

LA THERMODYNAMIQUE STATISTIQUE AU SERVICE DU MULTI- EHELLE:

EXEMPLES D'ÉQUATIONS PRÉDICTIVES ADAPTÉES À DES
PROBLÉMATIQUES INDUSTRIELLES (ACTIVITÉS, VOLATILITÉ DE
MÉLANGES AVEC ÉLECTROLYTES ET/OU COMPOSÉS
MULTIFONCTIONNELS)

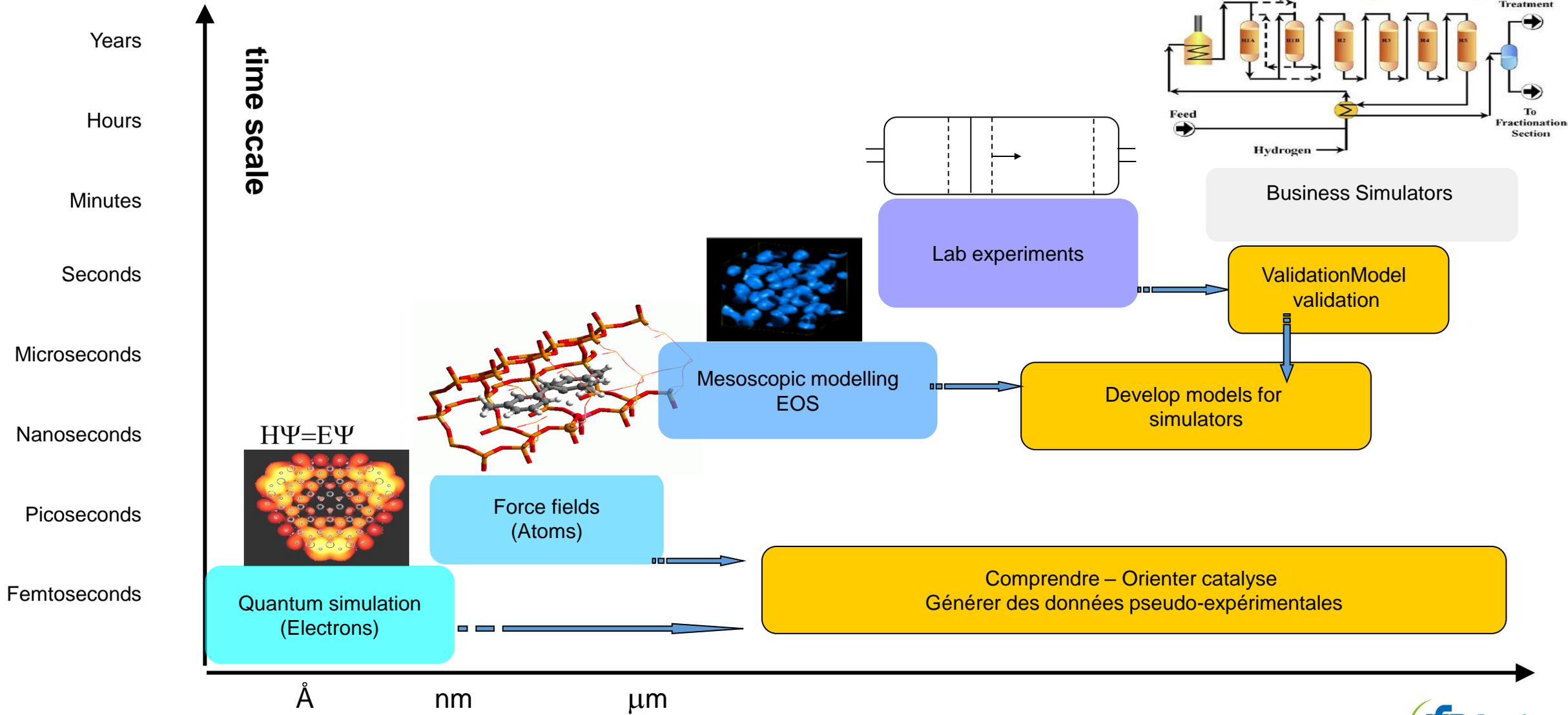
JC DE HEMPTINNE; R. LUGO, N. FERRANDO



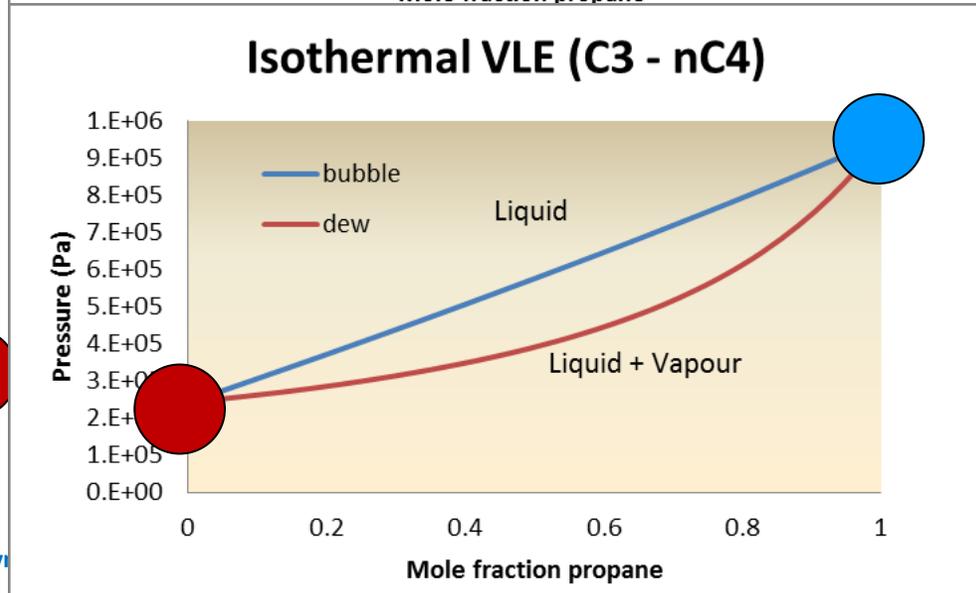
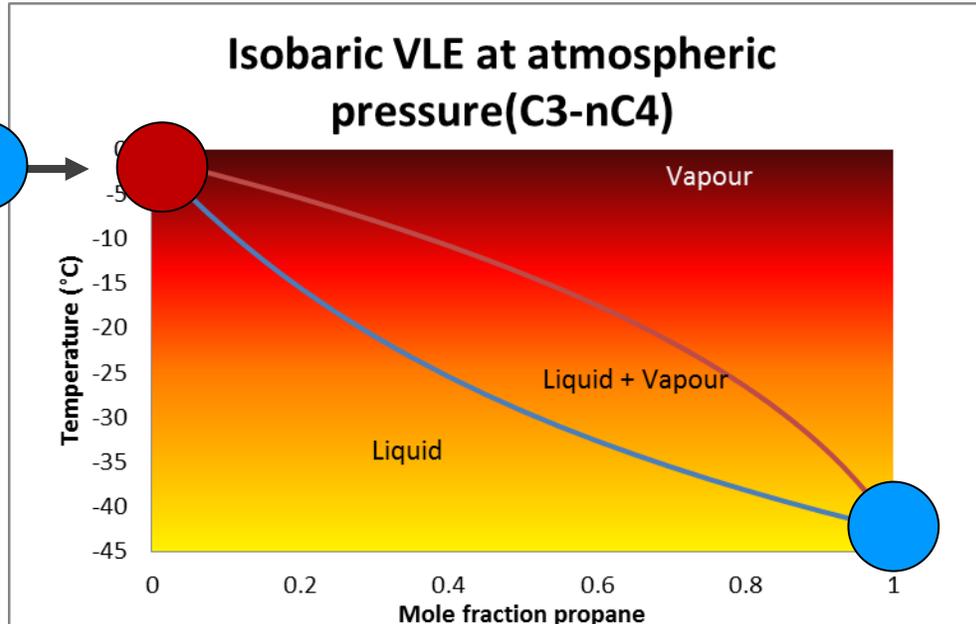
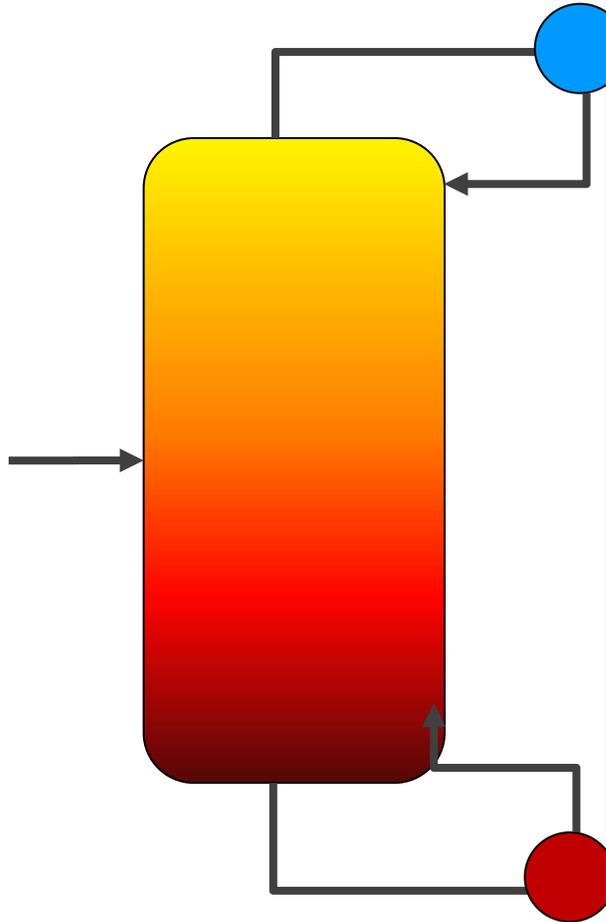
- Contexte
 - Objectif industriel
 - Quelques définitions
- Les phénomènes et les causes
- Un modèle statistique
- Conclusions/perspectives

CONTEXTE

Echelles de simulation



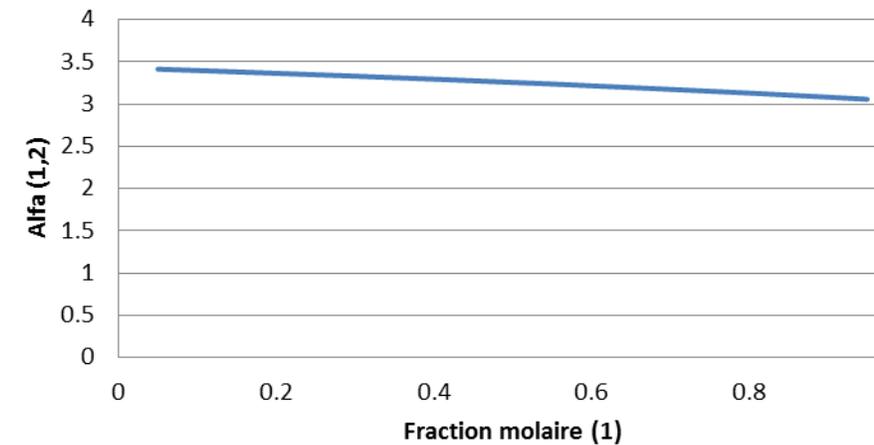
PRINCIPE DE SÉPARATION



Coefficient de partage:

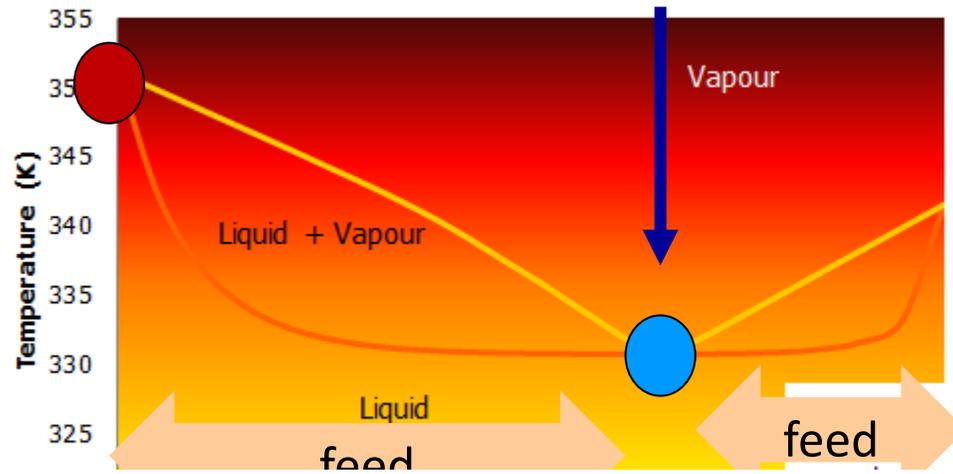
$$K_i = \frac{y_i}{x_i} \approx \frac{P_1^\sigma \gamma_1}{P}$$

Volatilité relative

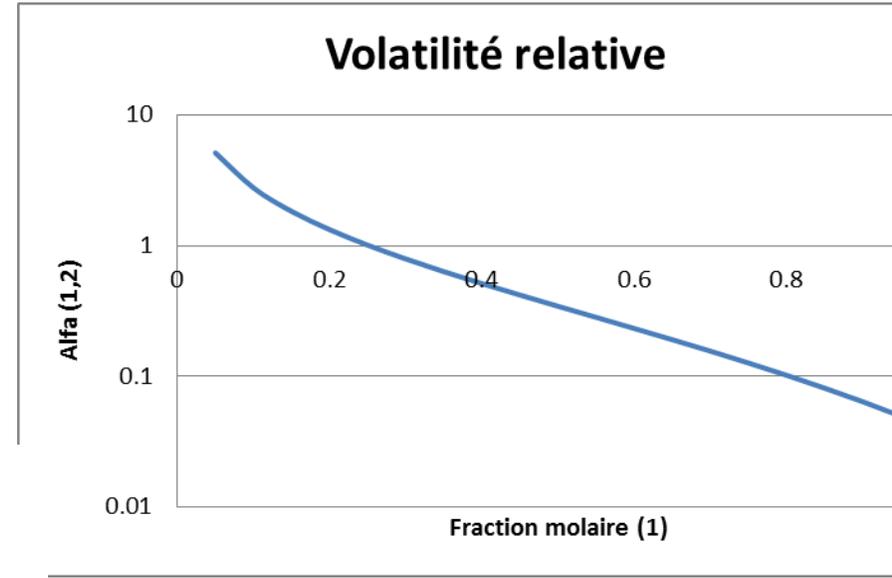
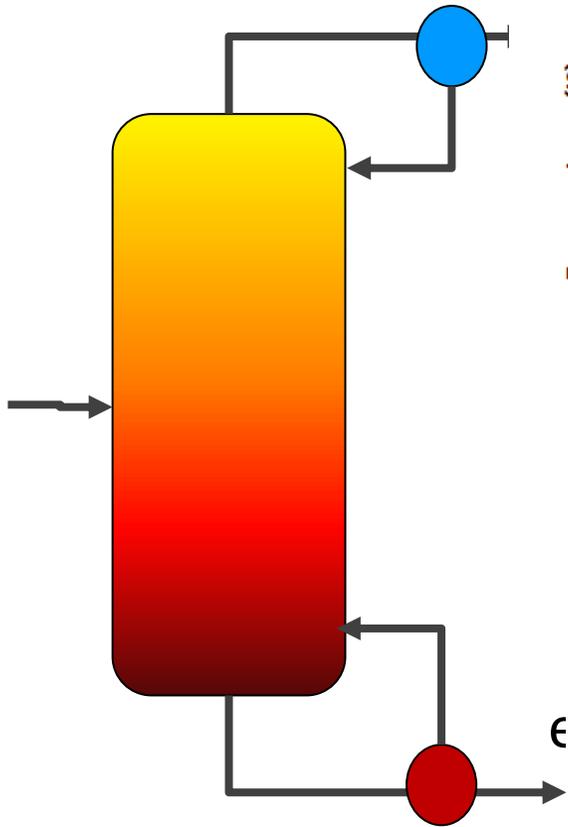
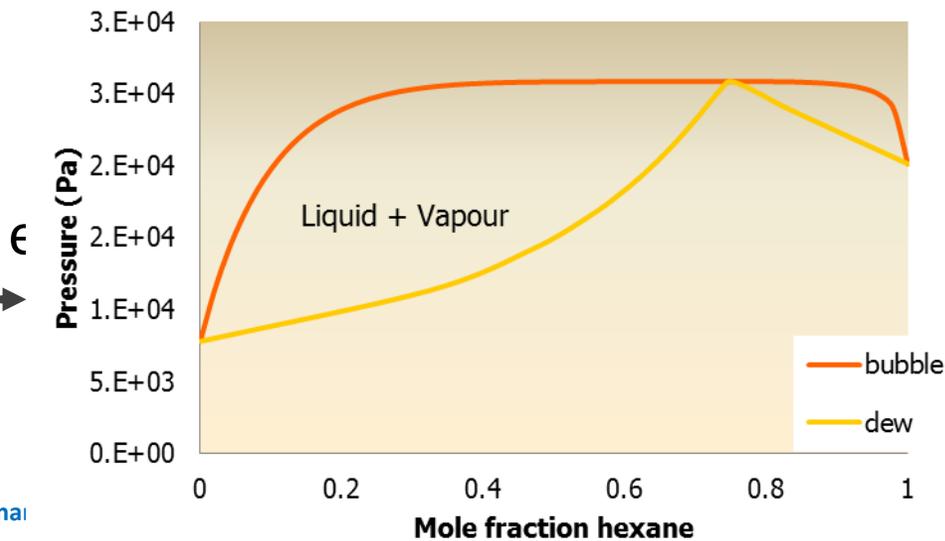


