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EQUIVALENCE OF POTENTIAL THEORY AND IDEAL ADSORBED SOLUTION (IAS) THEORY TREATMENTS OF THE DUBININ-RADUSHKEVICH EQUATION

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Multicomponent potential theory-based adsorption equilibria equations are derived using the IAS theory of Myers and Prausnitz. It is shown that both IAS and the potential theory lead to the same multicomponent equations when the potential theory equations are subject to a certain constraint. The constraint is that the potential theory equation satisfies $\beta q = F(\epsilon/\beta)$.

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PREFACE

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CONTENTS

FIGURES

EQUIVALENCE OF POTENTIAL THEORY AND IDEAL ADSORBED SOLUTION (IAS) THEORY TREATMENTS OF THE DUBININ-RADUSHKEVICH EQUATION

1. INTRODUCTION

The ideal adsorbed solution theory of Myers and Prausnitz[1] provides a means of determining multicomponent adsorption isotherms from pure component isotherms. It has the advantage of being applicable to all pure component isotherm equations regardless of form. It has the disadvantage of often requiring a numerical solution. In IAS, the spreading pressure is defined as an intensive thermodynamic quantity by the Gibbs isotherm. The following reviews the Ideal Adsorbed Solution theory, the Potential theory, and discusses the relationship between the two.

2. IDEAL ADSORBED SOLUTION THEORY

Using the Raoult's Law vapor-liquid expression, Myers and Prausnitz wrote

$$p_i = x_i \, p_i^0(\pi) \tag{1}$$

where p^0 is the pure component adsorbate partial pressure. The spreading pressure is denoted by π. Myers and Prausnitz assumed there would be no change in adsorption area with mixing. This led to the condition

$$\frac{1}{q_t} = \sum \frac{x_i}{q_i^0} \tag{2}$$

where q_t is the total number of moles adsorbed. The q_i^0 are the adsorbed-phase concentrations which correspond to the spreading pressure of the mixture subject to a particular pure component isotherm equation. The q_i^0 are expressed as implicit functions of the spreading pressure by use of the Gibbs adsorption isotherm.

$$\frac{\pi A}{RT} = \int_0^{p^0} \frac{q}{p} dp \qquad \text{(constant } T\text{)} \tag{3}$$

3. POTENTIAL THEORY

Adsorption isotherm relations based on the potential theory are commonly used to correlate data for activated carbons. For an adsorbate which may exist as a liquid at the adsorption temperature, the potential is defined

$$\varepsilon = RT \ln p / p^{sat} \tag{4}$$

where R is the gas constant, T is the adsorption temperature, p is the partial pressure over the adsorbent and p^{sat} is the partial pressure over the adsorbate as a liquid at T. A potential field strength is associated with a level of filling of the adsorption space. The potential of an adsorbate at a given position in the potential field depends on physical properties of the adsorbate as well. The potential *characteristic curve* may be defined

$$\theta = F(\varepsilon / \beta) \tag{5}$$

where β accounts for the adsorbate dependent contribution to the potential and is constant. The fractional filling of the adsorption space θ is defined

$$\theta = q / q^{sat} \tag{6}$$

where q^{sat} is the adsorbed-phase concentration at equilibrium with the saturation pressure at the adsorption temperature.

4. RELATIONSHIP BETWEEN IAS AND POTENTIAL THEORIES

The differential of Eq. (4) holding T constant is

$$d\varepsilon = d RT \ln p / p^{sat} = RT \frac{1}{p} dp \tag{7}$$

because p^{sat} is a function only of temperature. To determine the relationship between the spreading pressure π and the potential ε, Eq. (7) is substituted with Eq. (6) into Eq. (3) to give

$$\pi A = q^{sat} \int_{\varepsilon_{p=0}}^{\varepsilon_{p=p^0}} \theta \, d\varepsilon \tag{8}$$

Equation (5) may be written in an inverted form

$$\varepsilon = \beta F^{-1}(\theta) \tag{9}$$

Substituting Eq. (9) into Eq. (8), we have

$$\pi A = q^{sat} \beta \int_{F^{-1}(0)}^{F^{-1}(\theta^0)} \theta \, dF^{-1}(\theta) \tag{10}$$

