Abstract

Separation of simulated industrial food products, by method of adsorption, has been studied. A thermodynamic approach has been applied to study the liquid adsorption where benzene and cyclohexane have been used to simulate edible oils in a system that employs silica gel as the adsorbent. Different models suggested in the literature have been tested with experimental data in order to characterize properties of the system, such as the tendency to ideality, for both adsorbed and bulk liquid phases. The methods of determining thermodynamic properties such as free energy of adsorption, adsorption capacity and activity coefficients in the adsorbed phase have been studied.

It was observed that a model based on the assumption that adsorbed phase, but not liquid phase, is ideal gave a good for that may suffice for engineering design of liquid adsorption systems that may be applied in food
processing, such as decolourising crude sugar syrup, recovery of polypeptides and extraction of flavouring.

**Key Words:** Separation, food, model, adsorption, simulation and surface excess.

**Introduction**

Liquid adsorption techniques have been used industrially in purification and separation of liquid compounds, however the success of the process depends a great deal on the life span and regeneration of the adsorbent. Liquid adsorption process where solid adsorbents like activated carbon, zeolite and silica gel are applied have been used in industrial separation of substances whose saturated vapour pressures are so close that conventional methods area not practicable, and those that can not withstand high temperatures of the conventional distillation processes. For these types of mixtures, fractional crystallization, and vacuum, azeotropic and destructive distillations would be required. (Kipling, 1965). In the food industry, adsorption has been employed in processes like decolourising and drying of vegetable and animal oils, and recovery of vitamins. The decolouring of sugar syrup and extraction of flavouring compounds similarly employ liquid adsorption techniques. Fatty acids, amino acids, and enzymes, cannot withstand high temperature separation like in most distillation processes, therefore, adsorption is one of the separation processes that are commonly applied.

The efficiency of a separation process depends upon the degree of approach to equilibrium and the effectiveness of separation of the bulk liquid from the solid adsorbent after immersion. The physical and chemical structures of both the adsorbent and the adsorbate determine the overall mass transfer mechanism from the bulk liquid to the adsorbed phase. Molecular thermodynamics has emerged as an invaluable tool to study the intricate interplay between mass transfer and chemical kinetics (Prausnitz, 1965). Of particular interest is the energetic heterogeneity of the adsorbent and the non ideality of liquid mixtures. Adsorbents are often made of inert solid particles. However, there are some cases where chemisorption takes place, which may lead to deactivation of the adsorbent and sometimes difficulties in separation of adsorbate from the adsorbent. Most of the adsorption processes are carried out at an ambient temperature, where the process mechanics are due to reversible intermolecular forces rather than formation of new chemical bonds. Operation at an ambient or low temperature is necessary due to the fact that the rate of adsorption for most commonly applied adsorption processes decrease with an increase in temperature.

Conventionally, many of the measurement methods require sampling (at intervals) in order to determine the attainment of equilibrium. However, sampling does affect the liquid/adsorbent ratio, which has a significant
influence on the equilibrium. Therefore, online measurement method would produce better results.

In this work, a thermodynamic approach to multicomponent adsorption over an entire range of solute mole fraction, was applied to correlate the models with experimental data in order to determine the models that precisely fit the experimental data.

**Mathematical Models**

Modelling and simulation methods of analysis have the advantage that they give insight into the correlations among the operating parameters in systems where the number of parameters involved is enormous. The analysis of such correlations experimentally could be expensive and time consuming. There have been limitations as regards the application of the mathematical modeling approach due to the computation of cost. With the current fast computers, computation cost has been significantly reduced and is still being reduced further. Model formulation here involves representation of the chemical and physical characteristics of the system. The resulting model equations are solved in order to obtain the correlations among the operating parameters. Model equations formulation and the methods of solution depend on the system characteristics; for example, a multicomponent system will generate a more complex equation than a binary system.

