Intramolecular Hydrogen bonding for Lattice fluid EOS

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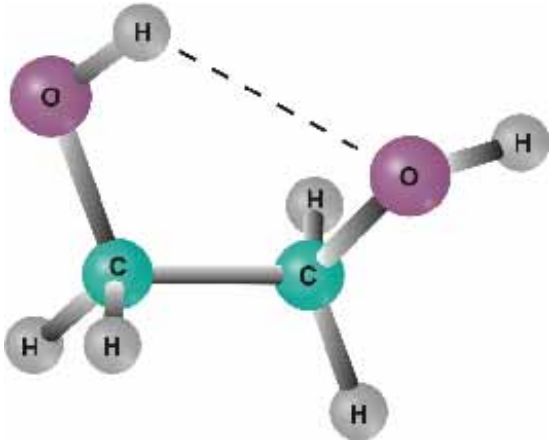
Scope

- Intramolecular Hydrogen bonding
- Models for intramolecular HB
- Proposed Model and model parameter
- Results
- Conclusion

Intramolecular Hydrogen Bond

- Intramolecular hydrogen bond

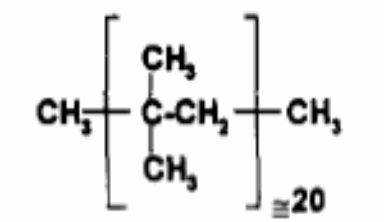
  A hydrogen bond formed between **two functional groups** of the same molecule



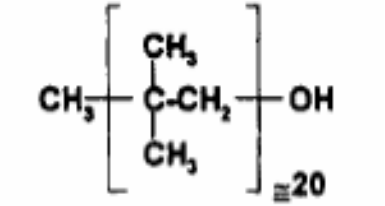
Intramolecuar HB plays an important role in **Protein folding**

Intramolecular HB - Polymer

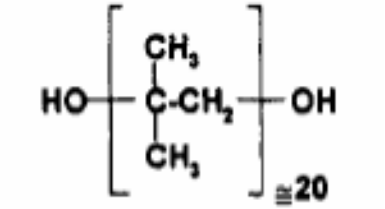
- Cloud-point pressure is decreased owing to intramolecular HB at polar solvents (Gregg et al, 1994)



Blank PIB



Monohydroxy PIB

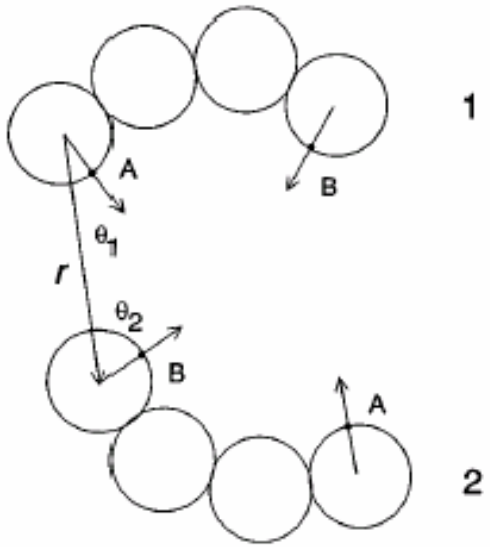


Dihydroxy PIB

Cloud point pressure
Medium
Large
Small

Previous Work –Ghonasgi(1994)

- For intermolecular association, Wertheim's thoery
- For intramolecular association, Ghonasgi(1994)'s theory was used.



$$X_A = \frac{X_o^{\mathbf{intra}}}{1+\rho X_A \Delta_{AB}^{\mathbf{inter}}} \qquad \frac{\rho_o}{\rho X_o^{inter}} = \frac{1}{1+\Delta^{\mathbf{intra}}}$$

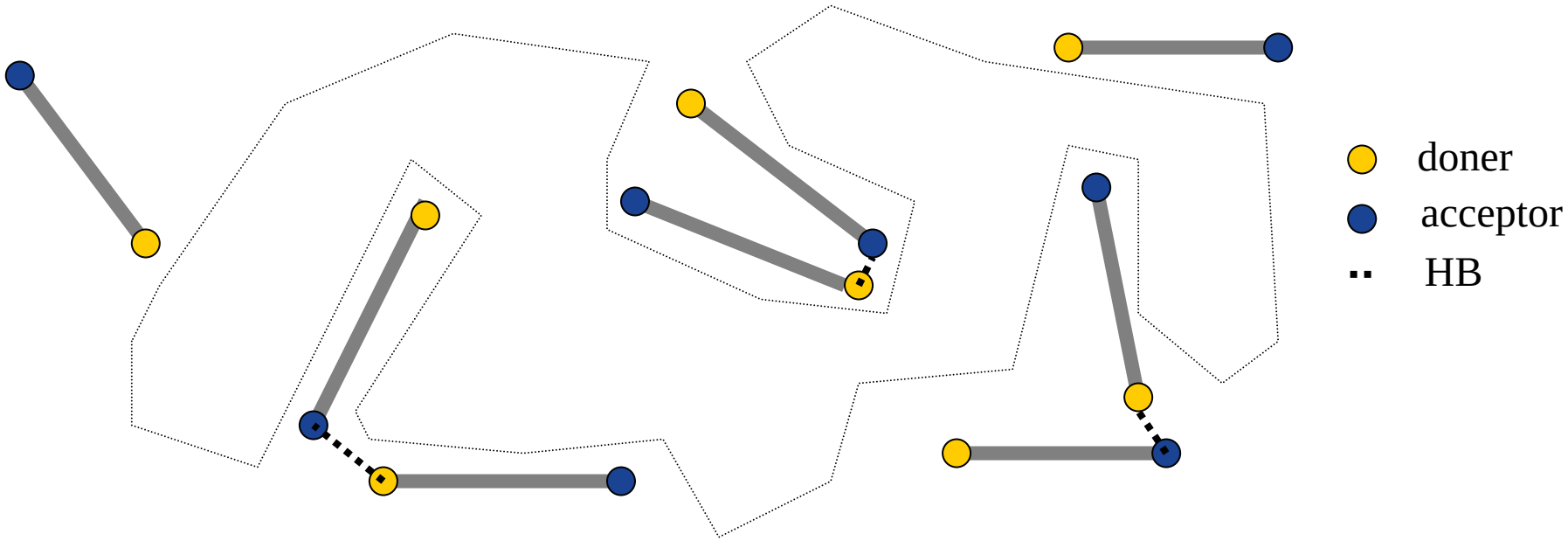
$$X_o = \frac{X_A^2}{X_o^{\mathbf{intra}}} \qquad X_o^{\mathbf{inter}} + X_o^{\mathbf{intra}} - X_o = 1$$

