Monte Carlo simulation of phase equilibria of aqueous systems

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Kwon, Cheong Hoon

Thermodynamics and Properties Lab.
Dept. of Chemical and Biological Engineering, Korea Univ.

Abstract

Monte Carlo simulation of aqueous systems

1. **Semi-empirical two-body potential models**
2. Representation of **vapor–liquid equilibria** of the pure water , including the critical region
3. The calculation of low and high pressure phase equilibria of **water–hydrocarbon**
4. The simulation of highly dense system(s) and systems of long chain molecules
5. The comparison of simulation results and experimental data

Introduction

1. The thermodynamic properties and phase behavior of aqueous systems
2. Necessities of molecular simulation
3. Intramolecular and intermolecular interactions
4. Two-body interactions vs. Many-body effects (such as polarizability)
5. The Gibbs ensemble Monte Carlo **(GEMC)** method

► **Semi-empirical two-body potential models** have gained considerable popularity for phase equilibrium calculations.

Procedure

The choice of appropriate potentials for **water and hydrocarbon**

↓

A suitable simulation procedure

↓

The **molecular simulations** performance

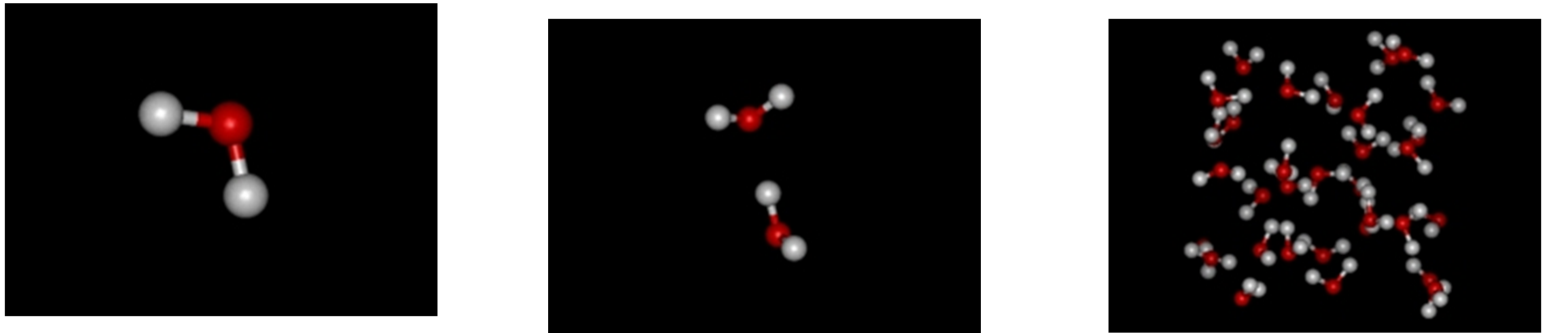
↓

The **comparison** of simulation results and experimental data

Potential models (1)

G.C. Boulougouris, I.G. Economou and D.N. Theodorou. (1998)