The adsorbed-phase concentration at saturation can be defined

$$q_i^{sat} = W_0 / V_{m,i} \tag{11}$$

where W_0 is a constant representing the capacity of a given adsorbent and is independent of the adsorbate. Substituting this into Eq. (10), we have

$$\pi A = \frac{W_0}{V_m} \beta \int_{F^{-1}(0)}^{F^{-1}(\theta^0)} \theta \, d F^{-1}(\theta) \tag{12}$$

If, as was suggested by Dubinin,[2] the correlative coefficient β is set equal to V_m there is a cancellation in Eq. (12). The following important result is obtained

$$\pi A = W_0 \int_{F^{-1}(0)}^{F^{-1}(\theta^0)} \theta \, d F^{-1}(\theta) \tag{13}$$

In Eq. (13), the spreading pressure is defined as a unique function of the fractional capacity. As long as all components in a mixture can be fit by a potential theory-based single component adsorption equilibria equation of the same form, $F^{-1}(\theta)$, Eq. (13) will hold for all adsorbates. We, therefore, have

$$p_i = x_i \, p_i^0 (\theta^0) \tag{14}$$

Equation (14) denotes that in place of determining p^0 as a function of the spreading pressure of the mixture, it is possible to determine p^0 as a function of θ^0 of the mixture and obtain identical results.

It is now necessary to use the IAS theory to determine θ^0 of the mixture. Multiplying both sides of Eq. (2) by q_t gives

$$1 = \sum \frac{q_i}{q_i^0} \tag{15}$$

Now dividing both the denominator and numerator of Eq. (15) by q_i^{sat}, we have

$$1 = \sum \frac{\theta_i}{\theta_i^0} \tag{16}$$

From Eq. (13) we know that all θ_i^0 are identical so multiplying by the ideal fractional loading the result is

$$\theta^0 = \sum \theta_i \tag{17}$$

When the IAS theory is applied with potential theory-based adsorption equilibria equations and $\beta = V_m$, the following analytical equation is derived

$$p_i = x_i\, p_i^0\left(\sum \theta_j\right) \tag{18}$$

It has been shown that Eq. (18) is the IAS multicomponent isotherm when the same potential theory pure component equation is used for each component and when the correlating coefficient β is set equal to the adsorbed-phase volume. Equation (18) is not a general IAS relation for the potential theory, but rather is only valid when

$$\beta q = F(\varepsilon / \beta) \tag{19}$$

The β is commonly assigned as a characteristic molar volume. It may be much more useful to regard the correlative coefficient as the inverse of the adsorbed-phase concentration at the saturation pressure, $\beta = 1/q^{sat}$. This is more general. The correlative coefficient β need not be defined as the liquid molar volume. All that is required for the IAS and the potential theory treatments of multicomponent adsorption to be equivalent is that Eq. (19) be satisfied. The generality is important because, as is discussed elsewhere,[3] the correlative coefficient which best fits data may not be equal to the molar volume of the liquid.

5. APPLICATION TO THE D-R EQUATION

A particularly useful form of Eq. (9) is the Dubinin-Radushkevich (D-R) equation[2]

$$RT \ln p / p^{sat} = -\beta E\left[-\ln \theta\right]^{1/2} \tag{20}$$

where V_m, the adsorbed-phase volume, is used to define β and E characterizes the potential field of the adsorbent. The D-R equation often fits data well over practical ranges of interest.

