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Excess Enthalpies of Mixing of Binary Mixtures of Isopropyl Benzene with Ethyl Acetate and Butyl Acetate at 298.15 K

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The excess enthalpies of mixing of two binary systems isopropylbenzene with ethyl acetate and butyl acetate have been experimentally determined using a Tronac-1250 isoperibol calorimeter at 298.15 K. Both the systems are endothermic in nature over the whole composition range. Three group contribution models, the UNIFAC, the UNIFAC-II and the ASOG, have been used to predict the enthalpies of mixing for the systems and are then compared with experimental values. It is observed that predictions by the ASOG and UNIFAC-II models are in close agreement with the experimental data for both the systems.

Key Words: Excess enthalpies, Binary mixtures, Calorimeter, UNIFAC, UNIFAC-II, ASOG models.

INTRODUCTION

Excess thermodynamic properties of organic liquid mixtures are proving to be increasingly useful. The development of research activity in this field has been motivated by the importance of these variables in developing new theoretical models as well as their use in design of separation equipments like distillation columns in chemical process industries. In this work the excess enthalpies of mixing of isopropylbenzene with ethyl acetate and butyl acetate are reported at 298.15 K. Both the systems are endothermic in nature over the entire composition range.

A number of empirical models are available to predict the enthalpies of mixing but the group contribution models have wider applicability. In these techniques, the interaction among molecules in terms of the functional groups of the molecules is considered. Three group contribution models, the UNIFAC, the UNIFAC-II and the ASOG, are used in this work for the prediction of excess enthalpies of mixing.

The UNIFAC model was considered first by Fredenslund *et al.*[1] and was further modified by Rupp *et al.*[2] and the interaction parameters reported by Dang and Tassios[3] have been used in this work. The ASOG (Analytical Solutions of Groups) model was used by Lai *et al.*[4] for prediction of excess enthalpies of mixing. The UNIFAC-II model as described by Larsen *et al.*[5] has been used. In this model the temperature dependence of group interaction terms has been taken into consideration, which triples the number of interaction parameters required for each group, over the original UNIFAC model. These models have been described in detail in our earlier works[6–8].

EXPERIMENTAL

Isopropylbenzene (Riedel, Germany), ethyl acetate (E. Merck, India) and butyl acetate (Riedel, India) were purified by standard procedures[9] and were stored over molecular sieves.

Densities were measured with the help of a bicapillary pycnometer and refractive indices were measured by a Bausch and Lomb Abbe-3L refractrometer. Densities were measured with a precision of $\pm 1 \times 10^{-4}$ g cm^{-3}. The accuracy of refractive indices was of the order of ±0.0001. The temperature was kept constant within ±0.02 K with the help of a cryostat (MK 70 MLW). The experimental values of densities and refractive indices are compared with literature values as given in Table-1.

TABLE-1
PHYSICAL PROPERTIES OF THE PURE COMPONENTS AT 298.15 K

Component	Density, ρ, (g cm^{-3})		Refractive index, n_D	
	Exp.	Lit.[9]	Exp.	Lit.[9]
Isopropyl benzene	0.8575	0.85751	1.4889	1.48890
Ethyl acetate	0.8946	0.89455	1.3698	1.36979
Butyl acetate	0.8763	0.87636	1.3918	1.39180

The excess enthalpies of mixing for two binary mixtures of isopropylbenzene with ethyl acetate and butyl acetate over the whole composition range were determined at 298.15 K using a Tronac-1250 model (Tronac Inc., USA) precision isoperibol titration calorimeter. The working of this calorimeter has been described earlier in detail[6, 7]. The principle of working of Tronac-1250 model calorimeter is essentially similar to that described by Christensen *et al.*[10,11] The calculation procedure used for the estimation of excess enthalpies of mixing has been described in detail by Eatough *et al.*[12] To the best of our knowledge, the data for these systems have not been reported in literature so far.

The calorimeter has been calibrated by experimentally studying the standard test system of benzene with cyclohexane at 298.15 K. The measured data for this system, as reported earlier by us[6,7], are in good agreement (within ±1%), with those reported in literature[13,14]. Similar studies on excess enthalpies of mixing of binary mixtures containing C_8 or C_9 hydrocarbons as one of the components were reported in our earlier works[15–17].

RESULTS AND DISCUSSION

The experimental data of excess enthalpies of mixing for both the systems studied are given in Table-2.

