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UNIFAC INTERACTION PARAMETERS FOR EXCESS ENTHALPIES OF MIXING

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ABSTRACT

The UNIFAC model is used to correlate the excess enthalpies of mixing. This model requires two interaction parameters per group pair, and values for 49 such pairs are obtained using experimental excess enthalpy data for binary systems. These parameters may be used in the prediction of excess enthalpies of mixing and for limited temperature-extrapolation of data with reasonable accuracy.

INTRODUCTION

Excess enthalpies, or heats of mixing are important both for fundamental studies of the interaction energies and for the rational study of approximate models used in chemical engineering thermodynamics. Analytical group solution models give a method to predict thermodynamic properties of liquid mixtures from limited experimental data on reference systems. They are easy to use and give predictions of an acceptable accuracy for engineering design. In this category, the engineering utility of UNIFAC (UNIQUAC Functional-group Activity Coefficients) group contribution method [1,2] has been shown in the estimation of phase equilibria under normal pressures. However, Nagata and Ohta [3] working with the analytical form of UNIFAC, found that a set of group interaction parameters different from that used for activity coefficients is required for reproducing experimental values of heats of mixing.

We present an extension of the UNIFAC method for the prediction of excess enthalpy of mixing. Interaction parameters for 49 pairs of groups have been obtained from experimental binary H^E data. These parameters should be useful in the prediction of excess enthalpies of mixing.

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TABLE 1

Excess enthalpy data used to determine group interaction parameters

Systems		No. of data points	Ref.
Components	Temp. (K)		
1-Hexanol–*n*-hexane	298.15	20	6
1-Hexanol–2-methyl pentane	298.15	20	6
Isobutanol–*n*-decanol	298.15	18	7
Cyclopentane–tetrachloroethylene	298.15	39	8
Benzene–cyclooctane	298.15	9	9
Benzene–*n*-heptane	318.15	16	10
Acetonitrile–benzene	298.15	16	10
Acetonitrile–*n*-heptane	318.15	14	10
Carbon tetrachloride–benzene	298.15	5	11
Ethylbenzene–toluene	298.15–303.15	9	11
Ethylformate–*n*-hexane	298.15	13	12
Acetic acid–*n*-heptane	308.15	5	12
Ethylformate–*n*-butanol	298.15–318.15	19	12
Ethanol–methyl acetate	298.15–318.15	20	13
Cyclopentane–carbon tetrachloride	288.15	5	14
Cyclohexane–carbon tetrachloride	298.15–318.15	7	14
Benzene–carbon tetrachloride	288.15–318.15	10	14
Tetrachloroethane–cyclopentane	298.15	4	14
Benzene–dichloromethane	298.15–303.15	8	14
Benzene–cyclohexane	298.15–323.15	7	14
Benzene–*p*-xylene	298.15	4	14
Benzene–chlorobenzene	303.15–308.15	7	14
Toluene–dichloromethane	298.15–303.15	7	14
o-Xylene–dichloromethane	298.15–303.15	7	14
Dichloromethane–tetrahydrofuran	303.15	19	15
Carbon tetrachloride–tetrahydrofuran	303.15	19	15
Benzene–cyclohexanone	298.15	21	16
Triethylamine–*n*-hexane	298.15	19	17
Tetrahydrofuran–benzene	303.15	19	18
Benzene–triethylamine	298.15	11	19
Hexafluorobenzene–triethylamine	298.15	19	20
Hexafluorobenzene–diethylether	298.15	19	20
Hexafluorobenzene–dimethylsulfoxide	298.15	19	20
Chlorobenzene–*n*-heptane	293.15–313.15	57	21

TABLE 1 (continued)

Systems		No. of data points	Ref.
Components	Temp. (K)		
Chlorobenzene–benzene	293.15–313.15	57	21
Chlorobenzene–toluene	293.15–313.15	57	21
Chlorobenzene–carbon tetrachloride	293.15–313.15	57	21
Carbon disulfide–cyclohexane	293.15	19	21
Carbon disulfide–toluene	293.15	19	21
Carbon disulfide–carbon tetrachloride	293.15	19	21
Benzaldehyde–benzene	298.15	7	22
Benzaldehyde–*n*-hexane	298.15	10	22
Carbon tetrachloride–*n*-heptane	298.15	7	18
Carbon tetrachloride–*n*-nonane	298.15	7	18
Acetic acid–cyclohexane	308.15	7	12
Acetic acid–methylacetate	308.15	7	12
Tetrahydrofuran–cyclohexane	303.15	10	18
Hexafluorobenzene–acetone	298.15	12	20

THEORETICAL BACKGROUND

The Gibbs–Helmholtz equation

$$\left(\frac{\partial(G^{E}/T)}{\partial T}\right)_{p,x} = -H^{E}/T^{2} \qquad (1)$$

where the differentiation at constant pressure and composition permits calculation of the excess enthalpy, H^{E}, from a model for the excess Gibbs energy, G^{E}.

