Measurement and Calculation of Excess Enthalpy with the Isothermal Microcalorimeter

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CONTENTS

I. Introduction

The Object of Study

The Needs of Excess Enthalpy

- Excess enthalpy data of binary mixture are important in understanding the nature of interactions between the molecules.
- Excess enthalpy data plays an important role in chemical engineering process design and operation.

Types of Calorimeter

■ **Three types of calorimeter**

: batch calorimeter, displacement calorimeter, flow calorimeter

► **flow calorimeter**

① To make measurements over a wide range of pressure and temperature conditions

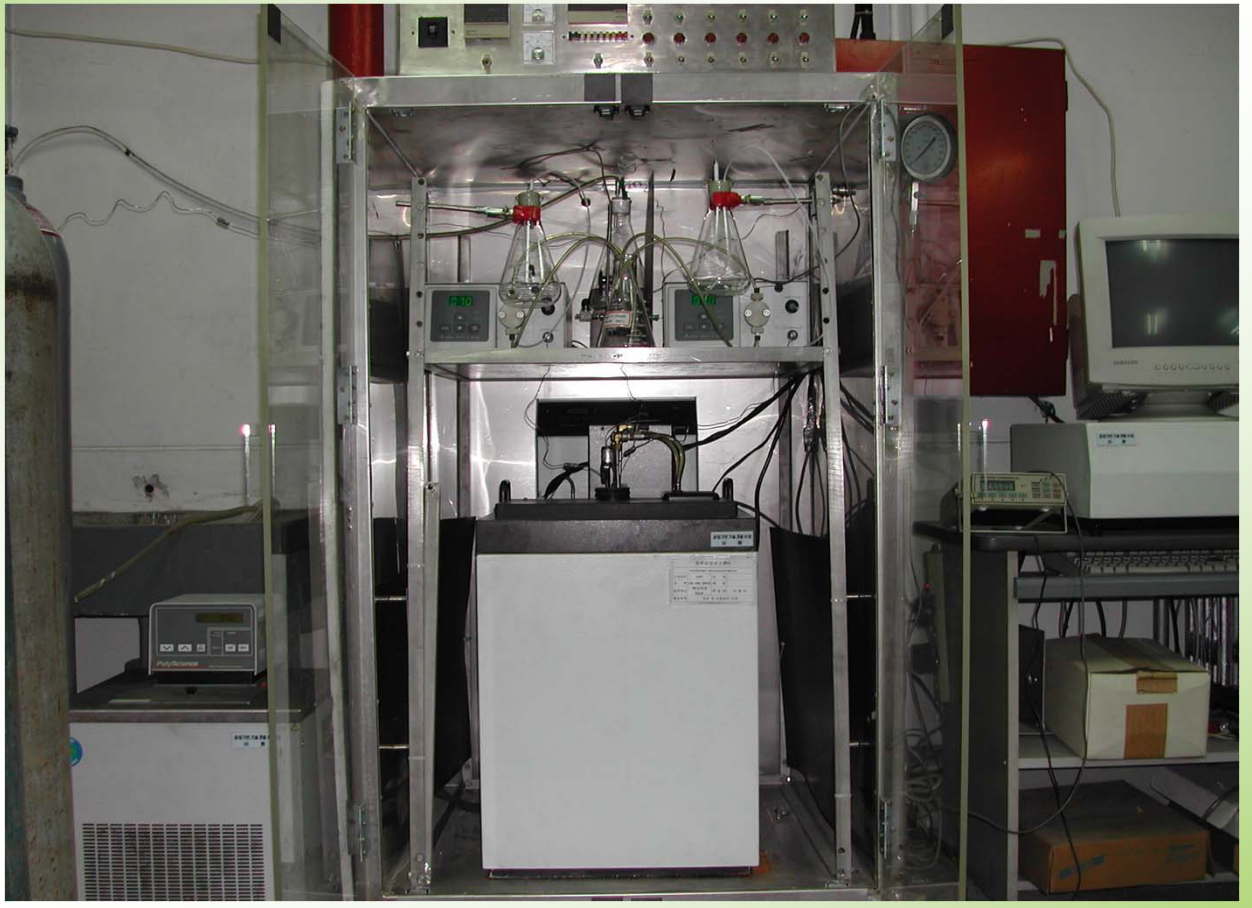
② The measurements of the excess enthalpy can be made for gases as well as liquids