1 **Water**



- a three-site model

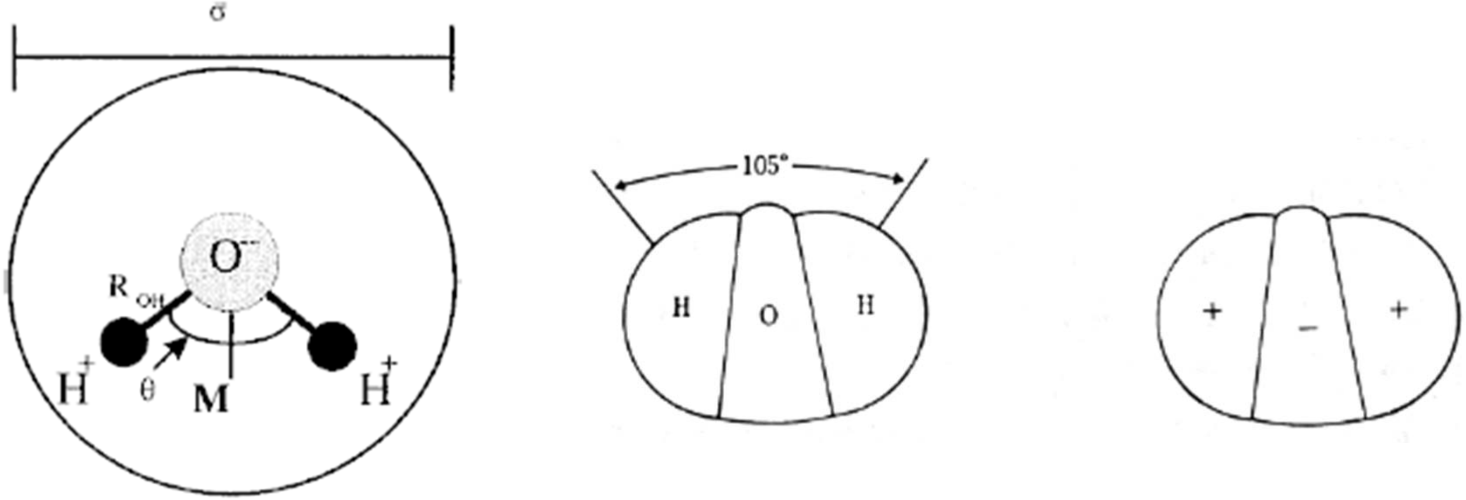
  : an oxygen site (exhibiting non-polar and electrostatic interactions)

  \+ two hydrogen sites (exhibiting electrostatic interactions, only)

Potential models (2)

G.C. Boulougouris, I.G. Economou and D.N. Theodorou. (1998)

■ SPC , SPC/E and MSPC/E model



Schematic representation of the molecular model [SPC-and SPC/E-] for water

Potential models (3)

The interaction energy between two water molecules

- For the SPC, SPC/E and MSPC/E model,

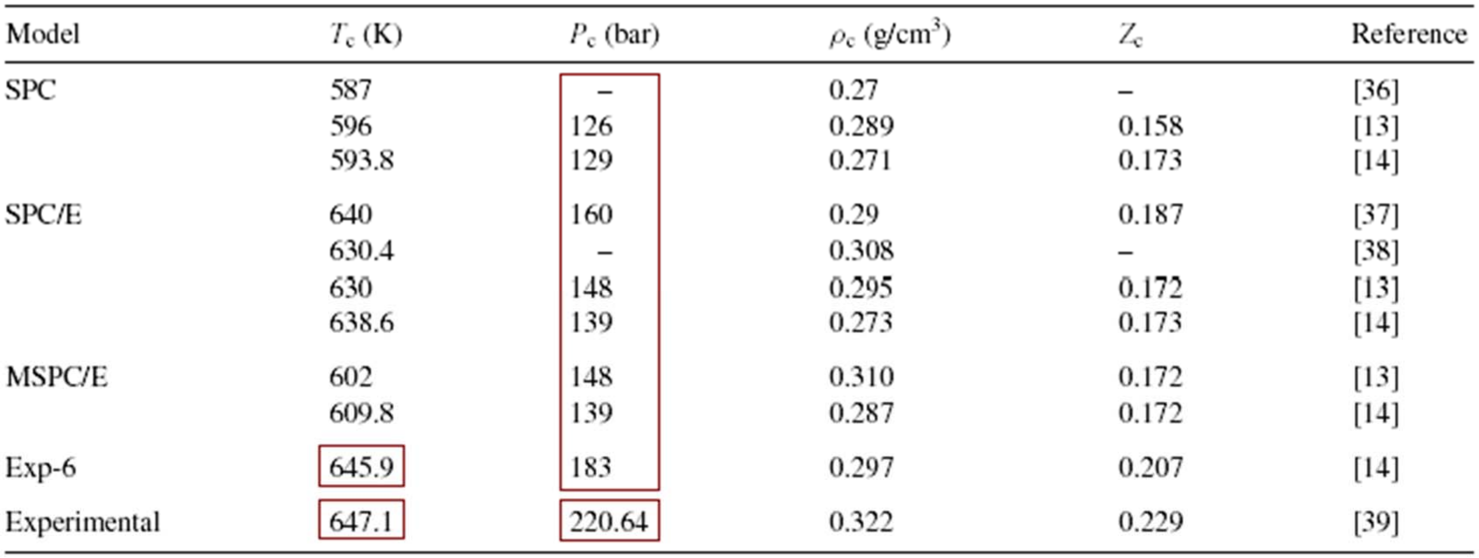
$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \sum_{\gamma=1}^{3}\sum_{\delta=1}^{3}\frac{1}{4\pi\varepsilon_0}\frac{q_\gamma q_\delta}{r_{\gamma\delta}}$$