PROBLÉMATIQUE AZÉOTROPE

Isobaric VLE (ethanol-nC6)

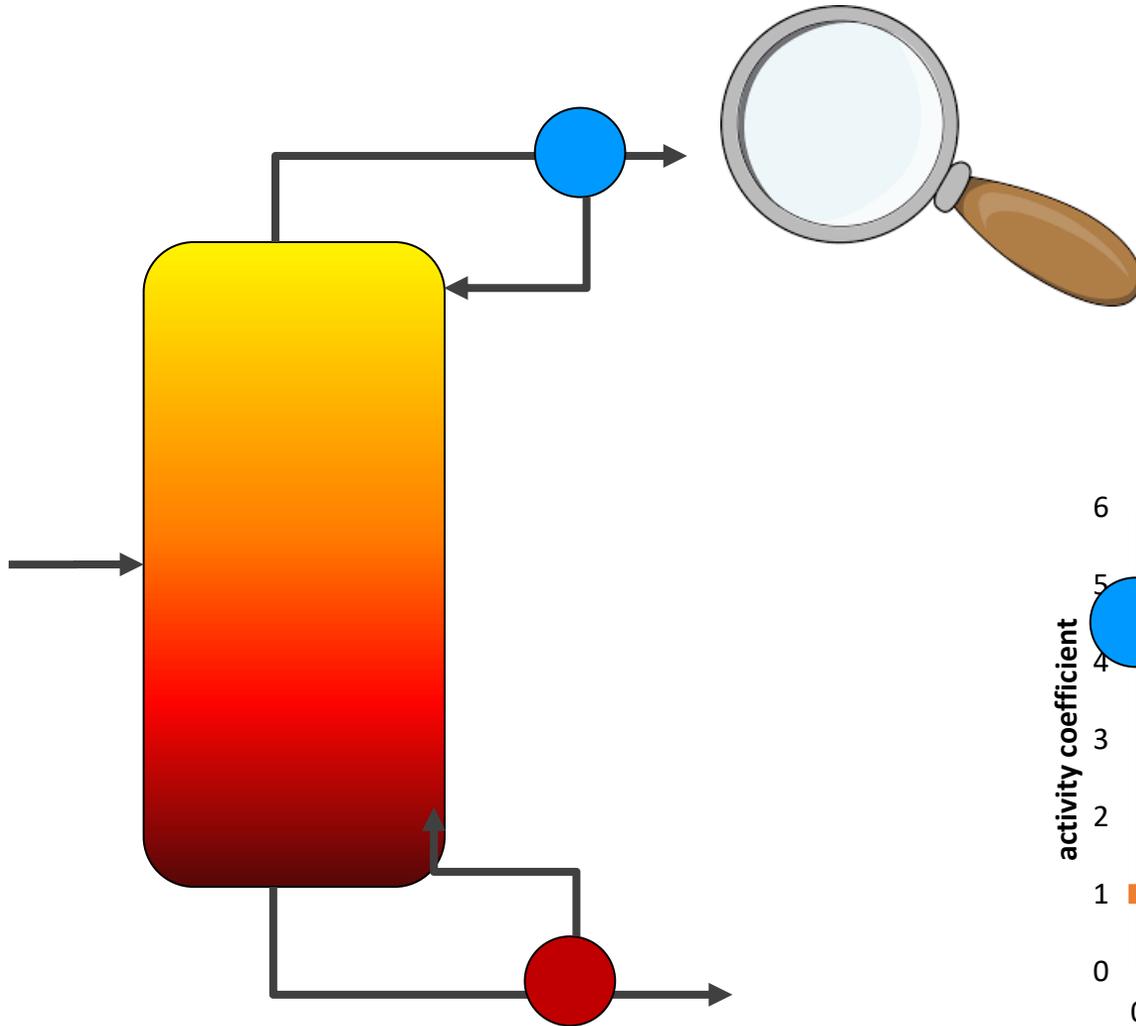


Isothermal VLE (ethanol - nC6)

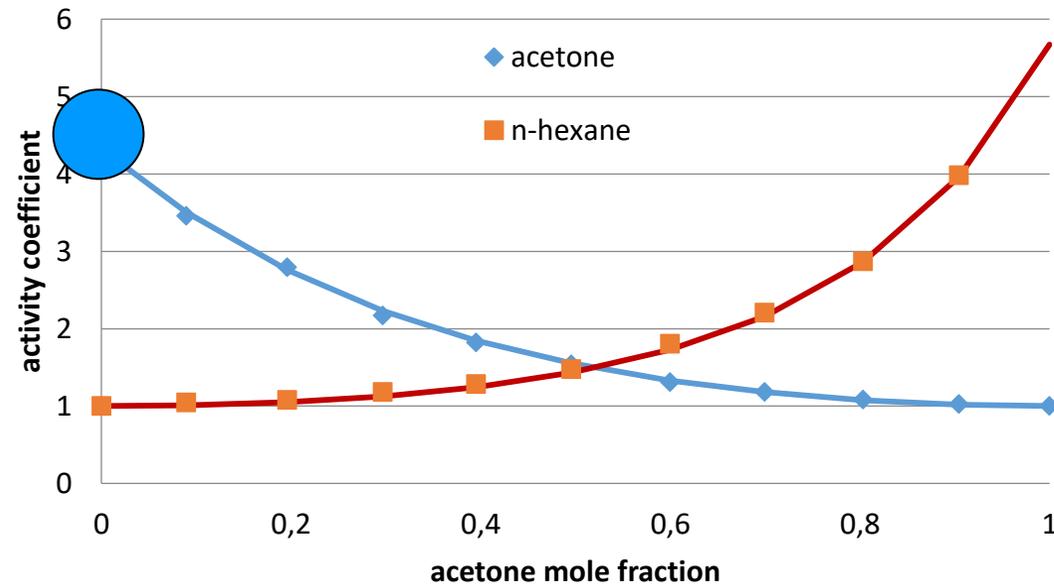


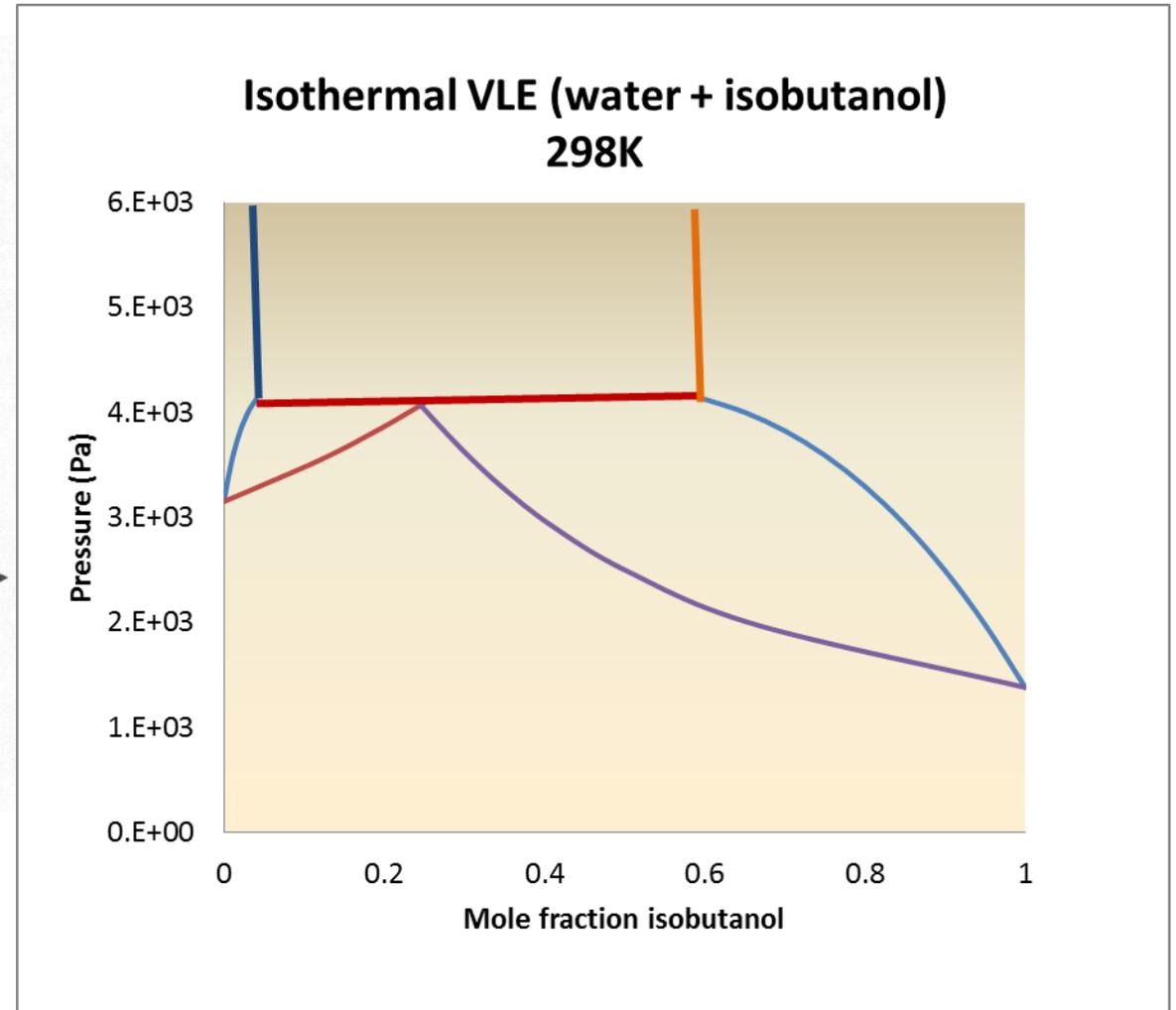
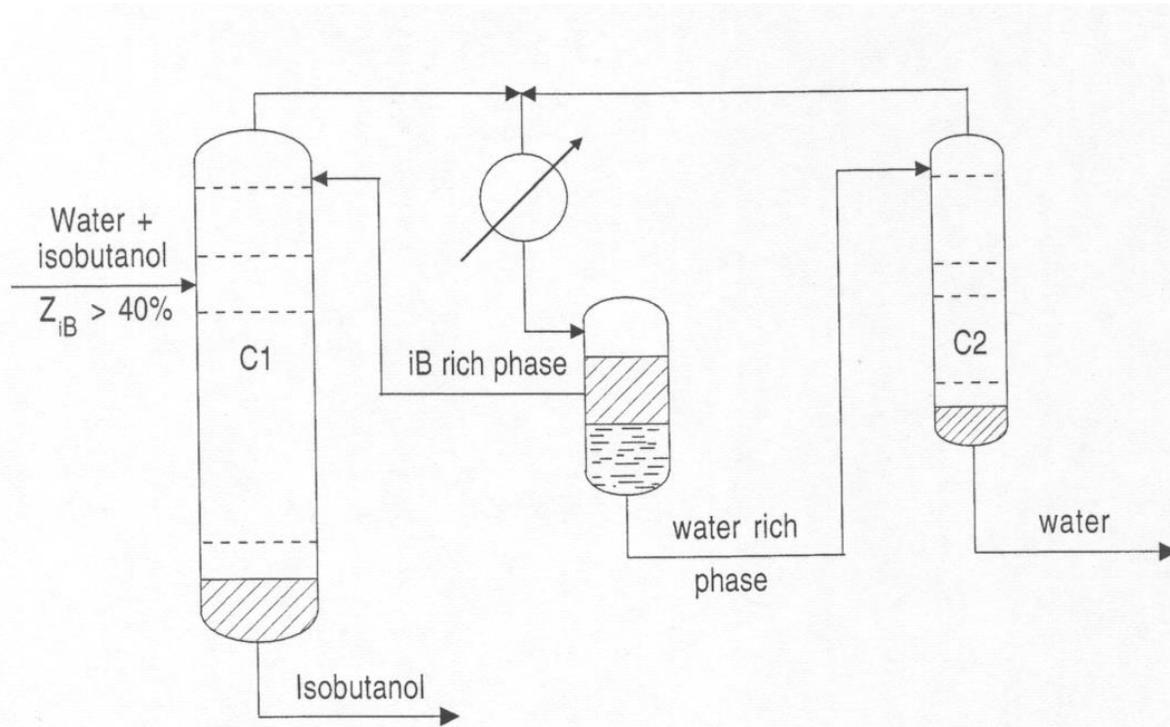
Volatilité relative:

$$\alpha_{1,2} = \frac{K_1}{K_2} = \frac{P_1^\sigma \gamma_1}{P_2^\sigma \gamma_2}$$



Activity coefficients at 318.15K





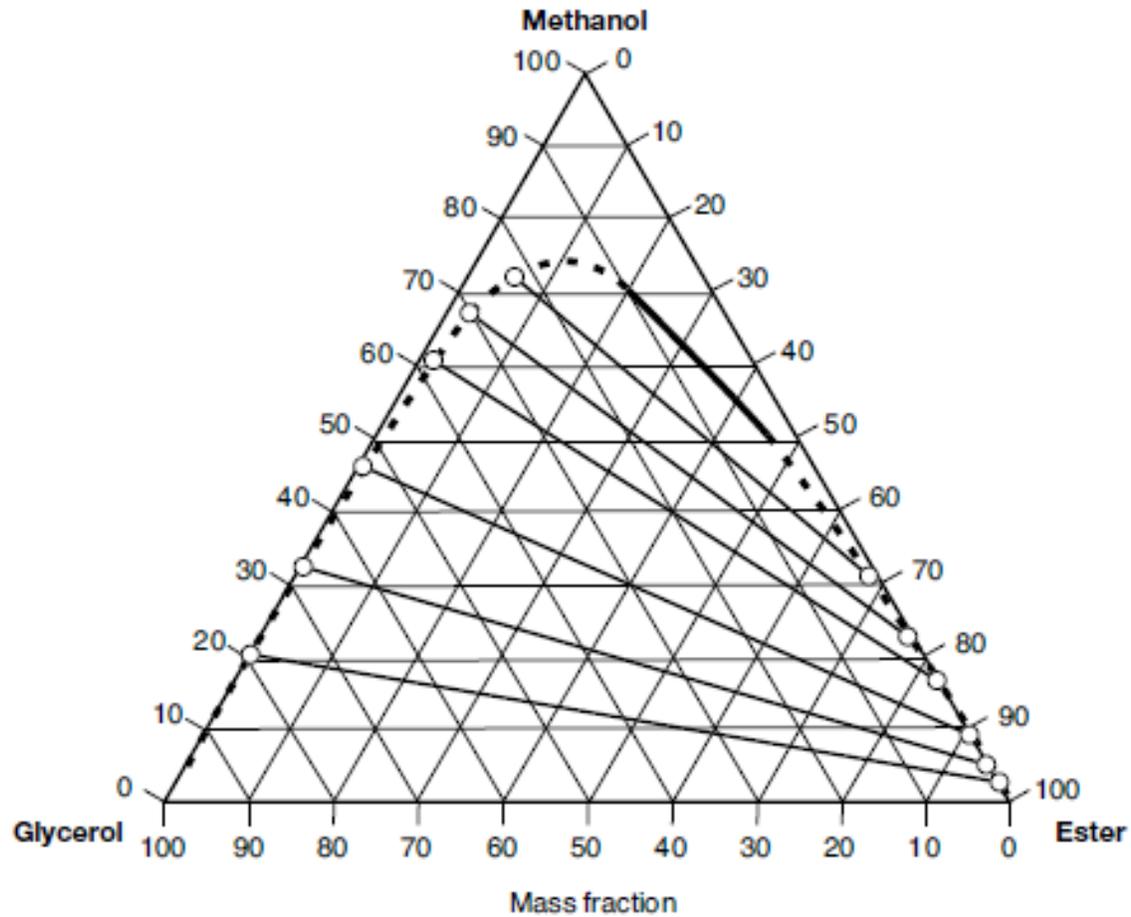
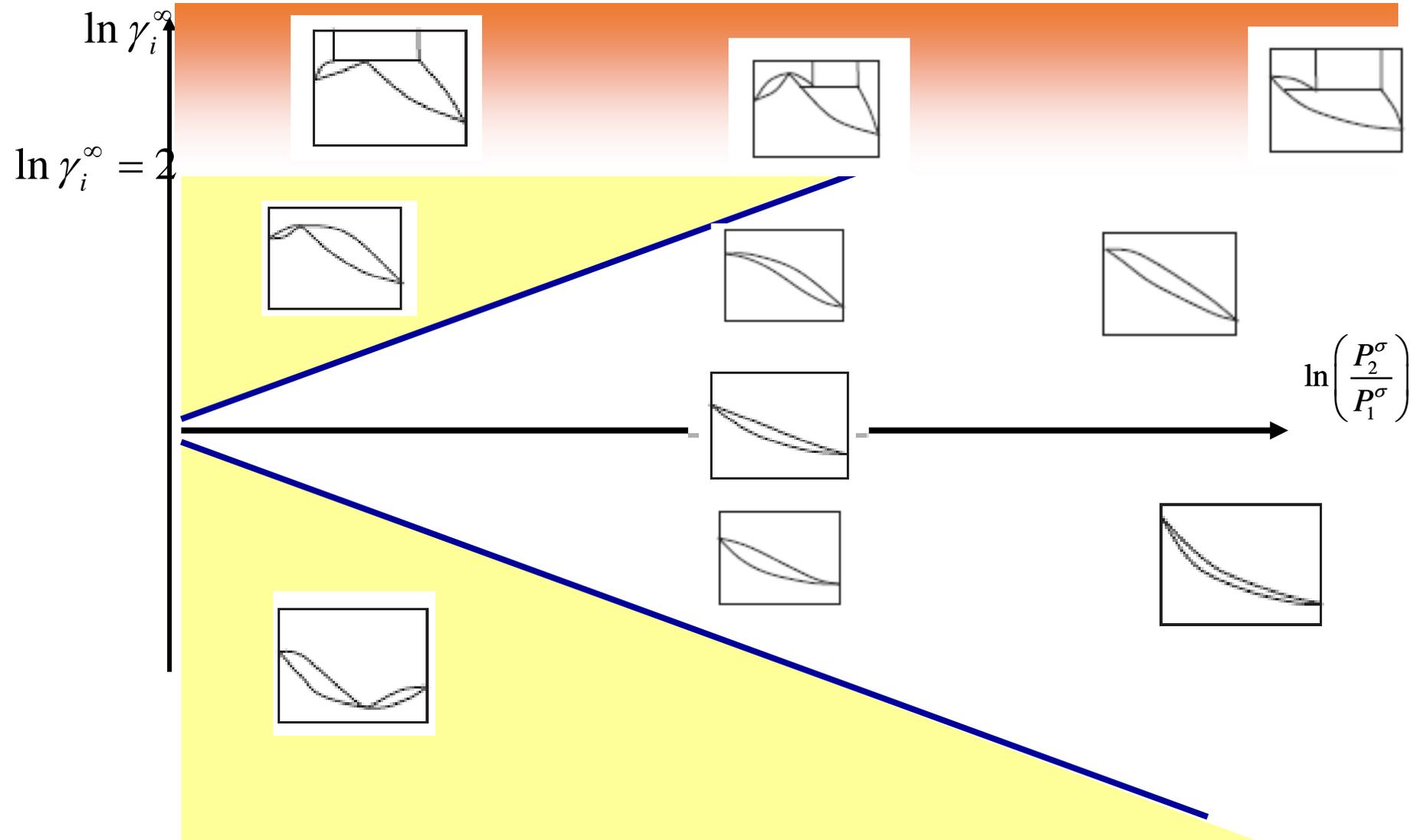