③ To require large amounts of chemicals

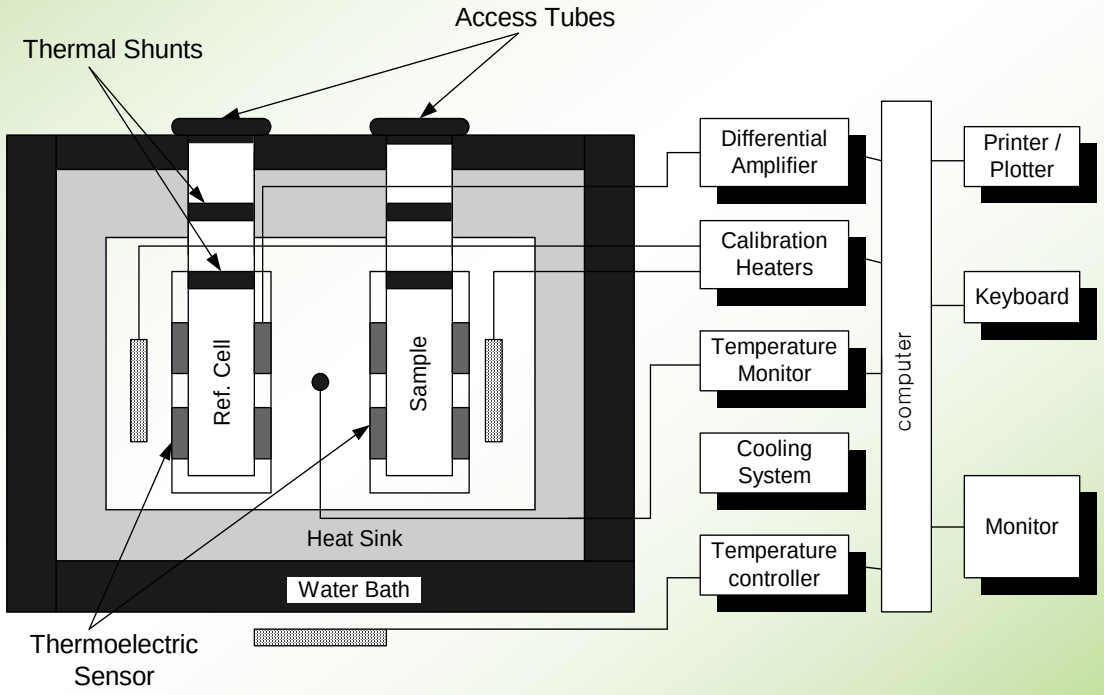
Apparatus

- **Isothermal Microcalorimeter (IMC)**
  - ► Model CSC 4400 (Calorimetry Sciences Corporation)
- **Pump :** a set of HPLC pump (Model Acuflow Series II)
  - ⟶ Accuracy of flow rate : ± 2%
- **Auxiliary equipments**
  - ► Air bath
  - ► Back pressure regulator
  - ► Control gas : compressed helium gas
  - ► Circulator (constant temperature)

