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EXCESS ENTHALPIES OF MIXING USING A MODIFIED AGSM APPROACH

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ABSTRACT

The temperature dependence of the interaction parameters of the Analytical Group Solution Model for excess enthalpies is modified. Interaction coefficients for 53 pairs of groups are reported. These may be used in predicting excess enthalpy data using the modified AGSM.

INTRODUCTION

Excess enthalpies of mixtures 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. Nguyen and Ratcliff [1], working with the Analytical Solution of Groups method, ASOG [2], for the calculation of activity coefficients in liquid mixtures, developed an Analytical Group Solution Model, AGSM, for the prediction of excess enthalpies. A set of group parameters different from that used for activity coefficients is required for reproducing experimental values of excess enthalpies, i.e., heats of mixing.

Lai et al. [3] have extended the AGSM by expressing the temperature dependence of group interaction parameters in terms of two temperature-independent group coefficients. In this work, the temperature dependence is modified and an expression analogous to that used in representing the group interaction parameters of the UNIFAC model [4,5] for activity coefficients is employed. This requires only one temperature-independent group coefficient and results in a saving in computing time. Interaction coefficients for 53 pairs of groups are obtained from experimental heats of mixing data for binary systems.

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THEORETICAL BACKGROUND

The Analytical Group Solution Model, AGSM, for excess enthalpy of mixing was given by Nguyen and Ratcliff [1] as follows

$$h^{E} = \sum_{i} x_i \sum_{k} \nu_{ki} \left(H_k - H_k^{(i)} \right) \tag{1}$$

where x_i is the mole fraction of pure component i, ν_{ki} is the number of structural groups of type k in pure component i and the contribution to enthalpy of group k in solution, H_k, is evaluated from the following equation for the group activity coefficient τ_k employed in the Analytical Solution of Groups, ASOG, formulation [2] for activity coefficients.

$$\ln \tau_k = 1 - \sum_{j} \left(X_j a_{jk} / \sum_{m} X_m a_{jm} \right) - \ln \sum_{j} X_j a_{jk} \tag{2}$$

Here, the group fraction of group j in the mixture, X_j, is given by

$$X_j = \left(\sum_{i} x_i \nu_{ji} \right) / \left(\sum_{m} \sum_{i} x_i \nu_{mi} \right) \tag{3}$$

The resulting equation for H_k is obtained as

$$\frac{H_k}{RT^2} \equiv -\frac{\partial \ln \tau_k}{\partial T} = \sum_{j} X_j b_{kj} / \sum_{k} X_j a_{kj} + \sum_{j} \left(X_j b_{jk} / \sum_{m} X_m a_{jm} \right) - \sum_{j} \left[X_j a_{jk} \left(\sum_{m} X_m b_{jm} \right) / \left(\sum_{m} X_m a_{jm} \right)^2 \right] \tag{4}$$

The contribution to enthalpy of group k in pure component i, $H_k^{(i)}$, is also evaluated from eqn. (4), but using the following equation for the group fraction of group j in pure component i, instead of eqn. (3) for the group fractions.

$$X_j^{(i)} = \nu_{ji} / \sum_{j} \nu_{ji} \tag{5}$$

Two important steps should be noted in the derivation of the AGSM: the size contribution to the activity coefficient in the ASOG formulation has been considered to be independent of temperature and the group interaction parameters a_{jk}, unlike those in the original ASOG, have been considered to be temperature dependent with

$$b_{jk} \equiv \partial a_{jk} / \partial T \tag{6}$$

Lai et al. [3] have expressed the temperature dependence of the group parameters in terms of two temperature-independent group interaction coefficients as

$$a_{jk} = \exp\left(A'_{jk} + B'_{jk} / T \right) \qquad a_{jk} \neq a_{kj} \tag{7}$$

TABLE 1

Excess enthalpy data used to determine group interaction coefficients

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

TABLE 1 (continued)

Systems		No. of data points	Ref.
Components	Temp. (K)		
Benzene–cyclohexanone	298.15	21	18
Triethylamine–*n*-hexane	298.15	19	19
Tetrahydrofuran–benzene	303.15	19	20
Benzene–triethylamine	298.15	11	21
Hexafluorobenzene–Triethylamine	298.15	19	22
Hexafluorobenzene–diethylether	298.15	19	22
Hexafluorobenzene–dimethylsulfoxide	298.15	19	22
Chlorobenzene–*n*-heptane	293.15–313.15	57	23
Chlorobenzene–benzene	293.15–313.15	57	23
Chlorobenzene–toluene	293.15–313.15	57	23
Chlorobenzene–carbon tetrachloride	293.15–313.15	57	23
Carbon disulfide–cyclohexane	293.15	19	23
Carbon disulfide–toluene	293.15	19	23
Carbon disulfide–carbon tetrachloride	293.15	19	23
Benzaldehyde–benzene	298.15	7	24
Benzaldehyde–*n*-hexane	298.15	10	24
Carbon tetrachloride–*n*-heptane	298.15	7	20
Carbon tetrachloride–*n*-nonane	298.15	7	20
Acetic acid–cyclohexane	308.15	7	14
Acetic acid–methylacetate	308.15	7	14
Tetrahydrofuran–cyclohexane	303.15	10	20
Hexafluorobenzene–acetone	298.15	12	22

