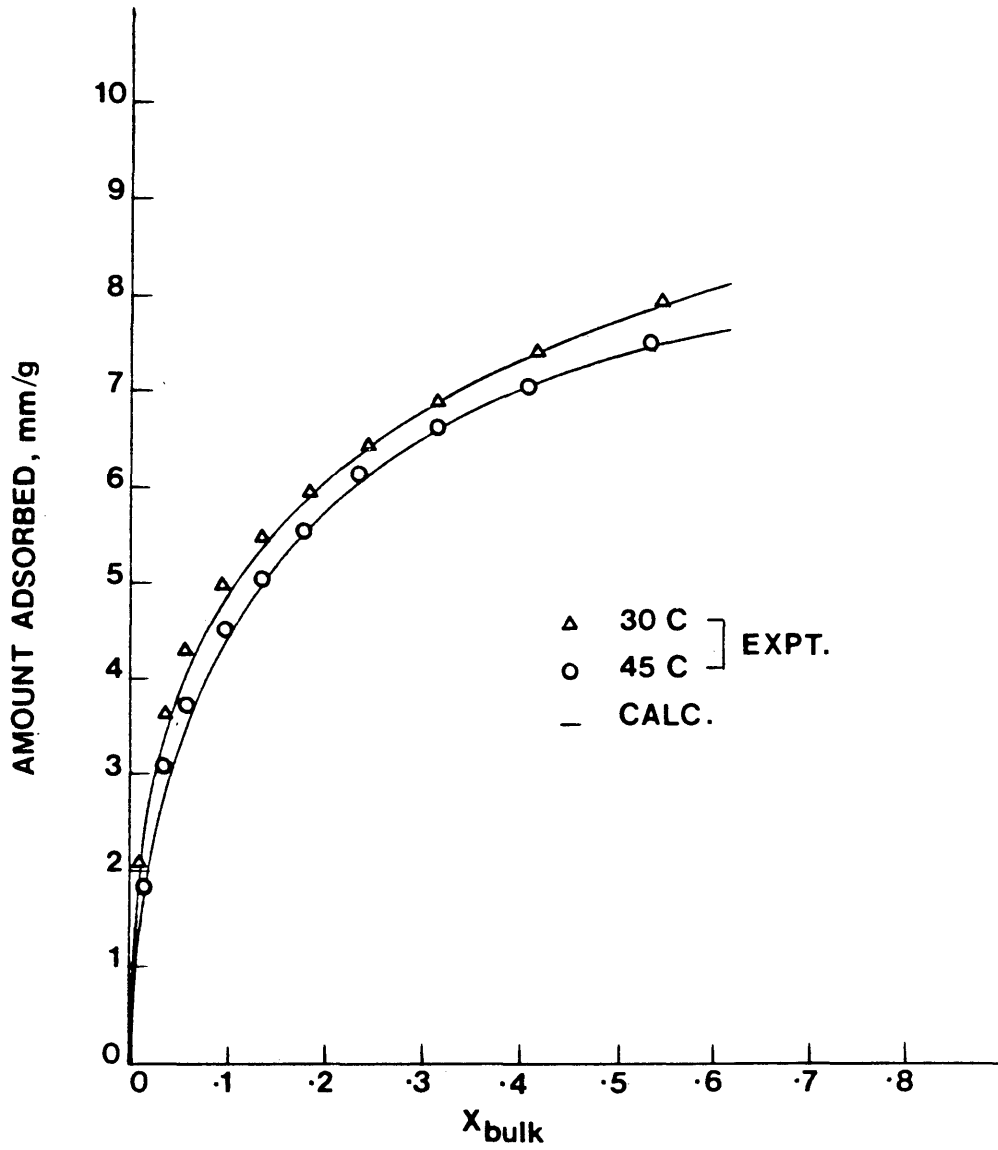


Fig (2) Adsorption of l-Propanol from Aqueous Solution

TABLE IX  
ADSORPTION OF 2-PROPANOL FROM AQUEOUS SOLUTION AT 30 °C

<u>X<sub>1</sub></u> <u>(bulk)</u>	<u>W<sub>1</sub> (exp.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (calc.)</u> <u>(mm/g)</u>
.0122	1.9413	2.011
.0318	3.4167	3.3034
.0575	4.2553	4.2409
.0881	4.8555	4.9067
.1285	5.404	5.4718
.1732	5.8547	5.8994
.2447	6.3407	6.4449
.3069	6.8022	6.7016
.4004	7.3055	7.0431
.5274	7.721	7.5930

TABLE XADSORPTION OF 2-PROPANOL FROM AQUEOUS SOLUTION AT 45 °C

<u>X<sub>1</sub></u> (bulk)	<u>W<sub>1</sub> (exp.)</u> (mm/g)	<u>W<sub>1</sub> (calc.)</u> (mm/g)
.0123	1.8447	1.7584
.0329	2.9965	2.9063
.0594	3.541	3.5495
.0916	4.2603	4.3722
.1333	4.8042	4.8934
.1784	5.3414	5.3786
.2347	6.0779	5.9837
.3133	6.5687	6.4553
.3951	7.0362	6.8785
.5365	7.4739	7.355

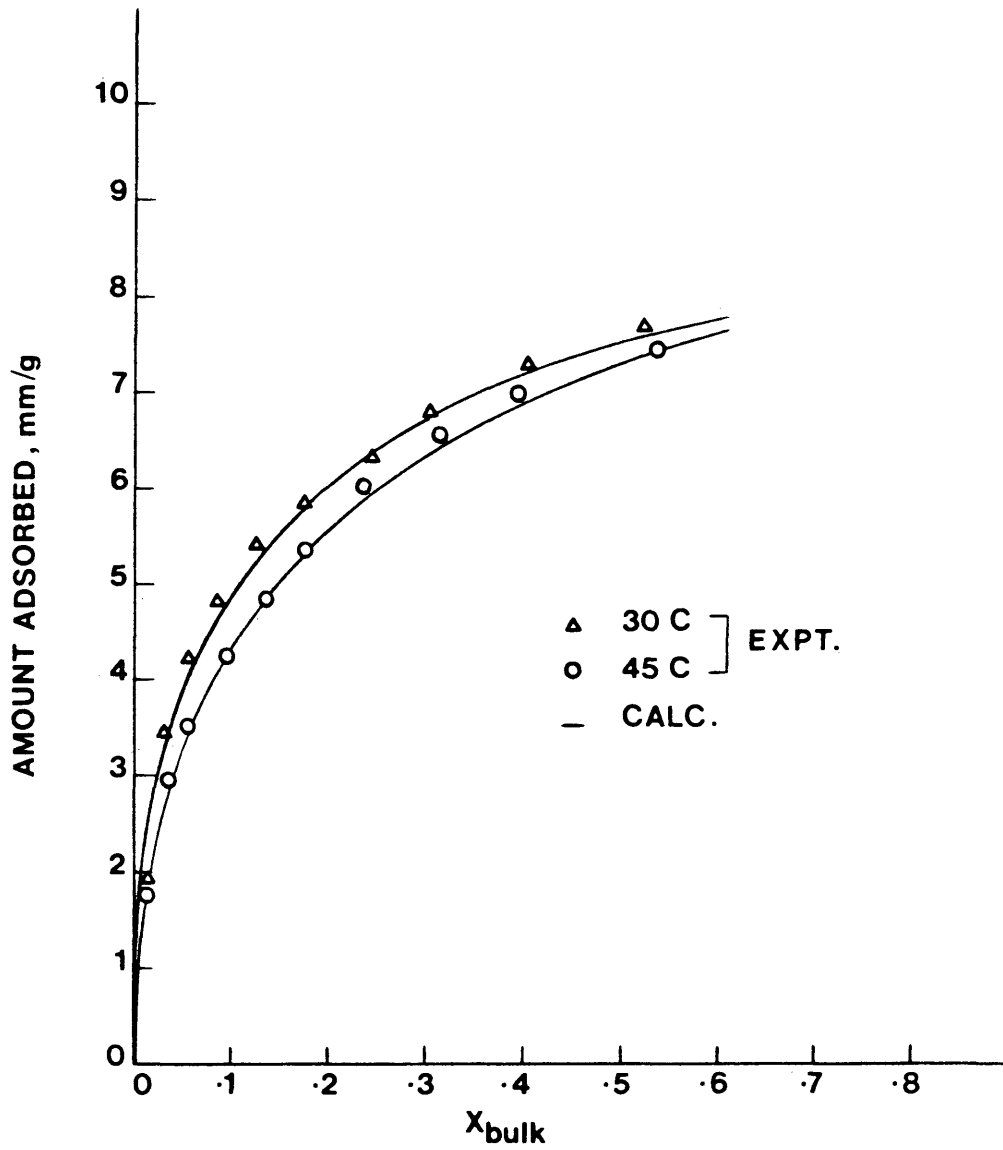


Fig. 3 Adsorption of 2-Propanol from Aqueous Solution

TABLE XIADSORPTION OF 1-BUTANOL FROM AQUEOUS SOLUTION AT 30 °C

<u>LOG<sub>X</sub></u> <u>(bulk)</u>	<u>W<sub>1</sub> (exp.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (calc.)</u> <u>(mm/g)</u>
-6.1658	.9297	.8579
-5.684	1.2565	1.1772
-5.426	1.4365	1.3903
-5.185	1.6527	1.6004
-4.9336	1.8662	1.8344
-4.7677	2.0351	1.9977
-4.6152	2.1676	2.1651
-4.5854	2.1878	2.2025
-4.4741	2.3	2.3367
-4.3125	2.4351	2.5707

TABLE XIIADSORPTION OF 1-BUTANOL FROM AQUEOUS SOLUTION AT 45 °C

<u>LOG X<sub>1</sub></u> <u>(bulk)</u>	<u>W<sub>1</sub> (exp.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (calc.)</u> <u>(mm/g)</u>
-5.684	1.0581	1.1023
-5.3602	1.3203	1.3422
-5.1328	1.5149	1.5351
-4.8665	1.7622	1.7726
-4.6995	1.9189	1.9373
-4.5952	2.0041	2.0495
-4.4654	2.1568	2.1890
-4.3505	2.2878	2.3229
-4.2199	2.40	2.5058
-4.0984	2.4649	2.6735