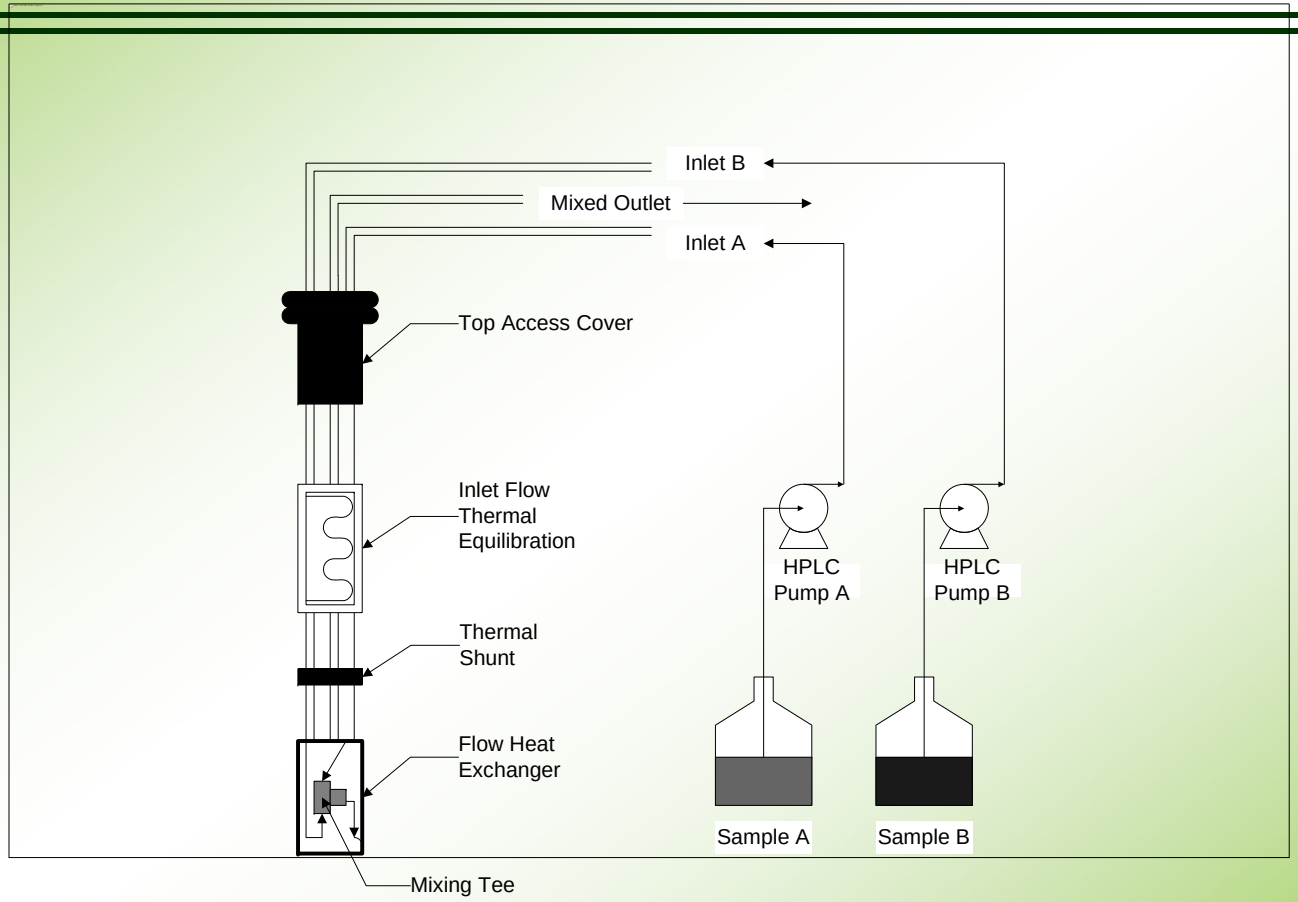
Experimental apparatus



Block diagram of IMC

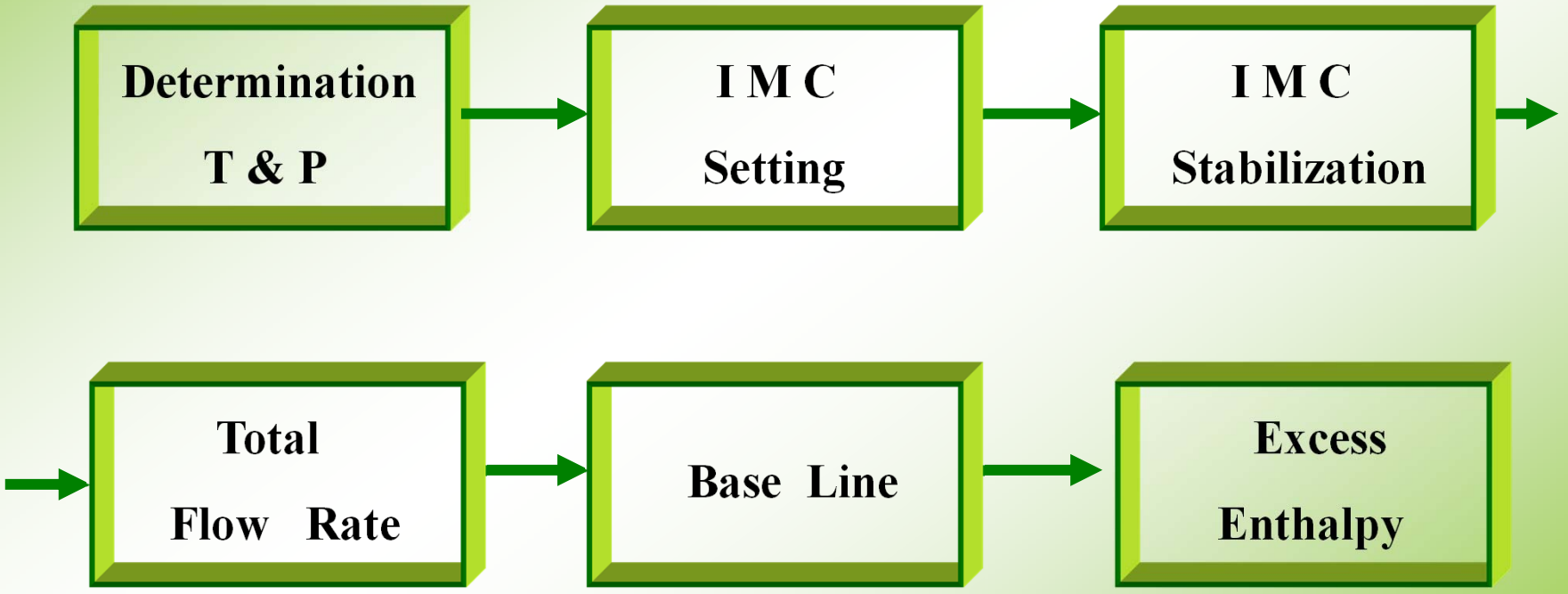


Schematic diagram of flow mixing cell



II. Experiments & Calculations

Procedure

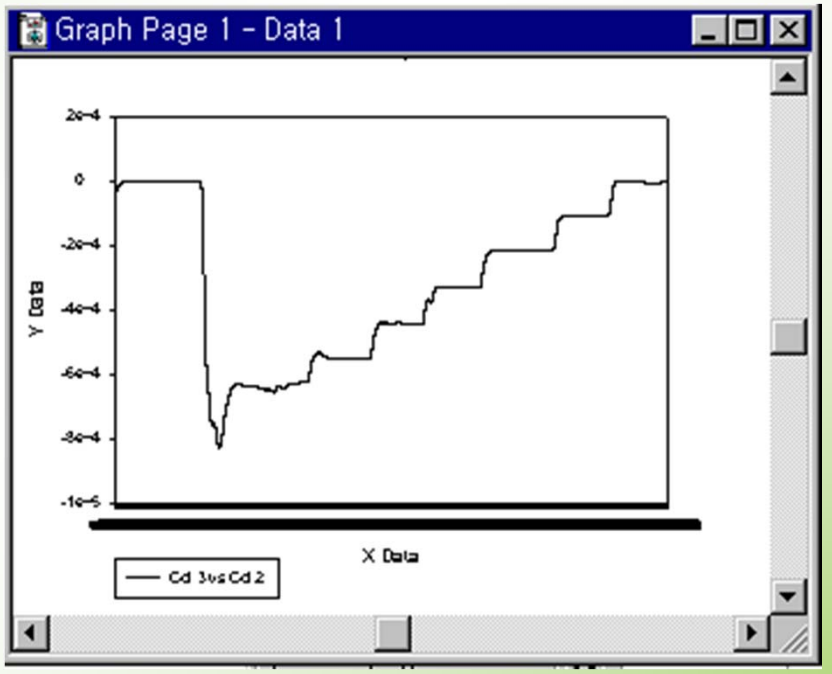

Determination
T & P
I M C
Setting
I M C
Stabilization
Total
Flow Rate
Base Line
Excess
Enthalpy

Course of H^E Calculation

- The raw data of experiment with IMC

Data 1

	-1-	-2-	-3-
1	29.97	-3863.22	t126.00
2	29.97	-3559.74	t144.02
3	29.97	-3280.90	t162.03
4	29.97	-3024.54	t180.05
5	29.97	-2788.51	t198.01
6	29.97	-2571.02	t216.02
7	29.97	-2370.58	t234.04
8	29.97	-2185.68	t252.00
9	29.97	-2014.81	t270.01
10	29.97	-1857.04	t288.03
11	29.97	-1711.38	t306.05
12	29.97	-1576.48	t324.01
13	29.97	-1451.68	t342.02
14	29.97	-1336.17	t360.04
15	29.97	-1229.12	t378.00
16	29.97	-1129.86	t396.01
17	29.97	-1037.88	t414.03
18	29.97	-952.60	t432.04
19	29.97	-873.34	t450.01
20	29.97	-799.80	t468.02
21	29.97	-731.44	t486.04
22	29.97	-667.85	t504.00
23	29.97	-608.78	t522.01
24	29.97	-553.80	t540.03
25	29.97	-502.64	t558.04
26	29.97	-455.05	t576.00
27	29.97	-410.68	t594.02
		Plot 1 Y Data	Plot 1 X Data