Figure 3.44

Ternary LLE diagram of the glycerol + methanol + methyl ester system.

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LES CAUSES

enthalpique

P

A

P

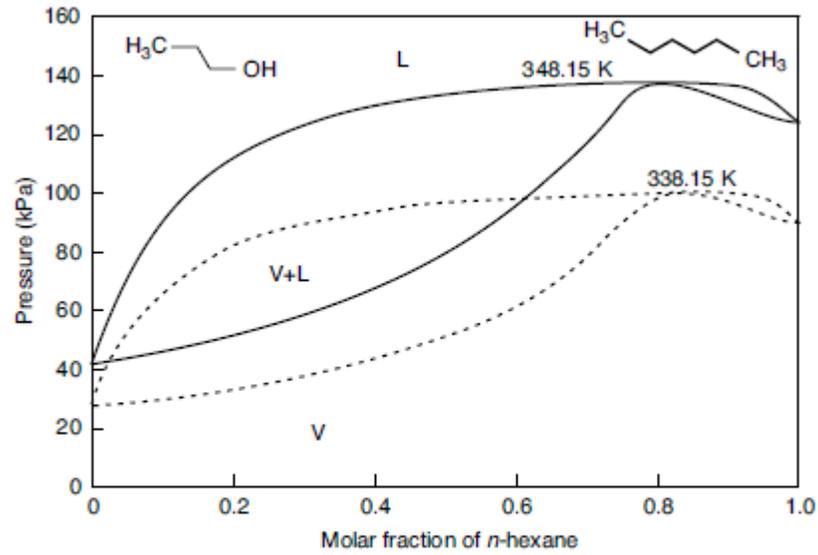


Figure 4.51
1-Propanol + *n*-hexane binary vapour-liquid equilibrium, from [256].

entropique

T

T

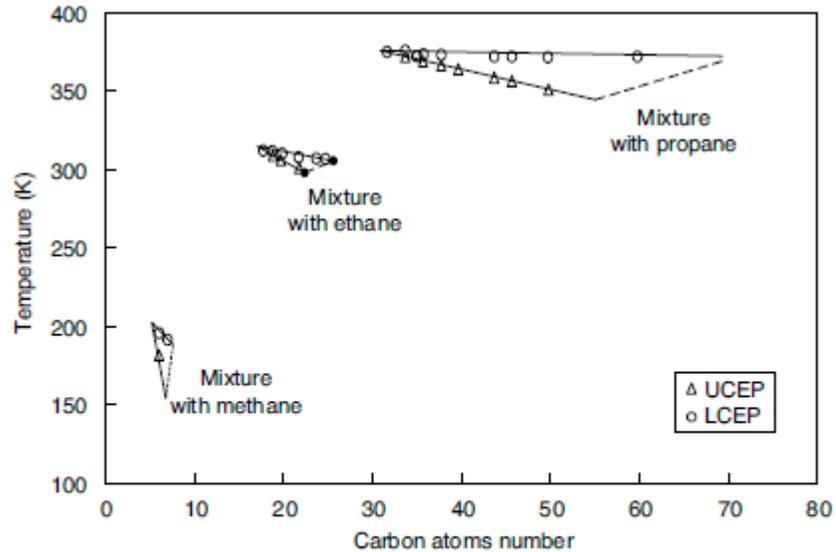
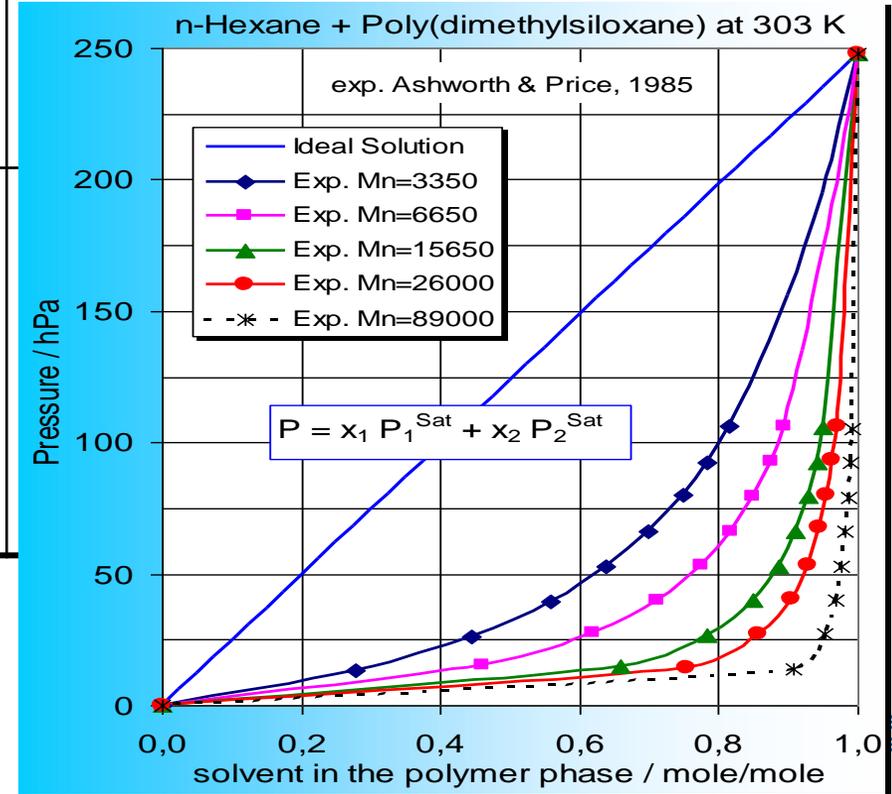
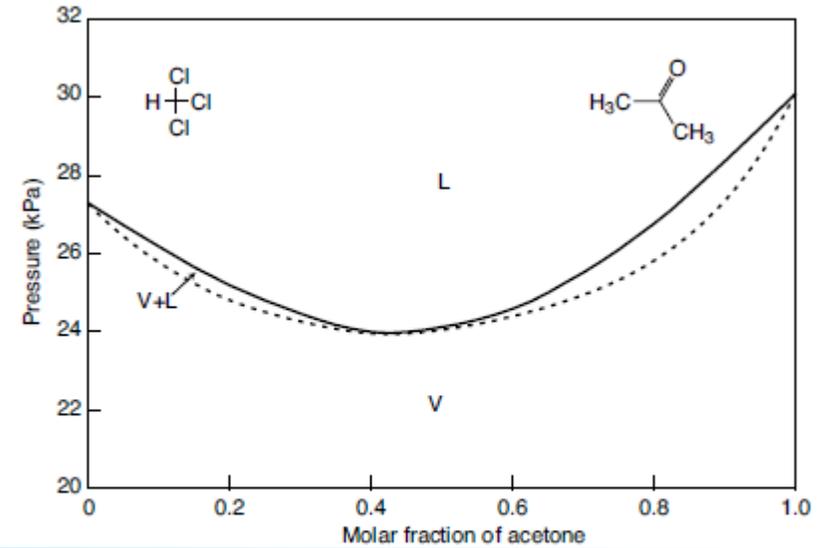
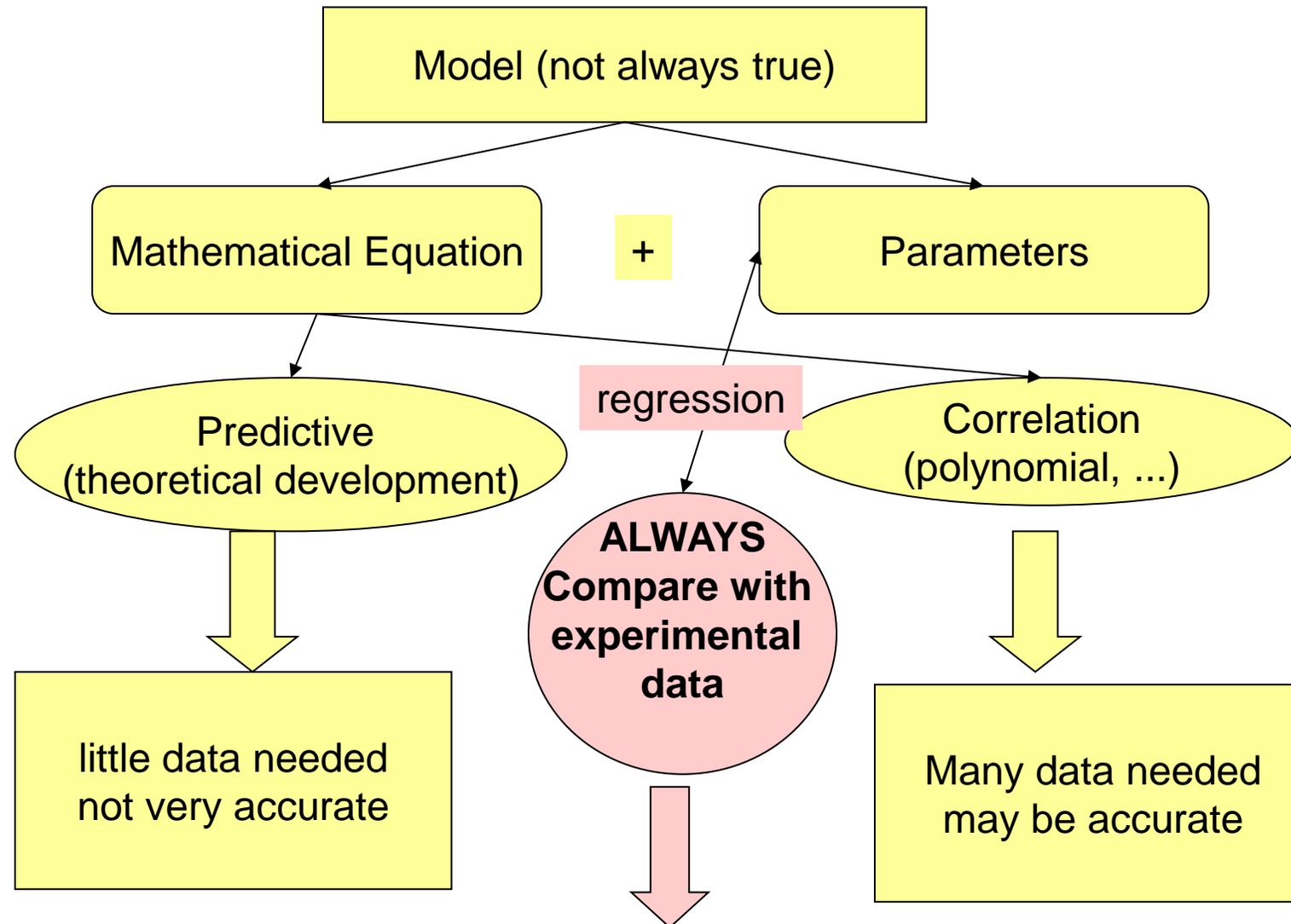


Figure 4.25
Position of the liquid-liquid equilibrium in asymmetric alkanes mixtures [46]





● Contexte

- Objectif industriel
- Quelques définitions

● Les phénomènes et les causes

● Un modèle statistique

- Construction du modèle
- Exemples d'application

● Conclusions/perspectives

- Les aspects entropiques
 - Répulsion sphère dure
 - Formation de chaînes
- Les aspects enthalpiques
 - Les liaisons hydrogène
 - La polarité

RELATIONS ENTRE PROPRIÉTÉS THERMODYNAMIQUES LA THÉORIE DE PERTURBATION

- Energy can be written as a sum of terms, each related to a specific energy contribution

- yielding:
$$A(T, V, \vec{N}) = A^{\#} + A_{\text{rép}} + A_{\text{attr}} + A_{\text{ass}} + A_{\text{polaire}}$$

- or:
$$P(T, V, \vec{N}) = \left. \frac{\partial A}{\partial V} \right|_{T, N} = 1 + P_{\text{rép}} + P_{\text{attr}} + P_{\text{ass}} + P_{\text{polaire}}$$

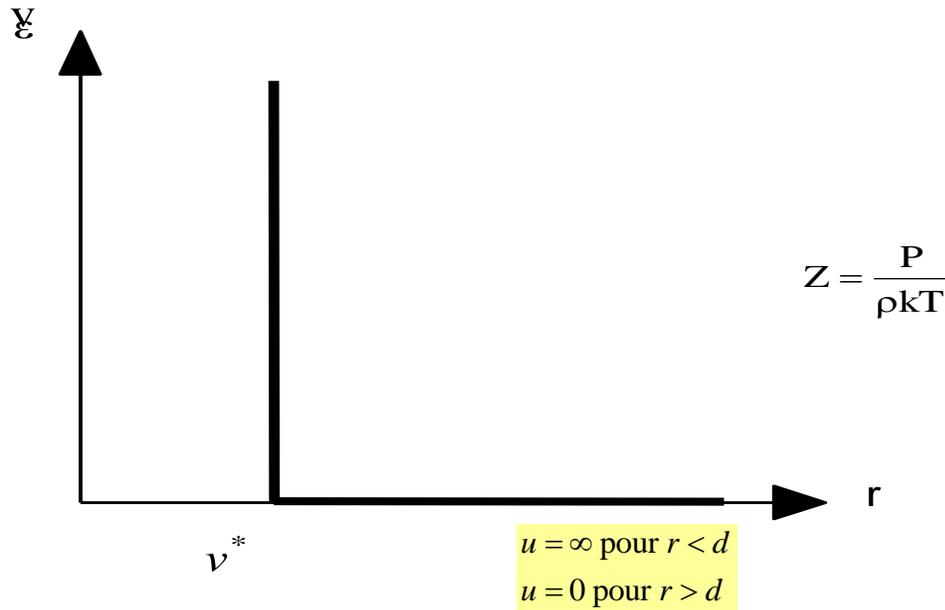
$$\frac{\mu_i}{RT}(T, V, \vec{N}) = \left. \frac{\partial A_i / RT}{\partial n_i} \right|_{T, V, n_{j \neq i}} = \frac{\mu_i^{\#}}{RT} + \frac{\mu_i}{RT}_{\text{rép}} + \frac{\mu_i}{RT}_{\text{attr}} + \frac{\mu_i}{RT}_{\text{ass}} + \frac{\mu_i}{RT}_{\text{polaire}}$$