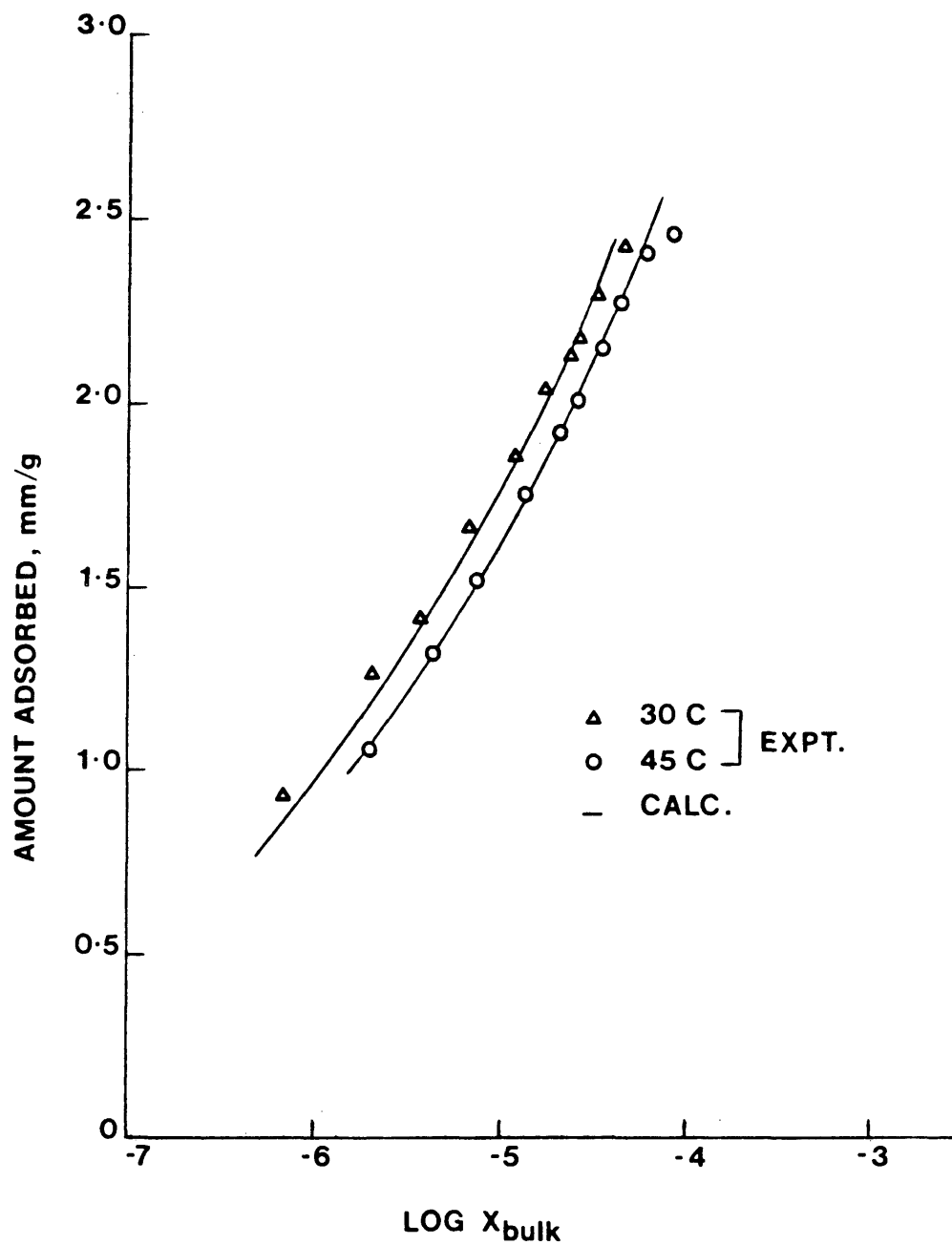


Fig. (4) Adsorption of 1-Butanol from Aqueous Solution

TABLE XIIIADSORPTION OF 1-PENTANOL FROM AQUEOUS SOLUTION AT 30 °C

<u>LOG X<sub>1</sub></u> <u>(bulk)</u>	<u>W<sub>1</sub> (exp.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (calc.)</u> <u>(mm/g)</u>
-7.4186	.475	.5157
-6.9078	.6682	.6790
-6.6454	.8068	.7975
-6.32	.9955	.9847
-6.1193	1.1398	1.1166
-5.7138	1.433	1.4416

TABLE XIVADSORPTION OF 1-PENTANOL FROM AQUEOUS SOLUTION AT 45 °C

<u>LOG X<sub>1</sub></u> <u>(bulk)</u>	<u>W<sub>1</sub> (exp.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (calc.)</u> <u>(mm/g)</u>
-7.2644	.4295	.4951
-6.6454	.6815	.6780
-6.5023	.7608	.7377
-6.2659	.9074	.8596
-6.0323	1.0619	1.0158
-5.6840	1.3511	1.3905

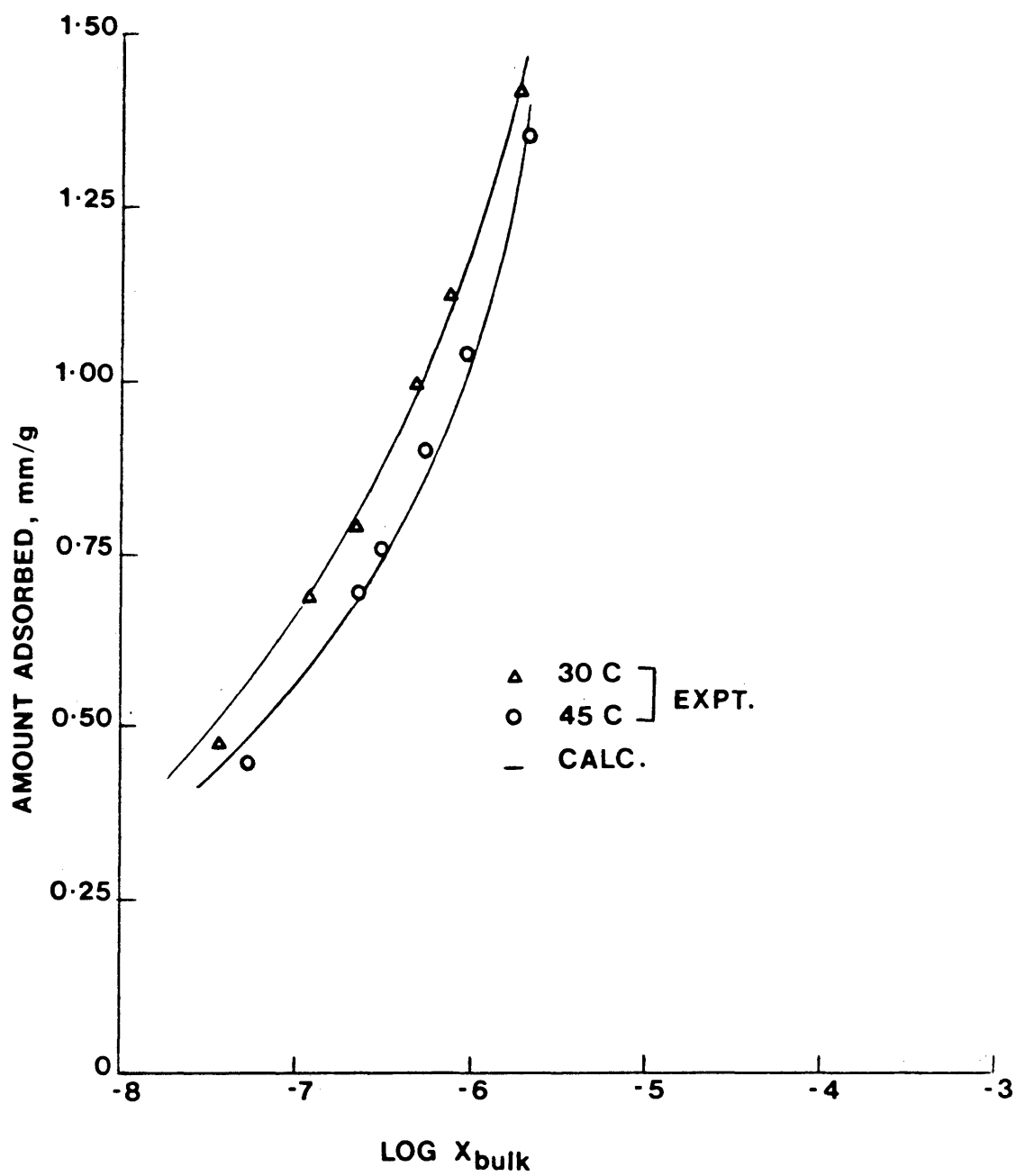


Fig. (5) Adsorption of 1-Pentanol from Aqueous Solution

TABLE XV

ADSORPTION OF BI-SOLUTE(ETHANOL (1) - 1-PROPANOL (2) - WATER (3)) AT 30 °C

$X_1$	$W_1$ (exp.)	$W_1$ (calc.)	$X_2$	$W_2$ (exp.)	$W_2$ (calc.)
_____	<u>(g/g)</u>	<u>(g/g)</u>	_____	<u>(g/g)</u>	<u>(g/g)</u>
.0221	.0682	.0663	.0164	.0822	.0809
.0506	.1153	.1138	.0365	.1319	.1314
.0782	.1488	.1368	.0599	.1712	.1643
.1156	.1720	.1609	.0831	.1845	.1766
.1528	.187	.1815	.1112	.2063	.1974
.1964	.1973	.1997	.1443	.2177	.2151
.2443	.2088	.2140	.1799	.2326	.2274
.2930	.2201	.2258	.2177	.2466	.2389
.3522	.2318	.2335	.2649	.2587	.2468
.4162	.2406	.2456	.3131	.2657	.2571

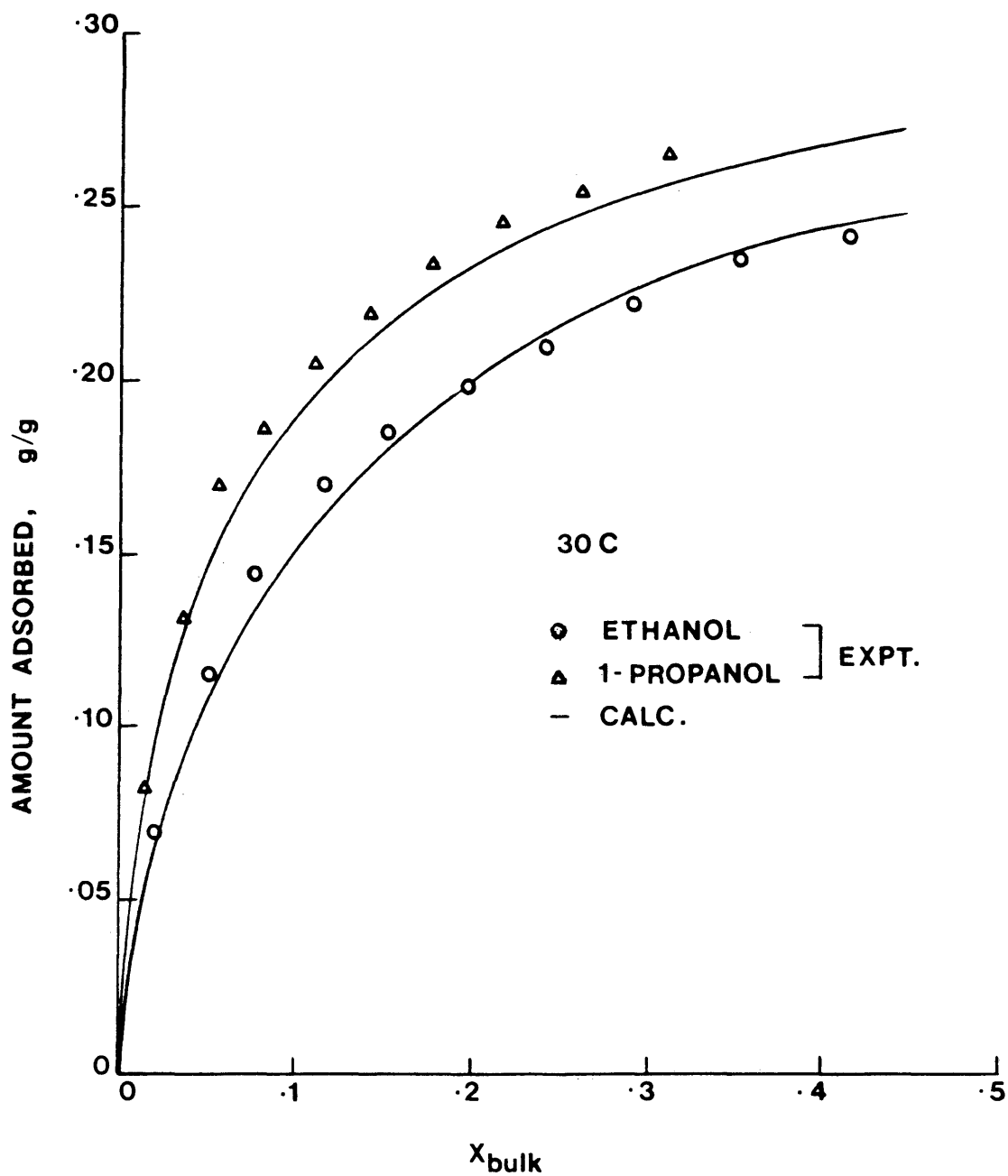


Fig. (6) Adsorption of Bi-solute at 30 °C  
(Ethanol(1)-1-Prop.(2)-Water(3))

TABLE XVIADSORPTION OF BI-SOLUTE SYSTEM AT 30 °C(ETHANOL(1) - 2-PROPANOL(2) - WATER(3))

$X_1$ (bulk)	$W_1$ (exp.) (g/g)	$W_1$ (calc.) (g/g)	$X_2$ (bulk)	$W_2$ (exp.) (g/g)	$W_2$ (calc.) (g/g)
.0222	.0703	.0622	.0158	.0728	.0626
.0497	.119	.1162	.0344	.1366	.116
.0819	.1525	.1601	.057	.1653	.1608
.1147	.1728	.1843	.0814	.1947	.1876
.1550	.1958	.2085	.1092	.198	.2083
.1937	.2103	.2185	.141	.2197	.2201
.2401	.2196	.2296	.1724	.2315	.2281
.2945	.2314	.2402	.2117	.2426	.2364
.3488	.2392	.2446	.2535	.2509	.2412
.411	.2484	.2527	.2956	.2542	.2447