Experimental single component data measured by Rudisill, et al.[4] for the hexane/BPL and the acetone/BPL systems was fit to the D-R equation. Fit constants are, for hexane/BPL, $q^{sat} = 3.41$ mol/kg, $\beta E/R = 2869\ \mathrm{K}^{-1}$, and for acetone/BPL, $q^{sat} = 4.82$ mol/kg, and $\beta E/R = 1822\ \mathrm{K}^{-1}$. The IAS theory was used to estimate mixture equilibria by numerically determining the solution of Eq. (1), Eq. (2) and Eq. (3) with the fit D-R equation. Multicomponent equilibria predictions were also made using Eq. (18). Predicted results are shown in Figure 1. Numerical IAS predictions and predictions of Eq. (18) are shown to differ to some extent. This is because Eq. (19) is not satisfied. This can be seen, noting that E is the same for both fits, so in order to satisfy Eq.(19) the ratio of the hexane and acetone fit molar volumes ($V_{m,\text{hex}}/V_{m,\text{ace}} = \dfrac{q_{ace}^{sat}/W_0}{q_{hex}^{sat}/W_0} = 1.413$) must be equal to the ratio of the hexane and acetone fit $\beta E/R$ values ($\beta E/R_{\text{hex}}/\beta E/R_{\text{ace}} = 1.575$). These ratios are within about 10% but are not equal. The predictions shown in Figure 1 are similarly close but not equal. The hexane $\beta E/R$ value in the numerical IAS code was then reduced by 5% and the corresponding acetone value was increased by about 5% in order to satisfy Eq. (19). The modified values are, for hexane $\beta E/R = 2726\ \text{K}^{-1}$, and for acetone $\beta E/R = 1928\ \text{K}^{-1}$. The numerical IAS result compared to the prediction of Eq. (18) for the case where Eq. (19) is satisfied are shown to be equivalent in Figure 2. This is numerical confirmation of the derivation presented thus far.

The derivation is now applied specifically to the D-R equation. For the D-R equation the adsorbed-phase concentration is related to the spreading pressure by substituting Eq. (20) into Eq.(3)

$$\frac{\pi A}{RT} = \frac{V_{m,i}E}{RT}\int_{\infty}^{\sqrt{-\ln\theta^0}} q_i^{sat}\theta \, d\sqrt{-\ln\theta} \tag{21}$$

where $\theta = q/q^{sat}$. Though it is not necessary to do so, the integral of Eq. (21) may be easily evaluated because it is proportional to the complimentary error function

$$\frac{\pi A}{RT} = \frac{q_i^{sat}V_{m,i}E}{RT}\int_{\infty}^{y^0} \exp\left(-y^2\right)dy \tag{22}$$

where $y = \sqrt{-\ln\theta}$. We see from Eq. (21) that the spreading pressure can be expressed as a unique function of the fraction of the adsorption space filled when $q_i^{sat} = W_0/V_{m,i}$. The arguments leading to Eq. (16) are then valid, and we have

$$p_i = x_i p_i^{sat} \exp\left(-\frac{\beta E}{RT}\left[-\ln\sum\theta_j\right]^{1/2}\right) \tag{23}$$

where the sum is over all components of the mixture.

6. DISCUSSION

It may also be mentioned that Eq. (18) can be readily obtained using only potential theory-based arguments. In this case, Eq. (14) is a starting point and Eq. (17) follows from the assumption that there is no volume change on mixing. Grant and Manes (1966)[5] provide an example of such a derivation. Though their result is in slightly different form, rearranging produces an identical result. The relation of Eq. (18) has also been used by Hacskaylo (1987)[6] where it was referred to as Raoult's law for adsorption. Equation (18) is by no means new, but to the author's knowledge its connection to the IAS theory has never been discussed.

7. CONCLUSION

When Eq. (19) is satisfied, multicomponent isotherms derived using the IAS theory are identical to those derived using the potential theory.

