Excess Enthalpies for the Binary Systems of N-Alkane + 1-Alkanol at 313.15 K

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Introduction

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.

System : N-alkane + 1-alkanol

- **Temperature condition : 313.15K**

Types of Calorimeter

■ Three types of calorimeter

: Batch calorimeter, Displacement calorimeter, Flow calorimeter

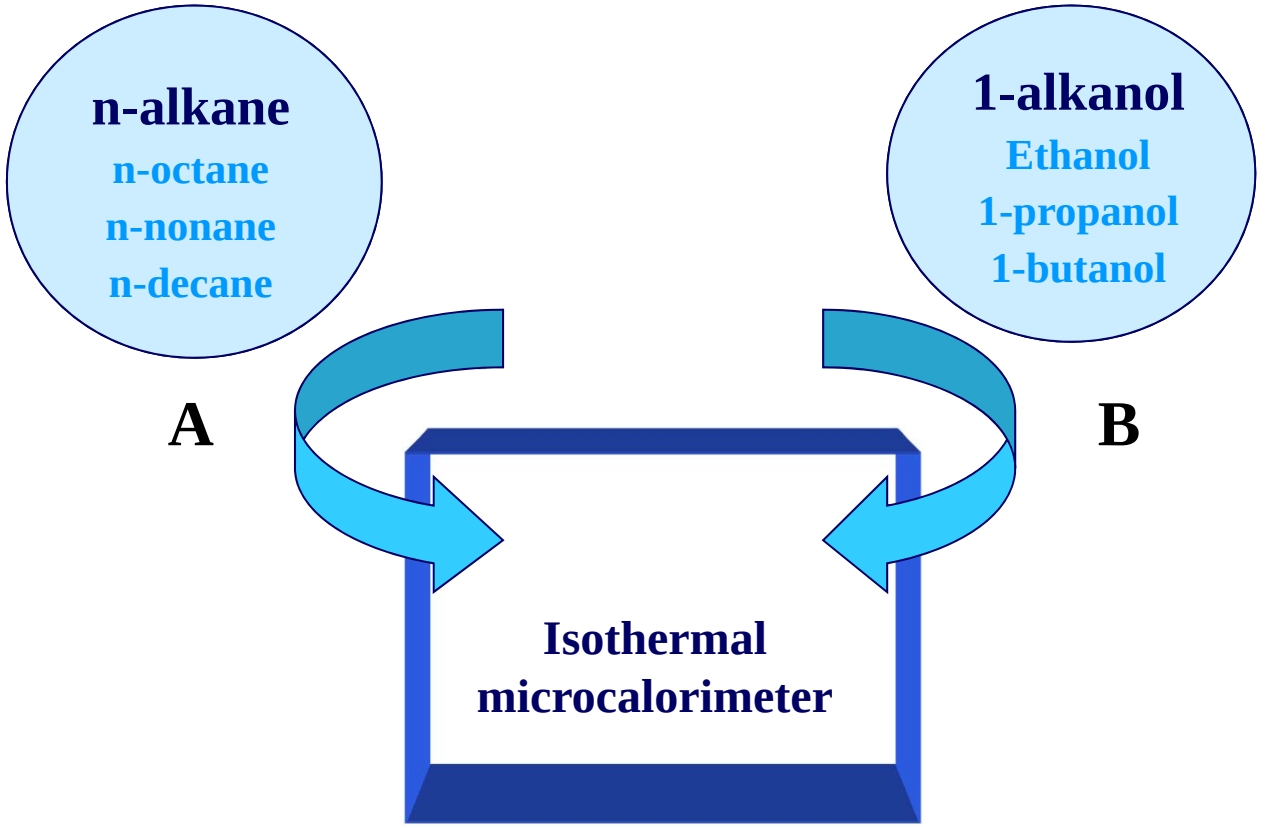
► Flow calorimeter

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

Materials