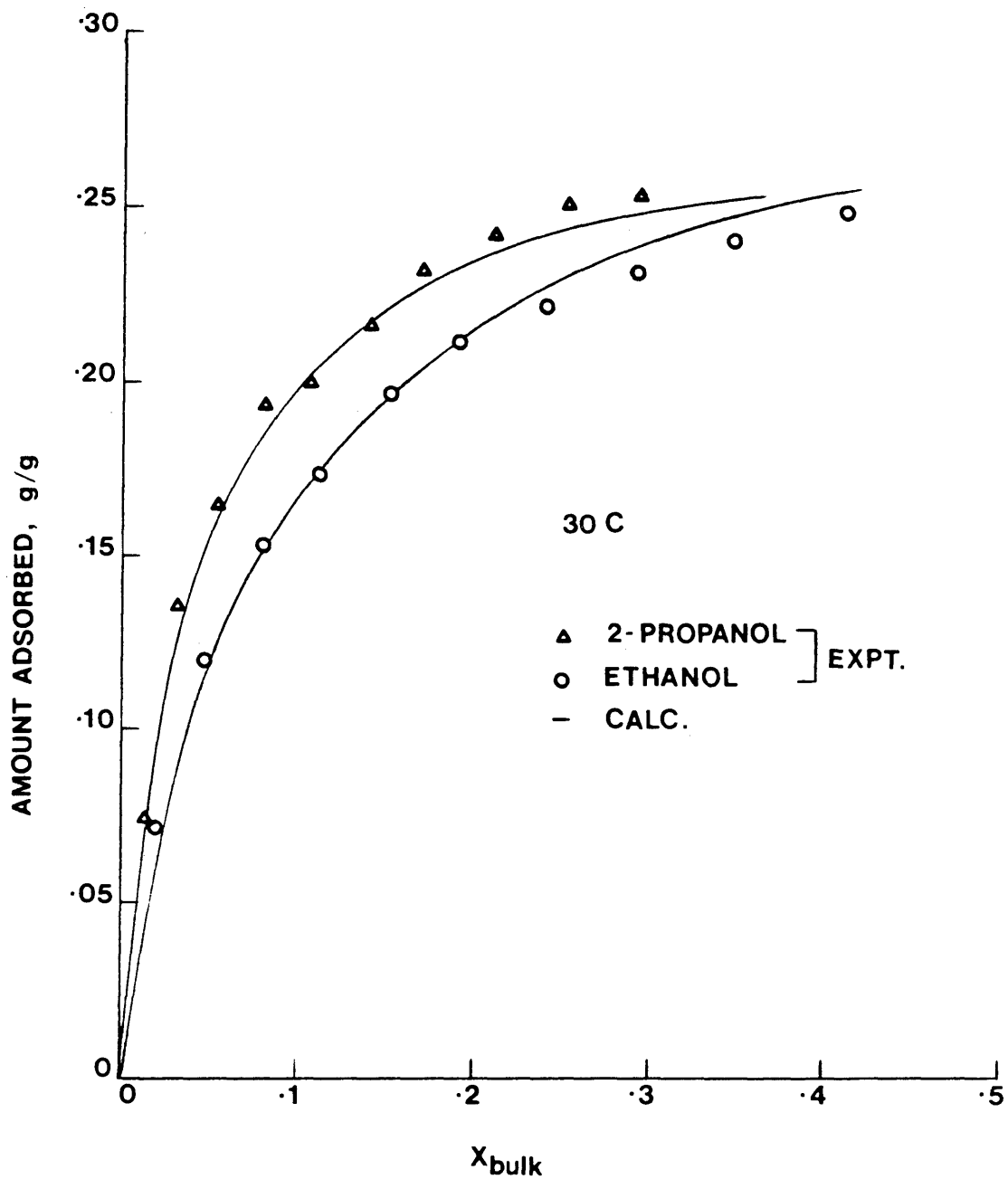


Fig. (7) Adsorption of Bi-solute at 30 °C  
(Ethanol(1)-2-Prop.(2)-Water(3))

TABLE XVIIADSORPTION OF 2-PROPANOL FROM AQUEOUS SOLUTION AT 25 °C (12)

<u>LOG X<sub>1</sub></u> <u>(bulk)</u>	<u>W<sub>1</sub> (exp.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (calc.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (P.T.)*</u> <u>(mm/g)</u>
-4.37	.0864	.0925	.157
-3.87	.1884	.1974	.2748
-3.22	.4142	.4602	.5364
-3.10	.5103	.5272	.6803
-1.93	1.413	1.629	1.9625

\*Potential Theory (12)

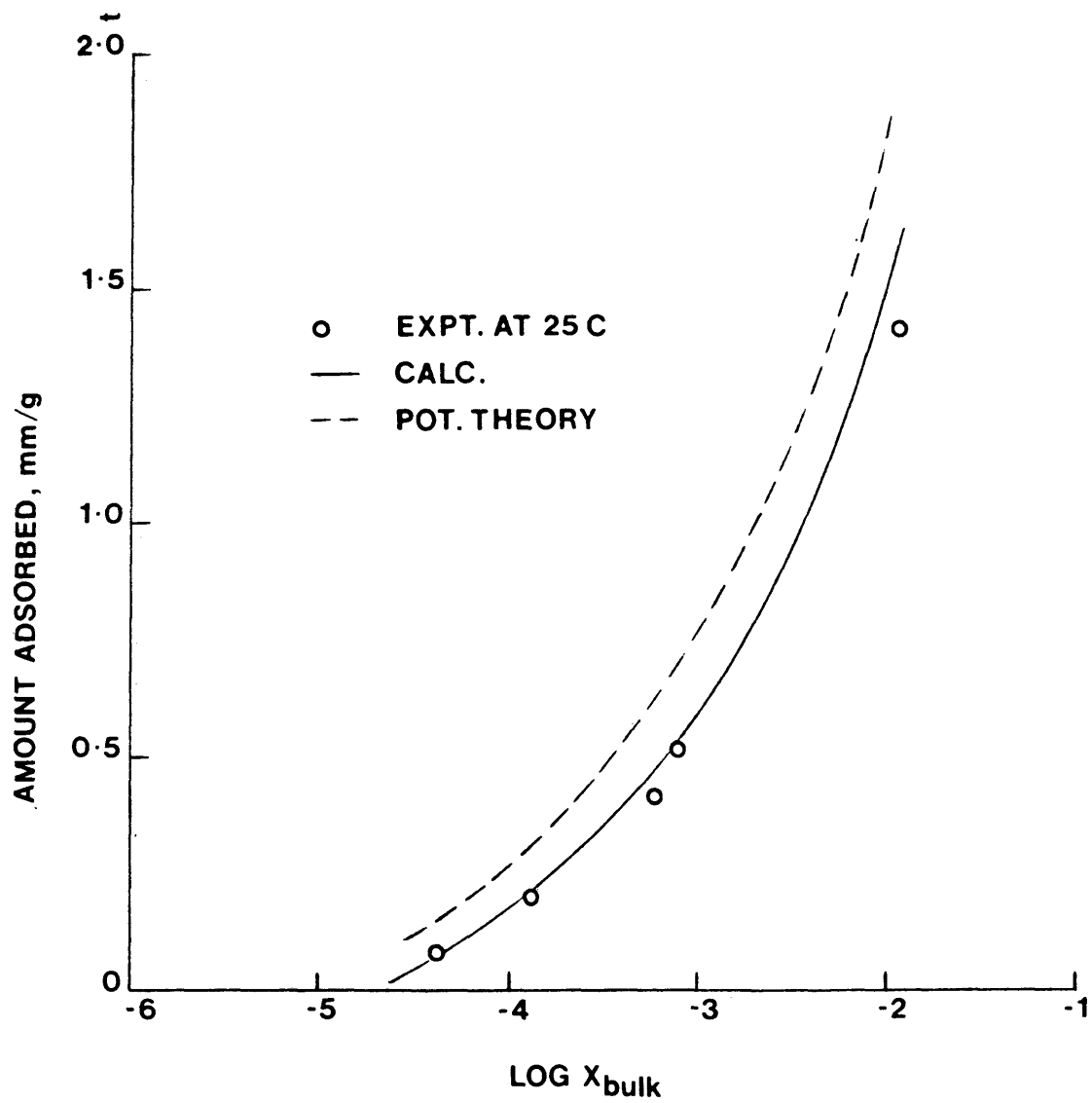


Fig. (8) Adsorption of 2-Propanol from Aqueous Solution

TABLE XIIIADSORPTION OF ACETONE FROM AQUEOUS SOLUTION AT 25 °C (61)

<u>LOG X<sub>1</sub></u> <u>(bulk)</u>	<u>W<sub>1</sub> (exp.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (calc.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (P.T.)</u> <u>(mm/g)</u>
-5.17	.0614	.0626	.0341
-4.72	.1173	.1053	.0696
-3.98	.2428	.2448	.1637
-3.67	.4801	.4857	.2728
-1.94	2.10	2.502	1.6366

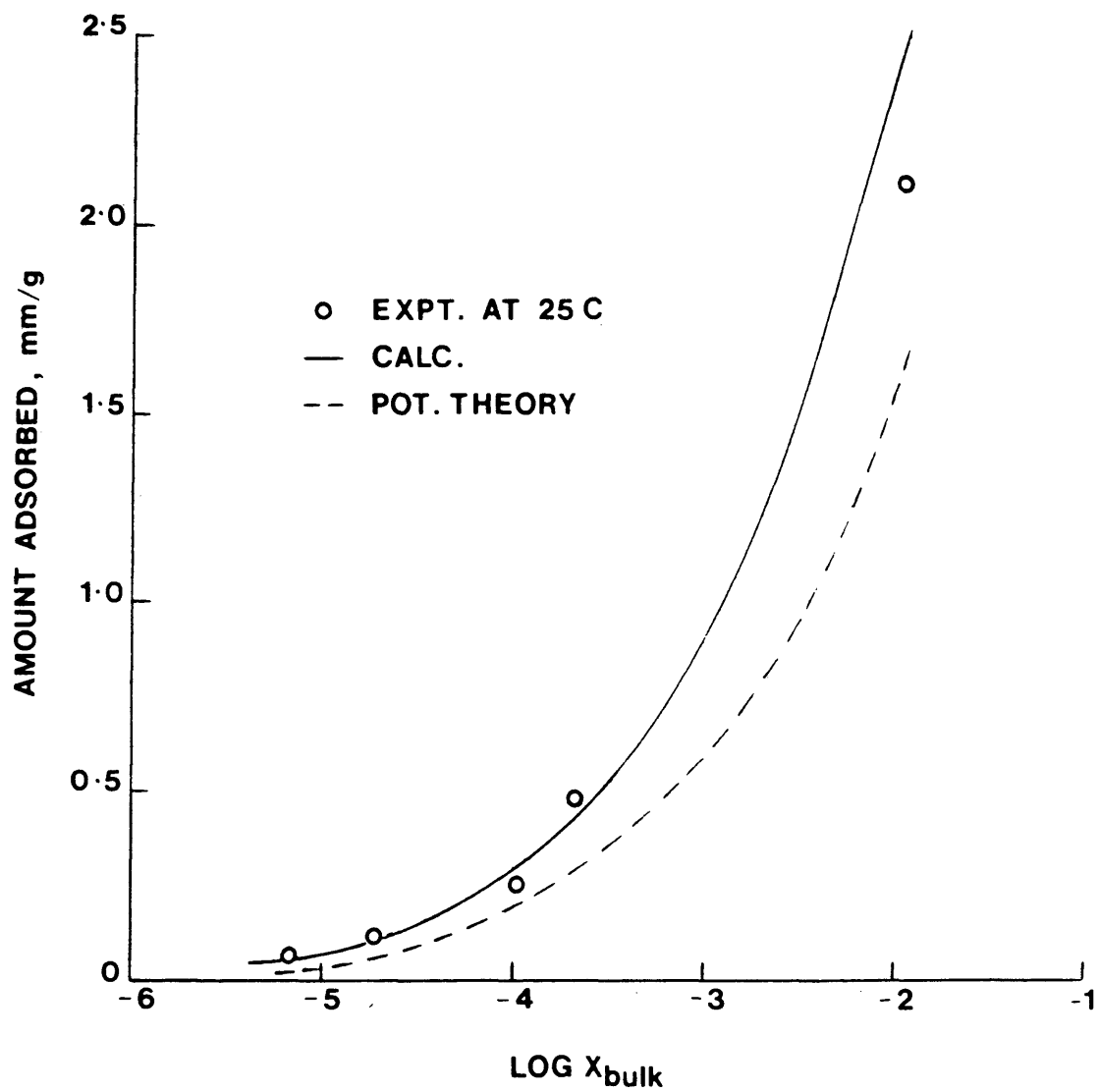


Fig. (9) Adsorption of Acetone from Aqueous Solution

TABLE XIVADSORPTION OF ACETIC ACID FROM AQUEOUS SOLUTION AT 25 °C (61)