- For the exp-6 model,

$$u(r) = \begin{cases} \dfrac{\varepsilon}{1-(6/\alpha)}\left[\dfrac{6}{\alpha}\exp\left(\alpha\left[1-\dfrac{r}{r_m}\right]\right) - \left(\dfrac{r_m}{r}\right)^{6}\right] + \displaystyle\sum_{\gamma=1}^{3}\sum_{\delta=1}^{3}\frac{1}{4\pi\varepsilon_0}\frac{q_\gamma q_\delta}{r_{\gamma\delta}} & \text{for } r > r_{\max} \\ \infty & \text{for } r < r_{\max} \end{cases}$$

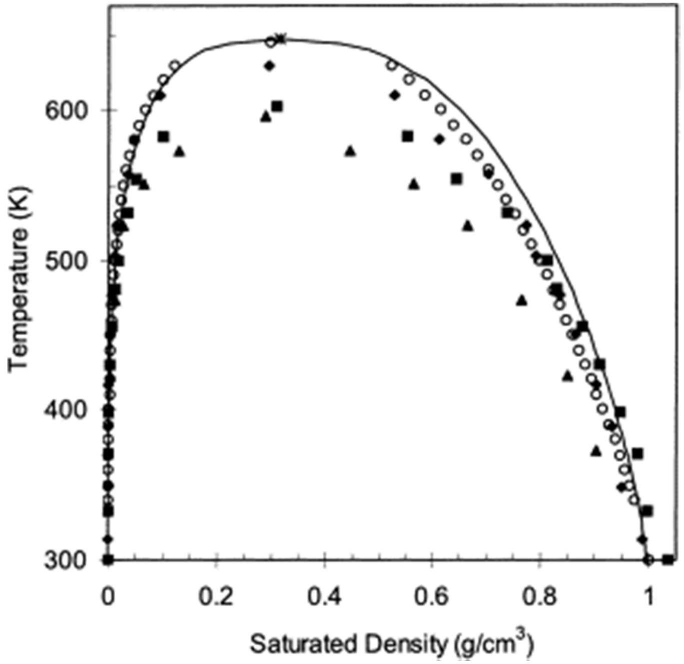
Potential models (4)

Table 1. Critical parameters for pure water



Model	T_c (K)	P_c (bar)	ρ_c (g/cm^3)	Z_c	Reference
SPC	587	–	0.27	–	[36]
	596	126	0.289	0.158	[13]
	593.8	129	0.271	0.173	[14]
SPC/E	640	160	0.29	0.187	[37]
	630.4	–	0.308	–	[38]
	630	148	0.295	0.172	[13]
	638.6	139	0.273	0.173	[14]
MSPC/E	602	148	0.310	0.172	[13]
	609.8	139	0.287	0.172	[14]
Exp-6	645.9	183	0.297	0.207	[14]
Experimental	647.1	220.64	0.322	0.229	[39]

Potential models (5)