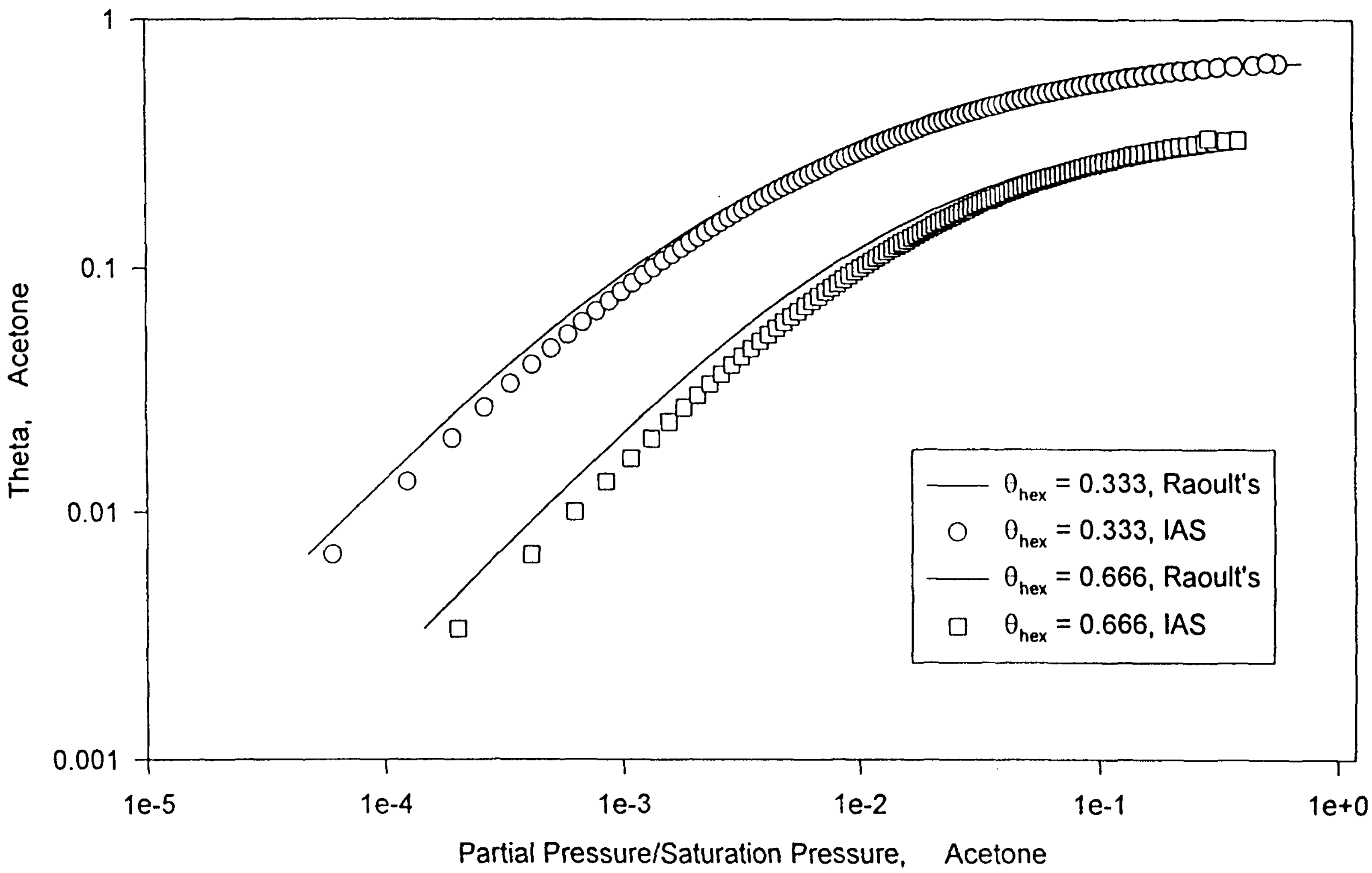

Figure 1. Comparison of Raoult's Law and IAS for a Hexane-Acetone Mixture on BPL: Fit D-R