Most of the work that has been reported confine adsorption to a mono-layer and consider binary system, where solutes are adsorbed with marked preference over the solvent. Consideration of the influence of the solvent forms the basis of multicomponent adsorption concept. In comparison to binary systems, multicomponent systems pose a considerable challenge due to the complexity of the model used to describe the adsorbent equilibrium characteristics. It has been reported (Myers, 1991) that Langmuir's theory applied to multicomponent systems fails in most cases. Unlike in a dilute binary system where one component is considered to be in excess, there is considerable competitive adsorption in multicomponent systems. It is expected that competitive adsorption is influenced by the difference in the strength of interaction between adsorbent and adsorbate (Ash, 1969). Apparently, the difference in adsorptive forces could be responsible for preferential adsorption which can be readily detected experimentally. The major utilities governing the thermodynamic accuracy of the experimental data include precision of equilibrium state and consistency of morphology of the adsorbent. The equilibrium and the morphology of the adsorbent are affected by temperature fluctuations, and consequently, the accuracy of the model in predicting the system performance is affected.

In liquid adsorption, unlike in gas adsorption, the assumption of an isothermal adsorption process is valid because
of large heat capacity of the liquid, and the fact that the adsorbent surface is completely covered. The influence of pressure is not as significant in liquid adsorption as it is in gas adsorption. Primarily, adsorption in pure gas is governed by pressure, and may be predicted from single gas adsorption isotherms. This approach is not applicable to liquid adsorption, given that adsorption in pure liquid is not a meaningful parameter due to the fact that the surface excess, \( n^e \), for any pure liquid is zero.

If some of the constants in the model equations are to be filled from the experimental data, then there is inevitably a need for an accurate experimental measurement without effect on the mixture volume. It is normally not practicable to measure directly the amount of adsorbates in the adsorbed phase. Therefore, the concept of surface excess has been introduced to indirectly determine the amount adsorbed. Surface excess has been defined as the difference between the amount adsorbed and the amount that could be adsorbed if the concentration of the adsorbed phase would be the same as that of the bulk phase (Sircar et al., 1989) Based on material balance, of the total number of moles of liquid phase, surface excess is given by:

\[
\begin{align*}
{n^e_i} &= n^0 (x_i^0 - x_i) \\
&= n^0 (x_i^0 - x_i) \\
&= n^0 (x_i^0 - x_i) \\
&= n^0 (x_i^0 - x_i)
\end{align*}
\]

Where \( n^0 \) is the number of moles of liquid brought into contact with a unit mass of the adsorbent; \( x_i^0 \) and \( x_i \) are, respectively, the mole fraction of components in liquid bulk phase before and after immersion. It is necessary to express \( n^e_i \) in terms of experimentally measurable variables such that \( n^e_i \) is found from the change in bulk liquid concentration (\( x_i^0 - x_i \)). In terms of mass balance in adsorbed phase:

\[
\begin{align*}
{n^e_i} &= n' (x_i' - x_i) \\
&= n' (x_i' - x_i) \\
&= n' (x_i' - x_i) \\
&= n' (x_i' - x_i)
\end{align*}
\]

where \( n' \) is the total amount adsorbed; \( x_i' \) is the mole fraction of components in adsorbed phase. The sum of the surface excess for all the components should add up to zero:

\[
\sum n^e_i = 0
\]
The assumption that surface excess in the bulk phase is equal to the surface excess in the vapour phase \( n_{1e} = n_{1ev} \) when liquid pressure tends to saturated vapour pressure leads to:

\[
\frac{\phi - \phi_1}{RT} = x_1 \int_{x=1}^{x_1} \frac{n_{1e}}{x_1 x_2 \gamma_1} d \gamma_1 x_1 \tag{4}
\]

In his earlier work, Sircar et al. (1970) considered pure liquid as the standard state and when equating the fugacities of the liquid phase and the adsorbed phase, Poynting correction factor was used. The introduction of this correction factor led to a relatively complicated integral equation for surface excess. From the fundamental principles of thermodynamics, it was taken that fugacity in the bulk phase and adsorbed phase are equal:

\[
f_i - f_i' = \tag{5}
\]

