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THERMODYNAMICS OF ASSOCIATED SOLUTIONS. EXCESS ENTHALPIES FOR ACETIC ACID–NON-POLAR COMPONENT MIXTURES

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ABSTRACT

An association model is used to reproduce well excess enthalpies for four binary systems of acetic acid with benzene, cyclohexane, *n*-heptane and tetrachloromethane. The model assumes a liquid phase dimerization equilibrium between monomeric and dimeric molecules of the acid and uses the NRTL equation with temperature-dependent energy parameters for a physical contribution.

INTRODUCTION

The isothermal vapour–liquid equilibrium data of solutions containing acetic acid and non-polar components have been successfully correlated using an association model with association in the vapour and liquid phases [1]. The model uses the thermodynamic equilibrium constant for the dimerization of acid molecules and takes into account the physical interactions between pairs of the monomer and dimer of the acid and non-polar components using the NRTL equation [2]. This paper presents some results on the workability of the proposed association model in representing the excess enthalpies of solutions of acetic acid with benzene, cyclohexane, *n*-heptane and tetrachloromethane.

SOLUTION MODEL

A_1 and A_2, and B denote the monomer and dimer of the acid and a non-polar component respectively. The thermodynamic dimerisation constant K_T in pure liquids or mixtures is defined in terms of activity by

$$K_T = \frac{x^*_{A_2}\gamma^*_{A_2}}{(x^*_{A_1}\gamma^*_{A_1})^2} = K_x^* K_\gamma^* = \frac{x_{A_2}\gamma_{A_2}}{(x_{A_1}\gamma_{A_1})^2} = K_x K_\gamma \qquad (1)$$

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where x_{A_1} and x_{A_2} are the true mole fractions of the monomer and dimer of the acid, γ_{A_1} and γ_{A_2} are the activity coefficients of the monomer and dimer, the liquid phase mole fraction dimerisation constant K_x is defined by $x_{A_2}/x_{A_1}^2$, the activity coefficient ratio K_γ is expressed as $\gamma_{A_2}/\gamma_{A_1}^2$ and the superscript * indicates the pure liquid reference state.

The present model assumes that the excess enthalpy of acid–non-polar mixtures is given as the sum of both chemical and physical contributions. The chemical term arises from the dimer formation of the acid and the physical term is due to non-specific interactions between the non-polar component and the monomeric and dimeric species of the acid.

The excess molar enthalpy h^E is expressed by

$$h^E = \frac{h_A K_x x_{A_1}^2}{x_{A_1} + 2K_x x_{A_1}^2 + x_{B_1}} - \frac{x_A h_A K_x^* x_{A_1}^{*2}}{x_{A_1}^* + 2K_x x_{A_1}^{*2}} + R\sum_I x_I \left\{ \frac{\sum_J x_J [\partial(\tau_{JI} G_{JI})/\partial(1/T)]}{\sum_K G_{KI} x_I} - \frac{\sum_J \tau_{JI} G_{JI} x_J \sum_K x_K [\partial(G_{KI})/\partial(1/T)]}{\left(\sum_K G_{KI} x_K\right)^2} \right\} \tag{2}$$

where

$$\tau_{JI} = a_{JI}/T \tag{3}$$

$$G_{JI} = \exp(-\alpha_{JI}\tau_{JI}) \tag{4}$$

The monomer mole fractions in the mixtures are related to the stoichiometric mole fractions of components:

$$x_A = \frac{x_{A_1} + 2K_x x_{A_1}^2}{x_{A_1} + 2K_x x_{A_1}^2 + x_{B_1}} \tag{5}$$

$$x_B = \frac{x_{B_1}}{x_{A_1} + 2K_x x_{A_1}^2 + x_{B_1}} \tag{6}$$

The sum of the mole fractions of all the chemical species present must be unity:

$$x_{A_1} + K_x x_{A_1}^2 + x_{B_1} = 1 \tag{7}$$

The value of $x_{A_1}^*$ is obtained from

$$x_{A_1}^* + K_x^* x_{A_1}^2 = 1 \tag{8}$$

In fitting the model to experimental excess enthalpy data, the non-randomness parameters for all I–J pairs are fixed as 0.3 and the energy parameters are set as follows: $a_{A_1A_2} = a_{A_2A_1} = -100$ K, which are taken to be temperature independent; $a_{A_1B} = 2a_{A_2B}$ and $a_{BA_1} = 2a_{BA_2}$, which are assumed to be expressed by a linear function of temperature, i.e.