EQUATION D'ÉTAT DE SPHERES DURES

$$\frac{A - A^\circ}{NkT} = a^{hs}$$

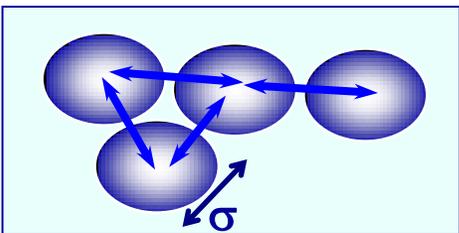
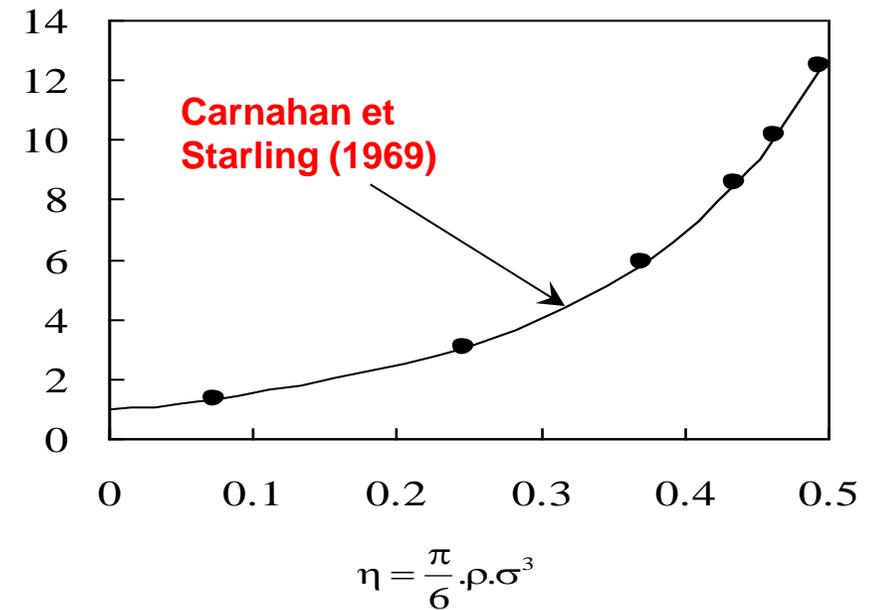
$$a^{hs} = \frac{4\eta - 3\eta^2}{(1-\eta)^2}$$

Carnahan et Starling (1969)



Comparison with MD

● Alder et Wainwright (1964)



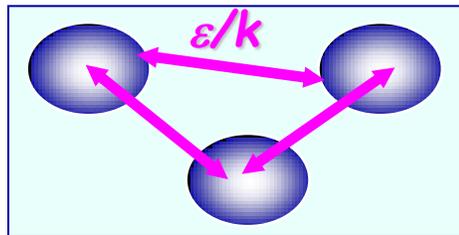
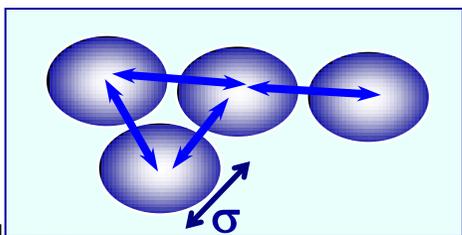
Sphère + Lennard-Jones

$$\frac{A - A^{\circ}}{NkT} =$$

$$a^{hs} + a^{disp}$$

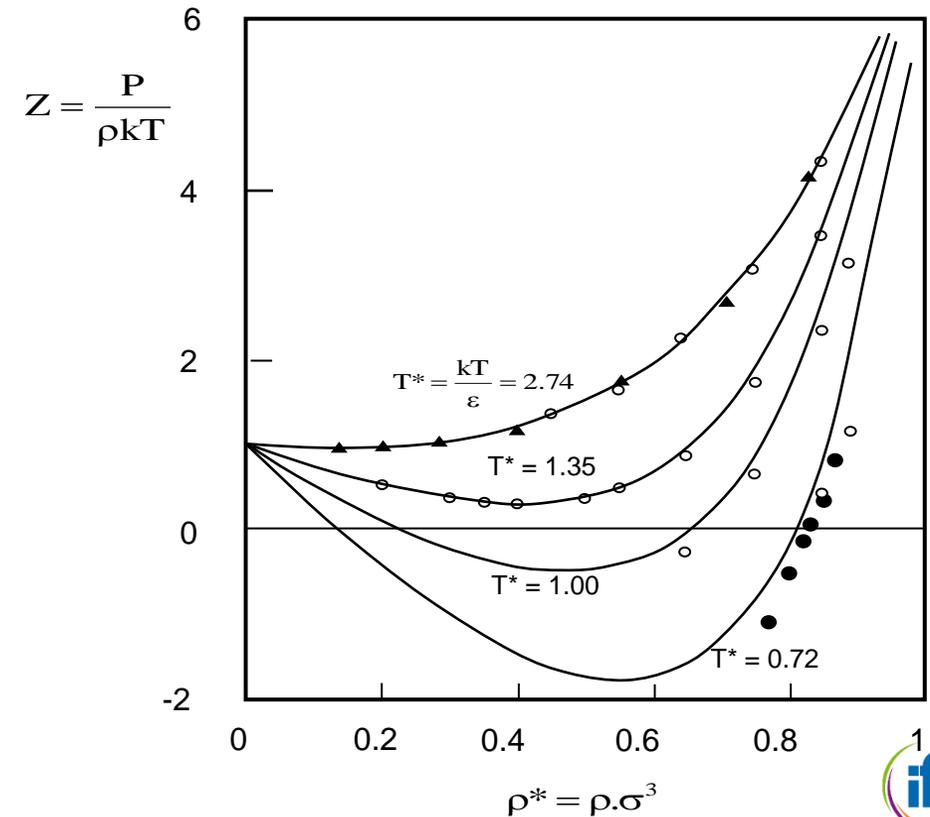
$$a^{disp} = a_1 + \frac{a_2}{T}$$

Barker et Henderson (1967)

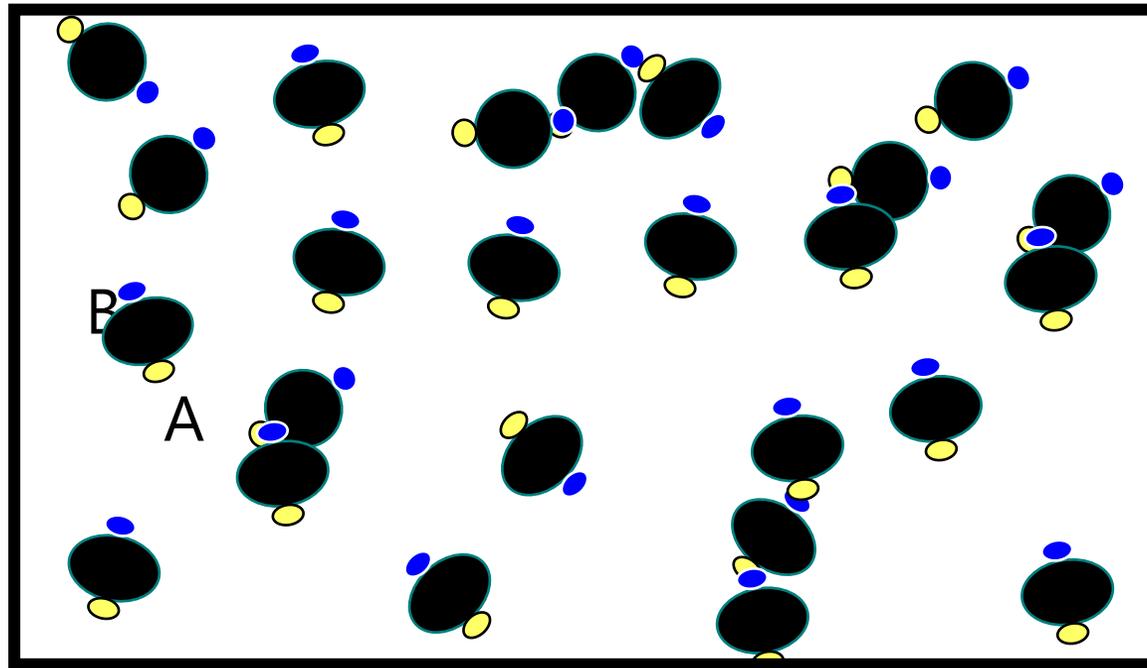


Comparison with MD/MC

● ○ ▲ Barker et al (1966), Verlet (1967), Wood et Parker (1957)



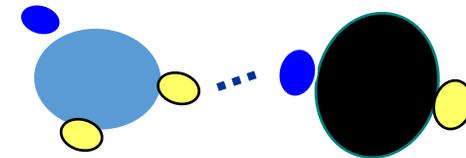
- Une des causes principales de la non-idéalité est le phénomène de liaisons hydrogène



● Consider sites A on molecule i and B on molecule j

● The equilibrium is written as:

● and the concentrations are:



$$\Delta^{A_i B_j} = \frac{[A_i B_j]}{[A_i][B_j]}$$

$$[A_i] = \frac{n_i X^{A_i}}{V} = \rho_i X^{A_i} \quad [B_j] = \frac{n_j X^{B_j}}{V} = \rho_j X^{B_j}$$

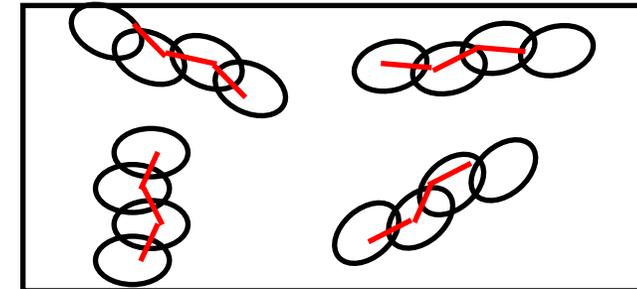
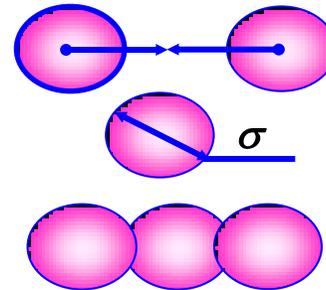
$$[A_i B_j] = \frac{n_i n_j}{V} X^{A_i B_j} = \frac{\rho_i \rho_j}{\rho} X^{A_i B_j}$$

- Chain formation
 - parameters:

ε

σ

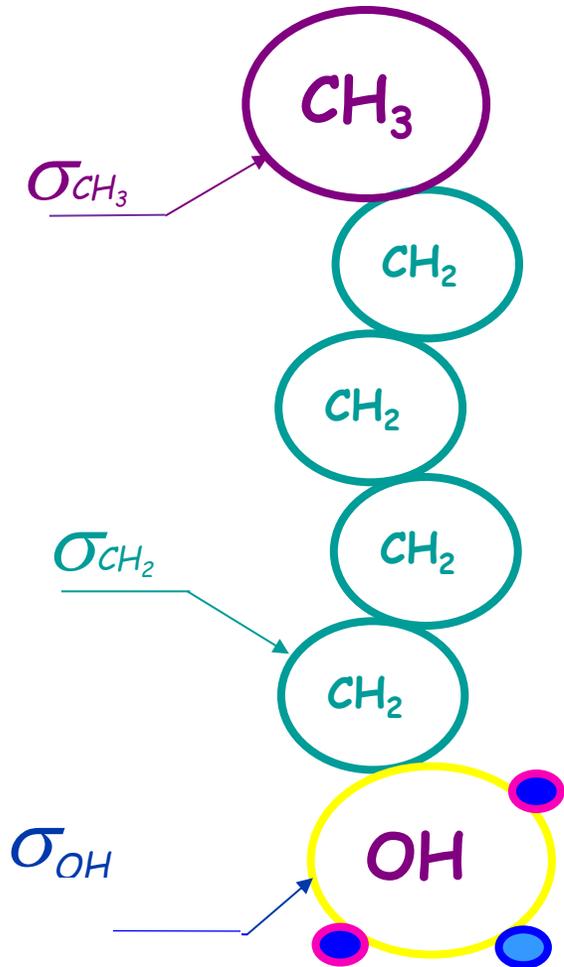
m



chain formation

$$A(T, v, \vec{N}) = A^{\#} + m(A_{rep} + A_{disp}) + A_{chain}$$

Molecular structure



Pure component parameters

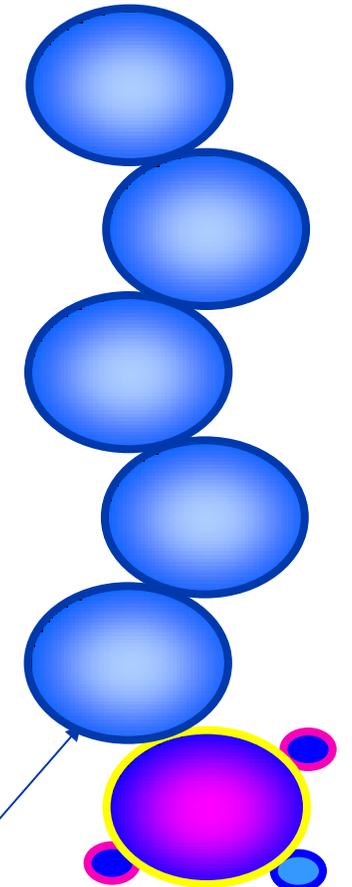
$$\varepsilon_{\text{molécule}} = (n_{\text{CH}_3} + n_{\text{CH}_2} + n_{\text{OH}}) \sqrt{\varepsilon_{\text{CH}_3}^{n_{\text{CH}_3}} \varepsilon_{\text{CH}_2}^{n_{\text{CH}_2}} \varepsilon_{\text{OH}}^{n_{\text{OH}}}}$$

$$\sigma_{\text{molécule}} = \frac{n_{\text{CH}_3} \sigma_{\text{CH}_2} + n_{\text{CH}_2} \sigma_{\text{CH}_2} + n_{\text{OH}} \sigma_{\text{OH}}}{n_{\text{CH}_3} + n_{\text{CH}_2} + n_{\text{OH}}}$$

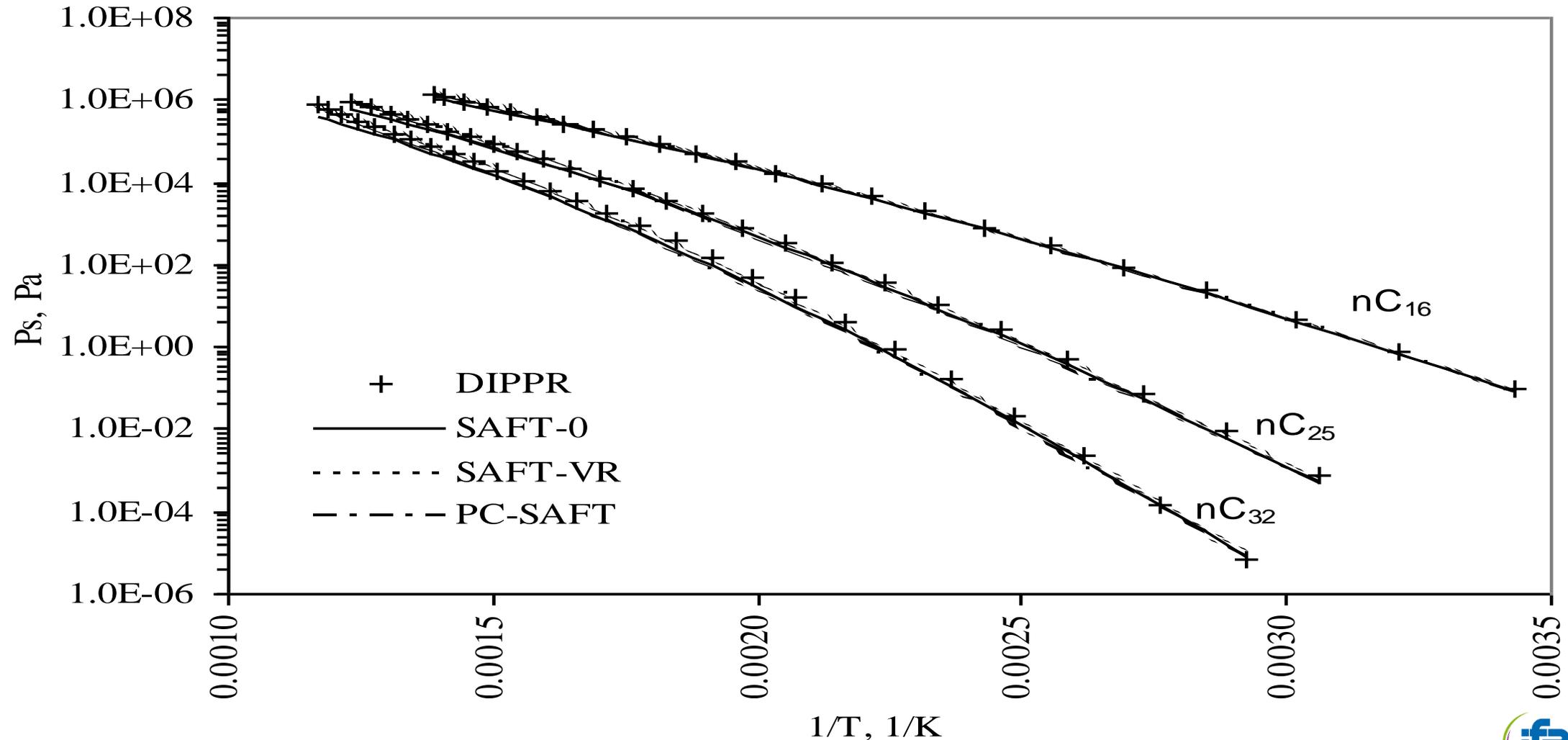


$$m_{\text{molécule}} = n_{\text{CH}_3} R_{\text{CH}_3} + n_{\text{CH}_2} R_{\text{CH}_2} + n_{\text{OH}} R_{\text{OH}}$$