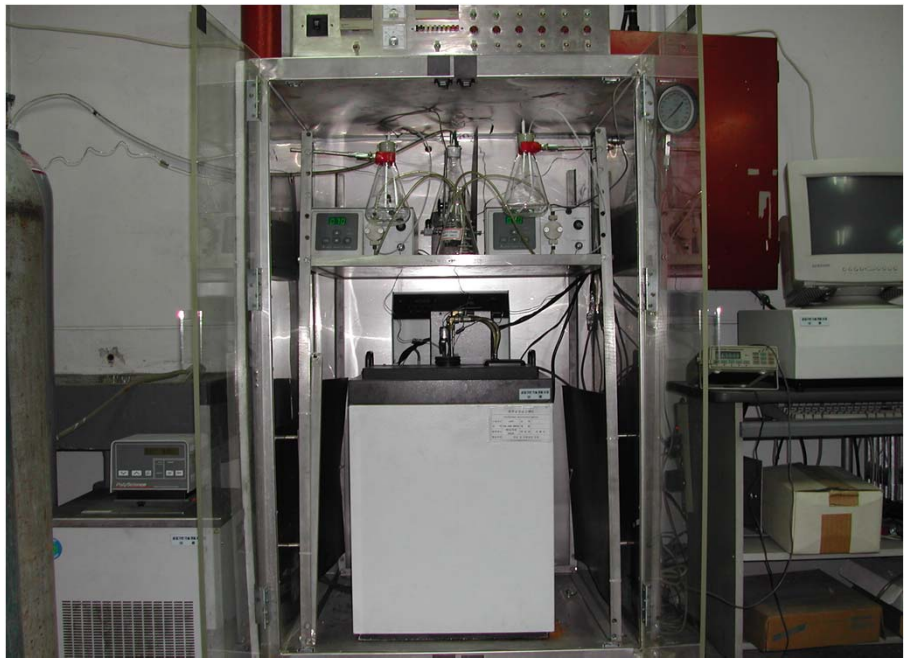

n-alkane
n-octane
n-nonane
n-decane
1-alkanol
Ethanol
1-propanol
1-butanol
A
B
Isothermal
microcalorimeter

Apparatus

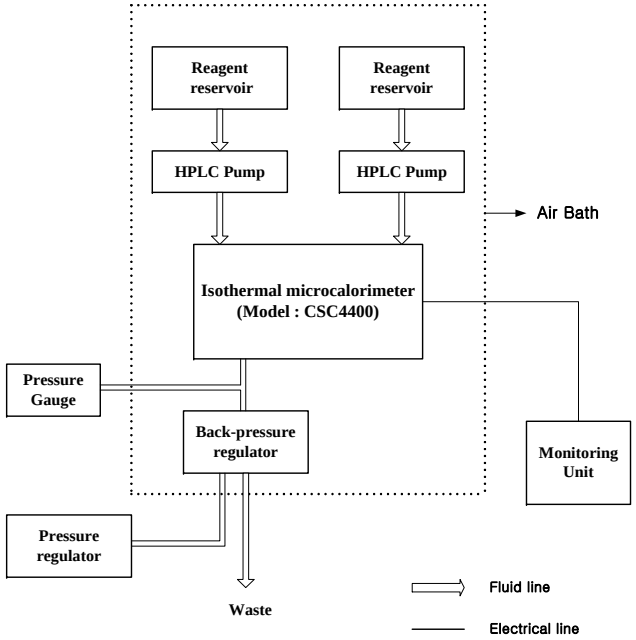
- **Isothermal Microcalorimeter (IMC)**
  - Model CSC 4400 (Calorimetry Sciences Corporation)
- **Pump :** a set of HPLC pump (Model Acuflow Series II)

  ⟹ Accuracy of flow rate : ± 2%
- **Auxiliary equipments**
  - Air bath
  - Back pressure regulator
  - Control gas : compressed helium gas
  - Circulator (constant temperature)