<u>LOG X<sub>1</sub></u> <u>(bulk)</u>	<u>W<sub>1</sub> (exp.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (calc.)</u> <u>(mm/g)</u>	<u>W<sub>1</sub> (P.T.)</u> <u>(mm/g)</u>
-4.86	.1592	.1523	.0175
-4.08	.3497	.3407	.0874
-3.5	.577	.6168	.2448
-3.04	.7903	.7795	.4196
-1.82	1.9582	2.2969	1.9582

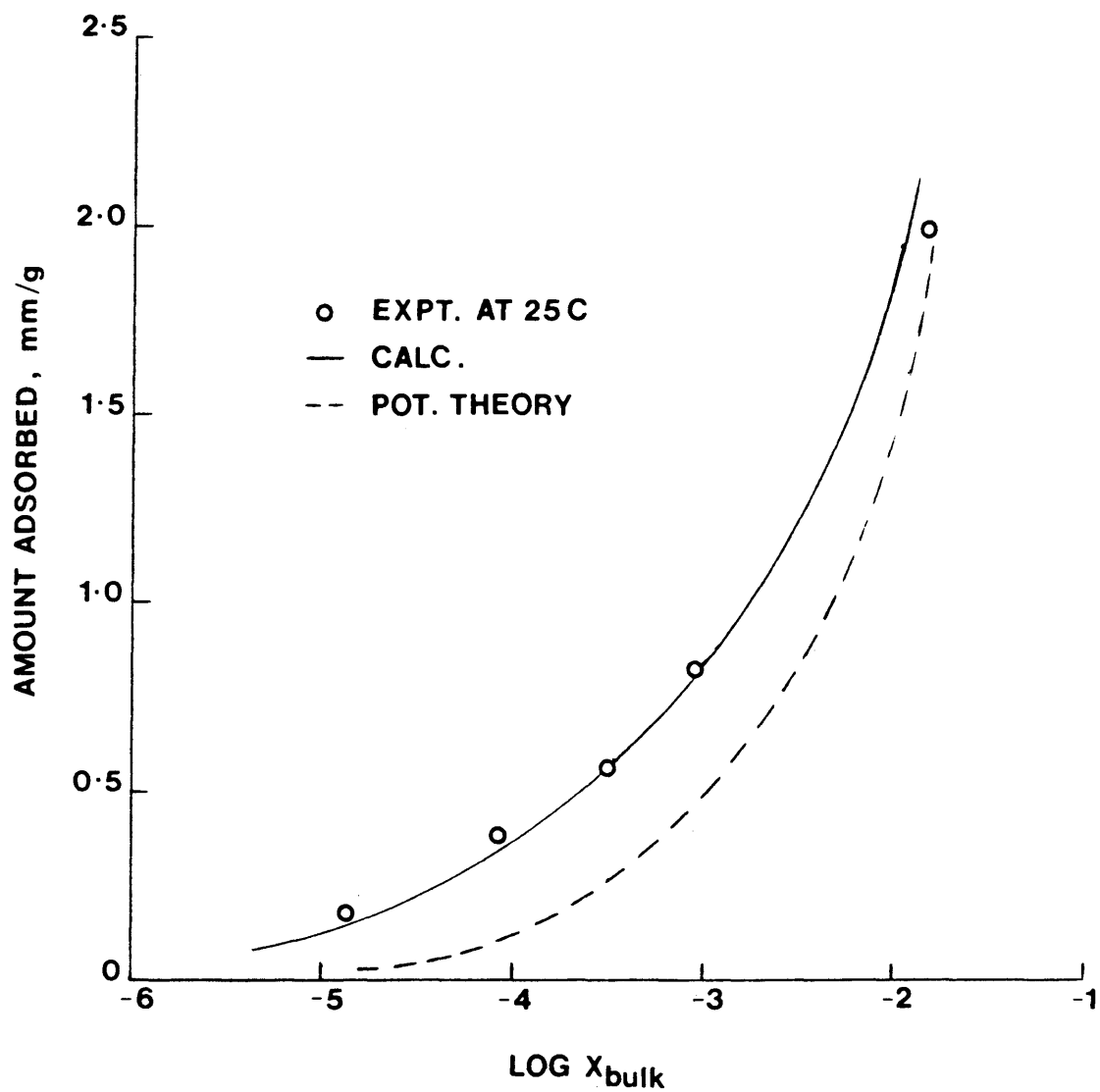


Fig. (10) Adsorption of Acetic Acid from Aqueous Solution

### CONCLUSIONS AND RECOMMENDATIONS

Equilibrium adsorption isotherms for five single solutes, and two bi-solute systems were studied at 30 and 45 °C. The adsorption isotherms covers wide ranges of loading and concentration. Adsorption of an individual component (absolute adsorption) rather than preferential or apparent adsorption which corresponds to the surface excess was determined in all of the above systems.

Determination of absolute adsorption leads to a much better understanding of the phenomena of adsorption and especially of the meaning of preferential adsorption. Using the experimental data for completely single solute adsorption at 30 °C, general thermodynamic correlations were developed to predict single solute systems at 45 °C, and bi-solute system at 30 °C. No bi-solute or single-solute data are required for this correlation, nor is there any restriction on whether or not the solutes are miscible in all proportions with the solvent.

The new developed correlation is more general than that of the potential theory or the ideal adsorbed solution theory. The generality of our correlation not only lies in reducing the study of multi-solute adsorption to the study of single-solute adsorption but also in the generality of the correlations, which is applicable to nonideal adsorption from

nonideal solutions at all concentration.

The new model is the most convenient to use in computer simulations. Its calculation is simple and direct, and an extrapolation beyond the experimental concentration range is not required which is the case in most of the models available in the literature.

Comparison with the potential theory for 2-propanol, acetone, and acetic acid at 25 °C, shows our correlations provide a better representation of these systems. This proves the validity of this correlation when applied to a highly nonideal systems in the bulk phase and in the adsorbed phase.

Beside its generality, the new model is subjected to neither an assumption about the behavior of the adsorbed phase (mobility versus immobility) nor an assumption concerning the characteristics of the solid (homogeneity versus heterogeneity). Nevertheless, these factors are accounted for by the activity coefficient, and the composition dependence of the activity coefficient may be affected by them. Finally extension to multi-solute systems and to mixed solvent systems is straight-forward without any mathematical difficulties.

Although, we conclude that our correlation can be applied to highly nonideal systems, the procedure and techniques developed in this work need further verification using more systems adsorbed on different activated carbons.

APPENDIX A

UNIFAC EQUATION IN BOTH PHASES

Following the development of Abrams (51), in a mixture, the activity coefficient  $\gamma_i$  (for component  $i$ ) is related to  $g^E$ , the excess Gibbs energy per mole of mixture, by

$$n_T g^E = RT \sum_i n_i \ln \gamma_i \quad (A1)$$

$$RT \ln \gamma_i = \left( \frac{\partial n_T g^E}{\partial n_i} \right)_{T,P, n_J (J \neq i)} \quad (A2)$$

To obtain activity coefficients, an expression which gives  $g^E$  as a function of composition, temperature, and pressure is needed. Such an expression is provided by Guggenheim's quasi-chemical lattice theory (51). The most important variable is composition, for liquid mixtures at ordinary pressures, the effect of pressure is negligible. The effect of temperature is not negligible, but often it is not large when consideration is restricted to a moderate temperature range.

For binary mixture containing  $N_1$  molecules of component 1 and  $N_2$  molecules of component 2, the Helmholtz energy of mixing is then given by

$$\Delta A = - kT \ln \frac{Z_{\text{lattice}}(N_1, N_2)}{Z_{\text{lattice}}(N_1, 0) Z_{\text{lattice}}(0, N_2)} \quad (A3)$$

Where  $Z_{\text{lattice}}$  refers to the situation where the center of every segment is coincident with a lattice site and  $k$  is Boltzmann's constant.

When attention is restricted to mixtures of nonelectrolyte liquids at low or modest pressures, we can substitute

for the excess Gibbs energy of mixing at constant temperature and pressure, the excess Helmholtz energy of mixing at constant temperature and volume.

$$g^E = \frac{\Delta A}{n_1 + n_2} - RT (x_1 \ln x_1 + x_2 \ln x_2) \quad (\text{A4})$$

Where R is the gas constant, x stands for mole fraction, and n for the number of moles.

Following Guggenheim, the lattice partition function is given by (51):

$$Z_{\text{lattice}} = \sum_{\text{all}} \omega(\theta) \exp(-U_0(\theta)/kT) \quad (\text{A5})$$

Where  $\omega$  is the combinatorial factor (number of ways that molecules can be arranged in space).

$$\omega = \omega_1 \omega_2 h(N_1, N_2) \quad (\text{A6})$$

$U_0$  is the potential energy of the lattice, that is the energy required to remove all molecules from the lattice.

Both  $\omega$  and  $U_0$  depend on the molecular configuration of the mixture, designated by the variable  $\theta$ . The molecular configuration of a mixture can be represented by the local area fraction, for example, the local area fraction for the two different molecules 1 and 2 can be explained as follows:

The composition of a region in the immediate vicinity of molecule 1. The local area fraction  $\theta_{21}$  is the fraction of external sites around molecule 1 which are occupied by segments of molecule 2. Similarly, local area fraction  $\theta_{11}$

is the fraction of external sites around molecule 1 which are occupied by segments of (another) molecule 1. A similar definition holds for  $\theta_{12}$  and  $\theta_{22}$ .

For a binary mixture, therefore, we have four local area fractions which describe the microstructure of the lattice; however only two of these are independent because

$$\theta_{11} + \theta_{21} = 1 \quad (\text{A7})$$

$$\theta_{12} + \theta_{22} = 1 \quad (\text{A8})$$

Equations (A7) and (A8) can be written for the adsorbed phase, representing the effect of the adsorbent.

$$\theta_{11} + \theta_{21} + \theta_{s1} = 1 \quad (\text{A9})$$

$$\theta_{12} + \theta_{22} + \theta_{s2} = 1 \quad (\text{A10})$$

$$\theta_{1s} + \theta_{2s} + \theta_{ss} = 1 \quad (\text{A11})$$

Where s represent the adsorbent.

The next derivation will be restricted to binary mixture, and extension to multicomponent is straightforward.

The lattice energy  $U_0$  is the sum of all interaction energies between pairs of nonbonded segments.

$$\begin{aligned} -U_0 = & \left(\frac{Z}{2}\right) q_1 N_1 (\theta_{11} U_{11} + \theta_{21} U_{21}) \\ & + \left(\frac{Z}{2}\right) q_2 N_2 (\theta_{22} U_{22} + \theta_{21} U_{12}) \end{aligned} \quad (\text{A12})$$

Where  $U_{ij}$  characterizes the energy of interaction between sites i and j. The number of external nearest neighbors is given by  $Zq$ , for a molecule of component 1, where

Z is the coordination number of the lattice and  $q_1$  is a parameter proportional to the molecule's external surface area. For convenience let  $U_{ij} = \left(\frac{Z}{2}\right) U_{ij}$ . Equation (A12) then becomes

$$-U_o = q_1 N_1 (\theta_{11} U_{11} + \theta_{21} U_{21}) + q_2 N_2 (\theta_{22} U_{22} + \theta_{12} U_{12}) \quad (\text{A13})$$

The minus sign in equation (A13) follows from the convention that the potential energy of the ideal-gas state (infinite separation between molecules) is taken as zero. In equation (A6), the number of distinguishable configurations  $\omega_1$  and  $\omega_2$  are approximated by

$$\omega_1 = \frac{(q_1 N_1 \theta_{11} + q_2 N_2 \theta_{12})!}{(q_1 N_1 \theta_{11})! (q_1 N_1 \theta_{21})!} \quad (\text{A14})$$

$$\omega_2 = \frac{(q_2 N_2 \theta_{22} + q_1 N_1 \theta_{21})!}{(q_2 N_2 \theta_{22})! (q_2 N_2 \theta_{12})!} \quad (\text{A15})$$

$$q_1 N_1 \theta_{21} = q_2 N_2 \theta_{12} \quad (\text{A16})$$

The function h depends only on  $N_1$  and  $N_2$ , it is a normalization factor to assume that the combinatorial factor satisfies a physically reasonable boundary condition. In UNIFAC the boundary condition is the combinatorial factor of Staverman (51) for mixtures of molecules with arbitrary size and shape but no attractive forces. To find h, the athermal case (all  $U_{ij}=0$  and therefore  $U_o=0$ ) has to be considered.