$$(\frac{1}{X_A})^3 + (\rho\Delta^{\mathbf{inter}} - \Delta^{\mathbf{intra}} - 1)(\frac{1}{X_A})^2 - 2\rho\Delta^{\mathbf{inter}}\frac{1}{X_A} - \rho^2(\Delta^{\mathbf{inter}})^2 = 0$$

Previous Work – Lattice HB

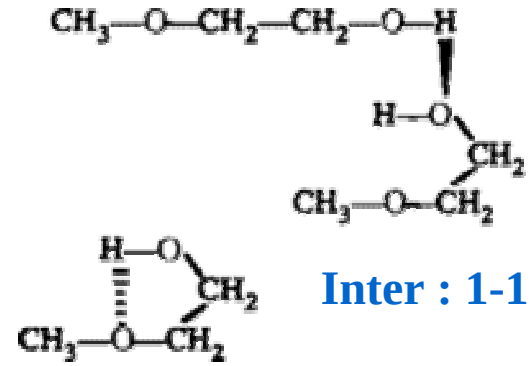
- Developed by Brinkley(1998) and Missopolinou (1999)

$$\Omega_{HB} = \Omega_{intra}\Omega_{inter}$$



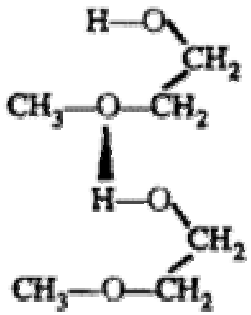
Brinkley (1998)

- **Analysis** of Intra- and Intermolecular HB of Glycol-ether using **FTIR** experiments.

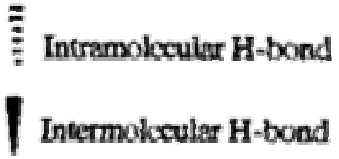


Intramolecular

Inter : 1-1



Inter : 1-2



- **H-bond**$_{OH\text{-}OH}$ =**H-bond**$_{OH\text{-}Ether}$
- One way of forming intramolecular HB for molecule ($Q_{intra} = 1$)

Problem – Brinkley's theory

- **No consideration** about distributing **Intramolecular** HB molecules among total molecules

$$P_{\mathbf{inter}} = \frac{c_M \rho}{N_T}$$

$$P_{\mathbf{intra}} = c_B$$

$$Q_{\mathbf{inter}} = \frac{(N_1 - B)!(3N_1 - B)!}{(N_1 - B - M)!(3N_1 - B - M)!M!}$$