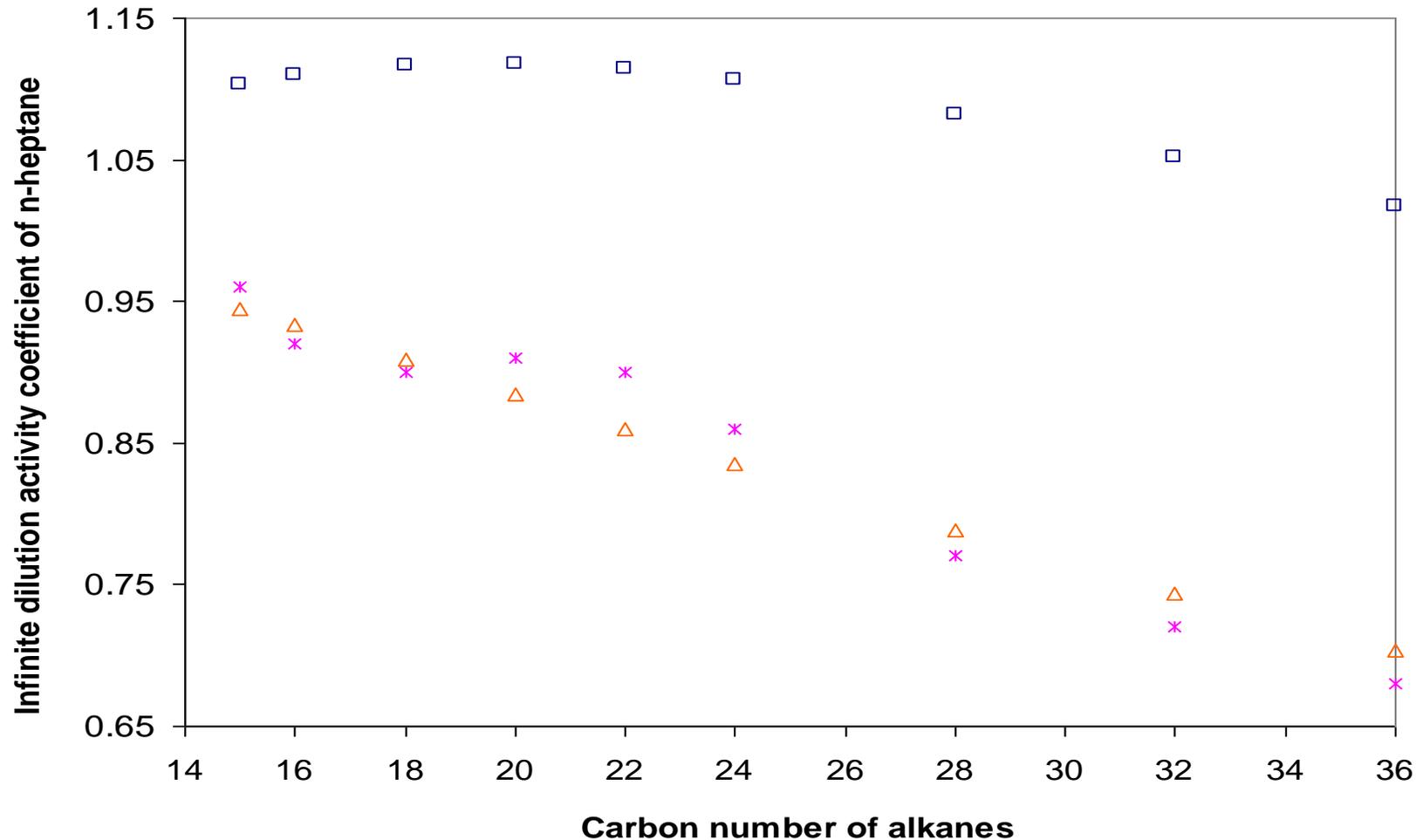
$\sigma_{\text{molécule}}$



PURE COMPONENT VAPOUR PRESSURES USING GC-PC-SAFT



COEFFICIENT D'ACTIVITÉ À DILUTION INFINIE

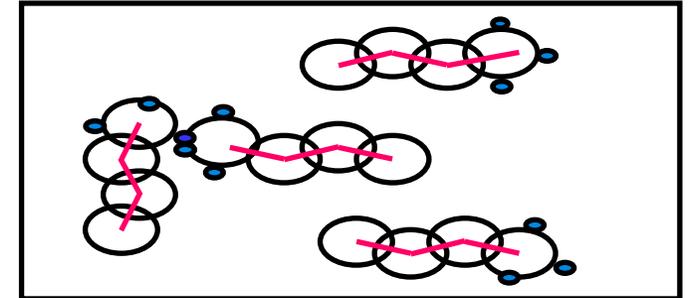
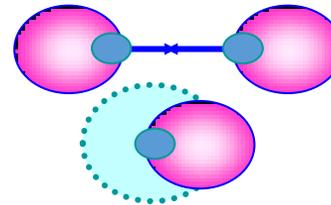


Infinite dilution activity coefficient of n-heptane in n-alkanes with different carbon numbers. Comparison of the experimental data (asterisks) from [78] and the modeling results of the GC-PPC-SAFT model with (squares) and without (triangle) the 'predictive' k_{ij} parameter. k_{ij} is estimated using the predictive rule given by Nguyen-Huynh [60].

- Association (e.g. hydrogen bonds)
 - parameters (between two segments or groups)

ϵ^{assoc}

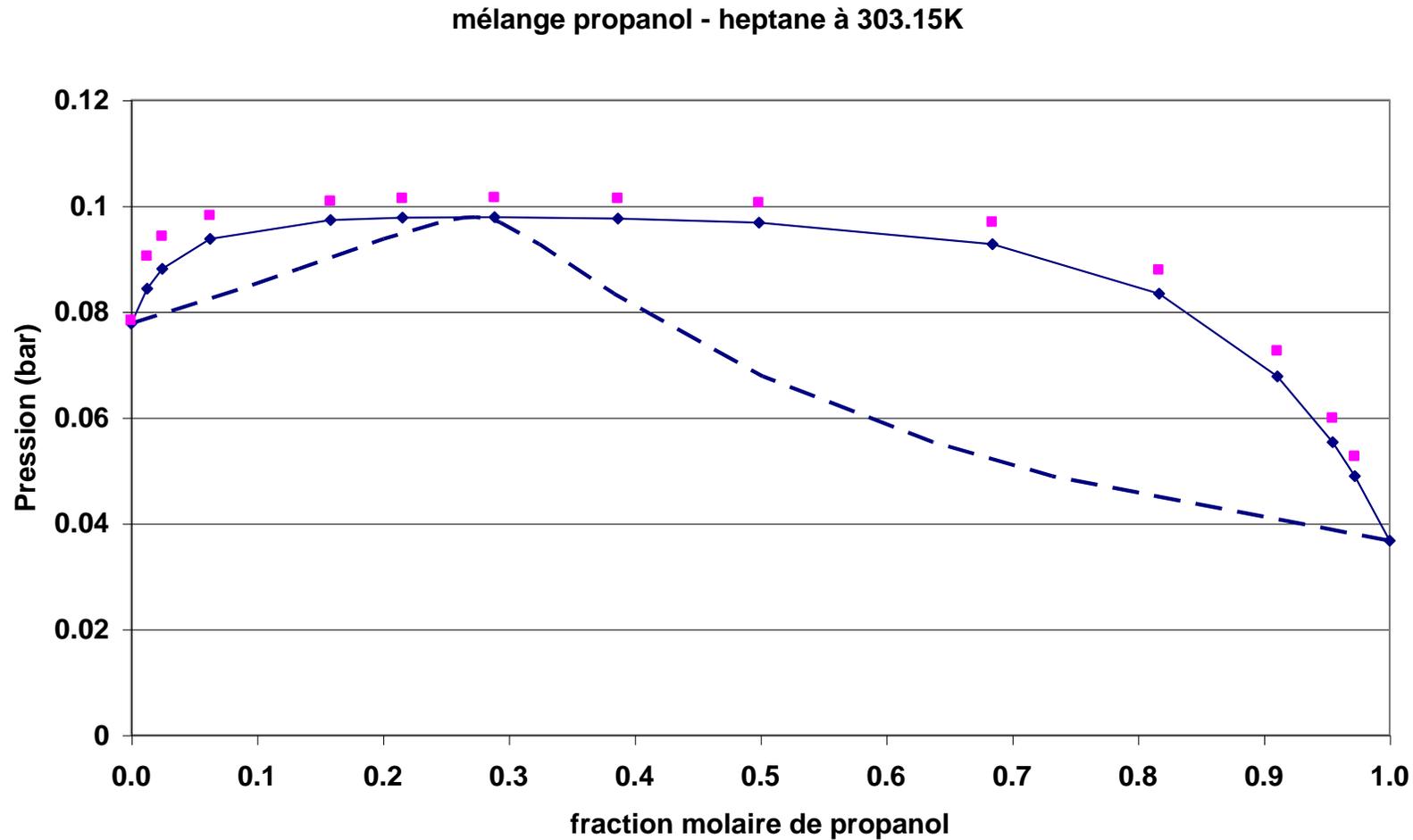
K^{assoc}



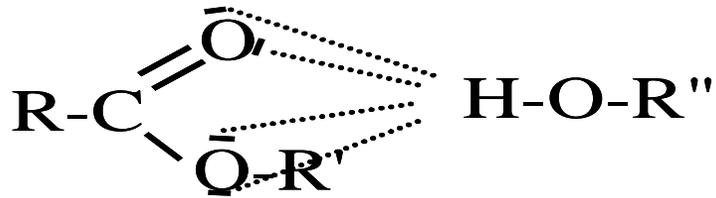
Association interactions

$$A(T, \nu, \vec{N}) = A^{\#} + m(A_{rep} + A_{disp}) + A_{chain} + A_{ass}$$

EFFECT OF THE ASSOCIATION (PREDICTIVE: KIJ=0)



ALCOHOL- ESTER CROSS ASSOCIATION: THE INTEREST OF IR SPECTROSCOPY



Kahn et al.

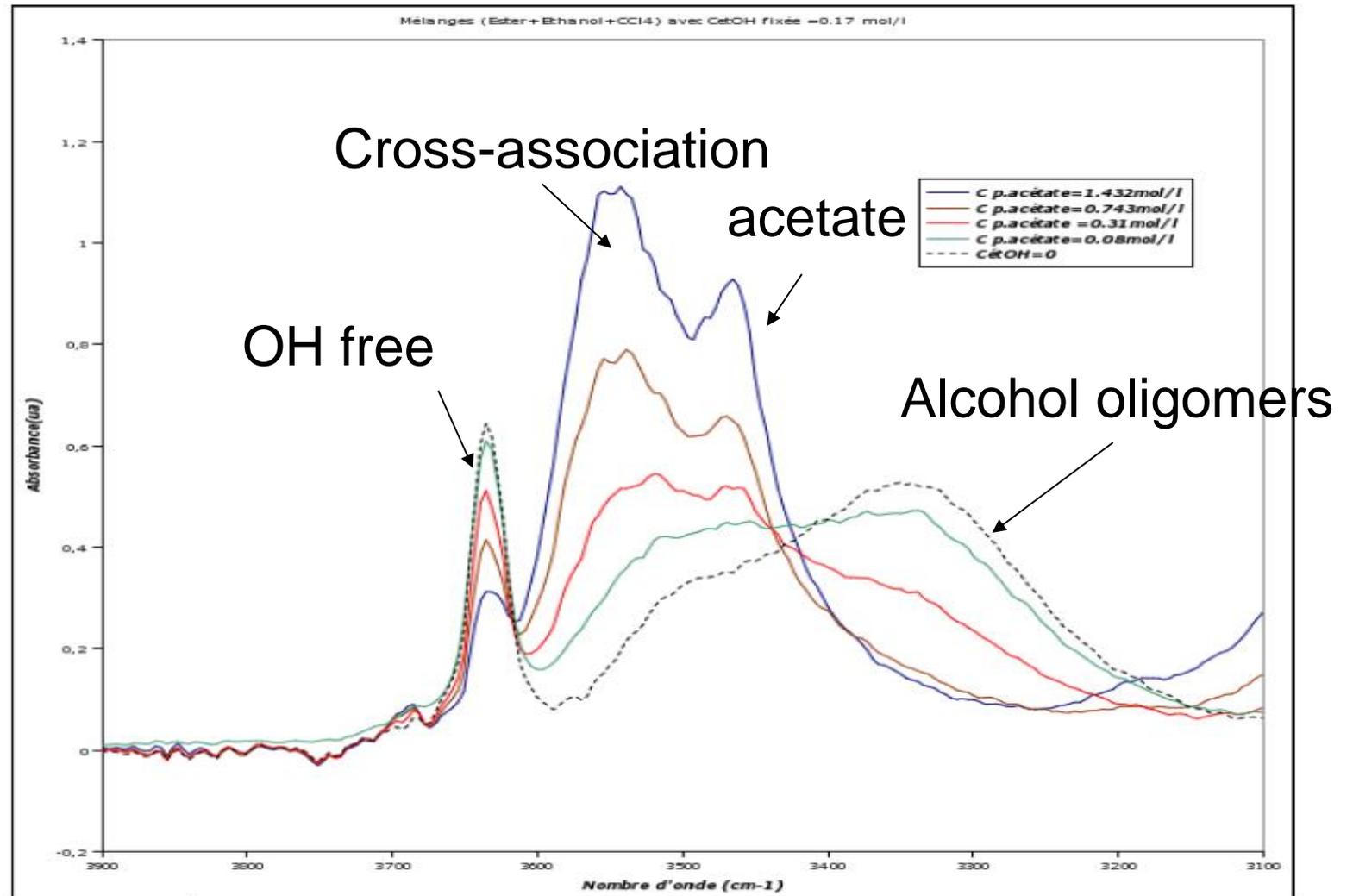
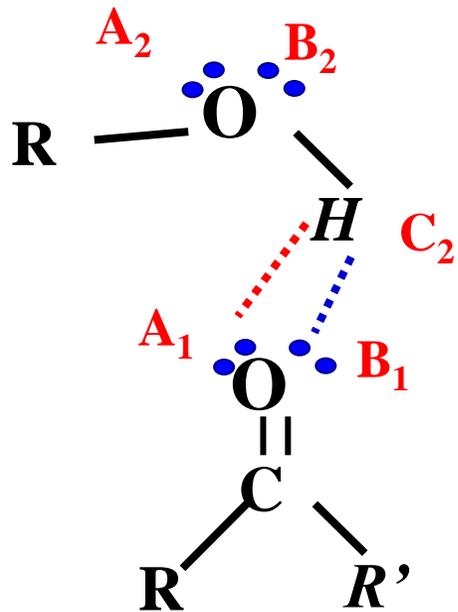