In equation (A5), the maximum term in the summation is found by separate differentiation with respect to  $\theta_{11}$  and  $\theta_{22}$ , and by setting the results equal to zero. Omitting mathematical details, the average local area fractions for an athermal mixture are given by (2):

$$\theta_{11}^{(o)} = \frac{q_1 N_1}{q_1 N_1 + q_2 N_2} \quad (A17)$$

$$\theta_{22}^{(o)} = \frac{q_2 N_2}{q_1 N_1 + q_2 N_2} \quad (A18)$$

Therefore, h can be found by substituting equations (A14) to (A18) into equation (A6):

$$h(N_{11}N_2) = \frac{\omega^o (q_1 N_1 \theta_{11}^{(o)})! (q_1 N_1 \theta_{21}^{(o)})! (q_2 N_2 \theta_{22}^{(o)})! (q_2 N_2 \theta_{12}^{(o)})!}{(q_1 N_1 \theta_{11}^{(o)} + q_2 N_2 \theta_{12}^{(o)})! (q_2 N_2 \theta_{22}^{(o)} + q_1 N_1 \theta_{21}^{(o)})!} \quad (A19)$$

Where  $\omega^o$  is the combinatorial factor given by Staverman.

Mass balance constraints give:

$$\theta_{12}^{(o)} = \theta_{11}^{(o)} = \theta_1 = \frac{q_1 N_1}{q_1 N_1 + q_2 N_2} \quad (A20)$$

$$\theta_{21}^{(o)} = \theta_{22}^{(o)} = \theta_2 = \frac{q_2 N_2}{q_1 N_1 + q_2 N_2} \quad (A21)$$

In the athermal case, therefore, the average local area fractions are the same as the average area fractions donated by  $\theta_1$  and  $\theta_2$ .

For the nonathermal case, that is, where  $U_{ij} \neq 0$ , and

$U_0 \neq 0$ , the resulting expression for  $Z_{\text{lattice}}$  is separately differentiated with respect to  $\theta_{11}$  and  $\theta_{22}$  and the result are set equal to zero. The average local area fractions are given by

$$\theta_{11}^{(1)} = \frac{\theta_1}{\theta_1 + \theta_2 \exp \frac{-(u_{21} - u_{11})}{RT}} \quad (22)$$

and

$$\theta_{22}^{(1)} = \frac{\theta_2}{\theta_2 + \theta_1 \exp \frac{-(u_{12} - u_{22})}{RT}} \quad (23)$$

Where superscript (1) denotes nonathermal case.

### Combinatorial Part

The combinatorial excess Gibbs energy per mole of the mixture is given by

$$g_{\text{comb}}^E = \frac{-RT}{N_1 + N_2} \ln \frac{\omega^{\circ}(N_1, N_2)}{\omega^{\circ}(N_1, 0) \omega^{\circ}(0, N_2)} - RT (x_1 \ln x_1 + x_2 \ln x_2) \quad (24)$$

$\omega^{\circ}$  is given by Staverman:

$$\omega(N_1, N_2) = \frac{(\rho_1)^{N_1} (\rho_2)^{N_2}}{N_1! N_2!} \left( \frac{(N_1 q_1 + N_2 q_2)!}{(r_1 N_1 + r_2 N_2)!} \right)^{\frac{1}{2}} (N_1 r_1 + N_2 r_2)! \quad (25)$$

Where  $\rho$  is the molar density, and  $r_1$  is the number of segments per molecule of component 1.

By using Stirling approximation:

$$\ln N! = N \ln N - N \quad (\text{A26})$$

$$\begin{aligned} \frac{\ln \omega^{\circ}(N_1, N_2)}{\omega^{\circ}(N_1, 0) \omega^{\circ}(0, N_2)} &= \ln \omega^{\circ}(N_1, N_2) - \ln \omega^{\circ}(N_1, 0) - \ln \omega^{\circ}(0, N_2) \\ &= \frac{Z}{2} N_1 q_1 \ln \frac{1}{\theta_1} + \frac{Z}{2} q_2 N_2 \ln \frac{1}{\theta_2} \\ &\quad + \left(\frac{qz}{2} - 1\right) r_1 N_1 \ln \phi_1 + \left(\frac{qz}{2} - 1\right) r_2 N_2 \ln \phi_2 \quad (\text{A27}) \end{aligned}$$

$$\frac{g_{\text{comb}}^E}{RT} = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \frac{Z}{2} (q_1 x_1 \ln \frac{\theta_1}{\phi_1} + q_2 x_2 \ln \frac{\theta_2}{\phi_2}) \quad (\text{A28})$$

By using equation (A2), the combinatorial activity coefficient is given by

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + \left(\frac{Z}{2}\right) q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (\text{A29})$$

$$\text{Where } l_j = \left(\frac{Z}{2}\right) (r_j - q_j) - (r_j - 1) \quad (\text{A30})$$

and where the average area fraction  $\theta$  and the average segment fraction  $\phi$  are defined by

$$\theta_i = \frac{q_i N_i}{\sum_j q_j N_j} = \frac{q_i x_i}{\sum_j q_j x_j} \quad (\text{A31})$$

$$\phi_i = \frac{r_i N_i}{\sum_j r_j N_j} = \frac{r_i x_i}{\sum_j r_j x_j} \quad (\text{A32})$$

Where  $x$  is the mole fraction. The combinatorial part was applied directly in the adsorbed phase without any modification. The summations in equation (A29) through (A32) are over all adsorbate only.

Residual Part

The residual excess Gibbs energy per mole of the mixture is given by

$$\begin{aligned} \frac{-E_R}{RT} &= \frac{1}{N_1+N_2} \ln \frac{Z_1(N_1, N_2)}{Z_1(N_1, 0) Z_1(0, N_2)} \\ &= \frac{1}{N_1+N_2} (\ln \omega_1 + \ln \omega_2 + \ln h(N_1, N_2) + \Delta(\text{exp})) \quad (\text{A33}) \end{aligned}$$

Where

$$\begin{aligned} \ln \omega_1 + \ln \omega_2 &= q_1 N_1 \theta_{11} \ln \frac{1}{\theta_{11}} + q_1 N_1 \theta_{21} \ln \frac{1}{\theta_{21}} \\ &\quad + q_2 N_2 \theta_{22} \ln \frac{1}{\theta_{22}} + q_2 N_2 \theta_{12} \ln \frac{1}{\theta_{12}} \quad (\text{A34}) \end{aligned}$$

$$\ln h(N_1, N_2) = q_1 N_1 \ln \theta_1 + q_2 N_2 \ln \theta_2 \quad (\text{A35})$$

$$\Delta(\text{exp}) = q_1 N_1 \theta_{21} \ln \tau_{21} + q_2 N_2 \theta_{12} \ln \tau_{12} \quad (\text{A36})$$

$$\tau_{21} = \exp \left[ - \frac{u_{21} - u_{11}}{RT} \right] \quad (\text{A37})$$

$$\tau_{12} = \exp \left[ - \frac{u_{12} - u_{22}}{RT} \right] \quad (\text{A38})$$

Substitute equations (A34) to (A38) into (A33)

$$\frac{-E_R}{RT} = -q_1 x_1 \ln(\theta_1 + \theta_2 \tau_{21}) - q_2 x_2 \ln(\theta_2 + \theta_1 \tau_{12}) \quad (\text{A39})$$

Equation (A39) for multicomponent system becomes

$$\frac{-g_R^E}{RT} = - \sum_i q_i x_i \ln \left( \sum_j \theta_j \tau_{ji} \right) \quad (\text{A40})$$

By using equation (A2), the residual activity coefficient is given by

$$\ln \gamma_i^R = q_i \left[ 1 - \ln \left( \sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right] \quad (\text{A41})$$

in equation (A41), the  $i$ 's represent the adsorbate groups only, and  $K, J$  represent the adsorbate groups and the adsorbent.

APPENDIX B

UNIFAC COMPUTER PROGRAM

```

C==== MAIN PROGRAM UNIF.F4 =====
C==== THIS PROGRAM USE UNIFAC TO CALCULATE =====
C==== THE ACTIVITY COEF. IN BOTH PHASES =====
C==== BY USING THE DEVELOPED PRAMETERS EPS =====
C==== ALONG WITH UNIFAC PRAMETERS EPS WHICH ARE =====
C==== AVAILABLE IN THE LITRATUPE =====
C==== CAP=1 BULK PHASE ACT. CALCULATION =====
C==== CAP=2 ADS. PHASE ACT. CALCULATION =====
C==== COP=1 OPTIMIZATION OF THE INTER. PRAM. =====
C==== COP=2 PRINT-OUT FOR THE CALCULATED =====
C==== ADSORBED PHASE COMPOSITION =====
C==== THE PROGRAM CAN BE USED TO CALCULATE =====
C==== THE ADSORBED PHASE COMP. IF THE =====
C==== ACT. COEF. IN BOTH PHASES ARE KNOWN =====
      DIMENSION Q1(10),Q2(10),R1(10),R2(10),AP1(10),
1      XP2(10),EXD1(40),EXD2(40),EP1(10,10),EP2(10,10)
1      ,F(40),XB1(40),XB2(40),ACP1(40),ACB2(40)
1      ,XD1(40),XD2(40),ACD1(40),ACD2(40),EXCA1(40)
1      ,EXCA2(40),XDC1(40),XDC2(40)
      COMMON Q1,Q2,P1,R2,XP1,XP2,XB1,XB2,ACB1,ACB2,
1      EXD1,EXD2,XD1,XD2,ACD1,ACD2,SQ11,SQ12,SQ21,SQ22,
1      SP12,SP22,SP21,EO1,EO2,ET1,ET2,ER1,ER2,EF1,EF2,
1      TQ1,TQ2,TT1,TT2,TR1,TR2,TF1,TF2,ES1,ES2,TS1,TS2,
1      N1,N2,NG1,NG2,EG1,EG2,EG3,TG1,TG2,TG3,NDP,DNP,F
1      ,EXCA1,EXCA2,XDC1,XDC2,SR11
      DATA EP1(1,1)/1./,EP1(1,2)/1./,EP1(1,3)/.0386/,
1      EP1(1,4)/.01295/,EP1(2,1)/1./,EP1(2,2)/1./,
1      EP1(2,3)/.0386/,EP1(2,4)/.01295/,EP1(3,1)/.597/,
1      EP1(3,2)/.597/,EP1(3,3)/1./,EP1(3,4)/.31164/,
1      EP1(4,1)/.37178/,EP1(4,2)/.37178/,EP1(4,4)/1./,
1      EP1(4,3)/2.1289/,EP2(1,1)/1./,EP2(1,2)/.37178/,
1      EP2(1,3)/.37178/,EP2(1,4)/2.1289/,EP2(2,2)/1./,
1      EP2(2,1)/.01295/,EP2(2,3)/1./,EP2(2,4)/.0386/,
1      EP2(3,1)/.01295/,EP2(3,2)/1./,EP2(3,3)/1./,
1      EP2(3,4)/.0386/,EP2(4,1)/.31164/,EP2(4,2)/.597/,
1      EP2(4,3)/.597/,EP2(4,4)/1./,SQ11/2.588/,SQ12/1.4/,
1      SP11/2.5755/,SP12/.92/,SQ21/1.4/,SQ22/2.588/,
1      SP21/.92/,SP22/2.5755/,Q1(1)/.848/,Q1(2)/.54/,
1      Q1(3)/1.2/,Q1(4)/1.4/,Q2(1)/1.4/,Q2(2)/.848/,
1      Q2(3)/.54/,Q2(4)/1.2/,R1(1)/.9011/,R1(2)/.6744/,
1      R1(3)/1./,R1(4)/.92/,R2(1)/.92/,R2(2)/.9011/,
1      R2(3)/.6744/,R2(4)/1./,EO1/1./,ET1/1./,ER1/1./,
1      EF2/1./,TQ1/1./,TT2/1./,TR2/1./,TF2/1./,
1      XP1(1)/.3333/,XP1(2)/.3333/,XP1(3)/.3333/,
1      XP2(1)/1./,ES1/3./,ES2/1./,TS1/1./,TS2/3./,
1      N1/3/,N2/1/,NG1/5/,NG2/5/,EG1/1./,EG2/1./,
1      EG3/1./,TG1/1./,ND1/1/,ND2/2/,NDP/36/,DNP/36./
      READ(ND1,84) (XP1(J),J=1,NDP)
      READ(ND2,84) (EXD1(J),J=1,NDP)
      FORMAT(5F)
      WRITE(4,85)