B : Intramolecular HB pair

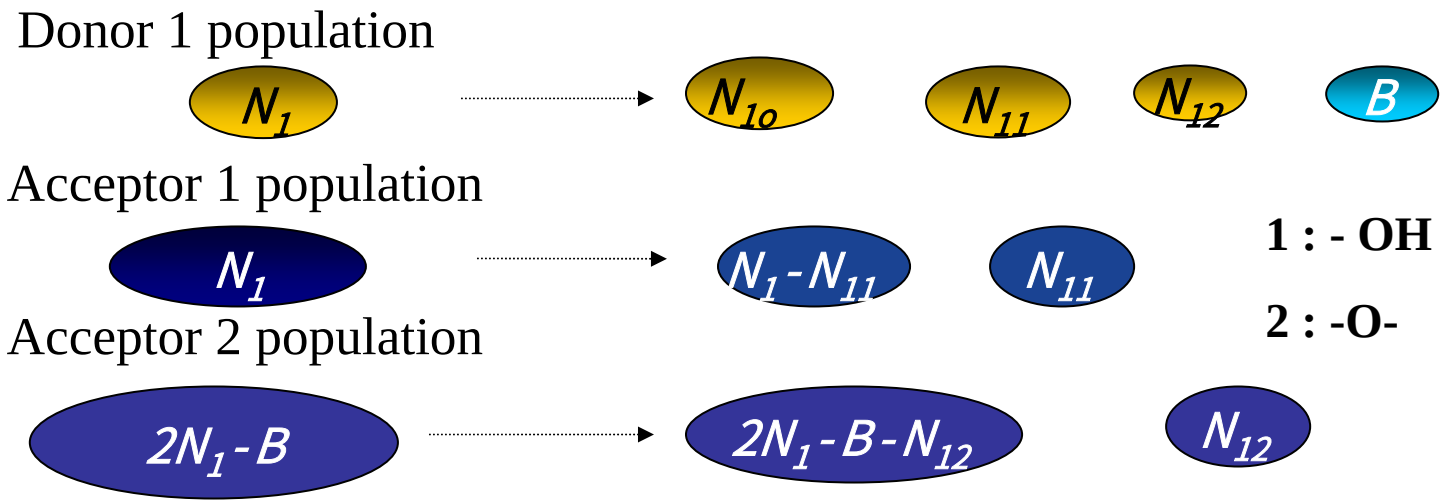
M : Intermolecular HB pair

c_B : probability for ring formation

$$Q_{\mathbf{HB}} = Q_{\mathbf{intra}} Q_{\mathbf{inter}} P_{\mathbf{intra}}{}^{B} P_{\mathbf{inter}}{}^{M} \exp\left(\frac{-\Delta F_B}{kT}\right) \exp\left(\frac{-\Delta F_M}{kT}\right)$$

Missopolinou (1999)

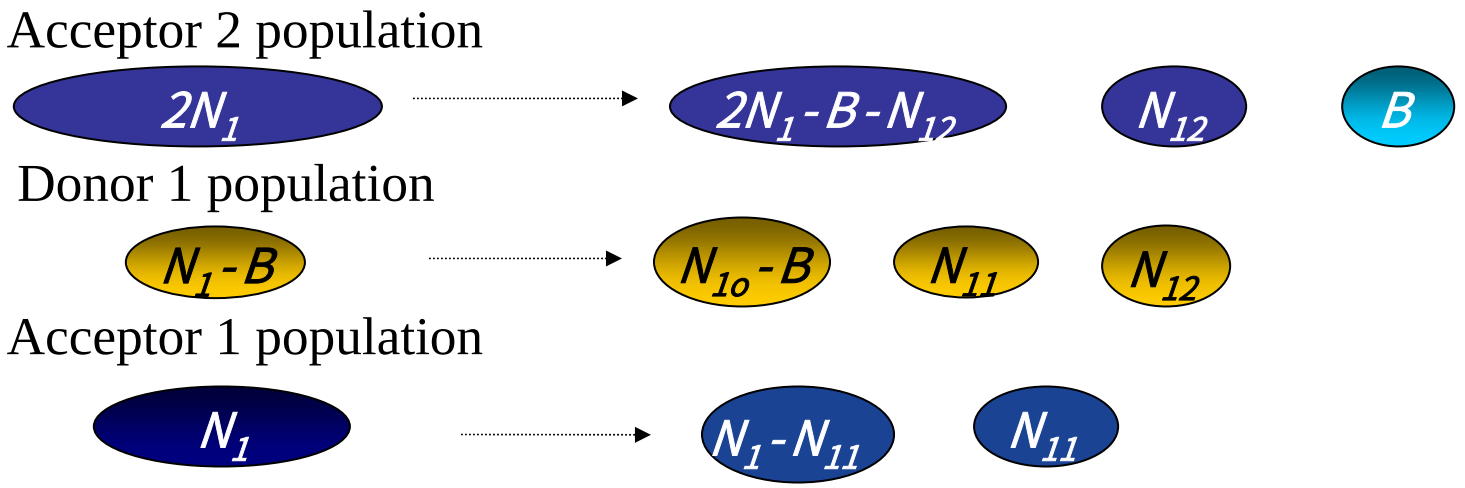
- First formalisms for **equation-of-state**
  - **H-bond**$_{OH\text{-}OH}$ **H-bond**$_{OH\text{-}Ether}$



$$Q_{HB} = \frac{2^B (N_1!)^2 (2N_1 - B)!}{B! N_{11}! N_{12}! N_{10}! (N_1 - N_{11})! (2N_1 - B - N_{12})!} \left(\frac{c_M \rho}{N_T}\right)^M (c_B)^B$$

Problem – Missopolinou's model

- If sequence of numbering is reversed, partition function is different.



$$Q_{\mathbf{HB}} = \frac{2^B (2N_1)! N_1! (N_1 - B)!}{B! N_{11}! N_{12}! N_{10}! (N_1 - N_{11})! (2N_1 - B - N_{12})!} \left(\frac{c_M \rho}{NT}\right)^M (c_B)^B$$

This Work

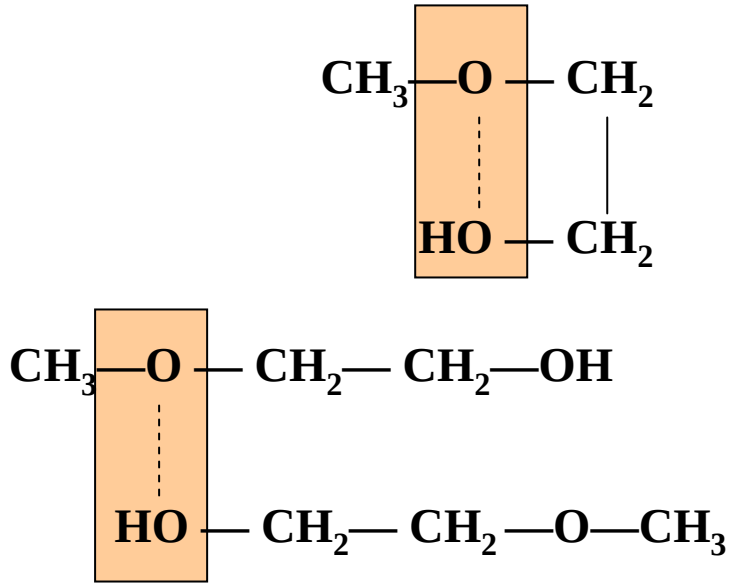
- Correct formalism of Q_{intra} and Q_{inter}
- General intramolecular HB model for any molecules