Bulk liquid phase fugacity;

\[
f_i = P_i^{LV} \gamma_i x_i \exp \left( \frac{\nu_i^L (P - P_i^{LV})}{m_i RT} \right) \tag{6}
\]

and fugacity in the adsorbed phase is given by:

\[
f_i' = P_i^s \gamma_i' x_i' \exp \left( - \left( \frac{\phi - \phi_i^o}{m_i RT} \right) \right) \tag{7}
\]

If the pressure \( P \) (in eq.(6)) tends to \( P_i^{LV} \), the Poynting factor (the exponential term in eq. (6), which accounts for
influence of pressure on fugacity in the bulk liquid phase, may be neglected. Thereafter, from eqs. (5) to (7), we get:

\[
\gamma_i x_i = \gamma'_i x'_i \exp\left(\frac{(\phi - \phi_i^o)}{m_i RT}\right) \quad (8)
\]

Surface excess with respect to component \(i\) may be expressed as; (Myers, 1991)

\[
n_i^e = \frac{\sum x_i x_j (1 - K_{ij})}{\sum x_j K_{jr} / m_j} \quad (9)
\]

Where 'r' is an arbitrary reference constant, and separation coefficient, \(K_{ij}\), is given by:

\[
K_{ij} = \frac{x_i x'_j}{x'_i x_j} \quad (10a)
\]

and from eq. (8)

\[
K_{ij} = \frac{\gamma'_i \gamma'_j}{\gamma'_j \gamma'_i} \exp\left(\frac{\phi - \phi_j^o}{m_j RT} - \frac{\phi - \phi_i^o}{m_i RT}\right) \quad (10b)
\]

Mole fraction in the adsorbed phase may be calculated as:
\[ x'_{i} = \frac{x_{i} K_{ij}}{\sum x_{i} K_{ij}} \]  \quad (11)

Taking \( r \) to be 1 and given that \( K_{11} = 1 \) for binary system, eq. (9) becomes:

\[ n_{1}^{e} = \frac{x_{1} x_{2} (1 - K_{12})}{\frac{x_{1}}{m_{1}} + \frac{x_{2} K_{12}}{m_{2}}} \]  \quad (12)

From Gibbs adsorption isotherm in eq. (4), the relative energy of immersion for a binary system may be calculated by solving the equation numerically. Analytical method was not possible given that \( n_{1}^{e} \) is not an explicit function. The sum of the differences should be zero. However, the equation becomes very complex if \( n_{1}^{e} \) is expressed in terms of \( K_{ij} \), and when pure liquid is considered as the standard state. If the adsorbed phase is taken as ideal, surface excess for a binary system can be expressed as:

\[ n_{1}^{e} = \frac{(a_{1} x_{2} - a_{2} x_{1} K^{o}_{12})}{\frac{a_{1}}{m_{1}} + \frac{a_{2} K^{o}_{12}}{m_{2}}} \]  \quad (13)

Where \( a_{1} \) and \( a_{2} \) are the activities of components 1 and 2, respectively and \( K^{o}_{12} \) is a constant similar to \( K^{o}_{ij} \)

If both adsorbed and bulk phases are ideal, activity coefficient for the phases will be 1, and eq. (13) simplifies to:
In some special cases and for computational purposes, it can be assumed that the adsorption capacity of both components in a binary system are equal \((m_1 = m_2)\). Then after rearrangement, eq. (14) becomes:

\[
\frac{n_i^e}{m} = \frac{X_1 X_2}{X_1 + X_2 K_{12}^o} K_{12}^o
\]

The methods given by equations (1) to (15) represent the chemical and the physical conditions of the adsorption process as well as the properties of the adsorbed phase and bulk liquid phases. It was, therefore the objective of this work to show how these models fit various experimental data from the literature.

