

A Priori Prediction of the Vapor-Liquid Equilibria of Mixtures of Acetic Acid and Water or Alcohols by Explicit Consideration of Hydrogen Bonded Dimers

Wei-Lin Chen and Shiang-Tai Lin*

Department of Chemical Engineering, National Taiwan University

AUTHOR INFORMATION

*corresponding author: stlin@ntu.edu.tw

A modified bubble point pressure calculation for the phase equilibrium of chemically reactive systems.

The bubble-point pressure calculation illustrated in Figure S1 is used to determine the vapor-liquid equilibrium of chemically reactive systems. This calculation procedure is similar to that of non-reactive systems, except that the liquid phase composition is obtained through a self-consistent iteration illustrated in Figure S2. At a given temperature and initial liquid composition (assuming only monomer for acetic acid), chemical equilibrium calculation is performed (with a guessed pressure) first in the liquid phase (phase with the smallest value of compressibility factor $z=PV/RT$) to ensure the chemical equilibrium. The variables in this calculation are the extent of reaction X_j of all independent reactions (R) in the reactive system. The new concentration is determined by a new set of extent of reactions X_j , i.e.,

$$n_i = n_i^o + \sum_{j=1}^R v_{ij} X_j \quad (\text{S.1})$$

$$x_i = n_i / \sum_{j=1}^c n_j \quad (\text{S.2})$$

where n_i^o is the number of moles of species i in the feed, n_i is the numbers of moles of species i under the extent of reaction \underline{X} . At a specified composition, the current chemical equilibrium constant can be determined from PR+ COSMOSAC EOS, i.e.,

$$K_{a,j}^{cal}(T, \underline{x}) = \prod_{i=1}^c \left[\frac{\bar{f}_i(T, P, \underline{x})}{f_i^o(T, P^o, x^o)} \right]^{v_{ij}} \quad (\text{S.3})$$

Finally, with the chemical equilibrium constant determined from experimental data the extent of reactions X is updated by the following equation,

$$X_j^{new} = X_j^{old} - \frac{K_{a,j}^{cal}(T, \underline{x}) - K_{a,j}^{exp}(T)}{K_{a,j}^{exp}(T)} \quad (\text{S.4})$$

Once the equilibrium phase composition is available, the bubble point pressure calculation is then performed for the vapor phase composition and the total pressure. For the vapor pressure of acetic acid, the same procedure is used except that the solvent composition is set to zero. The compressibility of pure acetic acid gas at given T and P is calculated through the Eq. S5.

$$z = PV/nRT \quad (\text{S.5})$$

where is the total number of moles of the gas. In the deal gas limit, almost all the dimers are in the form of cyclic dimer, i.e., $n = n_M + n_{CD}$. The experimental compressibility factor z^* is reported in terms of the total number of acetic acid monomer, i.e.,

$$z^* = PV/n_i^0 RT \quad (S.6)$$

where $n_i^0 = n_M + 2 n_{CD}$. The equilibrium composition n_M and n_{CD} are determined through cyclic dimerization reaction, Eq(13). Therefore, the experimental compressibility can be used to determine the chemical equilibrium constant of cyclic dimer.