```

```

85   FORMAT(/, ' CAP ', '/')
      READ(4,86) CAP
86   FORMAT(1F)
      C==== CALCULATE THE BULK PHASE ACT. COEF. =====
          CALL UNIT5(EP1,EP2,CAP,1)
          DO 27 I=1,NBP
      C==== FOR PREDICTION ASSUME STARTING VALUE OF =====
      C==== ADSORBED PHASE COMP. HERE =====
      C==== OPTIMIZATION OF THE UNIFAC PARAMETERS =====
      C==== IN THE ADSORBED PHASE =====
          WRITE(4,88) XE1(I),ACF1(I),XE2(I),ACF2(I)
88   FORMAT(4F12.5)
27   CONTINUE
87   CONTINUE
          WRITE(4,89)
89   FORMAT(/, ' EP1(5,1),EP1(3,5),EP1(4,5) ', '/')
          READ(4,90) EP1(5,1),EP1(3,5),EP1(4,5)
90   FORMAT(3F)
          WRITE(4,91)
91   FORMAT(/, ' DT,DP,DA,EP1(1,5),DT1,CAP,COP,IN ', '/')
          READ(4,99) DT,DP,DA,EP1(1,5),DT1,CAP,COP,IN
99   FORMAT(7F,1I)
          IF(COP.EQ.2.) GO TO 112
          IF(COP.EQ.3.) GO TO 115
          IF(COP.EQ.0.) GO TO 120
          IND=1
          CALL UNIT5(EP1,EP2,CAP,1)
          IF(IN=1) 92,93,92
93   DO 94 I=2,9
94   F(I)=F(1)
          GO TO 100
92   EP1(5,1)=EP1(5,1)+DT
          CALL UNIT5(EP1,EP2,CAP,2)
          EP1(5,1)=EP1(5,1)-DT
          EP1(3,5)=EP1(3,5)+DP
          CALL UNIT5(EP1,EP2,CAP,3)
          EP1(3,5)=EP1(3,5)-DP
          EP1(4,5)=EP1(4,5)+DA
          CALL UNIT5(EP1,EP2,CAP,4)
          EP1(4,5)=EP1(4,5)-DA
          EP1(1,5)=EP1(1,5)+DT1
          CALL UNIT5(EP1,EP2,CAP,5)
          EP1(1,5)=EP1(1,5)-DT1
          EP1(5,1)=EP1(5,1)-DT
          CALL UNIT5(EP1,EP2,CAP,6)
          EP1(5,1)=EP1(5,1)+DT
          EP1(3,5)=EP1(3,5)-DP
          CALL UNIT5(EP1,EP2,CAP,7)
          EP1(3,5)=EP1(3,5)+DP
          EP1(4,5)=EP1(4,5)-DA
          CALL UNIT5(EP1,EP2,CAP,8)

```

```

      EP1(4,5)=EP1(4,5)+DA
      EP1(1,5)=EP1(1,5)-DT1
      CALL UNIT5(EP1,FP2,CAP,9)
      EP1(1,5)=EP1(1,5)+DT1
      NF=1
      DO 95 I=2,9
95    IF(F(I).LT.F(NL)) NE=I
      IF(NE.EQ.1) GO TO 100
      IF(NE.EQ.2) EP1(5,1)=EP1(5,1)+DT
      IF(NE.EQ.3) EP1(3,5)=EP1(3,5)+DP
      IF(NE.EQ.4) EP1(4,5)=EP1(4,5)+DA
      IF(NE.EQ.5) EP1(1,5)=EP1(1,5)+DT1
      IF(NE.EQ.6) EP1(5,1)=EP1(5,1)-DT
      IF(NE.EQ.7) EP1(3,5)=EP1(3,5)-DP
      IF(NE.EQ.8) EP1(4,5)=EP1(4,5)-DA
      IF(NE.EQ.9) EP1(1,5)=EP1(1,5)-DT1
      F(1)=F(NL)
      WRITE(4,96) F(1)
96    FORMAT(1F12.5)
      INL=INL+1
      IF(INL.GT.14) GO TO 100
      GO TO 92
100   CONTINUE
      C==== FOR THE NEXT ITERATION LET THE ADSORBED =====
      C==== PHASE COMP. EQUAL TO THE CALCULATED VALUE =====
      WRITE(4,97)
97    FORMAT(/,'EP1(5,1),EP1(3,5),EP1(4,5),EP1(1,5),'/)
      WRITE(4,98) EP1(5,1),EP1(3,5),EP1(4,5),EP1(1,5)
98    FORMAT(5F12.5)
      C==== F(1) IS THE STANDARD DEVIATION =====
      WRITE(4,175)
175   FORMAT(/,' F(1) ,'/)
      WRITE(4,176) F(1)
176   FORMAT(1F12.5)
      GO TO 87
112   CONTINUE
      DO 113 N=1,NL
      C==== PRINT OUT OF THE CALCULATED ADSORBED =====
      C==== PHASE COMPOSITION =====
      WRITE(4,114) XDC1(N),EXD1(N),XDC2(N),EXD2(N)
114   FORMAT(4F12.5)
113   CONTINUE
      GO TO 87
115   CONTINUE
      DO 116 I=1,NL
      WRITE(4,118) XL1(I),ACD1(I),XD2(I),ACD2(I)
118   FORMAT(4F12.5)
116   CONTINUE
      GO TO 87
120   CONTINUE
      END

```

```

SUBROUTINE UNIT5(EP1,EP2,CAP,NE)
C===== CALCULATE ACTIVITY COEF. IN BOTH PHASES=====
  DIMENSION Q1(10),Q2(10),R1(10),R2(10),XP1(10),XP2(10),
  1 XC1(40),XC2(40),EP1(10,10),EP2(10,10),ELAC(40),GR(40),
  1 ACT1(40),ACT2(40),B1(40),B2(40),D1(40),D2(40),DIF(40),
  1 F(40),F2(40),XB1(40),XB2(40),XD1(40),XD2(40),
  1 ACH1(40),ACH2(40),ACD1(40),ACD2(40),CA1(40),CA2(40)
  1 ,DIF1(40),ADC1(40),XDC2(40),XP2(10),GR(40)
  1 ,EXCA1(40),EXCA2(40),EXD1(40),EXD2(40),DIF(40)
  COMMON Q1,Q2,R1,R2,XP1,XP2,XB1,XB2,ACH1,ACH2,
  1 EXD1,EXD2,XD1,XD2,ACD1,ACD2,SQ11,SQ12,SQ21,SQ22,
  1 SF12,SP22,SP21,ED1,ED2,ET1,ET2,ER1,ER2,EF1,EF2,
  1 TO1,TO2,TT1,TT2,TR1,TR2,TF1,TF2,ES1,ES2,TS1,TS2,
  1 N1,N2,NG1,NG2,EG1,EG2,EG3,TG1,TG2,TG3,NDP,DNF,F
  1 ,EXCA1,EXCA2,XDC1,XDC2,SR11
  IF(EP1(5,1).LT.0.0) EP1(5,1)=.001
  IF(EP1(3,5).LT.0.0) EP1(3,5)=.001
  IF(EP1(4,5).LT.0.0) EP1(4,5)=.001
  EP1(5,2)=EP1(5,1)
  EP2(1,5)=EP1(4,5)
  EP2(5,2)=EP1(5,1)
  EP2(5,3)=EP1(5,1)
  EP2(4,5)=EP1(3,5)
  IF(EP1(1,5).LT.0.0) EP1(1,5)=.001
  EP1(2,5)=EP1(1,5)
  EP1(5,3)=1.
  EP1(5,4)=1.
  EP1(5,5)=1.
  EP2(5,1)=1.
  EP2(2,5)=EP1(1,5)
  EP2(3,5)=EP1(1,5)
  EP2(5,4)=1.
  EP2(5,5)=1.
  F(NP)=0.0
  DO 10 J=1,NDP
  IF(CAP.EQ.1.) XC1(J)=XB1(J)
  IF(CAP.EQ.2.) XC1(J)=XD1(J)
  IF(CAP.EQ.1.) VP=1.
  IF(CAP.EQ.1.) S=0.0
  IF(CAP.EQ.2.) VP=1.121
  IF(CAP.EQ.2.) S=.0614
  XC2(J)=1.-XC1(J)
  IF(J.LE.12) GO TO 36
  IF(J.LE.24) GO TO 37
  IF(J.LE.36) GO TO 38
C===== ETHANOL-WATER SYSTEM =====
36 SQ11=2.588
   SF11=2.5755
   Q1(2)=.54
   R1(2)=.6744
   EP1=1.

```

```

      ET1=1.
      EG1=1.
      EG2=1.
      AP1(1)=.3333
      XP1(2)=.3333
      XP1(3)=.3333
      ES1=3.
      GO TO 40
C==== 1-PROPANOL-WATER SYSTEM =====
37      SQ11=3.128
      Q1(2)=.54
      SF11=3.2499
      R1(2)=.6744
      EP1=1.
      ET1=2.
      EG1=1.
      EG2=2.
      ES1=4.
      AP1(1)=.25
      XP1(2)=.5
      XP1(3)=.25
      GO TO 40
C==== 2-PROPANOL-WATER SYSTEM =====
38      SQ11=3.124
      SF11=3.2491
      Q1(2)=.228
      R1(2)=.4469
      EP1=2.
      ET1=1.
      EG1=2.
      EG2=1.
      ES1=4.
      AP1(1)=.5
      XP1(2)=.25
      AP1(3)=.25
      GO TO 40
40      SQ22=SQ11
      SF22=SF11
      TT2=EP1
      TR2=ET1
      Q2(3)=Q1(2)
      R2(3)=R1(2)
      TS2=ES1
      I1=J
      I2=J
      IF(XC1(J).EQ.0.0) GO TO 16
      CALL UNIT1(XC1,SQ11,SQ12,SF11,SF12,I1,CA1)
16      CONTINUE
      IF(CAP.EQ.1.) GO TO 25
      IF(J.EQ.11.OR.J.EQ.12) GO TO 25

```

```

IF(J.EQ.23.OR.J.EQ.24) GO TO 25
IF(J.EQ.35.OR.J.EQ.36) GO TO 25
IF(CAP.EQ.2.) GO TO 27
25 CALL UNIT4(Q1,XP1,EP1,N1,B1)
GO TO 30
27 CALL UNIT6(Q1,R1,XP1,EP1,N1,B1,VP,S)
30 CONTINUE
CALL UNIT3(Q1,R1,XC1,EP1,ES1,ES2,EO1,EO2,ET1,ET2,
1 EF1,EP2,EF1,EF2,NG1,N1,I1,D1,VP,S,CAP)
GP(J)=EG1*(D1(1)-R1(1))+EG2*(D1(2)-R1(2))
1 +EG3*(D1(3)-R1(3))
ELAC(J)=CA1(J)+GP(J)
ACT1(J)=EXP(ELAC(J))
IF(CAP.EQ.1.) ACH1(J)=ACT1(J)
IF(CAP.EQ.1.) XB1(J)=XC1(J)
IF(CAP.EQ.2.) XD1(J)=XC1(J)
IF(CAP.EQ.2.) ACD1(J)=ACT1(J)
IF(XC2(J).EQ.0.0) GO TO 17
CALL UNIT1(XC2,SQ21,SQ22,SR21,SR22,I2,C#2)
17 CONTINUE
IF(CAP.EQ.1.) GO TO 35
IF(J.EQ.11.OR.J.EQ.12) GO TO 35
IF(J.EQ.23.OR.J.EQ.24) GO TO 35
IF(J.EQ.35.OR.J.EQ.36) GO TO 35
IF(CAP.EQ.2.) GO TO 137
35 CALL UNIT4(Q2,XP2,EP2,N2,B2)
GO TO 140
137 CALL UNIT2(Q2,P2,XP2,EP2,N2,B2,VP,S)
140 CONTINUE
CALL UNIT3(Q2,R2,XC2,EP2,TS1,TS2,TO1,TO2,T11,TT2,
1 TF1,TR2,TF1,TF2,NG2,N2,I2,D2,VP,S,CAP)
GP(J)=TG1*(D2(1)-B2(1))+TG2*(D2(2)-B2(2))
1 +TG3*(D2(3)-B2(3))
ELAC(J)=CA2(J)+GP(J)
ACT2(J)=EXP(ELAC(J))
IF(CAP.EQ.1.) XB2(J)=XC2(J)
IF(CAP.EQ.1.) ACB2(J)=ACT2(J)
IF(CAP.EQ.2.) XD2(J)=XC2(J)
IF(CAP.EQ.2.) ACD2(J)=ACT2(J)
10 CONTINUE
IF(CAP.EQ.1.) GO TO 15
FFF1=ACD2(12)/ACD1(11)
CALL U8(FER1,ACB1,ACB2,XB1,XB2,ACD1,ACD2,
1 1,10,XDC1,XDC2,XD1,XD2,EXD1,EXD2,SUM1)
FFF2=ACD2(24)/ACD1(23)
CALL U8(FER2,ACB1,ACB2,XB1,XB2,ACD1,ACD2,
1 13,22,XDC1,XDC2,XD1,XD2,EXD1,EXD2,SUM2)
FER3=ACD2(36)/ACD1(35)
CALL U8(FER3,ACB1,ACB2,XB1,XB2,ACD1,ACD2,
1 25,34,XDC1,XDC2,XD1,XD2,EXD1,EXD2,SUM3)
SUM=SUM1+SUM2+SUM3