  - **Assumption**

    Number of distributing intermolecular molecules

$$Q_{\text{intra}} = \frac{N_1}{(N_1 - B)!B!}(c)^B \exp(-B\frac{A_{12}}{kT})$$

$$A_{\text{intra}} = A_{ij}(\text{inter})$$



This Work

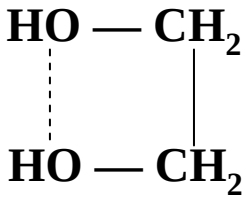
- **2-methoxy ethanol**

$$Q_{\text{intra}} = \frac{N_1}{(N_1 - B)!B!}(c)^B \exp(-B\frac{A_{12}}{kT})$$

$$Q_{\text{inter}} = \frac{(N_1 - B)!}{N_{11}!N_{12}!(N_1 - B - N_{11} - N_{12})!}\frac{N_1}{(N_1 - N_{11})!N_{11}!}(\frac{r_H}{N_r})^{N_{11}}$$

$$\times \frac{(xN_1 - B)!}{(xN_1 - B - N_{12})!N_{12}!} \times (\frac{r_H}{N_r})^{N_{12}} \times \exp(-N_{11}\frac{A_{11}}{kT} - N_{12}\frac{A_{12}}{kT})$$

- **Ethylene-glycol**



$$Q_{\text{intra}} = \frac{N_1}{(N_1 - B)!B!}(c)^B \exp(-B\frac{A_{\text{intra}}}{kT})$$

$$Q_{\text{inter}} = \frac{(2N_1 - B)!}{N_{11}!(2N_1 - B - N_{11})!}\frac{(2N_1 - B)!}{(2N_1 - B - N_{11})} \times (\frac{r_H}{N_r})^{N_{11}} \times \exp(-N_{11}\frac{A_{11}}{kT})$$

Result

- FTIR regression
  - Hydrogen bonding parameter from 35^{o}C and 45^{o}C experiment data
- Pure parameter fitting
- VLE calculation
  - Comparison with Intra HB and without Intra HB