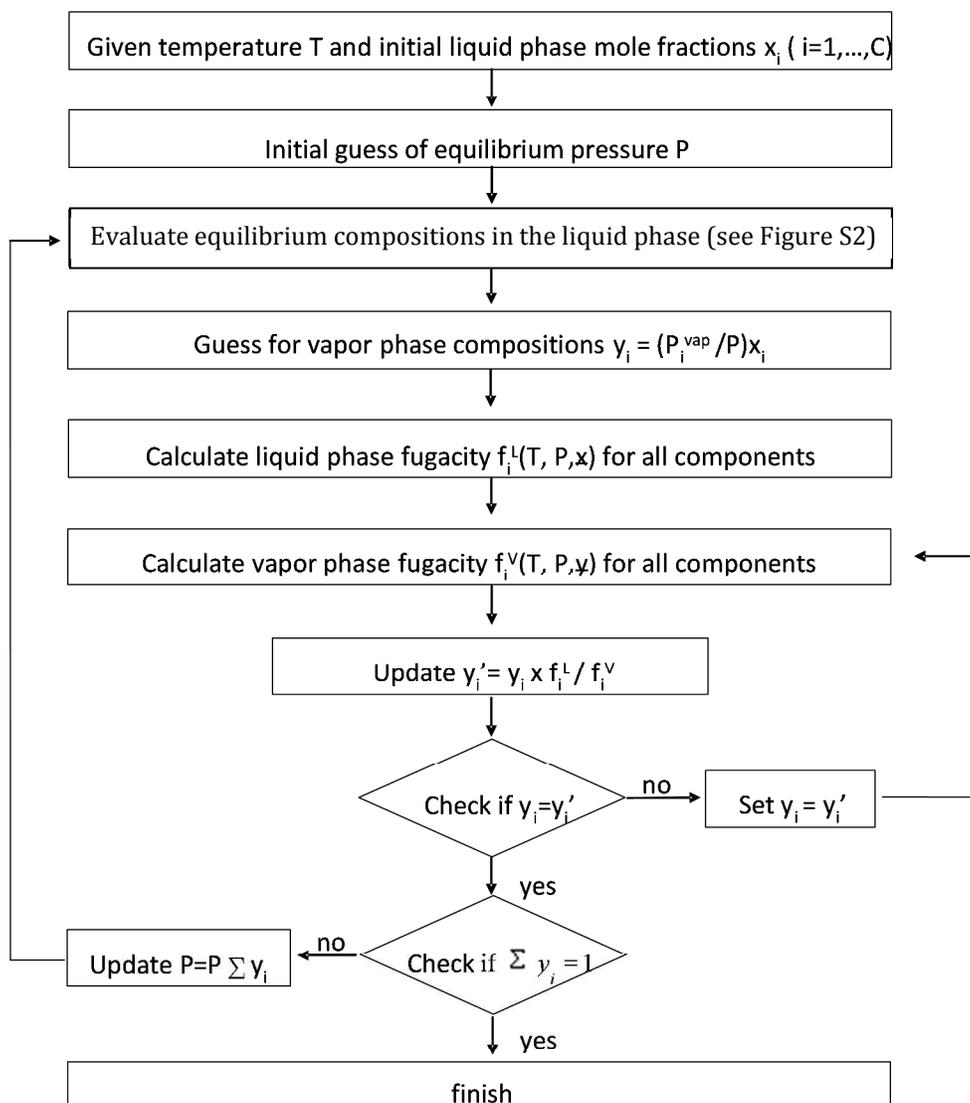


Figure S1 Modified bubble point pressure calculation for simultaneous phase and chemical equilibrium