According to UNIFAC model

$$G^{E}/RT = \sum_{i} x_i(\ln \gamma_i^{C} + \ln \gamma_i^{R}) \qquad (2)$$

since the logarithm of the activity coefficient of component i is assumed to be the sum of two contributions: a combination part, $\ln \gamma_i^{C}$, and a residual part, $\ln \gamma_i^{R}$.

Since the combinatorial activity coefficients do not depend upon temperature, only the residual part enters into the calculation of the excess enthalpy. The residual part of the activity coefficient is given by

$$\ln \gamma_i^{R} = \sum_{k} \nu_k^{(i)}(\ln \Gamma_k - \ln \Gamma_k^{(i)}) \qquad (3)$$

TABLE 2

UNIFAC group interaction parameters for excess enthalpy

Main groups		UNIFAC parameters (K)	
m	n	a_{mn}	a_{nm}
CH_2	C=C	15.92	19.88
CH_2	ACH	133.5	26.78
CH_2	$ACCH_2$	81.74	−118.1
CH_2	OH	622.2	−92.21
CH_2	CH_2CO	245.9	355.5
CH_2	CHO	782.5	342.9
CH_2	CCOO	521.3	234.0
CH_2	HCOO	279.8	−32.18
CH_2	CH_2O	553.9	192.8
CH_2	$(C)_3H$	228.5	182.7
CH_2	CCN	872.5	356.7
CH_2	COON	529.8	222.7
CH_2	CCl_2	−24.52	70.92
CH_2	CCl_3	−284.6	−125.2
CH_2	CCl_4	−15.17	37.28
CH_2	ACCl	50.71	−46.04
CH_2	CNO_2	−0.820	357.7
CH_2	CS_2	116.1	−1.871
CH_2	ACF	91.69	26.29
ACH	$ACCH_2$	38.58	82.27
ACH	OH	844.9	81.13
ACH	CH_2CO	104.1	−146.7
ACH	CHO	315.4	−71.54
ACH	CH_2O	8.690	−88.34
ACH	$(C)_3N$	−68.66	60.77
ACH	CCN	228.0	−41.67
ACH	CCl_2	−119.3	174.5
ACH	CCl_4	−9.101	32.65
ACH	ACCl	−55.15	59.25
ACH	CNO_2	−171.0	223.3
ACH	CS_2	43.75	−9.140
$ACCH_2$	OH	844.0	82.41
$ACCH_2$	CH_2CO	425.3	370.8
$ACCH_2$	CHO	−96.21	10.80
$ACCH_2$	CCN	104.2	83.34
$ACCH_2$	CCl_2	348.2	−79.36
$ACCH_2$	ACCl	−132.4	12.71
$ACCH_2$	CNO_2	292.3	377.9
$ACCH_2$	CS_2	216.6	143.6
OH	HCOO	107.0	83.62
CH_2CO	ACF	322.9	−59.76
CH_2O	CCl_2	−180.9	−134.2
CH_2O	CCl_3	228.5	−11.51
CH_2O	CCl_4	−100.8	2.190
CH_2O	ACF	−119.1	217.2

TABLE 2 (continued)

Main groups		UNIFAC parameters (K)	
m	n	a_{mn}	a_{nm}
$(C)_3N$	ACF	135.1	128.6
CCl_4	ACCl	−103.5	280.6
CCl_4	CS_2	79.25	1.131
Me_2SO	ACF	166.2	70.29

where $k = 1, 2, \ldots, N$ (all groups) and $\nu_k^{(i)}$, always an integer, is the number of groups of type k in molecule i; Γ_k is the group residual activity coefficient; and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i. The residual activity coefficient Γ_k is given by [2]

$$\ln \Gamma_k = Q_k\left[1 - \ln\left(\sum_m \theta_m \Psi_{mk}\right) - \sum_m \left(\theta_m \Psi_{km} / \sum_n \theta_n \Psi_{nm}\right)\right] \tag{4}$$

where m and $n = 1, 2, \ldots, N$ (all groups) and Q_k is the group area parameter of group k, and Q_k values are obtained from Gmehling et al. [4]. Ψ_{nm} is the group UNIFAC parameter between groups m and n ($\Psi_{mm} = \Psi_{nn} = 1$). Equation (4) also holds for $\ln \Gamma_k^{(i)}$. The area fraction of group m, θ_m, is given by