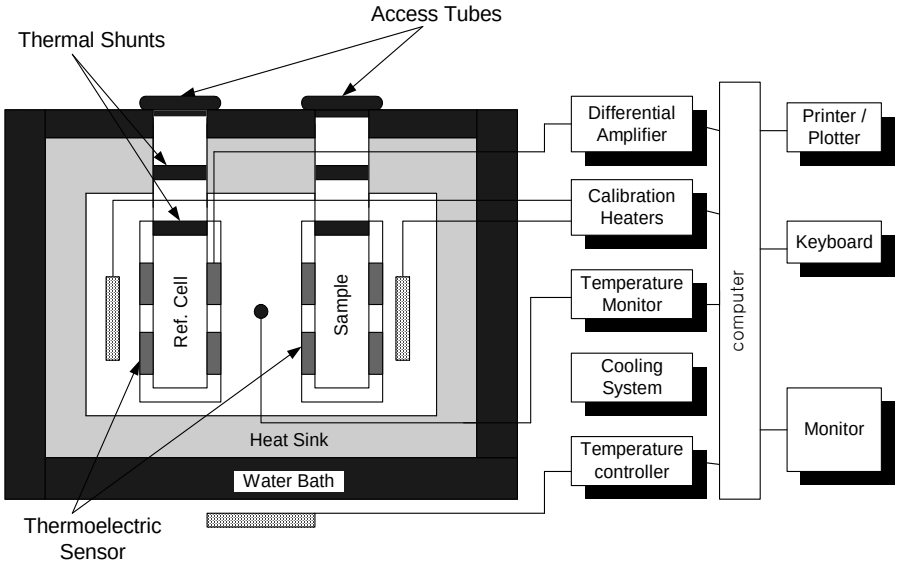
Experimental apparatus



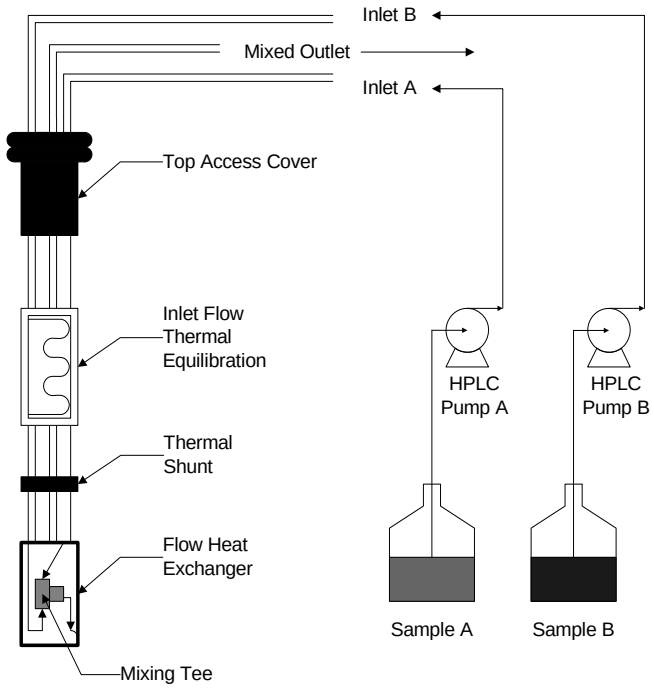
Block diagram of experimental apparatus



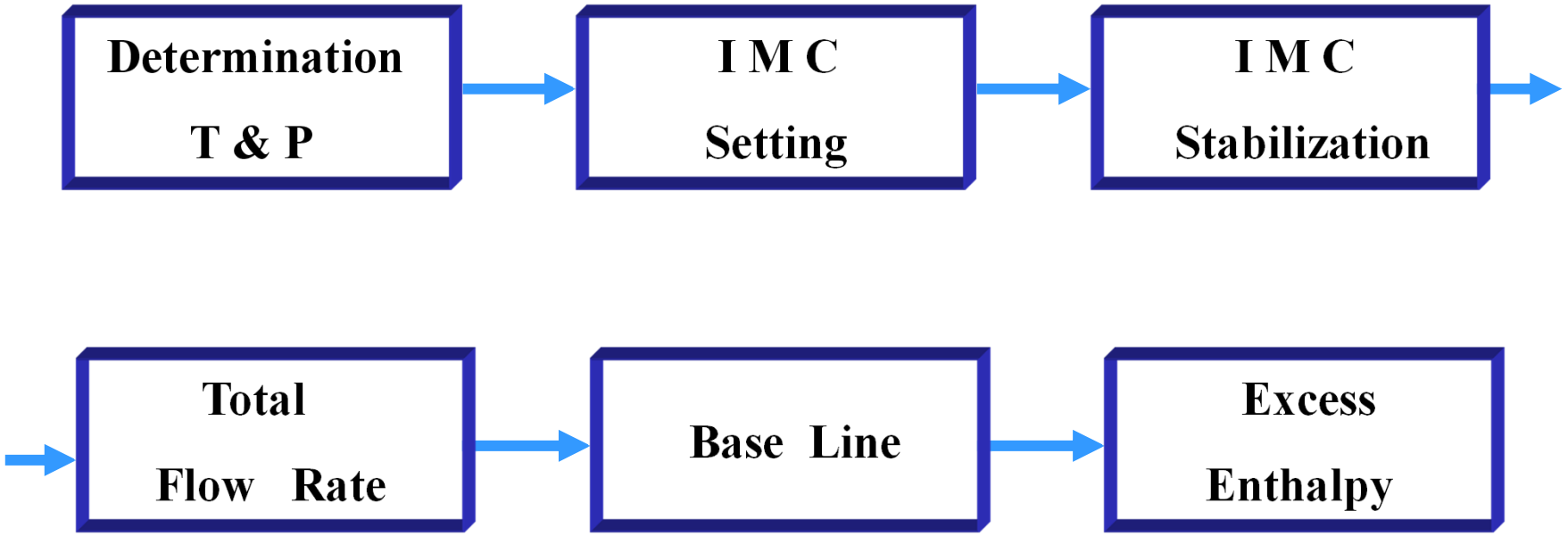
Block diagram of IMC



Schematic diagram of flow mixing cell



Procedure


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