X data : time , Y data : enthalpy

Course of H^E Calculation

Reagent	Density	M . W					
Water	0.997	18.02					
1 -butanol	0.80206	74.13					
Pump B Water	Pump A 1 -butanol	real flow rate of pump B	real flow rate of pump A	mole flow rate of pump B	mole flow rate of pump A	total mole flow rate	calory (micro Watt)
0	0.65	0	0.6976	0	0.007547782	0.007547782	284.0646
0.1	0.55	0.1047	0.603	0.00579278	0.006524244	0.012317024	-65866.20
0.15	0.5	0.1682	0.5471	0.009306071	0.005919426	0.015225497	-55080.5
0.2	0.45	0.2178	0.4918	0.012050311	0.0053211	0.01737141	-43957.2
0.25	0.4	0.2741	0.4377	0.015165244	0.004735757	0.019901001	-32641.8
0.3	0.35	0.3263	0.3848	0.018053335	0.004163398	0.022216733	-21520.9
0.35	0.3	0.3795	0.3374	0.020996754	0.003650547	0.024647301	-10636.2
0.4	0.25	0.4324	0.274	0.023923574	0.002964582	0.026888155	-379.307
0.45	0.2	0.4862	0.2196	0.026900189	0.002375993	0.029276182	6822.136
0.5	0.15	0.5414	0.1635	0.029954262	0.001769011	0.031723273	16399.98
0.55	0.1	0.5942	0.1092	0.032875549	0.001181505	0.034057054	25583.19
0.65	0	0.6943	0	0.038413824	0	0.038413824	269.8025
composition Pump B = x	composition Pump A = (1 -x)	Base line	final calory			Calory (J/mol)	
0.0000	1.0000	284.0646	0			0	
0.4703	0.5297	281.9546072	66148.15461			322.2279439	
0.6112	0.3888	280.7109229	55361.21092			218.1651421	
0.6937	0.3063	279.687084	44236.88708			152.7920405	
0.7620	0.2380	278.5725494	32920.37255			99.25241156	
0.8126	0.1874	277.5201995	21798.4202			58.8702761	
0.8519	0.1481	276.5147786	10912.71478			26.56529812	
0.8897	0.1103	275.334515	654.641515			1.460810167	
0.9188	0.0812	274.239957	-6547.896043			-13.41956968	
0.944236166	0.055763834	273.1105626	-16126.86944			-30.50164963	
0.965308074	0.034691926	272.0166332	-25311.17337			-44.59194835	
1	0	269.8025	0			0	

NLF-HB Theory

- Assumption : consideration of hole' non-randomness

Configurational partition function (Ω_c)

↓

Helmholtz Free Energy(A^c) derivation

↓

Nonrandom Lattice Fluid Theory Eos

Chemical potential , Fugacity

↓ **application**

- Equilibria of vapor-liquid,vapor-solid,liquid-liquid phase, and Multiphase equilibria including UCST behaviors
- Heat of mixing non polar- non polar, non polar- polar, polar - polar binary mixtures of simple and complex molecules

NLF-HB Theory

- Configurational partition function (Ω_c)

$$\Omega = \Omega_{PHYS}\ \Omega_{HB}$$

  - Ω_{PHYS} : [Physical term]… You et al. (1994)
  - Ω_{HB} : [Chemical term] … Extension of Veytsman statistics (Park et al. 2001)
    - Physical term

$$\Omega c = g_R g_{NR} \exp(-\beta U^c)$$

$$\Omega c = \left[\frac{N_r!}{\Pi N_i!}\right]\left[\frac{N_q!}{N_r!}\right]^{z/2}\left[\frac{\Pi N^o{}_{ii}\,\Pi\left[\left(\frac{N^o{}_{ij}}{2}\right)!\right]^2}{\Pi N_{ii}!\,\Pi\left[\left(\frac{N_{ij}}{2}\right)!\right]^2}\right]\exp(-\beta U^C)$$

NLF-HB Theory

- Hydrogen bonding term

$$\Omega_{HB} = \frac{N_{10}^{D0}!(2!)^{N_{11}^{H0}}}{N_{10}^{D}!(2!)^{N_{11}^{H}}} \prod_{k=1}^{M} \frac{N_{k0}^{H0}!}{N_{k0}^{H}!} \prod_{j=1}^{N} \frac{N_{0l}^{H0}!}{N_{0l}^{H}!} \prod_{k=1}^{M} \prod_{l=1}^{N} \frac{N_{kl}^{H0}!}{N_{kl}^{H}!} (P_{kl})^{(N_{kl}^{H} - N_{kl}^{H0})} \exp(-\beta A_{kl}^{H} N_{kl}^{H})$$

- Connection of thermodynamic function with configurational function

$$\beta A^{c} = -\ln \Omega^{c}$$

- The molar configurational internal energy for mixture

$$\frac{\beta U^{c}}{N} = -\left(\frac{T}{N}\right)\left(\frac{\partial \beta A^{c}}{\partial T}\right)_{N_0, N_i}$$

- **Expression of excess enthalpy**

$$H^{E} = (U^{C} + PV)_{mixture} - \sum x_i (U^{C} + PV)_{pure,i}$$

NLF-HB Theory

Physical Parameters

① Coordination number : $z = 10$

② Lattice volume : $V_H = 9.75\ cm^3/mol$

③ Pure parameters (r_i, ε_{ii}) :

$$r_i = r_a + r_b(T - T_0) + r_c[T\ln(T_0/T) + T - T_0]$$

$$\varepsilon_{ii}/k = \varepsilon_a + \varepsilon_b(T - T_0) + \varepsilon_c[T\ln(T_0/T) + T - T_0]$$