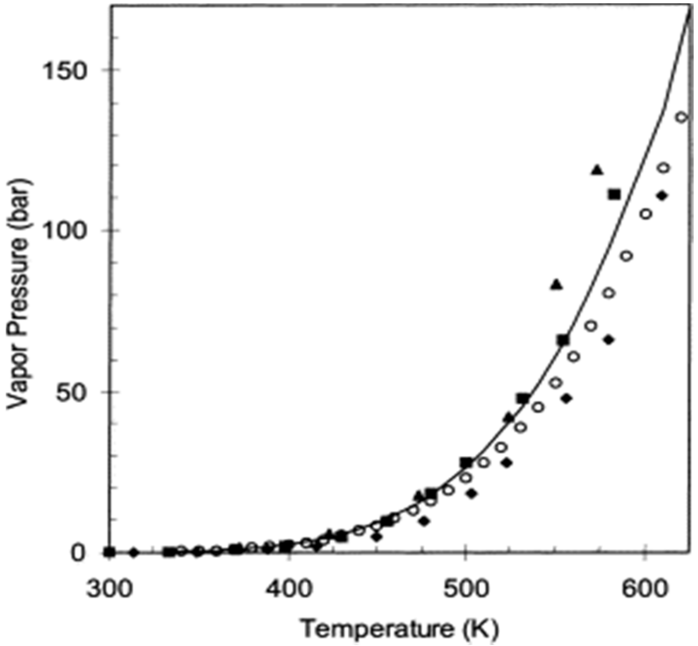
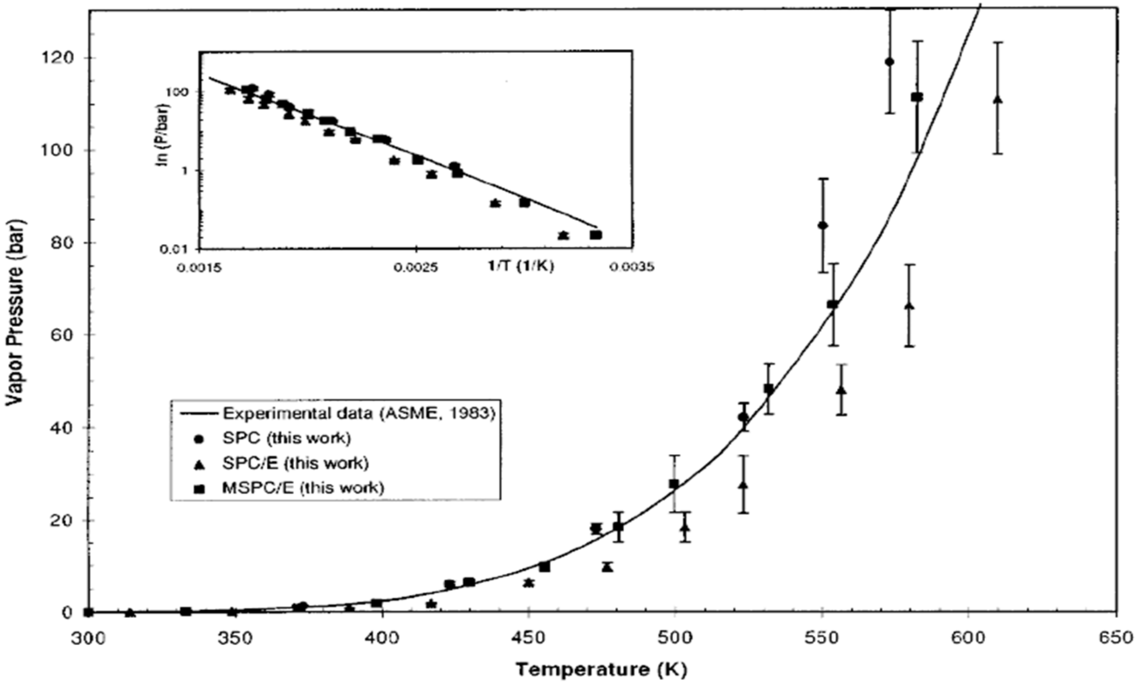


Fig. 1. Pure water vapor–liquid equilibria **Fig. 2. Pure water–vapor pressure.**

► Experimental data (solid line), and molecular simulation results from SPC (triangles), SPC/E (diamonds), MSPC/E (squares) and exp-6 (open circles) models

Potential models (6)

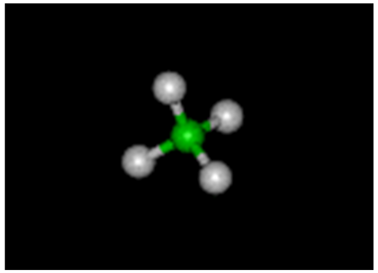
G.C. Boulougouris, I.G. Economou and D.N. Theodorou. (1998)