Comparison literature data and experimental data

- To test the accuracy of calorimeter measurements,
- **System : Octane + Ethanol [at 298.15K]**

  - ***Redlich-Kister Correlation***

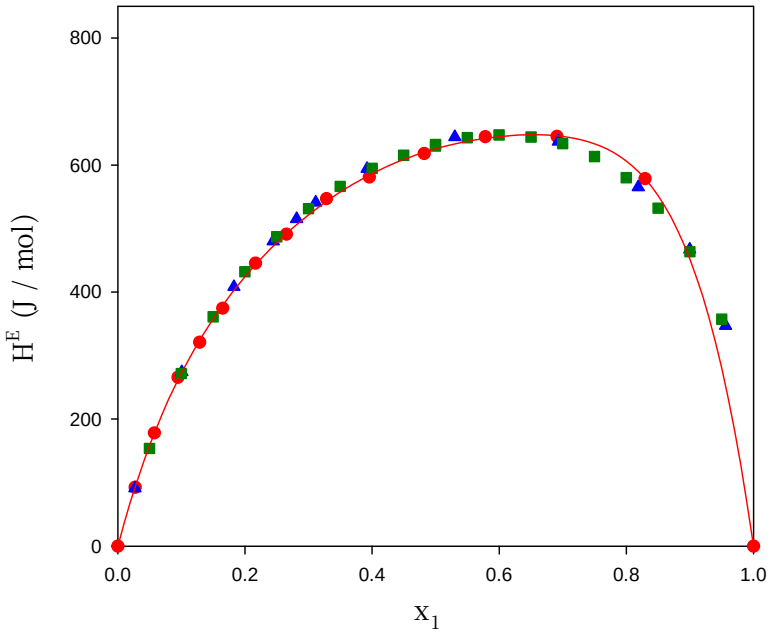
$$H^E / J \cdot mol^{-1} = x(1-x)\sum_{i=1}^{k} A_i (1-2x)^{i-1}$$