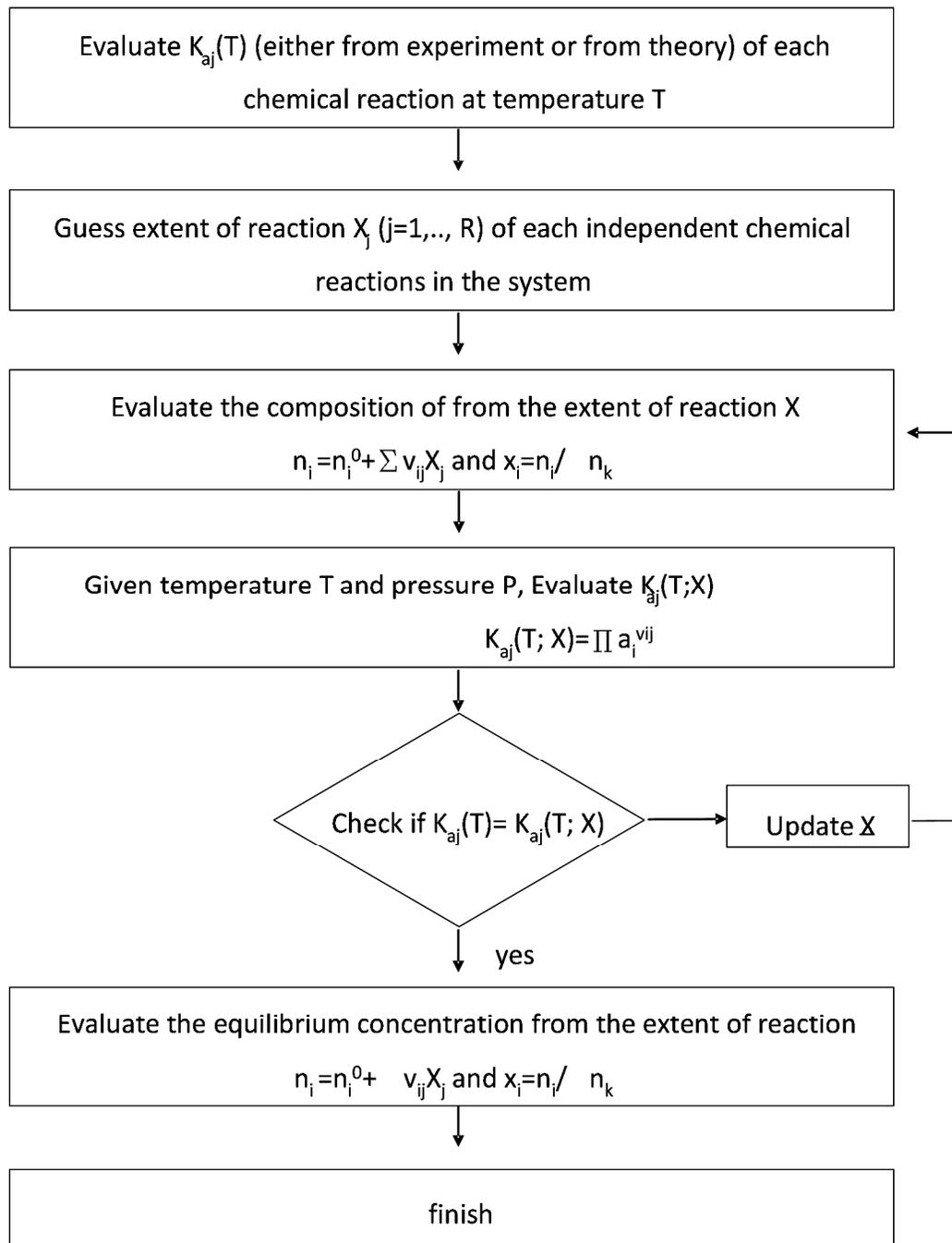


Figure S2 A self-consistent procedure for equilibrium composition of reactive systems