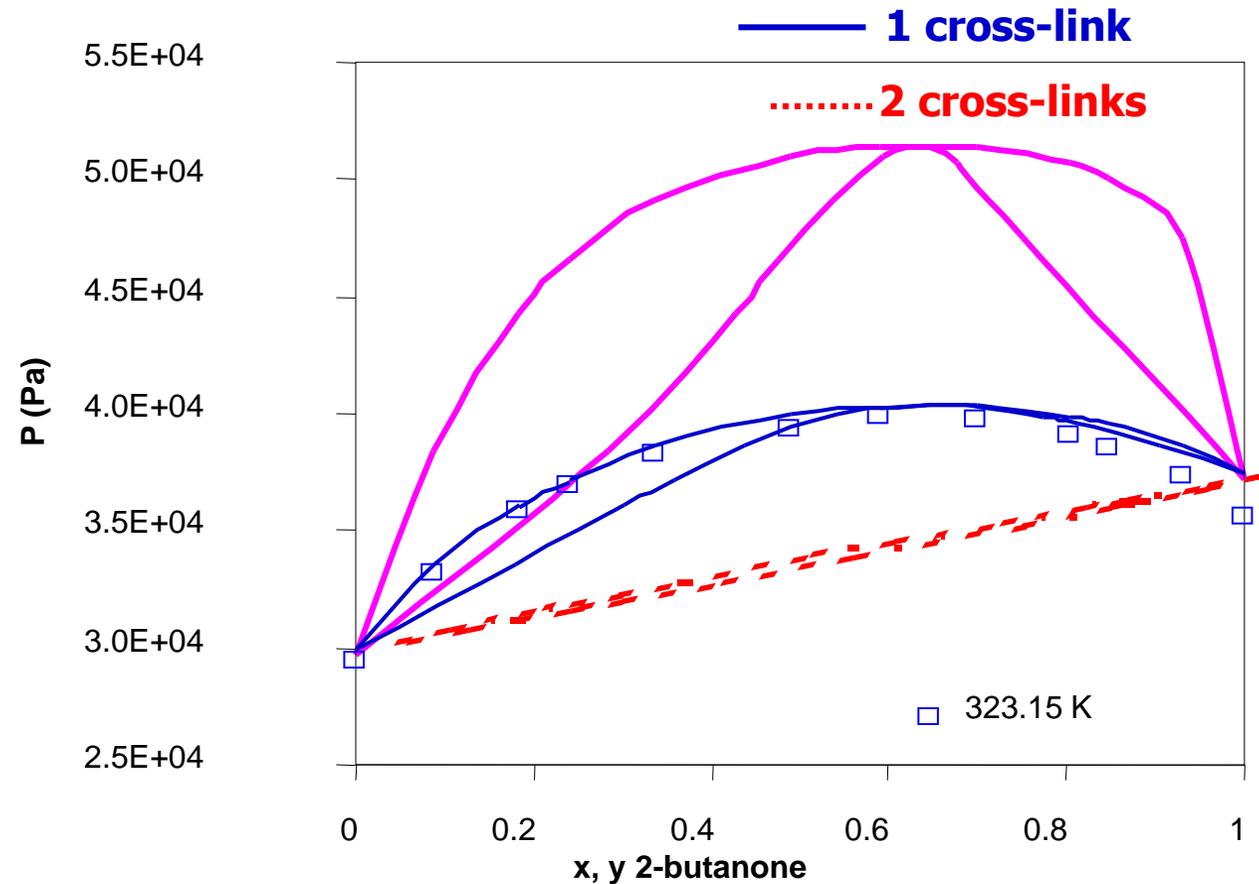
Figure 27: Évolution des spectres d'absorption en fonction de la concentration en propyl acétate (la concentration en éthanol est constante = 0,17 mol/l)



Hypothesis:

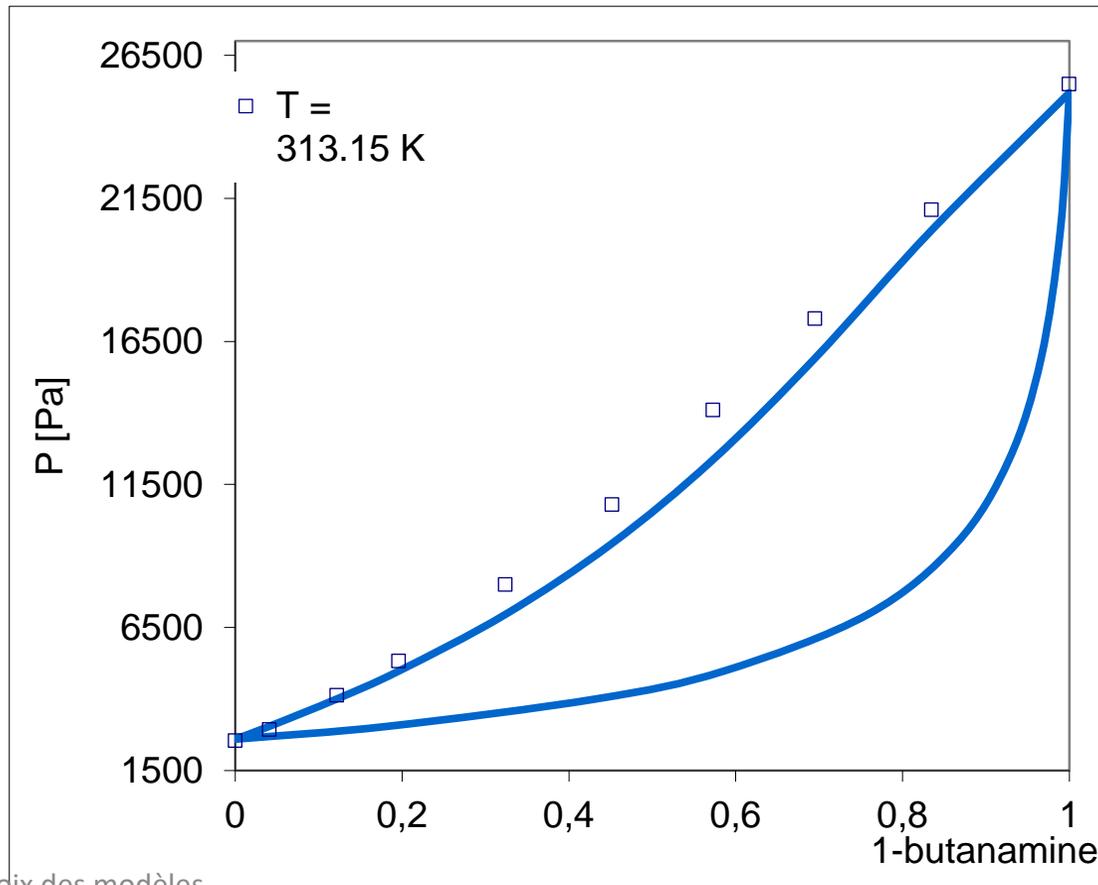
$$\varepsilon^{cross} = \varepsilon^{auto-OH}$$

$$K^{cross} = K^{auto-OH}$$

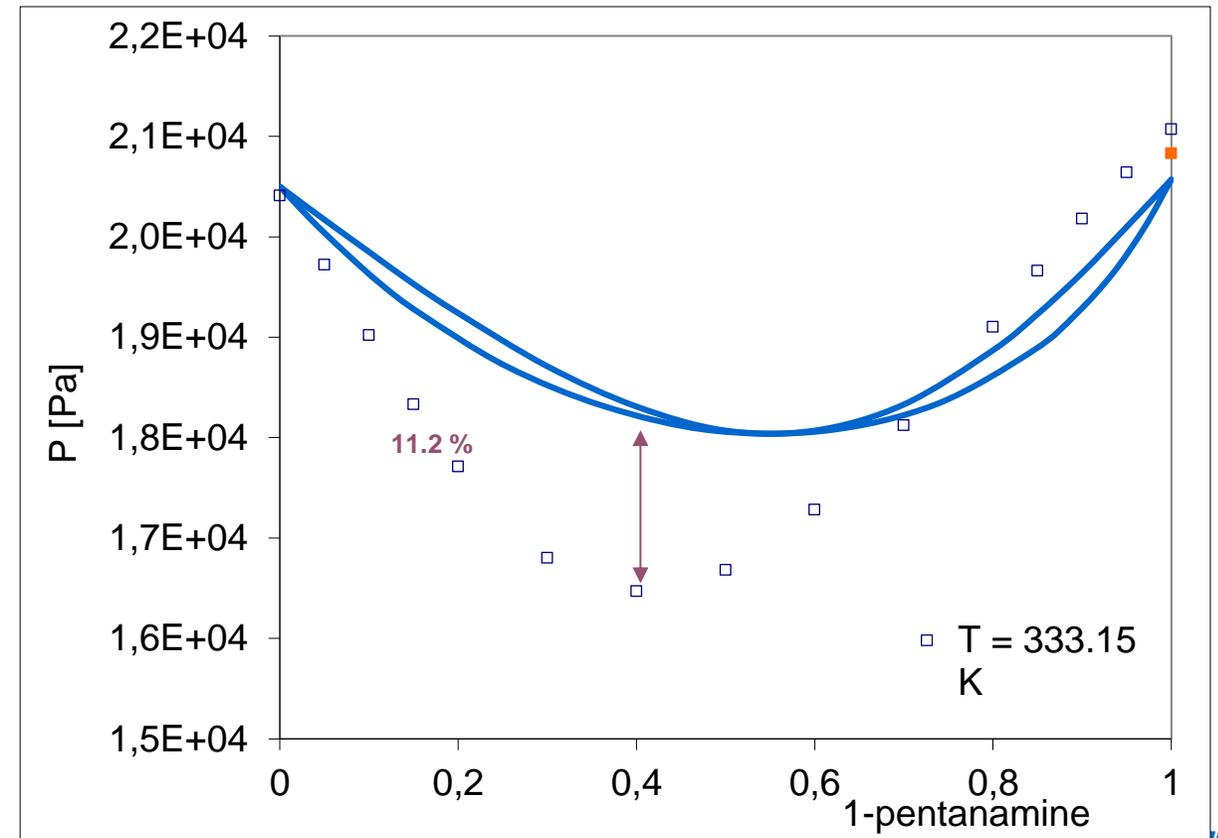


2-butanone + éthanol

- 1-butanamine + 1-butanol



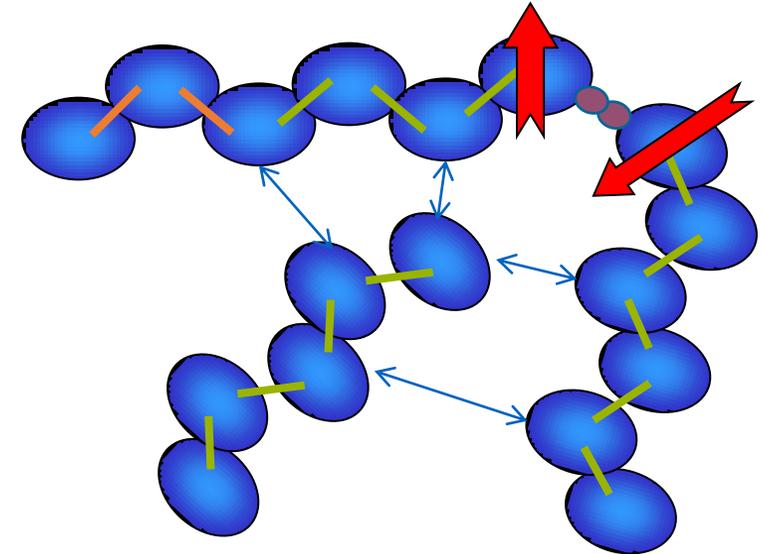
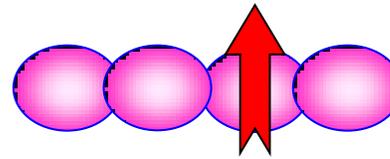
- ⌘ 1-pentanamine + 1-propanol



- Polar contribution
 - long distance dipole or quadrupole interactions
 - parameters (group parameters)

$$\mu, x_p^\mu$$

$$Q, x_p^Q$$



Jog et al. *Ind. Eng. Chem. Res.* (2001)

$$A(T, v, \vec{N}) = A^\# + m(A_{rep} + A_{disp}) + A_{chain} + A_{ass} + A_{polar}$$

Nguyen-Huynh et al., (2008) FPE, vol 264, pp62-75

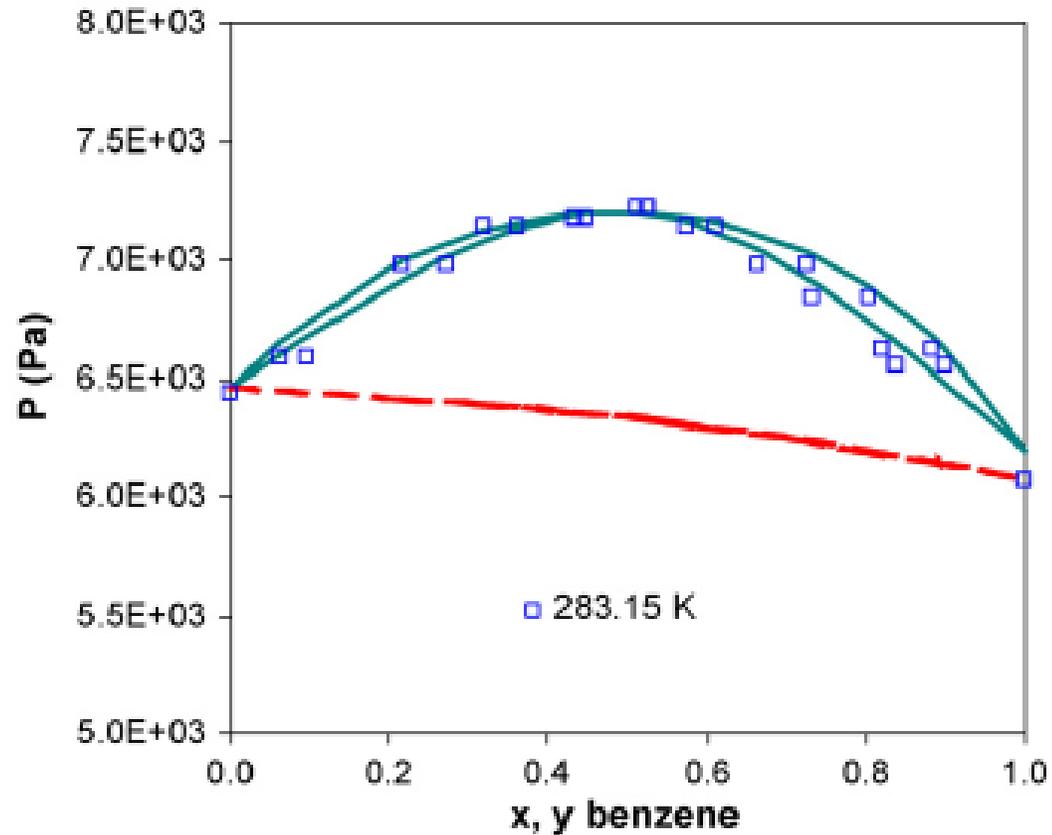


Fig. 9. Prediction of benzene + cyclohexane VLE using GC-VR-SAFT (—) and model of Tamouza et al. [12] (- - -) neglecting quadrupole moment of benzene.

● Definition

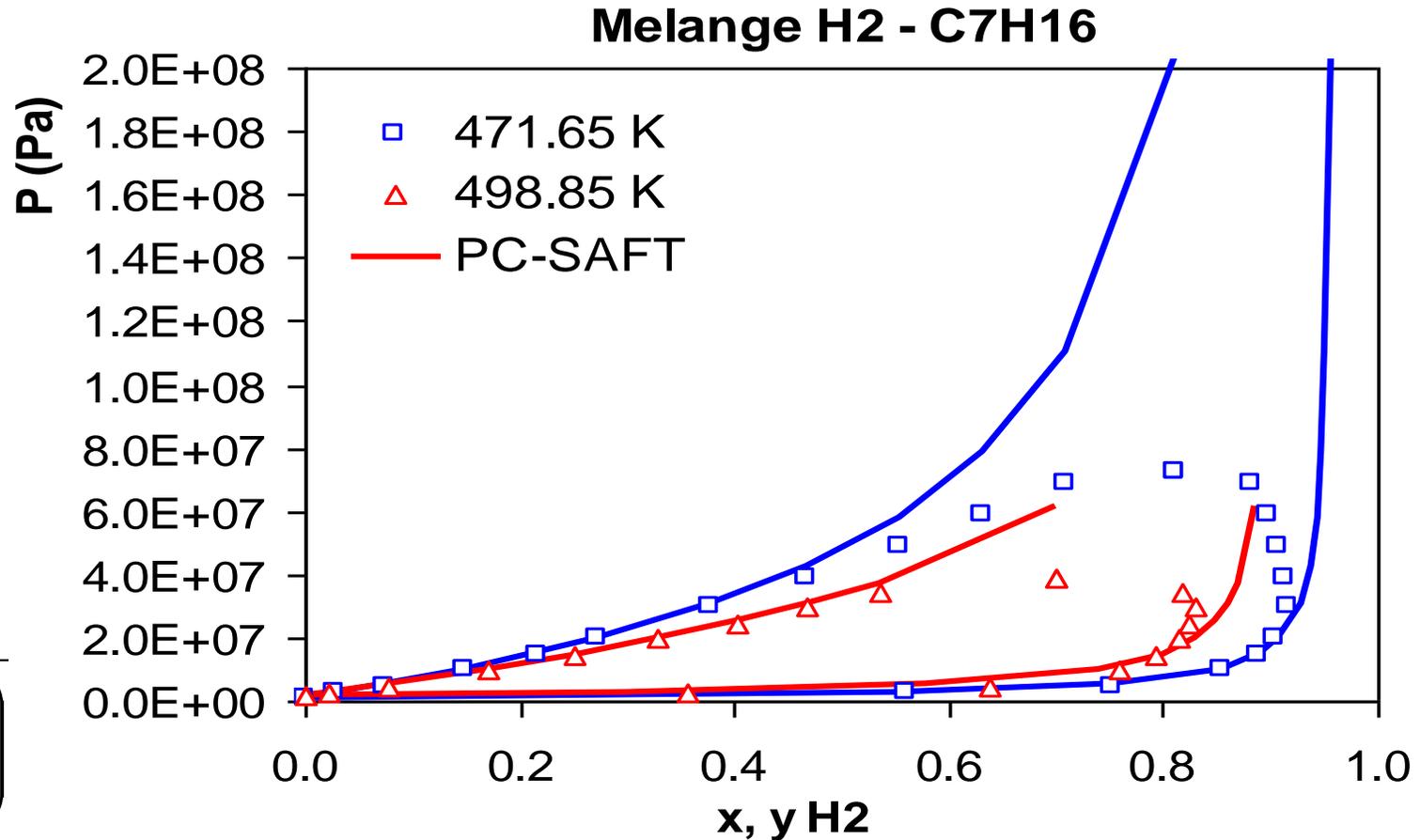
$$\varepsilon_{ij} = (1 - k_{ij}) \sqrt{\varepsilon_{ii} \varepsilon_{jj}}$$