Where, x is the mole fraction of component

A*i* is the adjustable parameter

  - **Result** → **S. D. ; 2.62%**

Redlich-Kister Correlation



Comparison experimental data H^E and literature value from n-octane + ethanol at 298.15K. • , This work ; ▲ , Ramalho R.S., Ruel M.Can. J. (1968); ■ , Zhu S., Shen S., Benson G..C., Lu B.C.-Y (1994)

NLF-HB Theory(1)

Configurational partition function (Ω_c)

↓

Helmholtz Free Energy(A^c) derivation

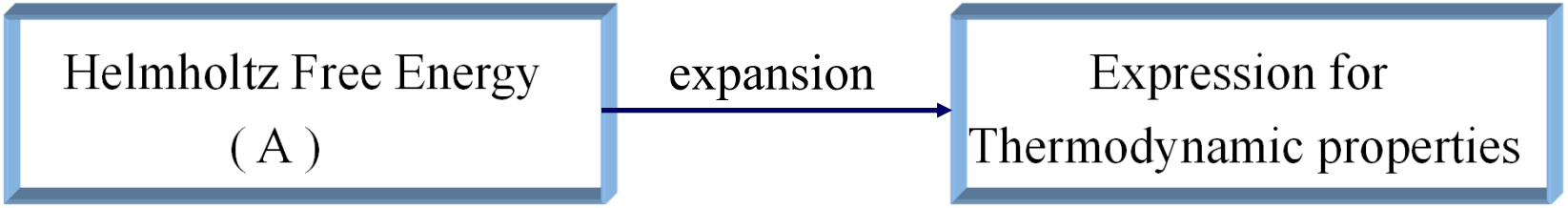
↓

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(2)



Partition Function

In a three-dimension lattice,

- The coordination number : z =10
- Unit cell volume : $V_H = 9.75\ cm^3/mol$
- Effective surface area : $zq_i = (z_i - 2)r_i + 2$

NLF-HB Theory (3)

- 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 (4)

- Hydrogen bonding term

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

- 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 (5)

Physical Parameters

① Coordination number : $z = 10$

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

③ Pure parameters (r_i, ε_{ii}) :

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

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

NLF-HB Theory(6)

The binary interaction parameters

- $\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}(1-k_{ij})$ $\qquad k_{ij} = A + B/T$

Hydrogen Bonding Parameters

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

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

Hydrogen bonding parameters for NLF-HB EOS

Results & Discussions (1)

	A1	A2	A3	A4	A5	s (J/mol)
n-Octane + Ethanol	3377.03	-857.84	1847.66	-1332.31	1028.53	8.62
n-Octane+1-Propanol	3587.15	-1304.61	1617.67	-2420.27	1896.63	4.13
n-Octane + 1-Butanol	3494.17	-1143.36	1211.19	-3068.19	1931.68	12.58
n-Nonane + Ethanol	3456.40	-842.37	1754.16	-846.86	1107.78	9.15
n-Nonane+1-Propanol	3733.21	-1303.01	1850.12	-2333.66	1805.08	3.51
n-Nonane + 1-Butanol	3635.14	-1200.29	1548.91	-2829.08	1732.21	11.19
n-Decane + Ethanol	3635.22	-1133.00	1659.25	-366.99	1802.66	5.10
n-Decane + 1-Propanol	3917.27	-1373.34	2071.94	-2214.13	1933.90	3.28
n-Decane + 1-Butanol	3844.24	-1192.97	1984.59	-2961.96	1422.91	12.97