TABLE 2

Temperature-independent group interaction coefficients, A_{jk} and A_{kj}

Main groups		Group interaction coefficients (K)	
j	k	A_{jk}	A_{kj}
CH_2	C=C	64.72	160.6
CH_2	ArCH	−71.75	128.2
CH_2	CyCH	−132.3	33.30
CH_2	OH	−30.95	328.9
CH_2	CO	−128.2	108.7
CH_2	O	153.5	−21.98
CH_2	CHO	1028	110.3
CH_2	COO	227.8	198.7
CH_2	COOH	81.64	131.5
CH_2	CN	103.8	327.8
CH_2	N	362.7	176.5
CH_2	NO_2	70.50	97.17
CH_2	CCl_2	75.42	63.09
CH_2	CCl_4	61.42	38.71
CH_2	ArCl	97.37	−125.1
CH_2	ArF	47.29	96.17
CH_2	CS_2	86.21	109.3
CH_2	SO	60.74	71.83
C=C	Cl	9.160	−10.25
ArCH	CyCH	75.36	71.78
ArCH	OH	−140.1	446.4
ArCH	CO	83.83	107.4
ArCH	O	126.7	54.66
ArCH	CHO	35.70	143.0
ArCH	CN	62.40	154.6
ArCH	N	−102.7	26.81
ArCH	NO_2	57.44	141.0
ArCH	CCl_2	70.22	−25.40
ArCH	CCl_4	22.81	35.04
ArCH	ArCl	63.52	−7.040
ArCH	ArF	142.5	95.78
ArCH	CS_2	11.76	114.5
ArCH	SO	55.33	176.3
CyCH	CO	181.6	385.0
CyCH	O	132.1	323.9
CyCH	COOH	226.3	−23.80
CyCH	Cl	66.59	21.75
CyCH	CCl_2	49.78	31.79
CyCH	CCl_3	−108.5	200.6
CyCH	CCl_4	31.39	27.32
CyCH	ArCl	74.44	−14.53
CyCH	CS_2	46.16	83.94
OH	COO	684.4	948.7
CO	ArF	−86.64	143.5
O	CCl_2	−20.69	193.6
O	CCl_3	4.030	95.17

TABLE 2 (continued)

Main groups		Group interaction coefficients (K)	
j	k	A_{jk}	A_{kj}
O	CCl_4	96.72	148.8
O	ArF	174.4	133.5
COO	COOH	17.60	85.36
N	ArF	84.38	62.99
CCl_4	ArCl	89.98	−16.78
CCl_4	CS_2	48.10	65.44
ArF	SO	93.21	167.2

Thus, according to eqn. (6)

$$b_{jk} = -a_{jk}B'_{jk}/T^2 \tag{8}$$

It should be emphasized that the group parameters required by AGSM for predicting heats of mixing are different from the group parameters used by ASOG for predicting activity coefficients.

In this work, the temperature dependence of the group interaction parameter, a_{jk}, is expressed as

$$a_{jk} = \exp(-A_{jk}/T) \tag{9}$$

with b_{jk} given by eqn. (6). This formulation is analogous to that used in representing the group interaction parameters of the UNIFAC model [4,5] for activity coefficients, and results in a reduction in computing time.

REDUCTION OF DATA

We adopted the classification of functional groups described by Kojima and Tochigi [6]. The temperature-independent group interaction parameters, A_{jk} and A_{kj}, were determined from the experimental h^E data for the systems listed in Table 1. The simplex method [7] 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.

RESULTS

Table 2 lists group interaction coefficients for 53 pairs of groups. The overall average value of the RMSRD (%) in h^E was 6.1 for the reference systems listed in Table 1.

CONCLUSION

The temperature dependence of the group interaction parameters in the extended AGSM has been modified. Interaction coefficients for 53 pairs of groups are obtained using experimental binary h^E data. These coefficients may be used in predicting h^E data using the modified AGSM.

NOMENCLATURE

a_{jk}	temperature-dependent group interaction parameter for the group pair $j-k$
A_{jk}	temperature-independent group interaction coefficient in eqn. (9) for the group pair $j-k$
A'_{jk}	temperature-independent group interaction coefficient in eqn. (7)
b_{jk}	derivative with respect to temperature of a_{jk}
B'_{jk}	temperature-independent group interaction coefficient in eqn. (7) for the group pair $j-k$ (K)
h^E	excess enthalpy (J mol^{-1})
H_k	contribution to enthalpy of group k in solution
$H_k^{(i)}$	contribution to enthalpy of group k in pure component i
R	Universal gas constant (J mol^{-1} K^{-1})
RMSRD(%)	$100 \times [\frac{1}{\text{data points}} \Sigma (\frac{\text{experimental} - \text{calculated}}{\text{experimental}})^2]^{1/2}$
T	absolute temperature (K)
x_i	mole fraction of pure component i
X_j	group fraction of group j in solution
$X_j^{(i)}$	group fraction of group j in pure component i

Greek symbols

ν_{ji}	number of structural groups of type k in pure component i
τ_k	group activity coefficient of group k in solution

Subscripts

i	component
j,k,m	group

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