④ Binary parameter (λ_{ij}) : $\varepsilon_{ij} = (\varepsilon_{ii} \cdot \varepsilon_{jj})^{1/2}(1 - \lambda_{ij})$

NLF-HB Theory

Hydrogen Bonding Parameters

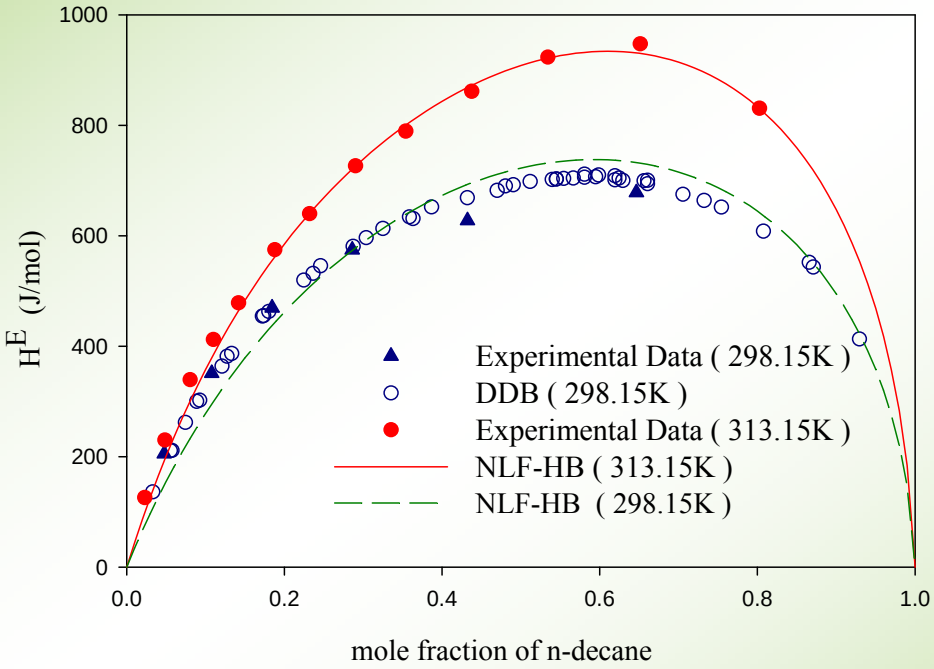
- $A_{kl}^{HB} = U_{kl}^{HB} - TS_{kl}^{HB}$

Hydrogen bonding parameters for NLF-HB EOS

	U_{kl}	S_{kl}
alcohols	$-25.1\times10^{3}\ J/mol$	$-26.5\ J/mol$
water	$-15.5\times10^{3}\ J/mol$	$-16.6\ J/mol$