FTIR regression

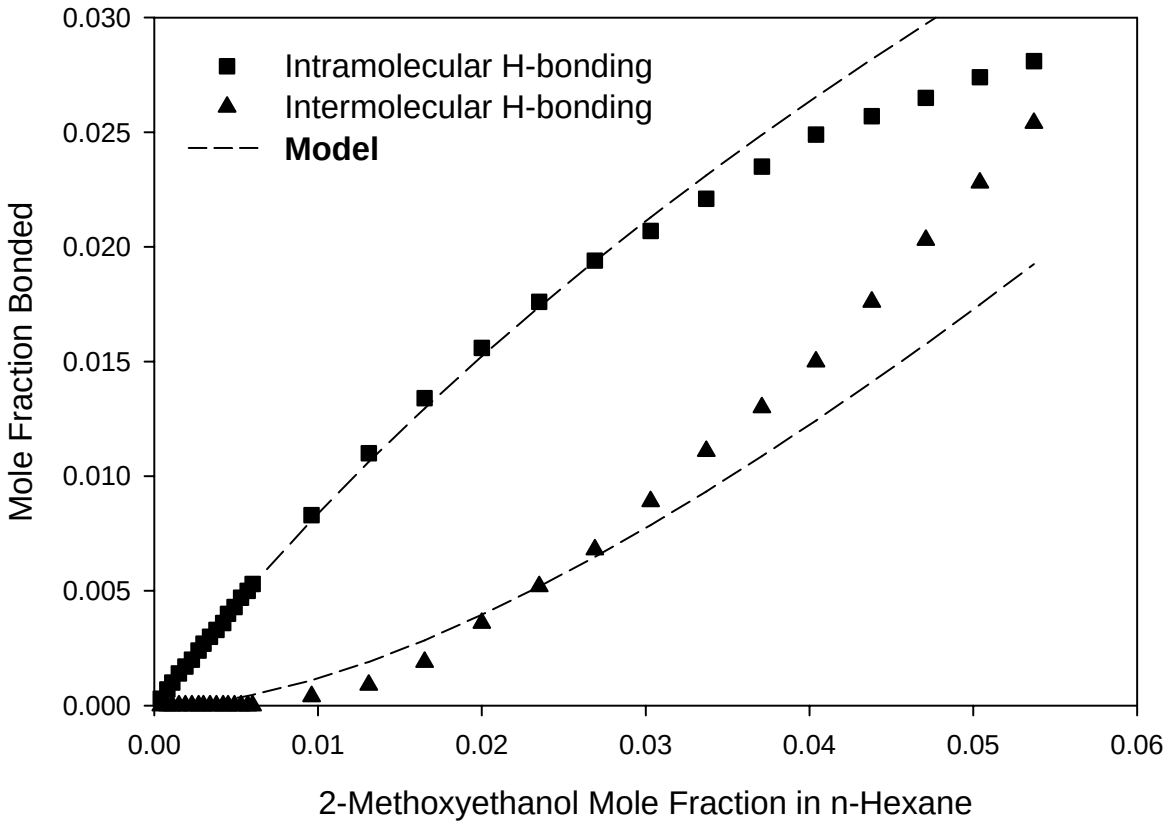


Fig. 1. Hydrogen bonding in 2-methoxy ethanol + hexane system at 35°C

FTIR regression

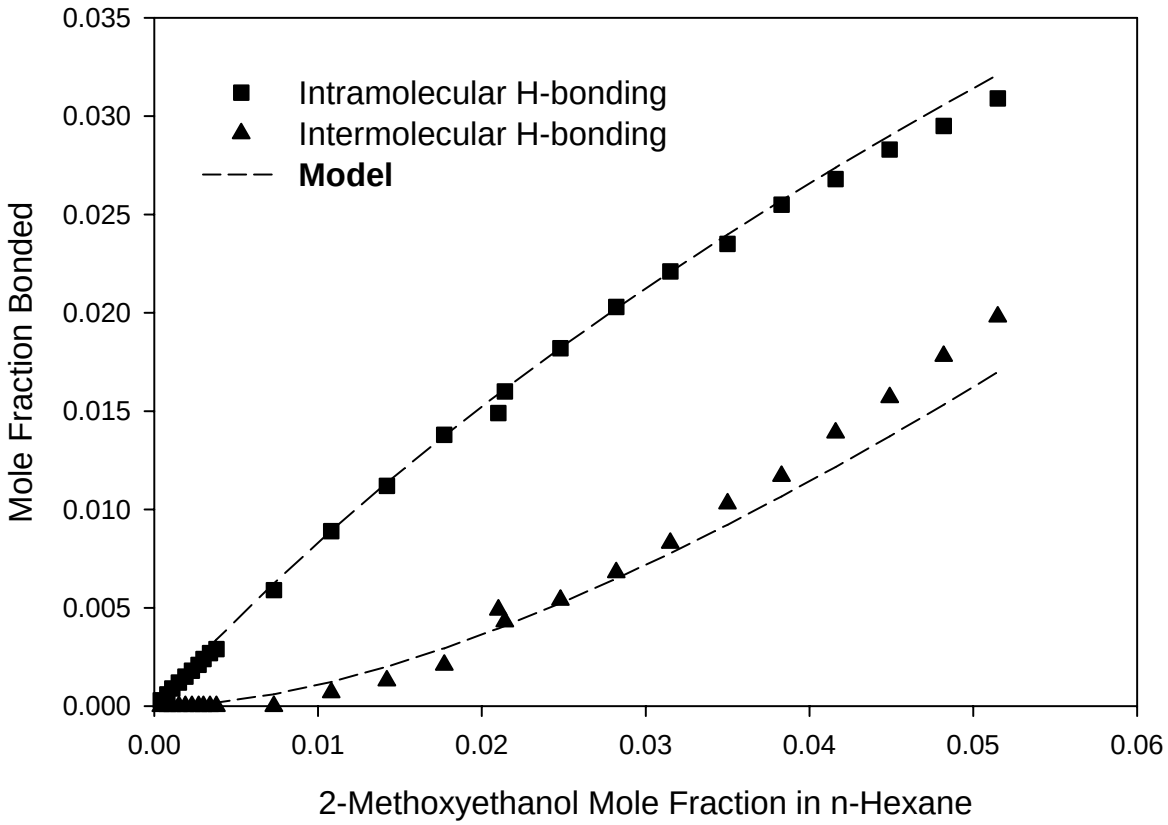


Fig. 2. Hydrogen bonding in 2-methoxy ethanol + hexane system at 45°C

Model characteristics

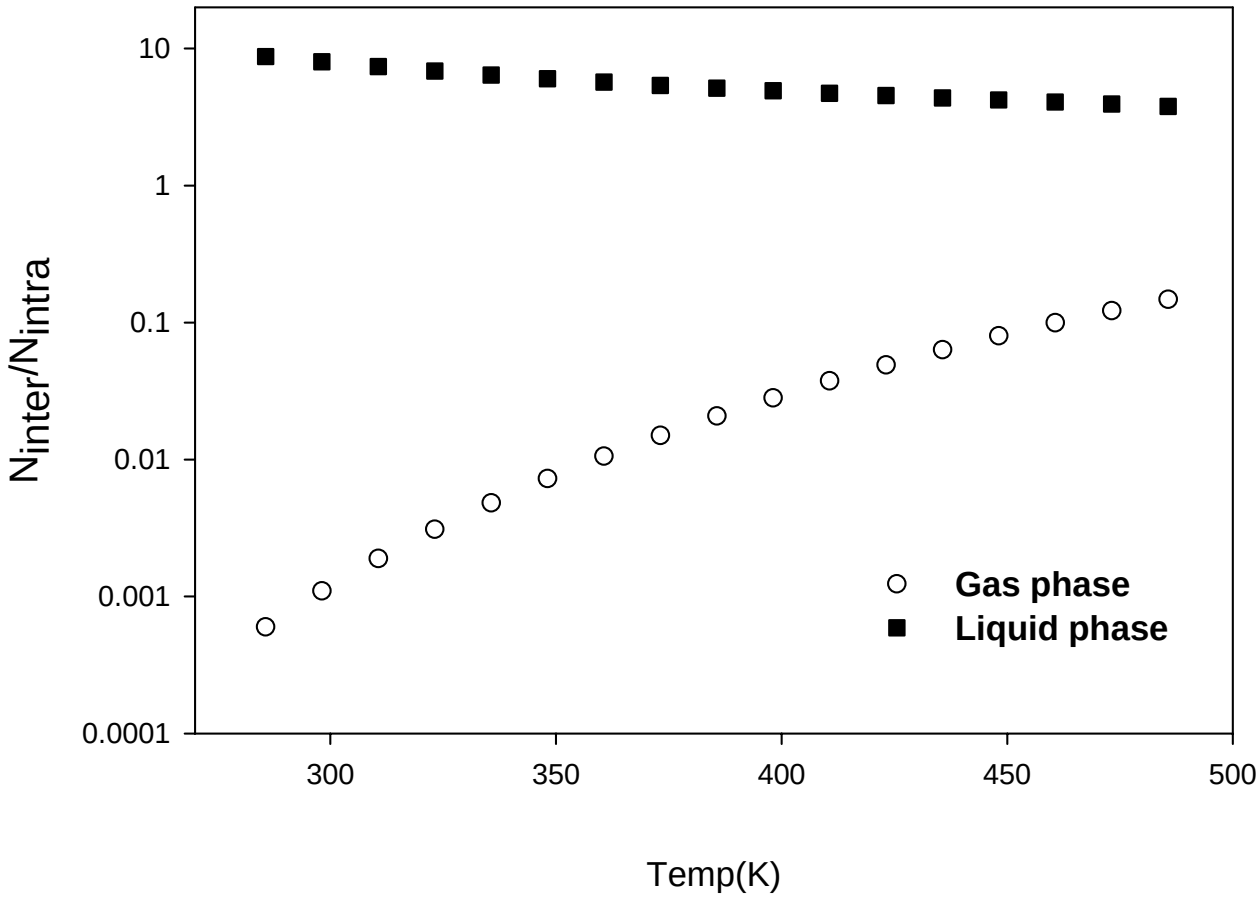


Fig. 3. Inter- and intramolecular hydrogen bond in 2-methoxy ethanol

Pure parameter fitting

- Regressed intramolecular parameter

	U_{HB}	S_{HB}	c
Alcohol	-4332	-2.98	-
Ether	**-2384**	-2.98	-
2-methoxyethanol	-	-	**0.005**

- Pure parameter for 2-methoxy ethanol

	r_A	r_B	r_C	e_A	e_B	e_C	DP(%)	Dρ(%)
Inter only	7.000	0.0038	-0.0024	93.15	0.175	0.162	4.04	0.054
Intra + Inter	7.578	0.015	-0.0013	123.0	-0.090	-0.299	**1.81**	**0.148**

$$DP(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|1-\frac{P_i^{calc}}{P_i^{\exp}}\right| \qquad D\rho(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|1-\frac{\rho_i^{calc}}{\rho_i^{\exp}}\right|$$