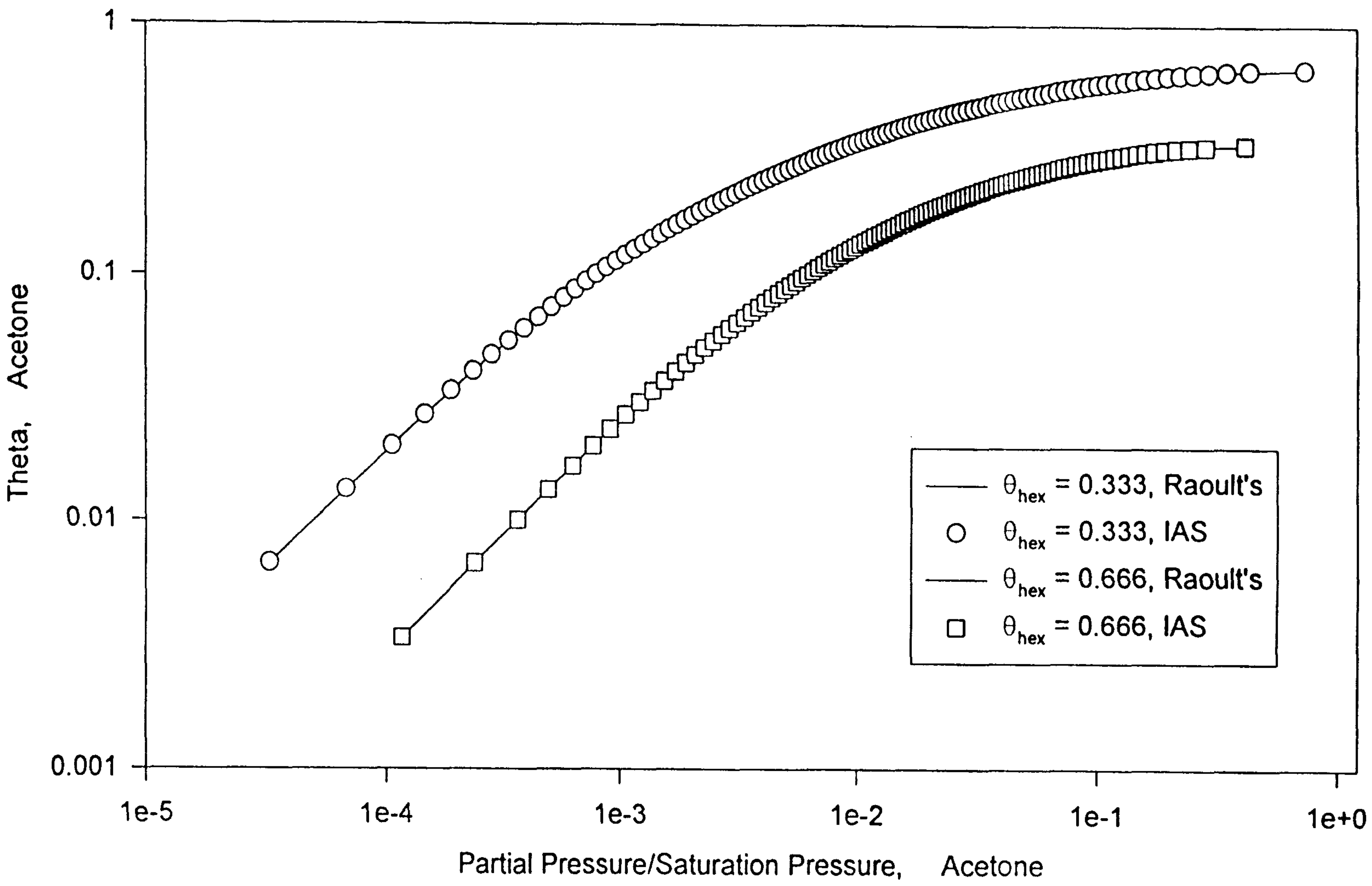

Figure 2. Comparison of Raoult's Law and IAS for a Hexane-Acetone Mixture on BPL: Eq. (19) Satisfied

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GLOSSARY

E - adsorbent potential field parameter of D-R equation (βE has units of J/mol)

F - general function

G - general function

p - partial pressure (Pa)

p^0 - pure component partial pressure (Pa)

p^{sat} - partial pressure at liquid saturation pressure (Pa)

q - adsorbed-phase concentration (mol/kg)

q^0 - adsorbed-phase concentration corresponding to the pure component partial pressure (mol/kg)

q^{sat} - adsorbed-phase concentration in equilibrium with the liquid saturation pressure (mol/kg)

q_t - total adsorbed-phase concentration of a mixture (mol/kg)

R - gas constant (J/mol-K)

T - temperature (K)

V_m - adsorbed-phase molar volume (cm^3/mol)

W_0 -adsorbent capacity (W_0/β has units of mol/kg)

x - mole fraction

y - variable

Greek

β – correlating coefficient of D-R equation (βE has units of J/mol)

ε - the adsorption potential (J/mol)

πA - product of spreading pressure and adsorption area (J/mol)

θ - fraction of the adsorption space filled

θ^0 - fraction of the adsorption space filled corresponding to the pure component partial pressure

Subscript

i - property of the *ith* component