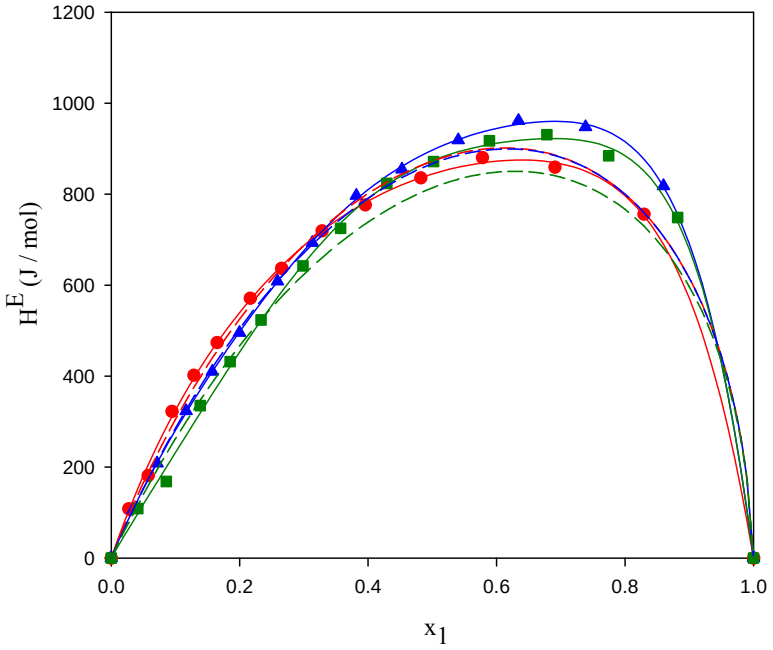
Coefficients, A_K, and Standard Deviation, s, for the Representation of H^E

Results & Discussions (2)

	e_a	e_b	e_c	r_a	r_b	r_c	Range (K)
n-Octane	100.590	.0356	-.0243	14.594	-.0019	.0075	273-533
n-Nonane	101.279	.0480	.0081	16.171	-.0027	.0060	373-575
n-Decane	101.689	.529	.0125	17.805	-.0034	.0057	368-598
Ethanol	84.918	.1791	.1674	4.945	.0019	-.0009	293-473
1-Propanol	90.291	.1362	.0827	6.523	.0001	-.0086	273-537
1-Butanol	89.946	.1917	.2471	7.810	.0061	.0104	275-545

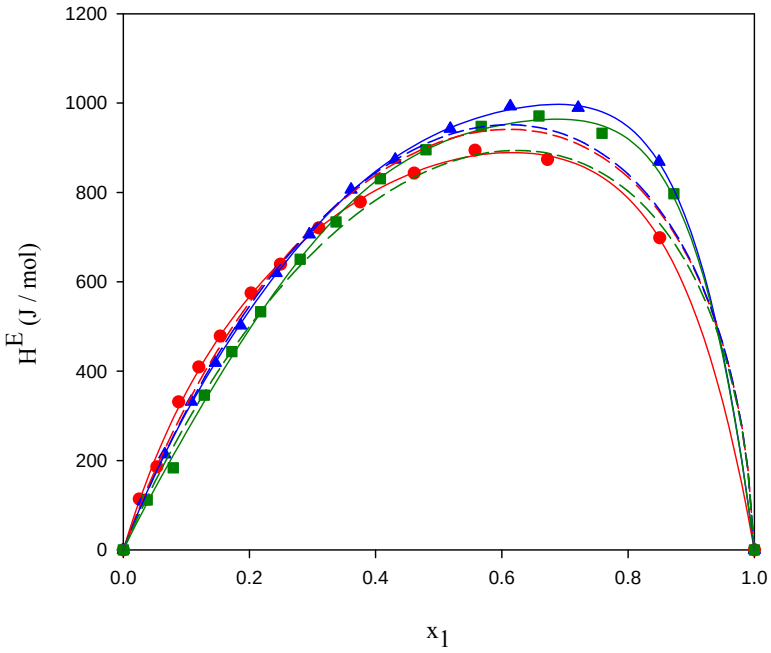
Pure parameters and temperature ranges of the NLF-HB equation of state