● Calculation

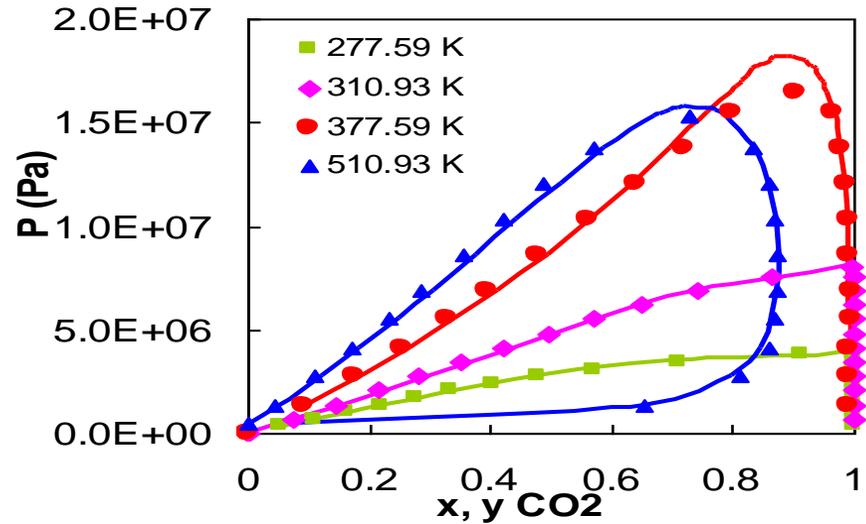
$$1 - k_{ij} = \frac{2\sqrt{(I_i I_j)}}{(I_i + I_j)}$$

● Group Contribution

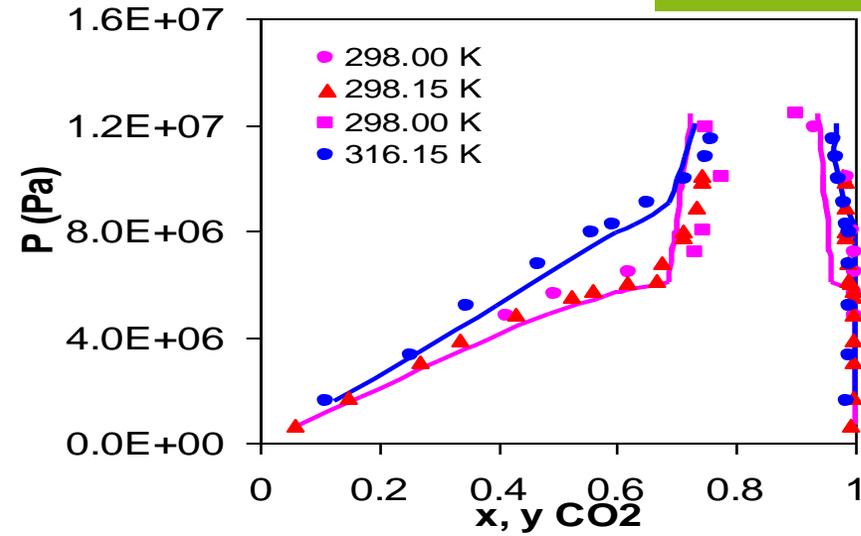
$$I_{molecule} = \sum_{i=1}^{n_{group}} n_i \sqrt{\left(\prod_{i=1}^{n_{group}} I_i^{n_i} \right)}$$



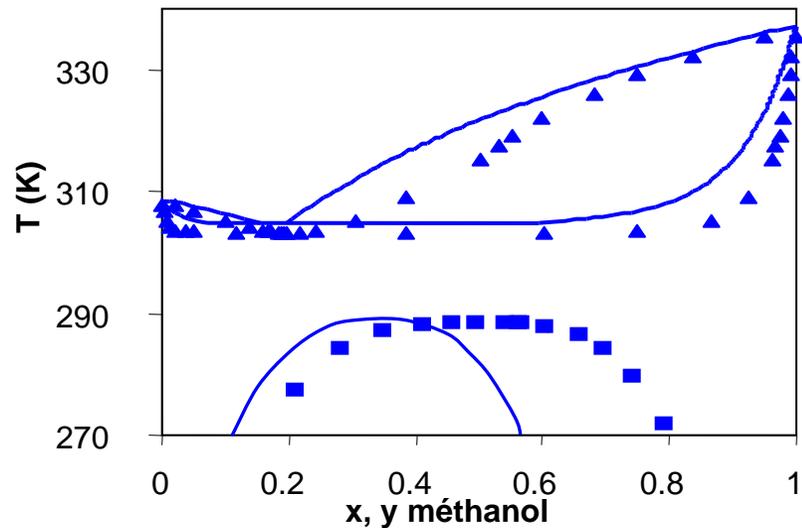
SYSTEMES QUI MONTRENT VLE ET LLE



$\text{CO}_2 + n\text{-décane}$

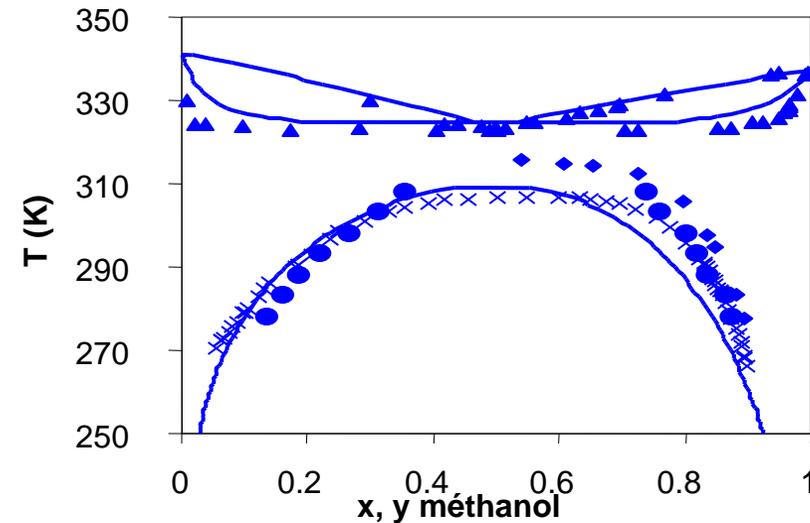


$\text{CO}_2 + 1\text{-heptanol}$



Méthanol + n-pentane

3B



Méthanol + n-hexane

MOLECULE MULTIFONCTIONNELLE ISSUE DE LA BIOMASSE: FURFURAL

NEW ENERGIES

L. Grandjean et al.: 26th European Symposium on Applied Thermodynamics, 2012

C. Pereira et al.: Guaiacol and its mixtures: new data and predictive models Part 1: Phase equilibrium Accepted for publication, FPE, 2017

M. Varfolomeev et al.: Guaiacol and its mixtures: new data and predictive models Part 2: Gibbs energy of solvation, Accepted for publication, FPE, 2017

Furfural + n-hexane

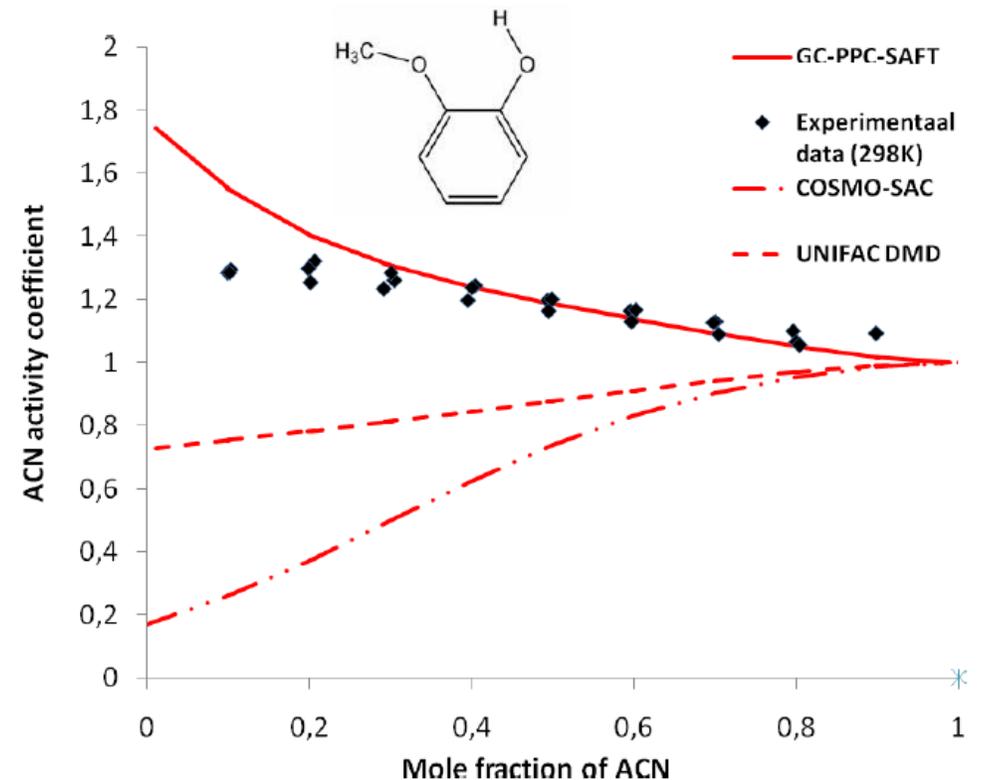
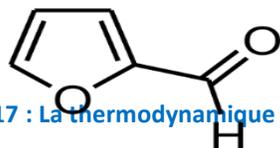
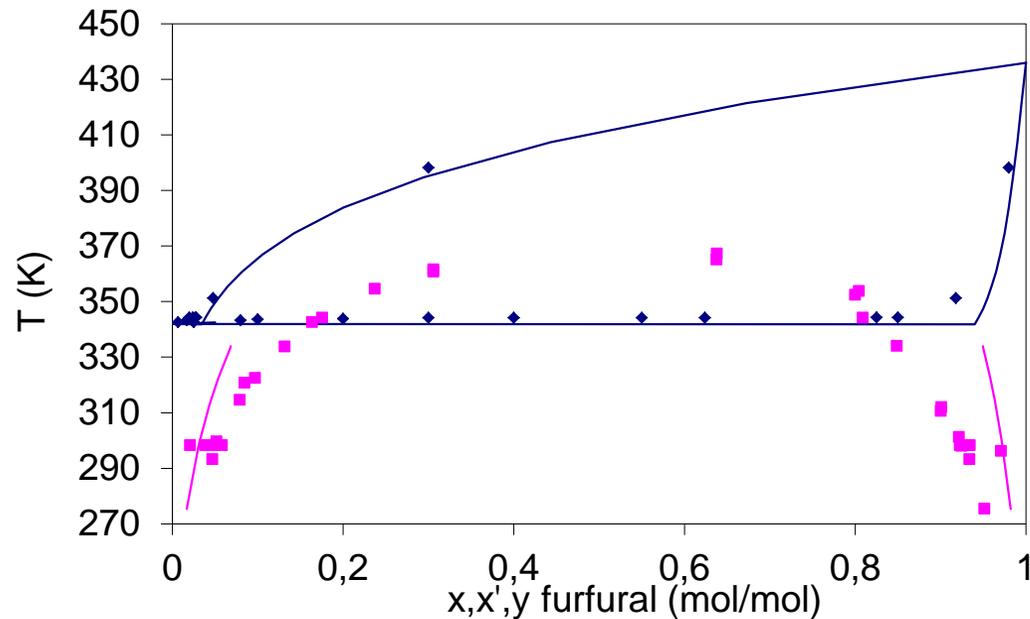
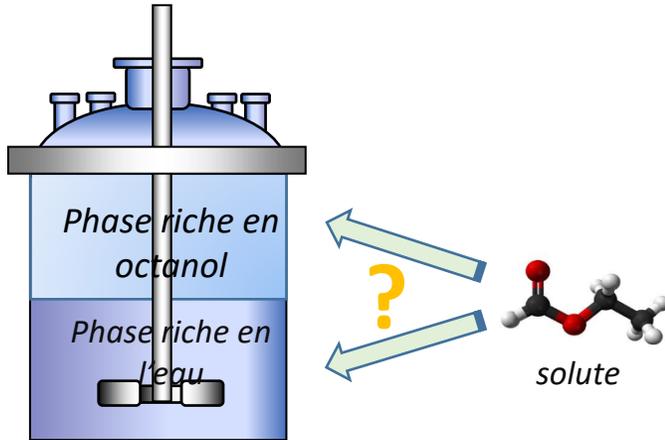


Fig.5. Activity coefficient of acetonitrile (ACN) acetonitrile-guaiacol solutions at 298K.

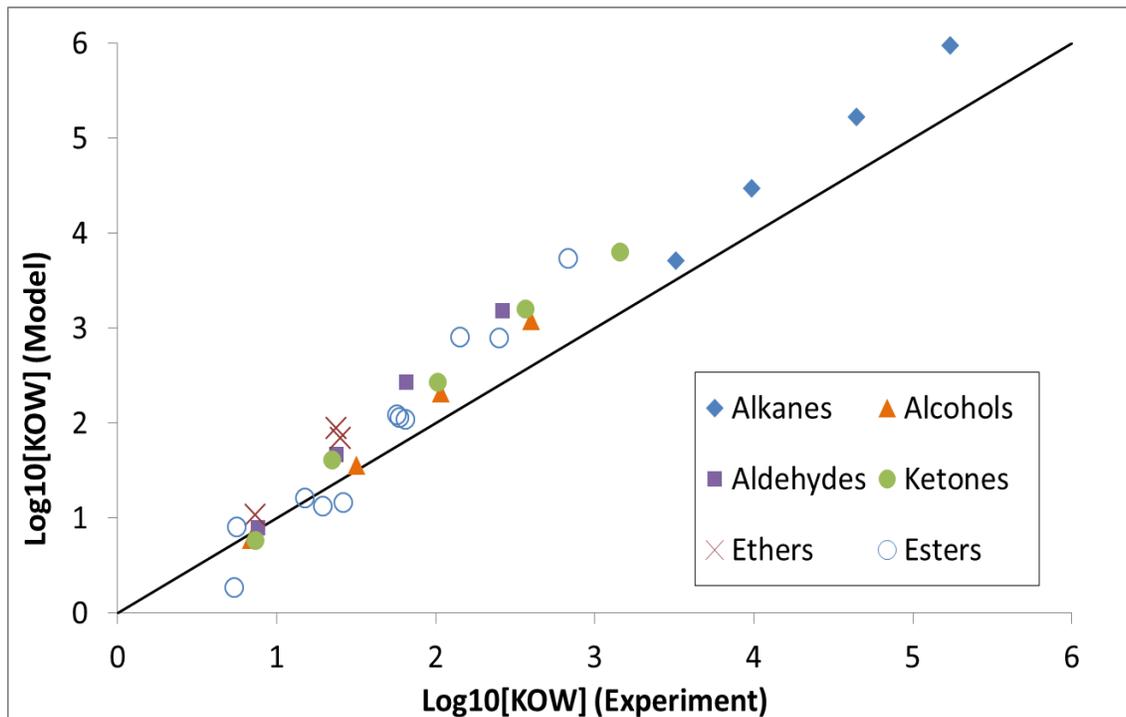
OCTANOL / L'EAU COEFFICIENT DE PARTAGE



$$K_{OW} = \frac{v^{aq} \cdot \gamma_i^{\infty,aq}}{v^{org} \cdot \gamma_i^{\infty,org}}$$