Results & Discussions

Results & Discussions

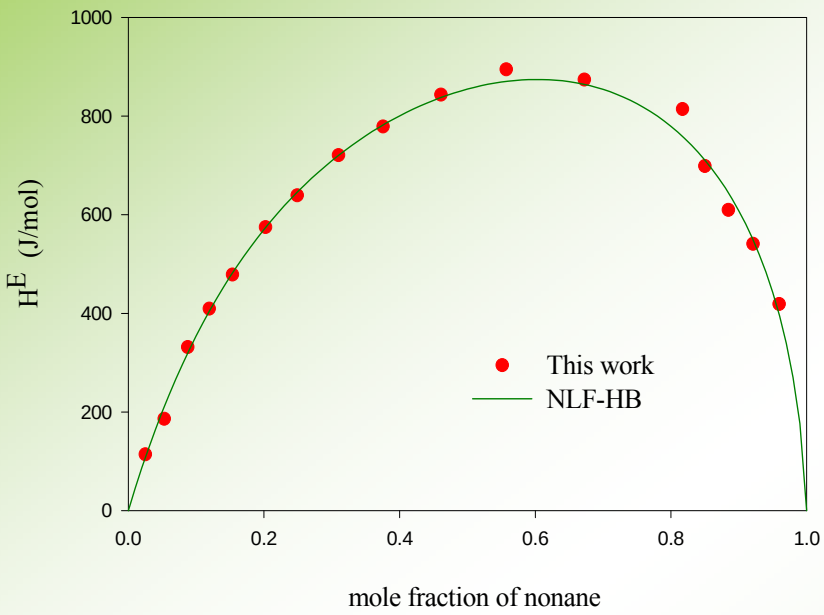


Comparison of experimental H^E for decane + ethanol

(1) 313.15K DATA ⟶ ERROR = 0.88 %

(2) 298.15K DATA ⟶ ERROR = 3.21 %

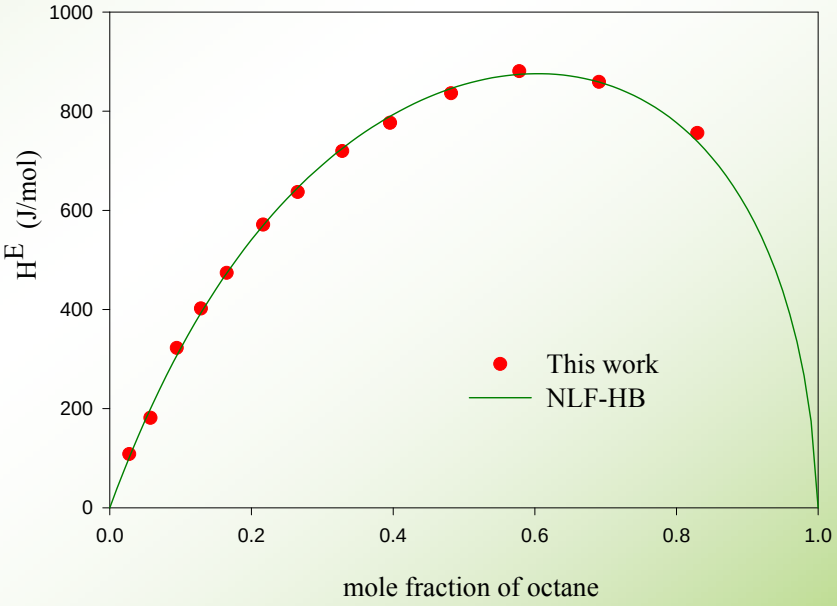
Results & Discussions



Comparison of experimental H^E

for nonane + ethanol at 313.15K

ERROR = 3.00%

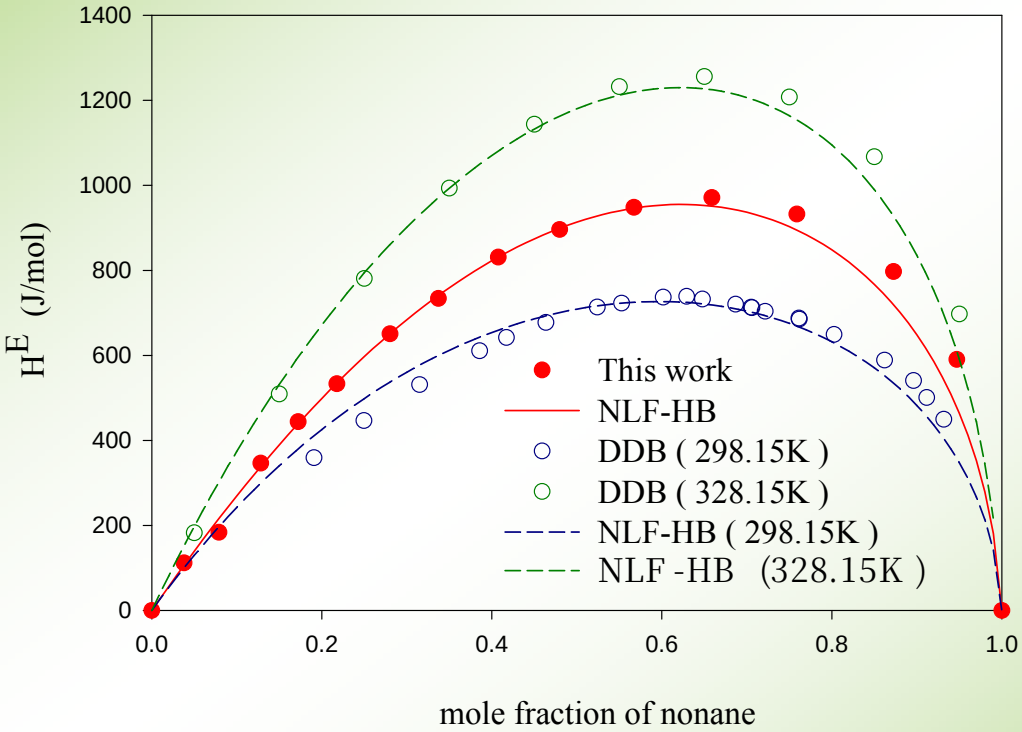


Comparison of experimental H^E

for octane + ethanol at 313.15K

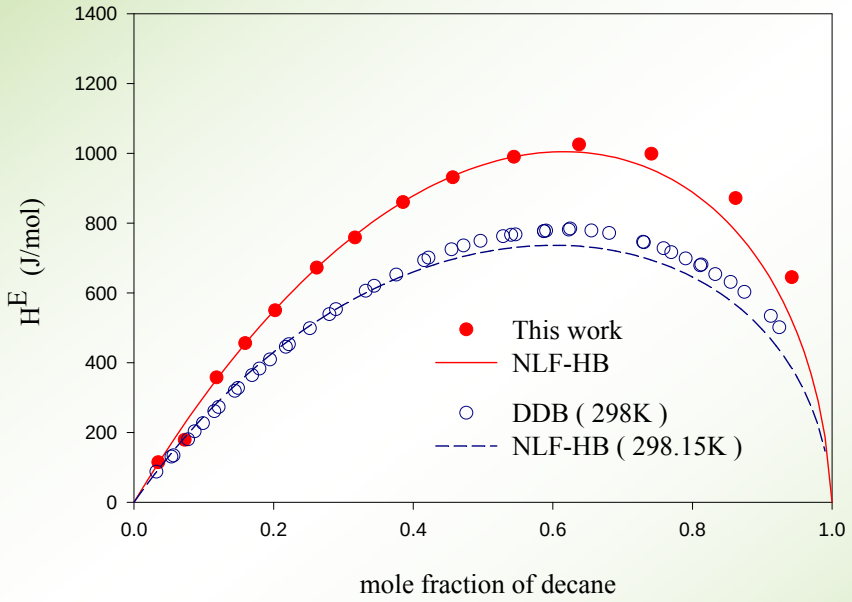
ERROR = 2.47%

Results & Discussions



Comparison of experimental H^E for nonane + 1-butanol at 313.15K

ERROR = 2.86 %

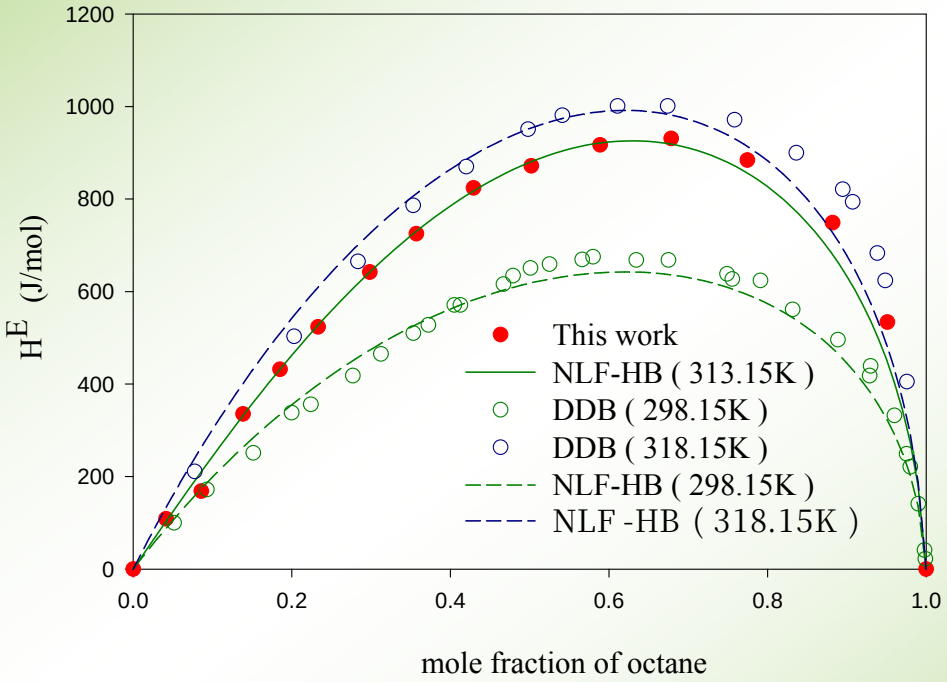


Comparison of experimental H^E

for decane + 1-butanol at 313.15K

ERROR = 4.28%

Results & Discussions



Comparison of experimental H^E for octane + 1-butanol at 313.15K

ERROR = 4.03%

III. Conclusion

Conclusion

1. Excess enthalpies for the various systems were measured with the isothermal microcalorimeter at 298.15K and 313.15K.
2. Experimental data were compared with calculated results using NLF-HB EOS.
3. The relative error for each system was within 5%.
4. The NLF-HB EOS is applied to binary mixtures of water , alcohol, alkane, acid , and amine, etc …

Future

- Systems : alcohol, alkane, amine, water, …
- The simultaneous representation of VLE and excess enthalpy
- The calculation of excess enthalpy using SAFT model