```

```
15      F(NE)=SQRT(SUM/60.)  
      CONTINUE  
      RETURN  
      END
```

```
      SUBROUTINE UNIT1(X1,SQ1,SQ2,SR1,SR2,IY,CA)
C==== COMBINATORIAL ACTIVITY COEFFICIENT =====
      DIMENSION X1(40),X2(40),PH(40),TH(40),CA(40)
      I=IY
      X2(I)=1.-X1(I)
      PH(I)=SR1*X1(I)/(SR1*X1(I)+SR2*X2(I))
      TH(I)=SQ1*X1(I)/(SQ1*X1(I)+SQ2*X2(I))
      EL1=5.*(SP1-SQ1)-(SR1-1.)
      EL2=5.*(SP2-SQ2)-(SR2-1.)
      A1=ALOG(PH(I)/X1(I))
      B1=CCP*SQ1*(ALOG(TH(I)/PH(I)))
      C1=PH(I)*(X1(I)*EL1+X2(I)*EL2)/X1(I)
      CA(I)=A1+B1+EL1-C1
      RETURN
      END
```

```

      SUBROUTINE UNIT2(Q,R,XP,EPS,NI,B,VP,S)
      C==== STANDARD ACTIVITY COEFFECIENT=====
      C==== UNIT2.F4 CALC. THE GROUP =====
      C==== ACT. COEF. IN ITS SOLUTION WITH THE =====
      C==== ADSORBENT =====
      DIMENSION Q(10),R(10),XP(10),EPS(10,10),B(40),
1    TE(10),EPSR(10,10)
      S1=0.0
      S2=0.0
      EPSR(1,1)=1.
      EPSR(2,1)=EPS(5,1)
      EPSR(1,2)=EPS(1,5)
      EPSR(2,2)=1.
      DO 10 I=1,NI
10    S1=S1+Q(I)*XP(I)
      S2=S2+R(I)*XP(I)
      DO 12 I=1,NI
      E1=VP*Q(I)*XP(I)/S2
      E2=(VP*S1/S2)+S
12    TE(I)=E1/E2
      TE(NI+1)=1.-TE(1)
      DO 14 K=1,NI
      SUM1=0.0
      SUM2=0.0
      SUM3=0.0
      DO 15 M=1,NI+1
15    SUM1=SUM1+TE(M)*EPSR(M,K)
      A=(1.)-ALOG(SUM1)
      DO 16 M=1,NI+1
      SUM2=0.0
      X=TE(M)*EPSR(K,M)
      DO 18 N=1,NI+1
18    SUM2=SUM2+TE(N)*EPSR(N,M)
16    SUM3=SUM3+(X/SUM2)
14    B(K)=Q(K)*(A-SUM3)
      RETURN
      END

```

```

SUBROUTINE UNIT3(Q,R,X1,EPS1,SN1,SN2,O1,O2,T1,T2,
1  K1,R2,F1,F2,NG,NGI,IJ,D,VP,S,CAP)
C==== RESIDUAL ACTIVITY COEF. =====
DIMENSION Q(10),R(10),A1(40),X2(40),EPS1(10,10),
1  GX(10),ST(10),D(40)
X2(IJ)=1.-X1(IJ)
SUM4=SN1*X1(IJ)+SN2*X2(IJ)
GX(1)=(O1*X1(IJ)+O2*X2(IJ))/SUM4
GX(2)=(T1*A1(IJ)+T2*A2(IJ))/SUM4
GX(3)=(P1*X1(IJ)+P2*X2(IJ))/SUM4
GX(4)=(F1*X1(IJ)+F2*X2(IJ))/SUM4
SUM5=0.0
SUM10=0.0
DO 10 K=1,NG-1
SUM5=SUM5+Q(K)*GX(K)
10  SUM10=SUM10+R(K)*GX(K)
DO 12 K=1,NG-1
E3=VP*Q(K)*GX(K)/SUM10
E4=(VP*SUM5/SUM10)+S
12  ST(K)=E3/E4
ST(5)=1.-ST(1)-ST(2)-ST(3)-ST(4)
DO 14 K=1,NGI
SUM6=0.0
SUM7=0.0
SUM8=0.0
DO 16 M=1,NG
16  SUM6=SUM6+ST(M)*EPS1(M,K)
C=1.-ALOG(SUM6)
IF(CAP.EQ.1.) JN=4
IF(CAP.EQ.2.) JN=5
DO 18 N=1,JN
SUM7=0.0
Y=ST(M)*EPS1(K,M)
DO 20 N=1,NG
20  SUM7=SUM7+ST(N)*EPS1(N,M)
18  SUM8=SUM8+Y/SUM7
14  D(K)=Q(K)*(C-SUM8)
RETURN
END

```

```

      SUBROUTINE UNIT4(Q,XP,EPS,NI,P)
      C==== REFERENCE ACTIVITY COEFFICIENT =====
      DIMENSION Q(10),XP(10),EPS(10,10),TE(10),B(40)
      S1=0.0
      DO 10 I=1,NI
10      S1=S1+Q(I)*XP(I)
      DO 12 I=1,NI
12      TF(I)=Q(I)*XP(I)/S1
      DO 14 K=1,NI
      SUM1=0.0
      SUM2=0.0
      SUM3=0.0
      DO 15 M=1,NI
15      SUM1=SUM1+TE(M)*EPS(M,K)
      A=1.-ALOG(SUM1)
      DO 16 M=1,NI
      SUM2=0.0
      X=TE(M)*EPS(K,M)
      DO 18 N=1,NI
18      SUM2=SUM2+TE(N)*EPS(N,M)
15      SUM3=SUM3+(X/SUM2)
14      B(K)=Q(K)*(A-SUM3)
      RETURN
      END

```

```

SUBROUTINE UNIT6(Q,P,XP,EP,NI,R,VP,S)
C==== STANDARD ACTIVITY COEFFICIENT =====
  DIMENSION Q(10),R(10),XP(10),EP(10,10),B(20),
  1 TE(10),EPSR(10,10),P(10,10)
  S1=0.0
  S2=0.0
  EPSR(1,1)=1.
  EPSR(2,2)=1.
  EPSR(3,3)=1.
  EPSR(1,2)=EP(1,2)
  EPSR(1,3)=EP(1,3)
  EPSR(2,1)=EP(2,1)
  EPSR(2,3)=EP(2,3)
  EPSR(3,1)=EP(3,1)
  EPSR(3,2)=EP(3,2)
  EPSR(4,1)=EP(5,1)
  EPSR(4,2)=EP(5,2)
  EPSR(4,3)=EP(5,3)
  EPSR(1,4)=EP(1,5)
  EPSR(2,4)=EP(2,5)
  EPSR(3,4)=EP(3,5)
  EPSR(4,4)=1.
  DO 10 I=1,NI
  S1=S1+Q(I)*XP(I)
10 S2=S2+R(I)*YP(I)
  DO 12 I=1,NI
  E1=VP*Q(I)*XP(I)/S2
  E2=(VP*S1/S2)+S
12 TE(I)=E1/E2
  TE(NI+1)=1.-TE(1)-TE(2)-TE(3)
  DO 14 K=1,NI
  SUM1=0.0
  SUM2=0.0
  SUM3=0.0
  DO 15 M=1,NI+1
15 SUM1=SUM1+TE(M)*EPSR(M,K)
  A=(1.-TE(4))-A*LOG(SUM1)
  DO 16 M=1,NI+1
  SUM2=0.0
  X=TE(M)*EPSR(M,M)
  DO 18 N=1,NI+1
18 SUM2=SUM2+TE(N)*EPSR(N,M)
16 SUM3=SUM3+(X/SUM2)
14 E(K)=Q(K)*(A-SUM3)
  RETURN
  END

```

```

SUBROUTINE US(FER,ACB1,ACB2,XB1,XB2,ACD1,ACD2,
1  M1,M2,XDC1,XDC2,XD1,XD2,EXD1,EXD2,SUM)
C==== CALCULATE ADSORBED PHASE COMPOSITION =====
  DIMENSION ACB1(40),ACB2(40),XB1(40),XB2(40),
1  XD2(40),ACD1(40),ACD2(40),EXD1(40),EXD2(40),
1  RA1(40),RA2(40),DIF(40),DIF1(40),RA(40)
1  ,XD1(40),XDC1(40),XDC2(40)
  SUM=0.0
  DO 10 I=M1,M2
    RA1(I)=(ACB1(I)*XB1(I))/(ACB2(I)*XB2(I))
    RA2(I)=FER*RA1(I)*ACD2(I)/(ACD1(I))
    XDC1(I)=RA2(I)/(1.+RA2(I))
    XDC2(I)=1.-XDC1(I)
    EXD2(I)=1.-EXD1(I)
    DIF(I)=(EXD1(I)-XDC1(I))/EXD1(I)
    DIF1(I)=(EXD2(I)-XDC2(I))/EXD2(I)
10  SUM=SUM+DIF(I)**2+DIF1(I)**2
  RETURN
  END

```

TABLE XV  
LIST OF VARIABLES FOR UNIFAC PROGRAM

Q1	Group surface area constant
R1	Group volume constant
EPS	Interaction parameters
XB	Mole fraction in the bulk phase
XD	Mole fraction in the adsorbed phase
ACB	Activity coefficient in the bulk phase
ACD	Activity coefficient in the adsorbed phase
XP	Fraction of the group in its solution
EXD	Experimental adsorbed phase composition
XDC	Calculated adsorbed phase composition
NDP	Number of data points, constant
DNP	Number of data points, variable
F	Standard deviation
ES,TS	Total number of groups
PH	Molecular volume fraction
TH	Molecular surface area fraction
CA	Combination activity coefficient
GR	Residual activity coefficient
B	Referance activity coefficient of the group
D	Residual activity coefficient of the group
GX	Mole fraction of the group in the solution
VP	Pore volume



APPENDIX C  
SAMPLE OF CALCULATION

The sample of calculation for 1-propanol(1)-water(2) is as follows:

Bulk Phase

$$x_1 = .1334 \quad x_2 = .8666$$

Combinatorial Part

$$\ln \gamma_1^c = \ln \frac{\phi_1}{x_1} + \left(\frac{z}{2}\right) q_1 \ln \frac{\theta_1}{\phi_1} + l_1 - \frac{\phi_1}{x_1} (x_1 l_1 + x_2 l_2) \quad (C1)$$

$$l_1 = \frac{z}{2} (r_1 - q_1) - (r_1 - 1) \quad (C2)$$

$$q_1 = \frac{z}{2} (r_2 - q_2) - (r_2 - 1) \quad z = 10 \quad (C3)$$

$$\begin{aligned} q_1 &= 3.128 & q_2 &= 1.4 \\ r_1 &= 3.2499 & r_2 &= .92 \\ l_1 &= -1.6404 & l_2 &= -2.32 \end{aligned}$$

The surface area fraction  $\theta_1$  and the volume fraction are given by:

$$\theta_1 = \frac{q_1 x_1}{q_1 x_1 + q_2 x_2} \quad (C4)$$

$$\phi_1 = \frac{r_1 x_1}{r_1 x_1 + r_2 x_2} \quad (C5)$$

$$\begin{aligned} \theta_1 &= .25592, & \theta_2 &= .74408 \\ \text{and } \phi_1 &= .35224, & \phi_2 &= .64776 \\ \ln \gamma_1^c &= .22093 \\ \text{and } \ln \gamma_2^c &= .02571 \end{aligned}$$

Residual Part

The activity coefficient of the group in its solution (Reference activity coefficient) is given by equation (25). 1-propanol contains 1 CH<sub>3</sub>(1), 2 CH<sub>2</sub>(2), and 1 OH(3), water contains 1 H<sub>2</sub>O(4). The activity coefficient of CH<sub>3</sub>(1) in its solution is given by:

$$\begin{aligned} \ln \Gamma_1^{(1)} = & q_1 \left[ 1 - \ln(\theta_{11}^{\tau_{11}} + \theta_{21}^{\tau_{21}} + \theta_{31}^{\tau_{31}}) - \right. \\ & - \frac{\theta_{11}^{\tau_{11}}}{\theta_{11}^{\tau_{11}} + \theta_{21}^{\tau_{21}} + \theta_{31}^{\tau_{31}}} - \frac{\theta_{21}^{\tau_{12}}}{\theta_{11}^{\tau_{12}} + \theta_{21}^{\tau_{22}} + \theta_{31}^{\tau_{32}}} - \\ & \left. - \frac{\theta_{31}^{\tau_{13}}}{\theta_{11}^{\tau_{13}} + \theta_{21}^{\tau_{23}} + \theta_{31}^{\tau_{33}}} \right] \end{aligned} \quad (C6)$$