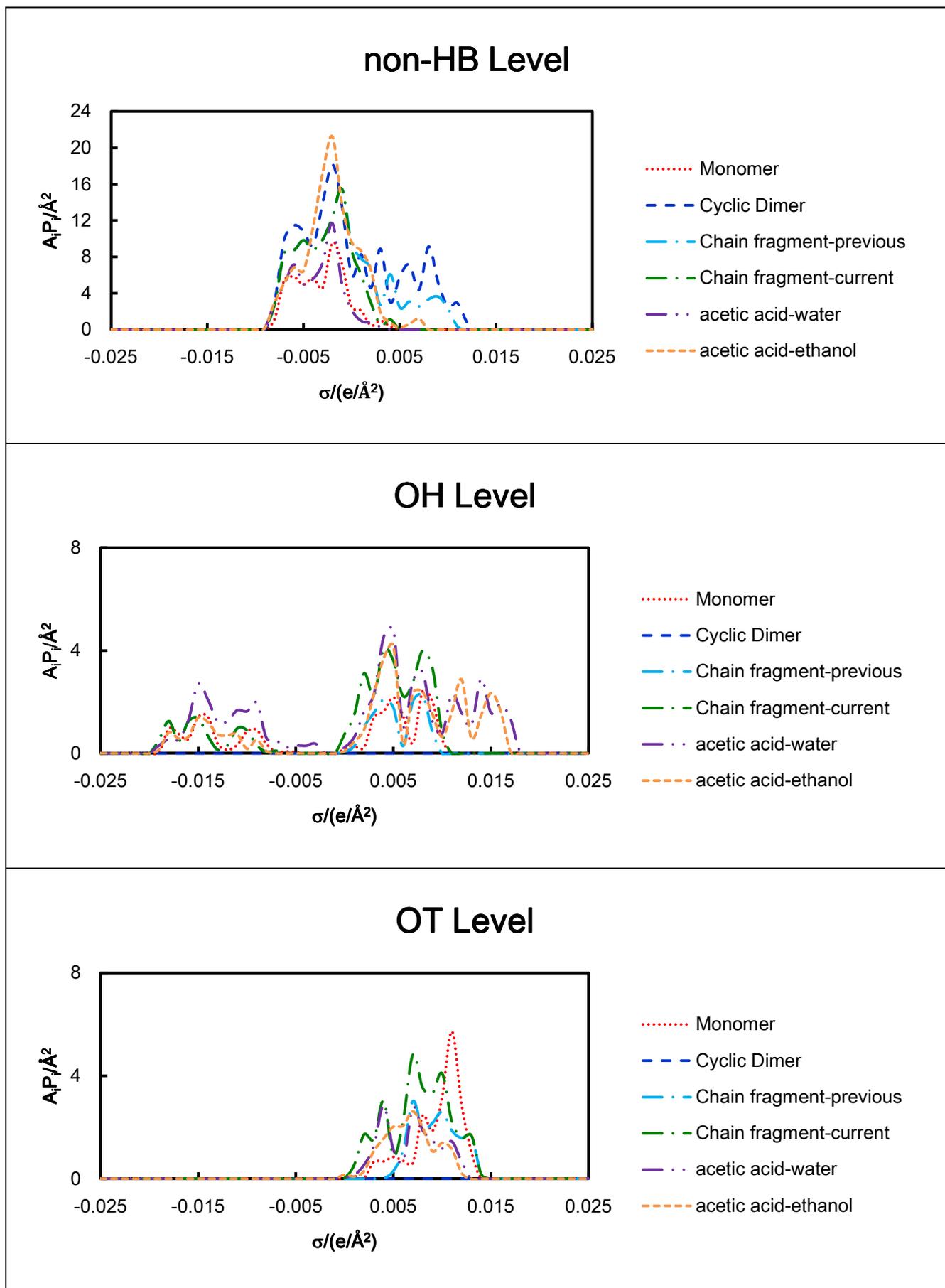


Figure S3 Sigma profile of the local fluid structures of acetic acid.

Table S1. The collected binary vapor-liquid equilibrium data that passed the thermodynamic consistent test performed by NIST.

Binary Mixtures	Data Points	Temperature range (K)	Press range (Pa)	Ref	
Water	225	293.15-502.9	1691-2778587	¹	
Methanol	9	318	8850-33890	²	
Acetic Acid	Ethanol	16	351.45-388.95	93990	³
	Ethanol	9	323.2	8200-29600	⁴
	1-Propanol	14	370.45-387.25	93990	³
	1-Hexanol	11	387.54-426.39	90000	⁵
	1-octanol	18	298.15-308.15	12-3587	²

Table. S2. Comparison of prediction accuracy in liquid-liquid equilibria of acetic acid and five alkanes based on different treatments of hydrogen bonding surface.

Compound	UCST/K ^a	M ^b	this work		previous work (ref. ⁶)	
			RMS ^c	Δ UCST/K ^d	RMS ^c	Δ UCST/K ^d
octane	291.8	8	0.071	-9.8	0.086	2.3
n-NONANE	302.3	8	0.073	-8.3	0.064	0.0
n-DECANE	314.1	12	0.066	-2.9	0.093	-6.1
n-NDECANE	325.5	11	0.078 ^e	2.5	0.126	-13.5
n-ODECANE	337	12	0.080 ^e	7.5	0.111	-19.0
Average			0.073		0.091	

^a The upper critical solution temperature (UCST) estimated from experimental LLE data

^b M mean the number of LLE system

^c $RMS = \left[\frac{1}{2M_{cal}} \sum_{j=1}^{M_{cal}} \sum_{k=1}^2 (x_j^{k,cal} - x_j^{k,expt})^2 \right]^{1/2}$, where superscript k indicates one of the two liquid phases in liquid-liquid equilibrium.

^d Experimental UCST minus calculated UCST.

Table. S3. Comparison of prediction accuracy in vapor-liquid equilibria of acetic acid and different solvents based on different treatments of hydrogen bonding surface.

Method Compound	this work		previous work (ref. ⁶)	
	AARD-P(%) ^a	AAD-y(%) ^b	AARD-P(%)	AAD-y(%)
Type I (non-hydrogen bonding solvent)				
Hexane	2.50	0.78	3.43	1.24
N-HEPTANE	1.32	1.18	1.95	1.46
CYCLOHEXANE	2.05	2.09	3.03	2.53
Octane	6.16	2.24	7.24	2.46
1-HEXENE	7.69	3.13	8.78	3.60
BENZENE	5.39	2.59	5.93	2.72
STYRENE	8.79	3.89	9.67	4.23
MONOCHLORO BENZENE	3.80	4.06	4.41	4.42
CARBON TETRA CHLORIDE	7.76	1.44	6.40	1.23
CHLOROFORM	26.10	0.53	25.06	0.47
Type I average	5.49	2.24	6.05	2.45
Type II (hydrogen acceptor solvent)				
ETHYL ACETATE	5.83	2.02	4.86	1.99
ACETIC ANHYDRIDE	8.80	4.62	10.68	5.22
ACETONE	18.84	2.34	16.11	2.17
BUTANAL	3.14	1.43	3.30	1.34
METHYL ETHYL KETONE	7.02	2.12	5.47	1.76
Type II average	9.72	2.36	8.50	2.28
Overall average	7.14	2.29	7.10	2.38

$$^a \text{AARD} - \text{P}(\%) = \frac{1}{N} \sum_{i=1}^N \frac{|p_i^{\text{calc}} - p_i^{\text{exp}}|}{p_i^{\text{exp}}}, \text{ calc and exp represent the data from calculation and experiment}$$

$$^b \text{AAD} - y = \frac{1}{N} \sum_{i=1}^N |y_i^{\text{calc}} - y_i^{\text{exp}}|$$

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