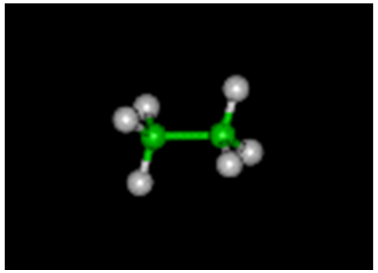


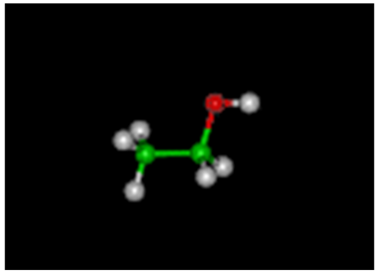
Pure water vapor pressure simulation data

Potential models (7)

2 Hydrocarbon molecules







- Non-bonded intramolecular and intermolecular interactions

  …. Using a Lennard–Jones potential, the so-called TraPPE potential and an exp-6 potential

- Non-polar interactions between unlike groups

  …. Using the Lorentz–Berthelot combining rules

Simulation methodologies (1)

- **Pure water vapor–liquid equilibrium**
  …. Using the GEMC-NVT method

- **The average pressure simulation**
  …. Using an equation based on the molecular virial expression

- **The size of the system** ; 200–250 molecules

- **Water–methane and water–ethane mixtures at high pressure**
  …. Using GEMC-NPT simulation
  …. In this case, a typical simulation consisted of approximately 200 water and 100 hydrocarbon molecules.

Simulation methodologies (2)

Small hydrocarbon solubilities in water

- Using standard thermodynamic relations, the Henry's law constant can be expressed in terms of the hydrocarbon excess chemical potential in water

$$H_{\mathrm{hc}\to\mathrm{w}} = \lim_{x_{\mathrm{hc}}\to 0}\left(\frac{\rho_{\mathrm{w}}}{\beta}\exp(\beta\mu_{\mathrm{hc}}^{\mathrm{ex}})\right)$$

where ρ_w : the pure water number density

$\beta=1/k_B T$

μ_{hc}^{ex} : By using the Widom test particle insertion method

Simulation methodologies (3)

D. Zanuy, S. Leon, C. Aleman, S.Munoz-Guerra. (2000)

Widom's test particle insertion method

- The infinite-dilution excess chemical potential
- To remove a test particle from the system (going from an *N*-molecule system to an (*N*-1)-molecule system) and calculate the corresponding energy change

$$\beta\mu^{\mathrm{ex}} = -\ln\left(\left\langle\frac{1}{V}\right\rangle \frac{Z(N,P,T)}{Z(N-1,P,T)}\right) = -\ln\left\langle\frac{1}{V}\right\rangle \left(\frac{\left\langle\prod_{i=1}^{N-1} H(r_{i,N})\right\rangle}{\left\langle\prod_{i=1}^{N-1} H(r_{i,N})\exp(\beta U^{(N)}(\vec{r}_1,\ldots,\vec{r}_N))/V\right\rangle_{N,P,T}}\right)$$

- The test-particle insertion method has been used successfully at low to moderate fluid densities.

Simulation methodologies (4)