Comparion : VLE calculation

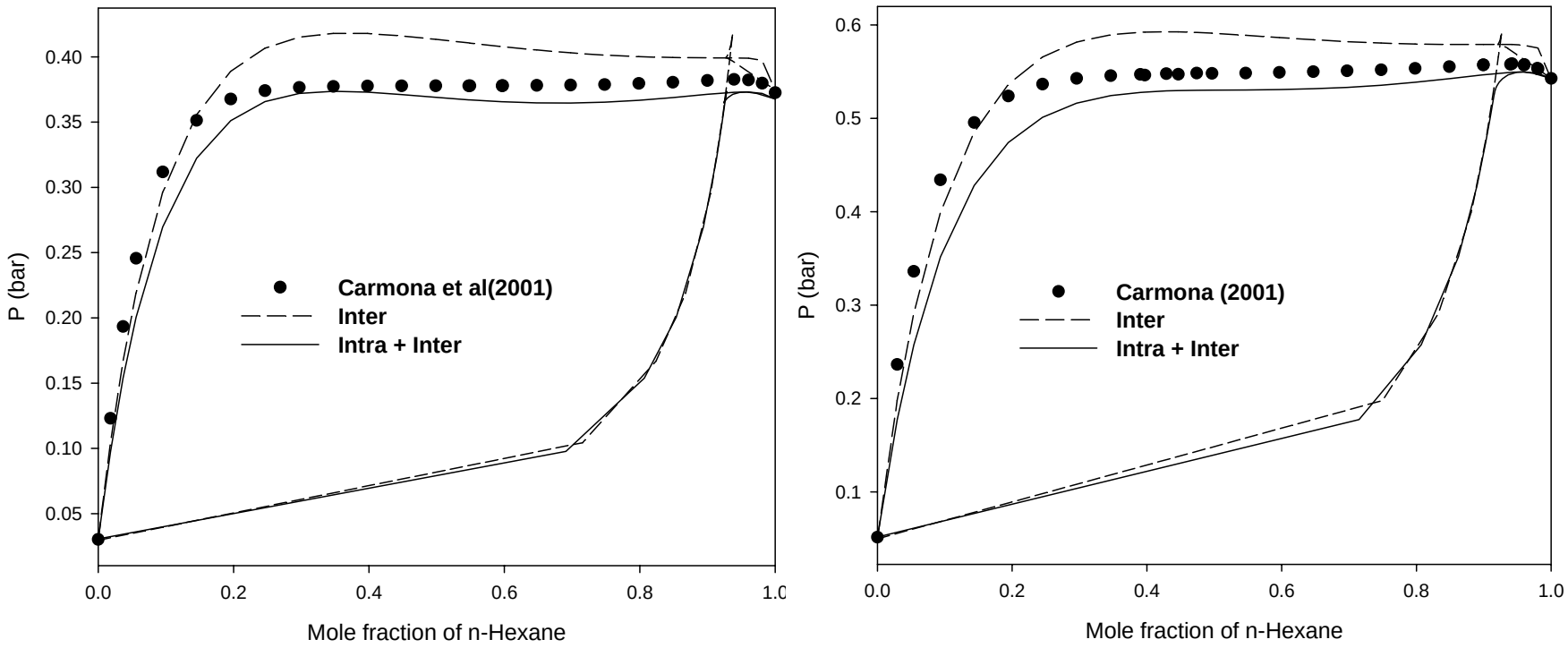


Fig. 4. n-Hexane + 2-methoxy ethanol at 40°C and 50°C

Comparion : VLE calculation

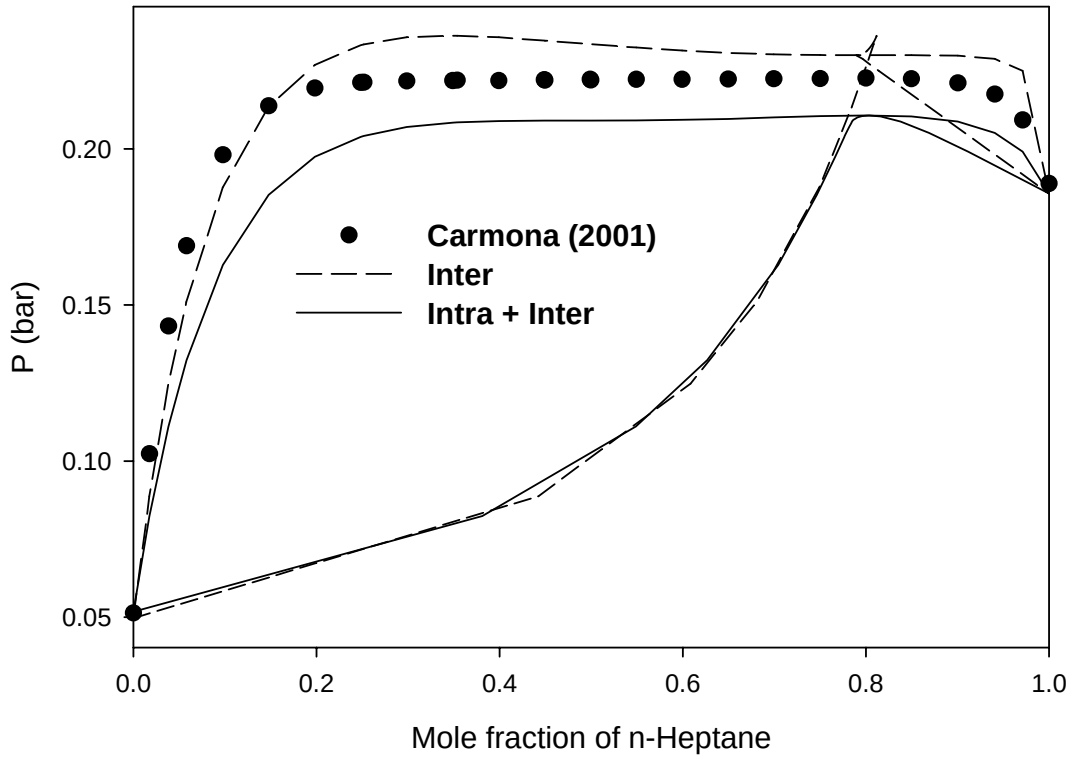
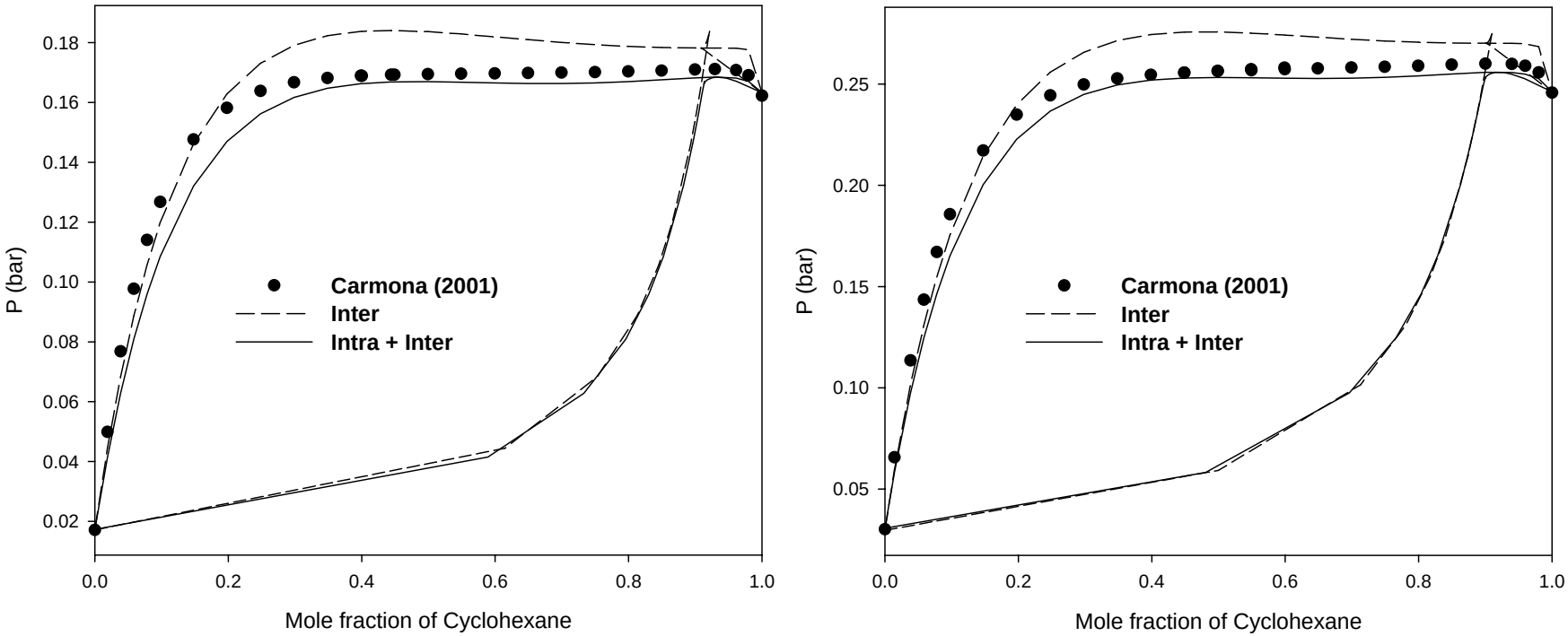