$$a_{A_1B} = C_{A_1B} + D_{A_1B}(T - 273.15)$$

$$a_{BA_1} = C_{BA_1} + D_{BA_1}(T - 273.15) \qquad (9)$$

CALCULATION PROCEDURE

The model is unable to correlate experimental binary excess enthalpy data for the acid–non-polar mixtures without any other thermodynamic information concerning the compositions of acid monomer and dimer as suggested by eqn. (1). In other words, it is only possible to calculate the true mole fractions of the monomer and dimer using binary parameters obtained in isothermal vapour–liquid equilibrium data reduction. Freedman [3] calculated the mole fraction equilibrium constant $K_x^* = 62$ at 20 °C and the enthalpy of hydrogen bond formation $h_A = -26$ kJ mol^{-1} for the dimerisation equilibrium between monomeric and dimeric molecules for pure acetic acid. These properties are used to estimate values of K_x^* at a specified temperature T_s by means of the van't Hoff relation and to calculate $x_{A_1}^*$ from eqn. (8) and $x_{A_2}^*$ from $K_A^* x_{A_1}^{*2}$. Values of $\gamma_{A_1}^*$ and $\gamma_{A_2}^*$ are computed using the NRTL equation together with $a_{A_1A_2} = a_{A_2A_1} = -100$ K and $\alpha_{A_1A_2} = \alpha_{A_2A_1} = 0.3$ for acetic acid [1]. Substitution of the values of K_x^*, $\gamma_{A_1}^*$ and $\gamma_{A_2}^*$ into eqn. (1) yields a value of K_T at T_s. From a set of the binary parameters obtained in the correlation of isothermal vapour–liquid equilibrium data whose temperature is close or identical to that for excess enthalpy data, it is possible to determine numerically values of x_{A_1} and x_{A_2} which satisfy eqn. (1) at T_s for any nominal mole fraction x_A.

The coefficients of eqn. (9) were obtained using the simplex method [4], which minimizes the objective function given by

$$F = \sum_{i=1}^{N} \left(h_{\text{exptl},i}^{E} - h_{\text{calc},i}^{E} \right)^2 \qquad (10)$$

CALCULATED RESULTS

Experimental vapour–liquid equilibrium and excess enthalpy data for four selected binary systems are available from the literature. In vapour–liquid equilibrium data reduction the fugacity coefficients of components

TABLE 1

Calculated results of vapour–liquid equilibrium data for acetic acid–non-polar component mixtures

System (A–B)	Temp. (°C)	Number of data points	Root-mean-square deviations				Parameters				Ref.
			δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	$a_{A_1A_2}$ (K)	$a_{A_1B_1}$ (K)	$a_{B_1A_1}$ (K)	α_{AB}	
Acetic acid–benzene	20	26	1.10	0.00	0.0	3.1	−100	207.75	405.92	0.8862	[8]
Acetic acid–cyclohexane	25	17	0.38	0.00	0.5		−100	916.41	891.93	0.4280	[9]
Acetic acid–*n*-heptane	20	12	0.71	0.00	0.0	5.9	−100	911.32	785.86	0.4122	[10]
	40	14	1.04	0.00	0.0	11.6	−100	984.40	822.20	0.4391	[10]
Acetic acid–tetrachloromethane	20	18	0.42	0.00	0.0		−100	369.91	654.98	0.8955	[11]

TABLE 2

Calculated results of excess enthalpy data for acetic acid–non-polar component mixtures

System (A–B)	Temp. (°C)	Number of data points	Parameters				Absolute arithmetic mean deviation (J mol^{-1})	Ref.	Temperature of vapour–liquid equilibrium data used (°C)
			$C_{A_1B_1}$ (J mol^{-1})	$D_{A_1B_1}$ (J mol^{-1} K^{-1})	$C_{B_1A_1}$ (J mol^{-1})	$D_{B_1A_1}$ (J mol^{-1} K^{-1})			
Acetic acid–benzene	20	10	55877.6	231.793	7203.3	9.1832	9.2	[13]	25
Acetic acid–cyclohexane	35	16	−2826.08	−12.5928	15253.0	−12.4526	6.4	[14]	25
Acetic acid–*n*-heptane	25	17	6288.71	0.3110	11879.9	−11.4881	5.6	[14]	20
	35	14	5697.63	−0.9149	11986.8	−7.1989	3.4	[14]	40
Acetic acid–tetrachloromethane	20	44	7325.36	18.1562	15913.5	42.1745	3.7	[15]	20