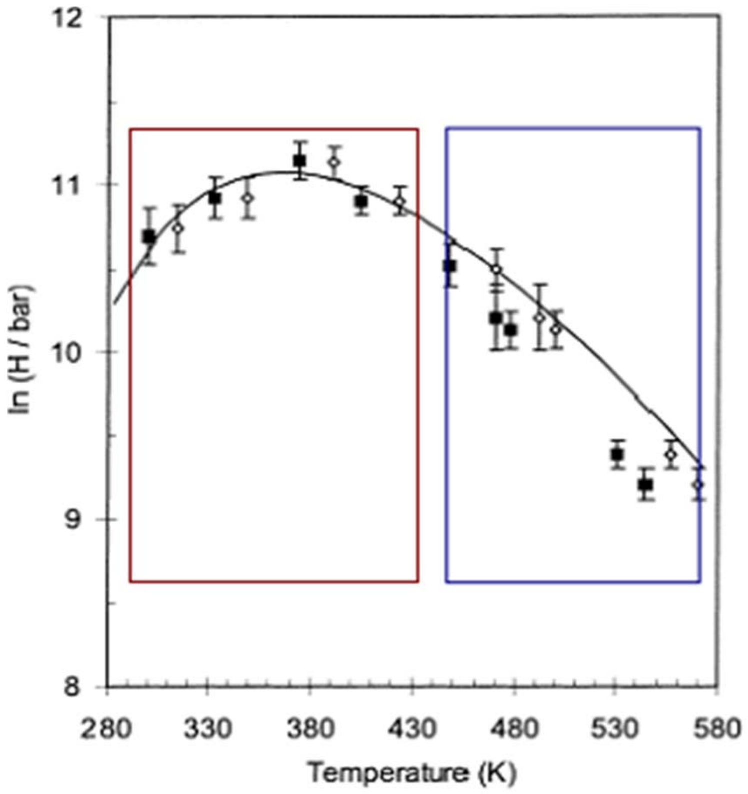


Fig. 3.

Henry's law constant of methane in water

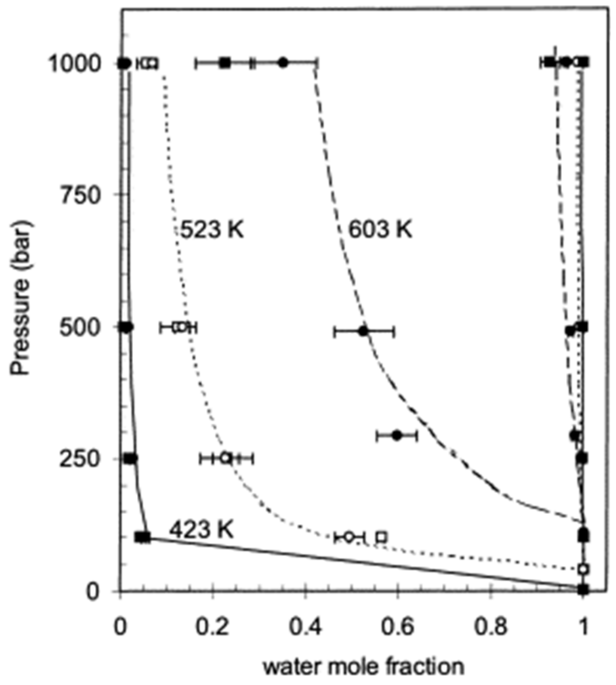
- ► Experimental data (solid line)
- ► Widom insertion Monte Carlo simulations
  - For water

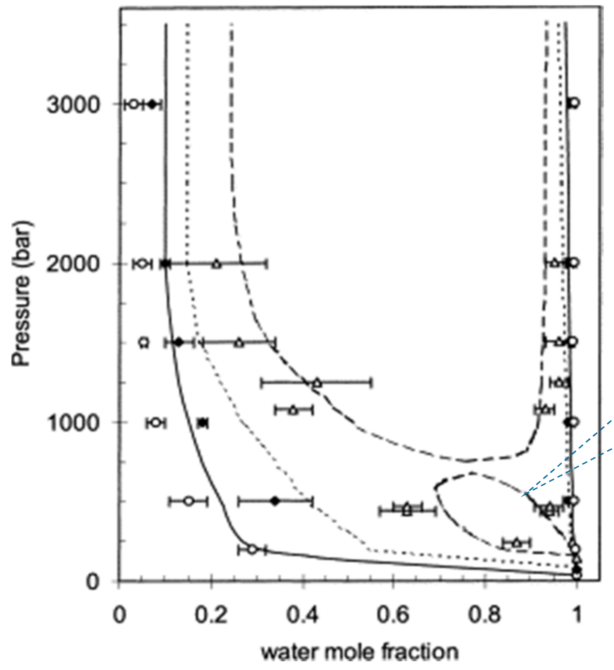
    * SPC/E model (diamonds)
    * MSPC/E model (squares)

  - For methane

    * TraPPE model

Results and discussion (1)





Complete miscibility

Fig. 4. Water–methane phase equilibria

Fig. 5. Water–ethane phase equilibra

Results and discussion (2)