Fig. 5. n-Heptane + 2-methoxy ethanol at 50°C

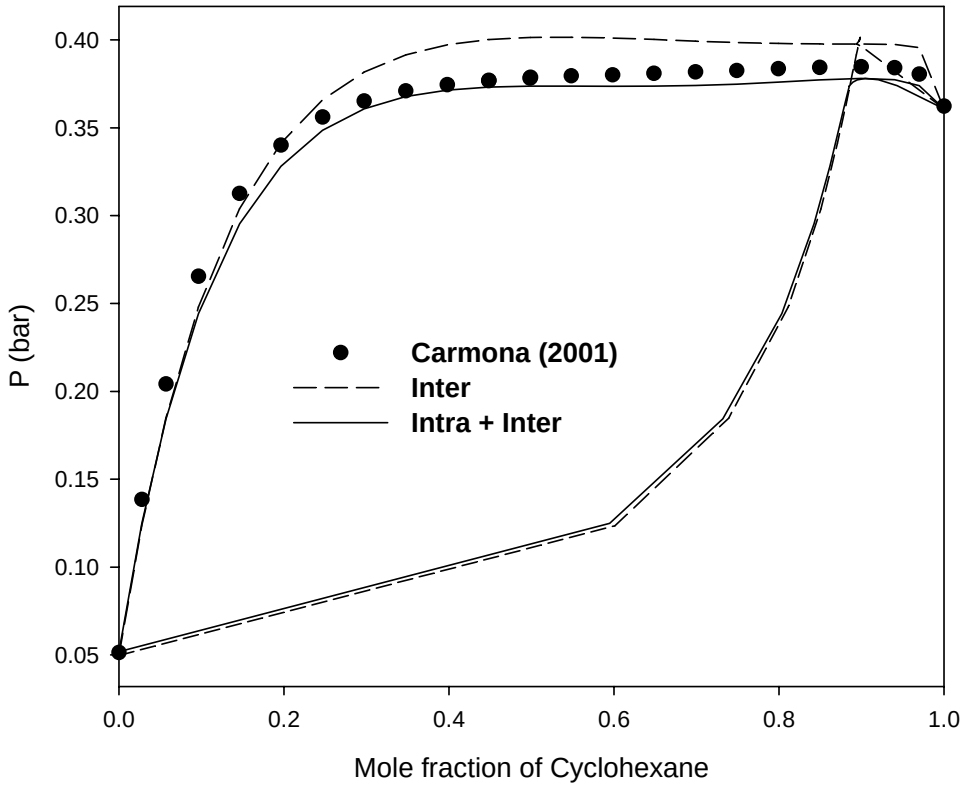
Comparion : VLE calculation



(a) (b)

Fig. 6. n-Cyclohexane + 2-methoxy ethanol at (a) 30 (b) 40 and (c) 50°C

Comparion : VLE calculation



(c)

Comparison

System	Temp (K)	DP(%)	
		Intermolecular only	**Intra and Intermolecular**
n-Hexane 2-methoxyethanol	313.15	**7.23**	**5.08**
	323.15	**6.01**	**5.12**
n-Heptane 2-methoxyethanol	323.15	**5.40**	**8.09**
Cyclohexane 2-methoxyethanol	303.15	**6.20**	**4.96**
	313.15	**5.77**	**3.69**
	323.15	**4.81**	**2.62**

$$DP(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|1-\frac{P_i^{calc}}{P_i^{\exp}}\right|$$

Conclusion

- Intramolecular hydrogen bonding based Lattice fluid statistics was proposed which considers **the number** of distributing **molecules with intermolecular bonds**

- Regressed Hydrogen bonding parameter and flexibility parameter showed **consistent behavior of FTIR experiment data** qualitatively and **possibility for application** to the equation of state.

- The models was found applicable to the calculation of **VLE of alkane-2-methoxy ethanol** in comparison with **the model with only intermolecular HB**