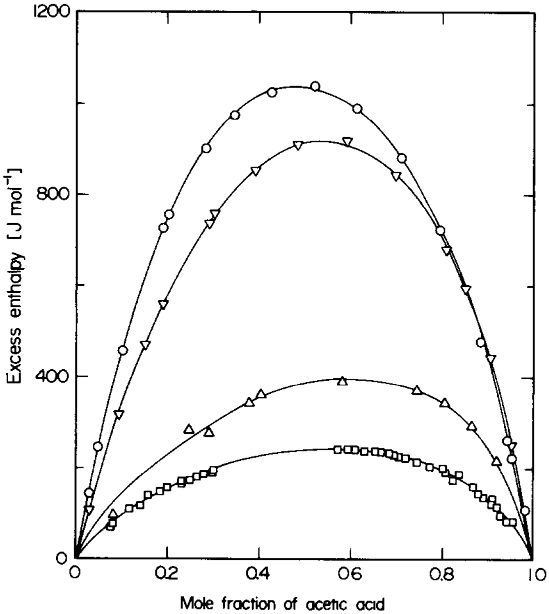

Fig. 1. Experimental (○, ▽, △, □) and calculated (———) excess enthalpies for four acetic acid–non-polar component systems: ○, acetic acid–cyclohexane at 35 °C [14]; ▽, acetic acid–*n*-heptane at 35 °C [14]; △, acetic acid–benzene at 20 °C [13]; □, acetic acid–tetrachloromethane at 20 °C [15].

were calculated using the chemical theory of vapour-phase imperfections. Details of pertinent property estimation and the parameter-seeking program are given by Prausnitz et al. [5]. Vapour pressures of the pure components were calculated from the Antoine equation whose constants are available [6,7]. Detailed results of the data reduction are shown in Table 1.

Experimental excess enthalpy data sets for the four systems listed in Table 1 are available from the compilation of Christensen et al. [12]: for acetic acid–benzene at 20 °C [13]; for acetic acid–cyclohexane at 35 °C [14]; for acetic acid–*n*-heptane at 25 and 35 °C [14]; for acetic acid–tetrachloromethane at 20 °C [15]. The observed temperatures of excess enthalpy and vapour–liquid equilibrium data for each system are identical or very close to each other. Table 2 gives calculated results obtained in fitting the model to the experimental excess enthalpy data and Fig. 1 compares the calculated results with the experimental values.

In conclusion, the proposed approach is able to correlate well the experimental excess enthalpy data of the acetic acid–non-polar component mixtures studied. Further extension of the association model to acetic acid–polar unassociated component mixtures is discussed in a forthcoming paper.

LIST OF SYMBOLS

A, B	carboxylic acid and a non-polar component
a_{IJ}	NRTL binary interaction parameter related to τ_{IJ}
C_{A_1B}, D_{A_1B}, C_{BA_1}, D_{BA_1}	binary coefficients of eqn. (9)
F	objective function as defined by eqn. (10)
G_{IJ}	coefficient as defined by $\exp(-\alpha_{IJ}\tau_{IJ})$
h^E	excess molar enthalpy
h_A	molar enthalpy of hydrogen-bonded dimer formation
K_T	liquid phase thermodynamic association constant
K_x	liquid phase mole fraction association constant as defined by $x_{A_2}/x_{A_1}^2$
K_γ	activity coefficient ratio is defined by $\gamma_{A_2}/\gamma_{A_1}^2$
P	total pressure
R	universal gas constant
T	absolute temperature
x_I	liquid phase mole fraction of component I or molecular species I

Greek letters

α_{IJ}	NRTL non-randomness parameter for the I–J pair
γ_I	activity coefficient of molecular species I
τ_{IJ}	NRTL binary parameter as defined by a_{IJ}/T

Subscripts

A_1, A_2	monomer and dimer of caroxylic acid
B_1	monomer of a nonpolar component
calc	calculated
exptl	experimental
I, J, K	molecular species

Superscript

$*$	pure liquid reference state

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