**Methodology**

The experimental data for a binary system of benzene and cyclohexane (designated as components 1 and 2, respectively) was used to simulate a food separation process. A plot of \(x_1 x_2 / n_i^e\), (from eq. (15)) against \(x_1\) gives a straight line with \(1/m\) as the slope and \(K_{12}^o/(1+K_{12}^o)\) as the \(y\)-intercept. This graphical method was used to obtain the first estimates of the parameters to be fitted. This graphical method was used to obtain the first estimates of the parameters to be fitted. A program was written based on eqs. (8) to (11). The program, based on Simplex method (Press *et al.*, 1992) fits the values of \(K_{12}^o m_1, m_2, (\bar{\Omega}-\bar{\Omega}_1^o)/RT\) and \((\bar{\Omega}-\bar{\Omega}_2^o)/RT\) from experimental data, using eq. (3) as the objective function. Alternatively, the energy of immersion may be calculated on the basis that chemical potentials in the bulk liquid phase are related by Gibbs-Duhem equation (Prausnitz, 1969; Myers, 1986).

A routine based on Wilson's equation was used in calculation of the activity coefficients, and consequently, the activity of the solutes. The thermodynamics study of liquid adsorption of binary systems was carried out with
models suggested by Myers and Sircar in their work from 1970 to 1991. All the fitting routines were based on the Simplex method. The fitting of the parameters such as free energy of adsorption and adsorption capacity, and the calculation of the activity coefficient were based on the experimental data reported by Sircar and Myers (1970) for benzene and cyclohexane mixture.

The major difference among the models studied here, was the description of the liquid bulk phase and adsorbed phase; either as ideal or real. The mathematical formulation, therefore, depended on whether the activity coefficients are to be calculated or assumed to be equal to 1 (for ideal condition). Consequently, calculation of the adsorption coefficient was governed by these assumptions, if made, and this was the distinguishing feature for the final expression for surface excess.

**Results and discussion**

The models that were studied include ideal-adsorbed-ideal-bulk phase and ideal-adsorbed phase. The results obtained in this work were comparable to those of other researchers, in spite of experimental condition not being exactly the same, as directed later.

**Liquid phase and adsorbed phase both ideal**

In eq.(14), both phases are assumed to be ideal and therefore, the activity coefficients in both phases are equal to 1. As shown in Fig. 1, the result of the fit obtained by this equation was very poor.

This implies that the assumption that both bulk liquid and adsorbed phases are ideal results in a significant deviation from the experimental date. There was an underestimation of the surface excess, and this could be due to the fact that the assumption that both phases are ideal probably underrates the difference between thermodynamic and kinetic properties of adsorbed and bulk liquid phases, and hence, lowering the value of the surface excess.

**Ideal Adsorbed Phase**

An ideal adsorbed phase mixture is one whose activity coefficient in the adsorbed phase, as opposed to bulk liquid phase, is equal to 1. The surface excess for such a mixture is described by eq. (13). And the whose results are shown in Fig. 2. The fit obtained was good for the entire range of the mole fraction, this is a sharp contrast to Fig. 1, whose model is similar to that of Fig. 2, except for the fact that an assumption that liquid bulk phase is ideal was
made in the former case.

**Adsorption Capacity of Benzene and Cyclohexane are equal \((m_1 = m_2)\)**

The equality of the adsorption capacity, thus, \(m_1 = m_2\), is a condition that makes the quantity \(\bar{\Omega}\) in equation (10) disappear. The parameters left for fitting were, therefore, \(K_{12}\), \(m\) (representing both \(m_1\) and \(m_2\)) and \((\bar{\Omega}_1 - \bar{\Omega}_2)/ RT\), whose fit values were -16.0, 2.755 and -5.99, respectively. These values were obtained by both Admo and Ads2 routines, the fit curve is shown in Fig. 3.

The fitting seems to be better at low mole fraction of benzene, and this may be an indication that this model could be more applicable at low concentration range. The routine Admo was a Numerical Recipe library routine which was also used for testing the working of the programs that were written. The routines that were written for this model gave identical results with those of the library routine, and the set of the results overlap as shown in Fig. 3. The values obtained here differ with the ones reported by Sircar *et al.*, (1970) as \((\bar{\Omega}_1 - \bar{\Omega}_2)/ RT = -6.33\) and \(m = 3.24\).) However, unlike in this case, the reported values of \(m_1\) and \(m_2\) were measured from saturated vapours of the pure adsorbates, and this could be the cause of the small difference between the fit parameter values obtained here and the literature ones.