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{5}$$

Here X_m is the group fraction of group m in the mixture given by

$$X_m = \frac{\sum_j \nu_m^{(j)} x_j}{\sum_j \sum_n \nu_n^{(j)} x_j} \tag{6}$$

where $j = 1, 2, \ldots, M$ (all components); $n = 1, 2, \ldots, N$ (all groups) and x_j is the mole fraction of component j. The group UNIFAC parameter, Ψ_{nm} is a function of temperature given by

$$\Psi_{nm} = \exp(-a_{nm}/T) \tag{7}$$

where a_{nm} is the temperature-independent group interaction parameter ($a_{nm} \neq a_{mn}$). From eqns. (1), (2) and (3), the resulting expression for H^E is obtained as follows

$$H^E = -RT \sum_i \sum_k x_i \nu_k^{(i)} \left[T\left(\frac{\partial \ln \Gamma_k}{\partial T}\right)_{p,x} - T\left(\frac{\partial \ln \Gamma_k^{(i)}}{\partial T}\right)_{p,x}\right] \tag{8}$$

where

$$T\left(\frac{\partial \ln \Gamma_k}{\partial T}\right)_{p,x} = Q_k \sum_m \theta_m \left[\frac{\Psi_{mk} \ln \Psi_{mk}}{\sum_n \theta_n \Psi_{nk}} + \frac{\Psi_{km} \sum_n \theta_n \Psi_{nm} \ln(\Psi_{km}/\Psi_{nm})}{\left(\sum_n \theta_n \Psi_{nm}\right)^2} \right] \tag{9}$$

A similar expression holds for $T\left(\frac{\partial \ln \Gamma_k^{(i)}}{\partial T}\right)_{p,x}$.

REDUCTION OF DATA

We adopted the classification of functional groups described by Gmehling et al. [4]. The group interaction parameters were determined from the experimental H^E data for binary systems listed in Table 1. The simplex method [5] was used to obtain the parameters by minimizing the sum of squares of deviations in experimental and calculated H^E values for all data points of relevant systems.

RESULTS

Table 2 lists the interaction parameters for 49 pairs of functional groups. The overall average value of RMSRD (%) in H^E was 5.2 for the reference

TABLE 3

Experimental and predicted excess enthalpy data for the system acetonitrile (1)–benzene (2) at 318.15 K

x_1	H^E (J mol^{-1})	
	Experimental [10]	Predicted
0.1778	249.8	227.6
0.2537	326.8	308.8
0.3309	393.3	378.7
0.4048	442.7	431.4
0.4812	477.4	468.2
0.5403	491.2	482.8
0.5708	493.3	485.3
0.6025	491.6	483.7
0.6460	482.0	475.3
0.6481	478.6	474.5
0.6805	465.7	460.7
0.7408	430.5	422.2
0.8016	372.8	363.2
0.8669	283.7	274.5
0.9361	153.1	148.5

systems listed in Table 1. Table 3 compares the calculated H^{E} values at 318.15 K with the experimental values for the acetonitrile–benzene system using interaction parameters evaluated from the experimental data at 298.15 K. It is seen that the UNIFAC method can be used for limited extrapolation of H^{E} values to another temperature with reasonable accuracy.

CONCLUSION

UNIFAC interaction parameters for 49 pairs of groups are obtained using experimental binary H^{E} data. These parameters may be used in predicting H^{E} data and for obtaining reasonable estimates of H^{E} values at mildly extrapolated temperatures.

NOMENCLATURE

a_{nm}	temperature-independent group interaction parameter for the group pair n–m (K)
G^{E}	excess Gibbs energy (J mol^{-1})
H^{E}	excess enthalpy (J mol^{-1})
p	pressure (Pa)
Q_k	group area parameter of group k
R	Universal gas constant (J mol^{-1} K^{-1})
RMSRD (%)	$100\left[\frac{1}{\text{data points}}\sum\left(\frac{\textit{experimental} - \textit{calculated}}{\textit{experimental}}\right)^2\right]^{1/2}$
T	absolute temperature (K)
x_i	mole fraction of pure component i
X_m	group fraction of group m in solution

Greek letters

$\nu_k^{(i)}$	number of groups of type k in molecule i
γ_i	activity coefficient of molecular component i
Γ_k	group residual activity coefficient of group k in solution
$\Gamma_k^{(i)}$	group residual activity coefficient of group k in pure component i
θ_m	area fraction of group m in solution
Ψ_{nm}	temperature-dependent group UNIFAC parameter

Subscripts

i, j	component
k, m, n	group

Superscripts

C	combinatorial
R	residual

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