The surface area fraction of the group in its solution is given by:

$$\theta_1 = \frac{q_1 x_1}{q_1 x_1 + q_2 x_2 + q_3 x_3} \quad (C7)$$

where  $q_1$ ,  $q_2$ , and  $q_3$  are the group surface area parameters which are given in Table (II).

$$q_1 = .848 \qquad q_2 = .54 \qquad q_3 = 1.2$$

$x_1$ ,  $x_2$ , and  $x_3$  are the mole fraction of the group in its solution.

$$\begin{aligned} x_1 = .25 & \qquad x_2 = .5 & \qquad x_3 = .25 \\ \theta_1 = .2711 & \qquad \theta_2 = .3453 & \qquad \theta_3 = .3836 \end{aligned}$$

By using the adsorbate-adsorbate interaction parameters, Table (III) at 30°C, and by using equation (29), the reference activity coefficient of each group are:

$$\begin{aligned} \ln \Gamma_1^{(1)} &= .848 \quad 1 - \ln((.2711)(1) + (.3453)(1) + .3836(.597)) - \\ &\quad - \frac{(.2711)(1)}{.2711(1) + .3453(1) + .3836(.597)} - \\ &\quad - \frac{(.3453)(1)}{(.2711)(1) + .3453(1) + .3836(.597)} - \\ &\quad - \frac{(.3836)(.0386)}{(.2711)(.0386) + (.3453)(.0386) + (.3836)(1)} \\ &= .3413 \\ \ln \Gamma_2^{(1)} &= .21734 \\ \ln \Gamma_3^{(1)} &= .62532 \end{aligned}$$

The activity coefficient of each group in the solution of 1-propanol(1)-water(2) is given by equation (26):

$$\begin{aligned} \ln \Gamma_1 &= q_1 \left[ 1 - \ln(\theta_1^{\tau_{11}} + \theta_2^{\tau_{21}} + \theta_3^{\tau_{31}} + \theta_4^{\tau_{41}}) - \right. \\ &\quad - \frac{\theta_1^{\tau_{11}}}{\theta_1^{\tau_{11}} + \theta_2^{\tau_{21}} + \theta_3^{\tau_{31}} + \theta_4^{\tau_{41}}} - \\ &\quad \left. - \frac{\theta_2^{\tau_{12}}}{\theta_1^{\tau_{12}} + \theta_2^{\tau_{22}} + \theta_3^{\tau_{32}} + \theta_4^{\tau_{42}}} - \right] \end{aligned}$$

$$\begin{aligned}
 & - \frac{\theta_{3^{\tau}13}}{\theta_{1^{\tau}13} + \theta_{2^{\tau}20} + \theta_{3^{\tau}33} + \theta_{4^{\tau}43}} - \\
 & - \frac{\theta_{4^{\tau}14}}{\theta_{1^{\tau}14} + \theta_{2^{\tau}24} + \theta_{3^{\tau}34} + \theta_{4^{\tau}44}} \quad (C6)
 \end{aligned}$$

The surface area fraction of the group in the solution is given by equation (27):

$$\theta_1 = \frac{q_1 x_1}{q_1 x_1 + q_2 x_2 + q_3 x_3 + q_4 x_4} \quad (C7)$$

where  $x_1$ ,  $x_2$ ,  $x_3$ , and  $x_4$  are the mole fraction of the group in the solution.

$$\begin{aligned}
 x_1 &= .0953, & x_2 &= .1905 \\
 x_3 &= .0953, & x_4 &= .6189 \\
 \theta_1 &= .0694, & \theta_2 &= .0883 \\
 \theta_3 &= .0982, & \theta_4 &= .7441
 \end{aligned}$$

By substitution in equation (C6):

$$\begin{aligned}
 \ln \Gamma_1 &= 1.16408 \\
 \ln \Gamma_2 &= .74128 \\
 \ln \Gamma_3 &= -.08574
 \end{aligned}$$

The residual activity coefficient of 1-propanol is the combination of residual activity coefficient of its groups:

$$\begin{aligned}
 \ln \gamma_1^R &= (1.16408 - .3413) + 2(.74128 - .21734) + \\
 &+ (.62532 - (-.08574)) = 1.1596
 \end{aligned}$$

The activity coefficient of 1-propanol is given by equation (20):

$$\ln\gamma_1 = .22093 + 1.1596 = 1.38053$$

$$\gamma_1 = 3.97701$$

By following the same procedure, the activity coefficient of water  $\gamma_2 = 1.10346$ .

### Adsorbed Phase

Knowing the adsorbate-adsorbent interactions Table (IV), the calculation of the activity coefficient in the adsorbed phase and prediction of the amount adsorbed is straight forward.

1. Assume a value of the composition in the adsorbed phase for the first iteration.

$$\text{Let } x'_1 = .244, \quad x'_2 = .756$$

2. Use equations (20) through (35) to calculate  $\gamma'_1$  and  $\gamma'_2$ . Equations (C1) through (C5) for the combinatorial part are the same in the adsorbed without any modification.

$$\ln\gamma_1^c = .0884, \quad \ln\gamma_2^c = .0549$$

The residual part activity coefficient of the group is the activity coefficient of the group in the solution and the adsorbent less the activity coefficient in its solution and the adsorbent.

The activity coefficient of the group in its solution and the adsorbent is given by:

$$\begin{aligned}
\ln \Gamma_1^{(1)} &= q_1 \cdot 1 - \ln(\theta_1^{\tau_{11}} + \theta_2^{\tau_{21}} + \theta_3^{\tau_{31}} + \theta_s^{\tau_{s1}}) - \\
&\quad - \frac{\theta_1^{\tau_{11}}}{\theta_1^{\tau_{11}} + \theta_2^{\tau_{21}} + \theta_3^{\tau_{31}} + \theta_s^{\tau_{s1}}} - \\
&\quad - \frac{\theta_2^{\tau_{12}}}{\theta_1^{\tau_{12}} + \theta_2^{\tau_{22}} + \theta_3^{\tau_{32}} + \theta_s^{\tau_{s2}}} - \\
&\quad - \frac{\theta_3^{\tau_{13}}}{\theta_1^{\tau_{13}} + \theta_2^{\tau_{23}} + \theta_3^{\tau_{33}} + \theta_s^{\tau_{s3}}} - \\
&\quad - \frac{\theta_s^{\tau_{1s}}}{\theta_1^{\tau_{1s}} + \theta_2^{\tau_{2s}} + \theta_3^{\tau_{3s}} + \theta_s^{\tau_{ss}}} \quad (C8)
\end{aligned}$$

where  $s$  stands for the adsorbent, and  $\theta$  is given by equation (34):

$$\begin{aligned}
\theta_1 &= .2565, & \theta_2 &= .3267 \\
\theta_3 &= .363, & \theta_s &= .0538
\end{aligned}$$

By using Table (III) and Table (IV) at 30°C:

$$\begin{aligned}
\ln \Gamma_1^{(1)} &= .848 \left[ 1 - \ln(.2565 + .3267 + (.363)(.597) + \right. \\
&\quad \left. + (.0538)(3.02)) - \right. \\
&\quad - \frac{(.2565)(1)}{.2565(1) + (.3267)(1) + (.363)(.597) + (.0538)(3.02)} \\
&\quad - \frac{(.3267)(1)}{(.2565)(1) + (.3267)(1) + (.363)(.597) + (.0538)(3.02)} \\
&\quad \left. - \frac{(.363)(.0386)}{(.2565)(.0386) + (.3267)(.0386) + (.363)(1) + (.0538)(1)} \right]
\end{aligned}$$

$$\begin{aligned}
 & - \frac{(.0538)(2.598)}{(.2565)(2.598) + (.3267)(2.598) + (.363)(.08) + (.0538)(1)} \\
 & = .2654 \\
 \ln \Gamma_2^{(1)} & = .169 \\
 \ln \Gamma_3^{(1)} & = .75814
 \end{aligned}$$

The activity coefficient of the group in the solution and the adsorbent is given by:

$$\begin{aligned}
 \ln \Gamma_1 & = q_1 \left[ 1 - \ln(\theta_1^{\tau_{11}} + \theta_2^{\tau_{21}} + \theta_3^{\tau_{31}} + \theta_4^{\tau_{41}} + \theta_s^{\tau_{s1}}) - \right. \\
 & - \frac{\theta_2^{\tau_{12}}}{\theta_1^{\tau_{12}} + \theta_2^{\tau_{22}} + \theta_3^{\tau_{32}} + \theta_4^{\tau_{42}} + \theta_s^{\tau_{s2}}} - \\
 & - \frac{\theta_3^{\tau_{13}}}{\theta_1^{\tau_{13}} + \theta_2^{\tau_{23}} + \theta_3^{\tau_{33}} + \theta_4^{\tau_{43}} + \theta_s^{\tau_{s3}}} - \\
 & - \frac{\theta_4^{\tau_{14}}}{\theta_1^{\tau_{14}} + \theta_2^{\tau_{24}} + \theta_3^{\tau_{34}} + \theta_4^{\tau_{44}} + \theta_s^{\tau_{s4}}} - \\
 & \left. - \frac{\theta_s^{\tau_{1s}}}{\theta_1^{\tau_{1s}} + \theta_2^{\tau_{2s}} + \theta_3^{\tau_{3s}} + \theta_4^{\tau_{4s}} + \theta_s^{\tau_{ss}}} \right] \quad (C9)
 \end{aligned}$$

Again, by using Table (III) and Table (IV):

$$\begin{aligned}
 \ln \Gamma_1 & = .72386 \\
 \ln \Gamma_2 & = .46095 \\
 \ln \Gamma_3 & = 0.84132
 \end{aligned}$$

$$\ln\gamma_1^R = (.72386 - .2654) + 2(.46095 - .169) + (.084132 - .75814) = .36835$$

$$\ln\gamma'_1 = .0884 + .36835 \\ = .45675$$

$$\gamma'_1 = 1.5789$$

By following the same procedure,  $\gamma'_2 = 1.3604$ .

### Exponential Term

In equation (38), the molar free energy of immersion of the adsorbent in the solution can be eliminated by using both equations (36) and (37). However, the molar free energy of immersion of the adsorbent in the pure component can be calculated as follows:

### Combinatorial Part

The combinatorial part is equal to zero for the pure component.

$$\ln\gamma_{1p}^c = 0 \\ \text{and } \ln\gamma_{2p}^c = 0$$

The pure component activity coefficient equation (17) can be calculated from the combination of the activity coefficient of the group and the adsorbent less the activity coefficient of the group in its solution

$$\gamma_{1p} = .96101 \\ \text{and } \gamma_{2p} = 1.03204$$

Now, equation (38) can be used to calculate the amount adsorbed for each component as follows:

$$\frac{x'_1}{x'_2} = \left( \frac{.1334}{.8666} \right) \left( \frac{3.97701}{1.10346} \right) \left( \frac{1.3604}{1.5789} \right) \left( \frac{1.03204}{.96101} \right) = .5134$$

$$\text{but } x'_1 + x'_2 = 1$$

$$x'_1 = .3392$$

$$\text{and } x'_2 = .6607$$

Repeat the calculation for the adsorbed phase until the calculated value of the composition is equal to the assumed value. The amount adsorbed can be calculated by using equation (7).

APPENDIX D  
ERROR ANALYSIS

The random errors associated with the experimental amount adsorbed and the predicted amount adsorbed can be estimated from the errors associated with each variable uncertainties which is given as follows:

<u>Experimental Variables</u>	<u>Uncertainty</u>
Initial weight of solute $W_I$	$\pm .00001$ g
Weight of adsorbent $W_C$	$\pm .00001$ g
Initial volume of solution $V_I$	$\pm 1$ ml
Temperature	$\pm .1^\circ\text{C}$
Final weight of the solute $W_F$	2%

The final weight of the solute uncertainty was estimated by preparing standard solutions to check the accuracy of the analysis. Reproducibility of about 3% was found for single solutes and about 4% for the bi-solute systems. This error is the combined errors of all the above mentioned experimental variables, including the errors in the GLC conditions and the digital integrator.

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