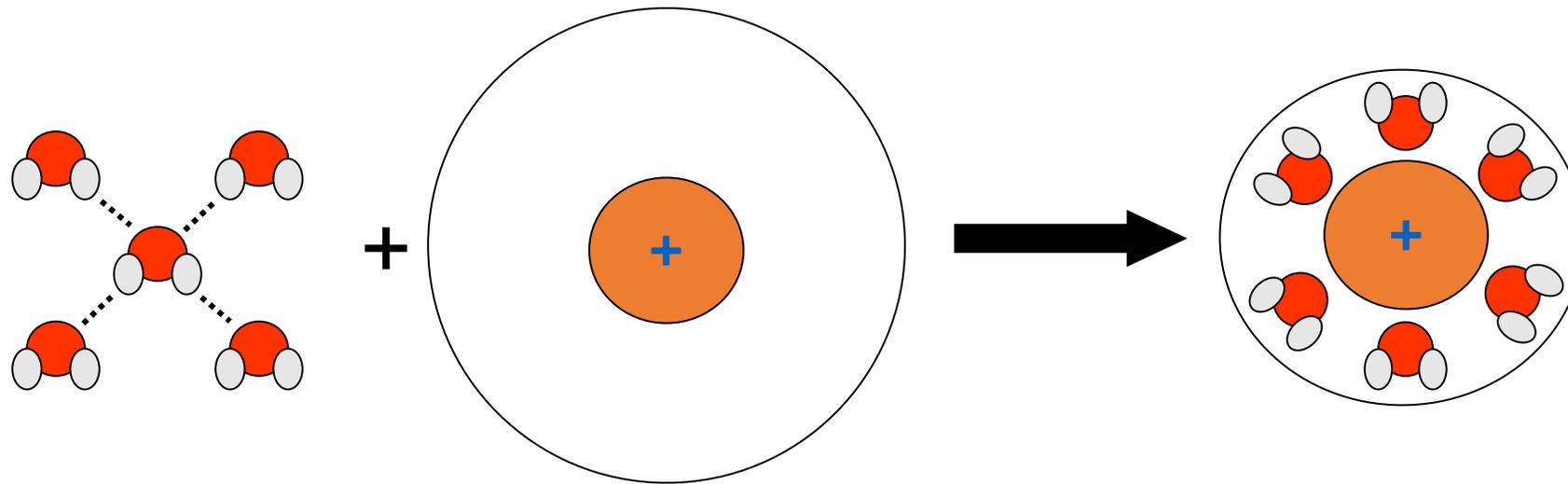
$$\gamma_i^{\infty} = \frac{\varphi_i^{\infty}}{\varphi_i^0}$$

Les volumes molaires et les coefficients de fugacité de notre nouveau modèle



Familles	Deviations Moyennes
n-Alcanes	18%
éthers	15%
Ketones	12%
Alcools	9%
Aldéhydes	8%
Esters	7%

La structure de l'eau est perturbée par l'ajout de sels (ions)



Interactions non-électrolytiques

+

Effets des électrolytes

Effet de la charge
= Born

Effet des interactions coulombiques
longue-distance
= MSA (Debye Hückel)

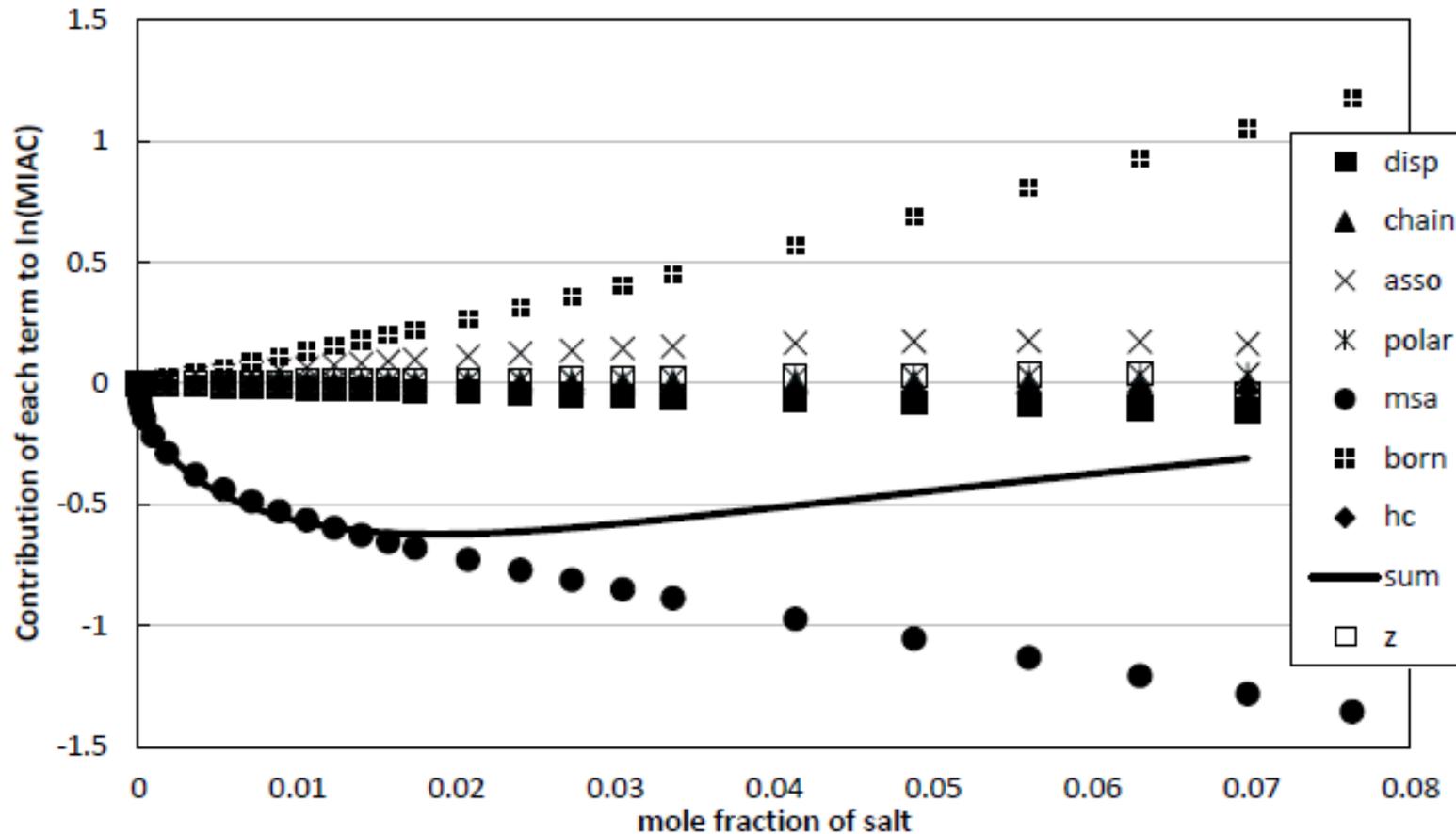
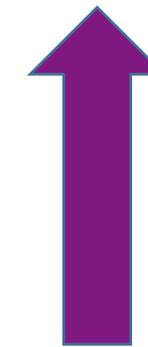
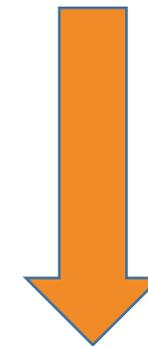


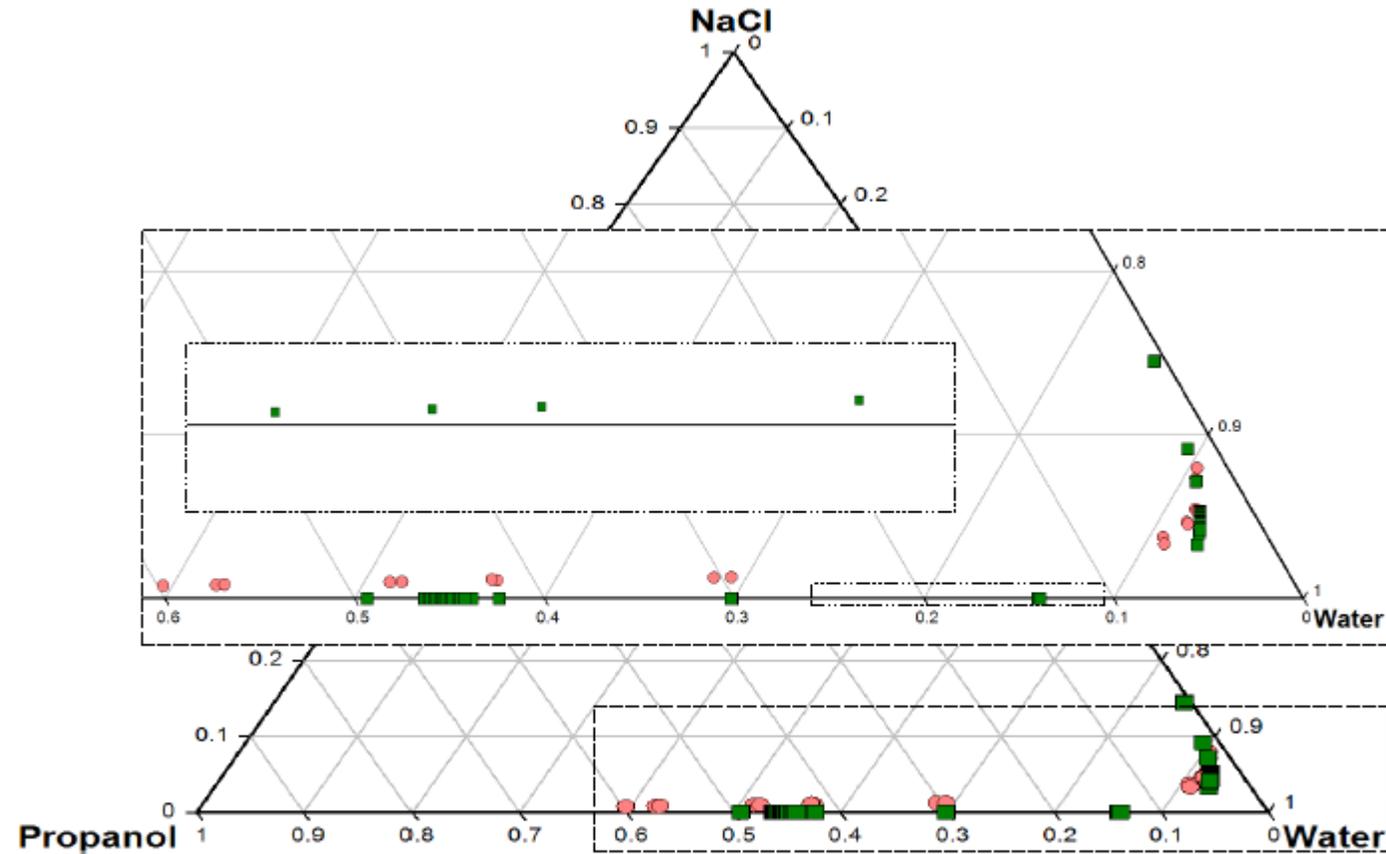
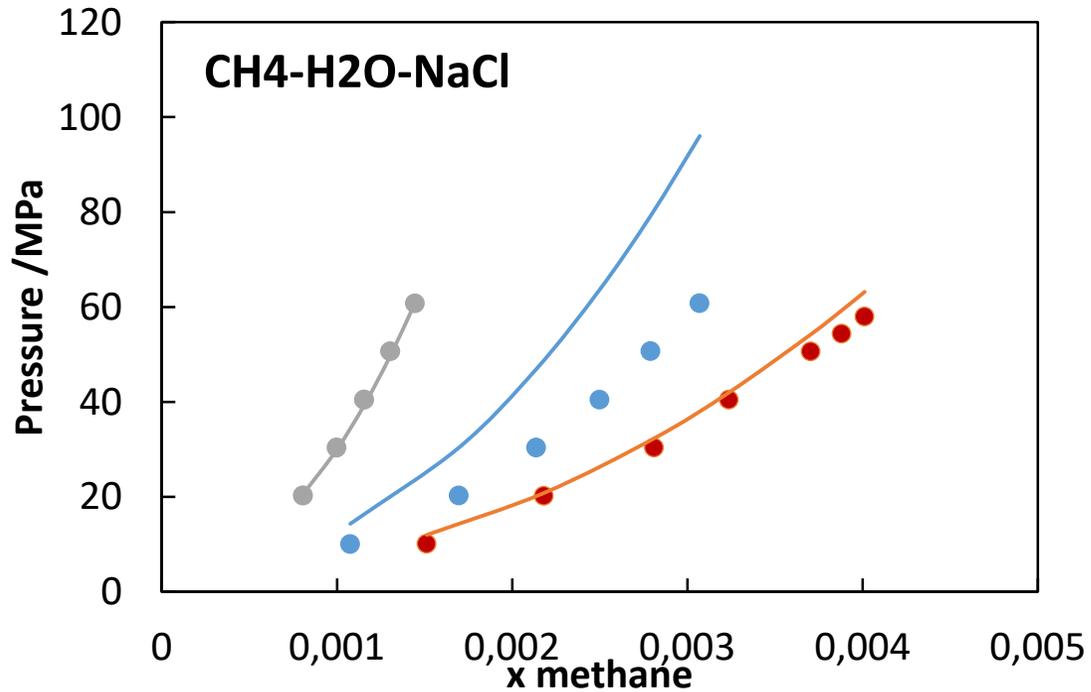
Figure 4 Effect of the various terms on the logarithm of the mean ionic activity coefficient (MIAC). The model used is that presented in section 3 along with the parameter presented in table 6.



L'ion préfère la solution salée:
Born exprime le comment le changement de constante dielectrique affecte l'activité des ions



L'ion préfère l'eau pure:
MSA (Debye Hückel) exprime comment l'augmentation de la force ionique diminue la portée des charges

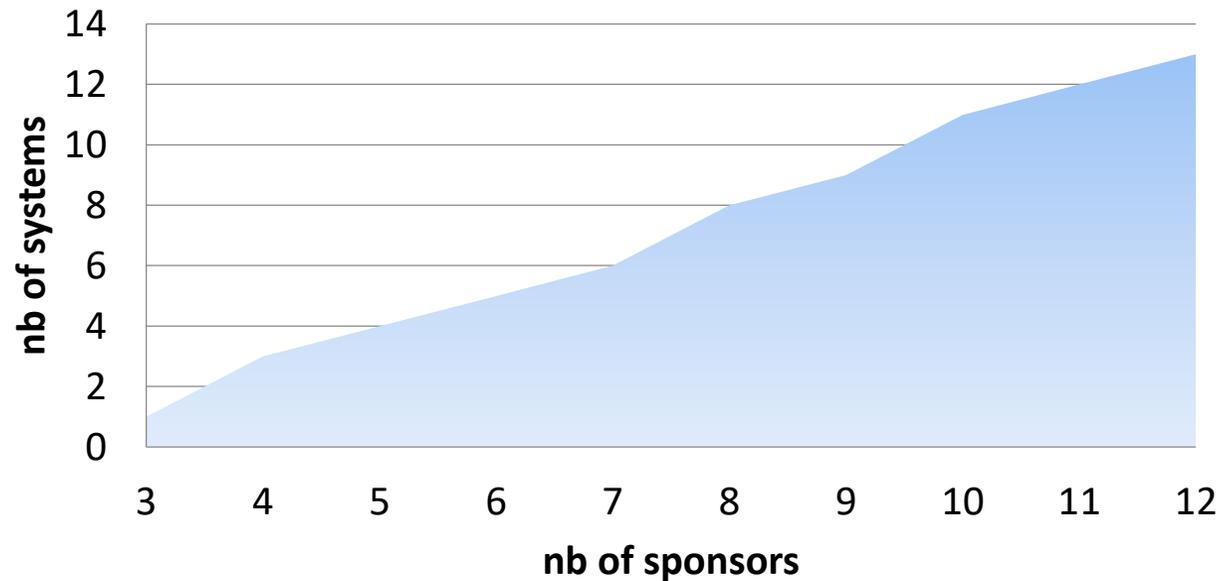


1-Propanol– Water – NaCl LLE at 298.15K, red circles are experimental data and green squares are prediction from model

- Un modèle prédictif est nécessaire lorsqu'on désire l'utiliser dans un domaine étendu (i.e. sans avoir recours à des mesures complémentaires)
- Le modèle statistique GC-PPC-SAFT permet de capter les interactions physiques intermoléculaires :
 - entropie (longueur de chaîne); dispersion; polarité; liaison hydrogène
- Un jeu de paramètres unique est utilisé pour tous les équilibres
 - VLE; GLE; LLE
- La contribution de groupe permet d'étendre les calculs à des systèmes n'ayant pas de données expérimentales

- Traitement de la biomasse:
 - Volatilité des matières organiques (acides gras) en fonction de la charge ionique et du pH
- Corrosion:
 - Spéciation des métaux en fonction de la fugacités des gaz acides, CO₂ et H₂S
- Batteries:
 - activité des espèces électrolytiques pour le calcul de potentiels redox
- Extraction Liquide-liquide:
 - Effet des sels et du pH sur la partition de molécules cibles
- Capture de CO₂:
 - Description de l'absorption dans des solvants physiques + chimiques
- Stockage du carbone:
 - Equilibres liquide-solide en présence de CO₂ dissous + mélange de minéraux
- flow assurance :
 - SLE of various scales in water containing various amounts of alcohols
- ...

- Benchmark systems of partner companies on existing simulator models



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