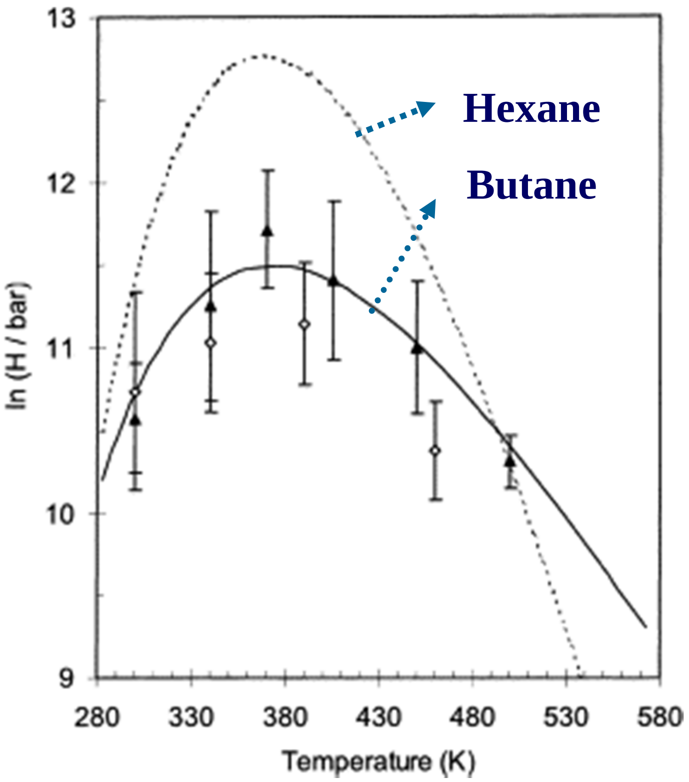


Fig. 6. Henry's law constant of *n*-butane and of *n*-hexane in water

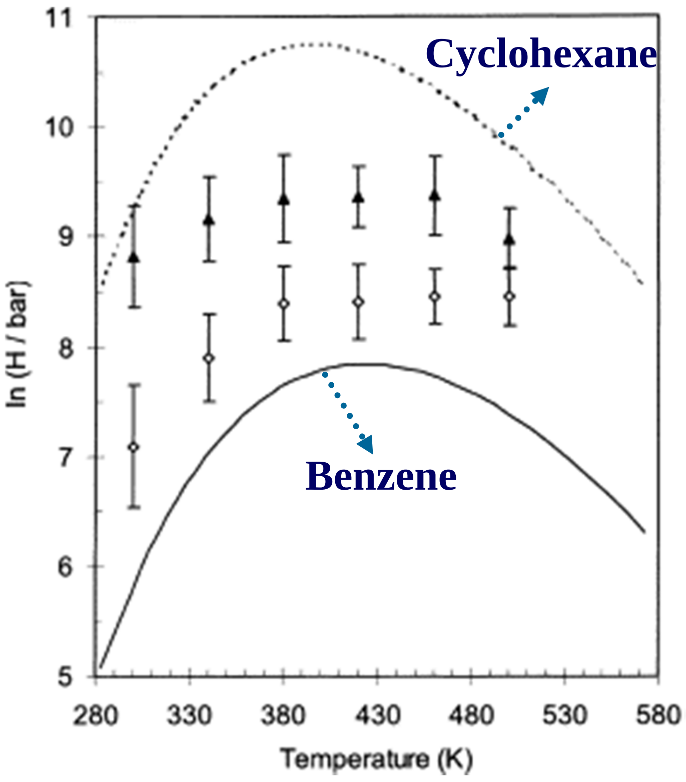


Fig. 7. Henry's law constant of cyclohexane and of benzene in water

Conclusion

1. **Significant advances have been made recently in the development of novel methodologies for the efficient molecular simulation of highly non-ideal mixture phase equilibria.**

2. **It is possible to obtain quantitative results for systems at remote conditions, as for example at very high pressure.**

3. **Based on the results presented here and elsewhere, it is apparent that more complex potentials that account explicitly for polarizability and other many body effects are necessary.**

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