Results & Discussions (4)



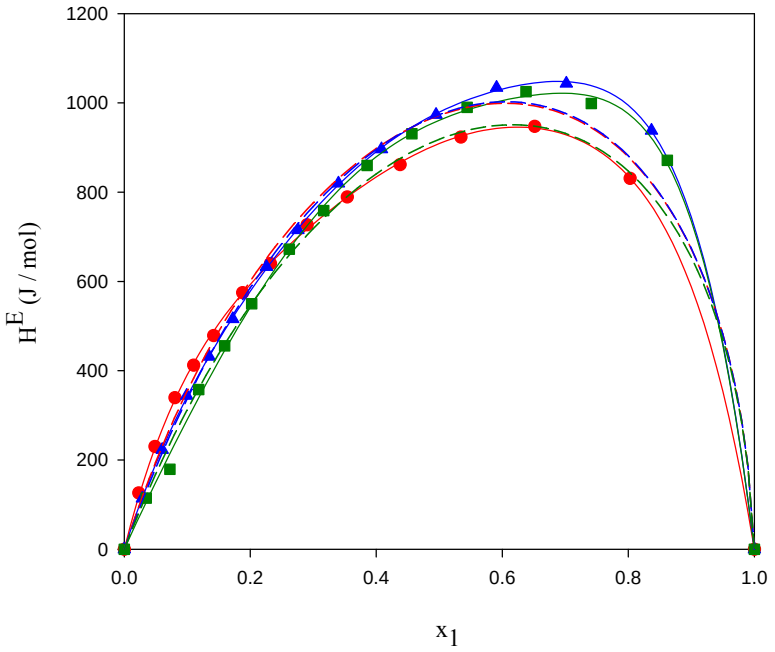
Excess enthalpy H^E at 313.15K for alkane(1) + alkanol(2). Experimental data ; • , octane +ethanol ; ▲ , octane + 1-propanol; ■ , octane +1-butanol

Results & Discussions (5)



Excess enthalpy H^E at 313.15K for alkane(1) + alkanol(2). Experimental data ; • , nonane +ethanol ; ▲ , nonane + 1-propanol; ■ , nonane +1-butanol

Results & Discussions (6)



Excess enthalpy H^E at 313.15K for alkane(1) + alkanol(2). Experimental data ; • , decane + ethanol ; ▲ , decane + 1-propanol ; ■ , decane + 1-butanol

Results & Discussions (3)

	A (dimensionless)	B (K^{-1})	AADH (%)
Octane + Ethanol	0.0267	9.9827	3.4988
Octane + 1-Propanol	0.0210	9.9855	2.9523
Octane + 1-Butanol	0.0281	9.9815	7.3946
Nonane + Ethanol	0.0279	9.9816	5.275
Nonane + 1-Propanol	0.0213	9.9853	2.263
Nonane + 1-Butanol	0.0282	9.9813	5.690
Decane + Ethanol	0.0267	9.9826	7.048
Decane + 1-Propanol	0.0215	9.9852	2.621
Decane + 1-Butanol	0.0272	9.9824	5.716

Binary interaction parameters from NLF-HB

Summary

■ The features of this work

1. All excess enthalpies have positive values and their graphical shapes are asymmetric.
2. They have maximum value of the mole fraction between 0.60 ml/min and 0.80 ml/min.
3. The H^E data was increased for all systems with the addition of the carbon number.
4. As compared the H^E experimental results by following each 1-alkanol systems, the discrepancies were wholly smaller at n-alkane systems of mixing with 1-propanol than those with ethanol and 1-butanol.