**General Model**

The routine 'mast2' was based on a general thermodynamic relationships expressed by eqs. (4) to (9). It involved fitting of four parameters namely; \(m_1\), \(m_2\), \((\bar{\Omega} - \bar{\Omega}_1)/ RT\) and \((\bar{\Omega} - \bar{\Omega}_2)/ RT\). This model provided a good fit for the entire range of mole fraction of benzene, comparable to the fit obtained by assuming that only the adsorbed phase is ideal. The values obtained were; \(m_1 = 2.8861\), \(m_2 = 0.0005\), \((\bar{\Omega} - \bar{\Omega}_1)/ RT = 0.5781\) and \((\bar{\Omega} - \bar{\Omega}_2)/ RT = -2.376\). The value of \((\bar{\Omega} - \bar{\Omega}_2)/ RT\) is less than that obtained by Sircar *et al.* (1970). However, the value of \(m_1\) and the literature value of \(m\) are comparable.

Calculation of the adsorption capacity from experimental data is just an approximation, owing to the fact that \(m_i\) is a quantity of a pure solute. Therefore, the presence of other components in the bulk liquid mixture resulting into molecular interaction is likely to influence the value of \(m_i\). The influence could be more significant if such interactions resulted in electrostatic forces as is often the case with aqueous electrolyte solutions. A more precise...
method would be to determine $m_i$ from vapour liquid equilibrium of a pure component. The sum of the values of free energy that were obtained from experimental data was not equal to zero as expected of a thermodynamically consistent data. The fact that the sum was not zero indicates that either the data used was not thermodynamically consistent or free energy differences are not independent variables, which is one of the requirements for Simplex method.

**Fig 4**

All the fit curves are shown if Fig 5 for comparison purposes and it is evident that the fit obtained by assumption that all phases are ideal gave the worst fit. The fit, obtained by assuming that the adsorbed phase is ideal (Onidel) was better than that of mast2 at low benzene mole fraction, whereas poorer at higher benzene mole fraction. This tendency at lower a concentration is in consistence with the theory that the tendency to ideal solution increases with dilution. Therefore, the ideal bulk phase model can be used to predict the surface excess more precisely in dilute solution.

**Conclusion**

The assumption that both the bulk phase and the adsorbed phase are ideal has a profound influence on the calculated values of the surface excess, causing a significant deviation from the experimental data. This model, therefore, may not be relied upon for industrial applications.

The ideal adsorbed phase model may be applies to a broad range of solute concentration. However, with better results at lower concentrations. The general model gave the best fit for the entire range of the concentration, and this could be due to the fact that no assumptions such as the ones in other models was made, however, fit values need to be re-examined. The assumption that the adsorption capacities are equal gives inaccurate results. Therefore, these values could be measured and the assumption could only be used as an initial guess for further iteration.

**Acknowledgement**

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**References**

**Notations**

\( f_i \) - fugacity
\( m_i \) - adsorption capacity (mol/kg)
\( K_{ij} \) - separation coefficient for i-j binary system (defined in eqs. 10)
\( P^0 \) - vapour pressure of the adsorbate at standard state (kPa)
\( P_{LV} \) - vapour pressure of bulk liquid (kPa)
\( R \) -universal gas constant (cal/mol K)
\( T \) - temperature (K)
\( n_i^e \) - surface excess of i (mol/kg)
\( x_i^o \) - mole fraction in the bulk liquid of before immersion
\( x_i \) - mole fraction in the bulk liquid of after immersion
\( x_i' \) - mole fraction of in the adsorbed phase

**Subscripts**

\( i \) - \( i^{th} \) component
\( ij \) - system of components i and j

**Superscripts**
e - surface excess
' - adsorbed phase
o - pure state

**Greek letters**
Ø - free energy of immersion (mJ/m²)
g - activity coefficient

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