The experimental values of h^E for the systems studied are fitted to a Redlich-Kister type equation,

$$h^E = x(1-x) \sum_{j=1}^{n} A_{j-1}(2x-1)^{j-1} \qquad (1)$$

TABLE-2
EXPERIMENTAL EXCESS ENTHALPIES OF MIXING, h^E (J mol^{-1}) at 298.15 K

Isopropylbenzene (1) + ethyl acetate (2)		Isopropylbenzene (1) + butyl acetate (2)	
x_1	h^E (J mol^{-1})	x_1	h^E (J mol^{-1})
0	0	0	0
0.0668	141.93	0.0864	53.11
0.1252	228.85	0.1591	108.61
0.1766	284.90	0.2210	153.73
0.2225	321.44	0.2745	186.69
0.2635	345.81	0.3211	210.03
0.3003	362.49	0.3620	224.77
0.3336	372.33	0.3980	233.41
0.3640	378.24	0.4305	237.56
0.3917	382.52	0.4652	238.86
0.4643	380.44	0.5365	228.89
0.4980	375.07	0.5720	219.32
0.5360	364.21	0.6102	206.02
0.5810	347.20	0.6524	187.83
0.6341	319.23	0.7010	164.56
0.6979	275.31	0.7570	135.73
0.7760	208.35	0.8237	98.34
0.8740	111.42	0.9033	54.86
1.0000	0	1.0000	0

The values of the constants A_{j-1} along with the standard deviations (σ) are given in Table-3.

TABLE-3
VALUES OF COEFFICIENTS FOR REDLICH-KISTER EQUATION (1) AND STANDARD DEVIATION (σ).

	Isopropylbenzene+ ethyl acetate	Isopropylbenzene + butyl acetate
A_0	1497.7480	941.4182
A_1	−446.6272	−263.3611
A_2	95.6658	−437.2458
A_3	−488.4919	338.5516
σ	0.2679	0.3365

The excess enthalpy, h^E, data for these two systems are predicted by the use of the ASOG, the UNIFAC and the UNIFAC-II models, which are summarized by the following equations:

The ASOG model

$$h^E = \sum_i \bar{h}_i x_i \tag{2}$$

$$\bar{h}_i = \sum_k N_{ki}(H_k - H_k^*) \tag{3}$$

$$\frac{H_k}{RT^2} = \frac{\sum\limits_i X_j b_{kj}}{\sum\limits_j X_j c_{kj}} + \sum_j \frac{X_j b_{jk}}{\sum\limits_m X_m c_{jm}} - \sum_j \frac{X_j c_{jk} \left(\sum\limits_m X_m b_{jm}\right)}{\left(\sum\limits_m X_m c_{jm}\right)} \tag{4}$$

X_m = mole fraction of group in the mixture.

$$= \frac{\sum\limits_i x_i N_{mi}}{\sum\limits_k \sum\limits_i x_i N_{ki}} \tag{5}$$

and group interaction parameters b_{kj} and c_{kj} are given as

$$b_{kj} = \frac{\partial}{\partial T}(c_{kj}) \tag{6}$$

$$c_{kj} = A_{kj} + B_{kj}/T \tag{7}$$

The UNIFAC model

$$\frac{H_k}{RT^2} = Q_k \left[\frac{\sum\limits_m \theta_m \psi'_{mk}}{\sum\limits_m \theta_m \psi_{mk}} + \sum_m \left\{ \frac{\theta_m \psi'_{mk}}{\sum\limits_n \theta_n \psi_{nm}} - \frac{\theta_m \psi_{km} \left(\sum\limits_n \theta_n \psi'_{nm}\right)}{\left(\sum\limits_n \theta_n \psi_{nm}\right)^2} \right\} \right] \tag{8}$$

$$\theta_m = \frac{Q_m X_m}{\sum\limits_n Q_n X_n} \tag{9}$$

$$\psi_{mn} = \exp\left(-\frac{Za_{mn}}{2T}\right) \tag{10}$$

where a_{mn} is the temperature-independent interaction parameter between groups m and n.

$$\psi'_{mn} = \frac{\partial}{\partial T}\psi_{mn} \tag{11}$$

$$Z = 35.2 - 0.1272T + 0.00014T^2 \tag{12}$$

where Z is temperature-dependent coordination number.

The UNIFAC-II model

The inclusion of new temperature dependent terms in UNIFAC-II model triples the number of interaction constants required for each group, over that of original UNIFAC. The total interaction between groups i and j as given by UNIFAC-II is

$$a_j = a_{ji,1} + a_{ji,2}(T - 298.15) + a_{ji,3}[T \ln(298.15/T) + (T - 298.15)] \tag{13}$$

The values of parameters $a_{ji,1}$, $a_{ji,2}$, $a_{ji,3}$ are available in literature[5] and the same have been used in the present study.

The experimental data are then compared with predicted values from these models as shown in Figs. 1 and 2. The ASOG parameters for group pairs, [CH_2/COO, COO/CH_2] and [COO/ACH, ACH/COO] which were reported earlier[16] have been used in this work. Adequate computer programs have been made for the use of these models.

The absolute per cent errors (S) for each system for all the three models are calculated using the equation:

$$S = \frac{100}{N}\sum_{i}^{N}\left|\frac{h^E(\text{expt.}) - h^E(\text{ASOG/UNIFAC/UNIFAC–II})}{h^E(\text{expt.})}\right| \tag{14}$$

where N = No. of data points.

The experimental data of enthalpies of mixing for the systems isopropylbenzene with ethyl acetate and butyl acetate at 298.15 K has been given in Table-2. Both the systems studied are endothermic in nature over the whole composition range.

The experimental data for these systems as mentioned above have been compared with the predicted values from the ASOG, the UNIFAC and the UNIFAC-II models in the form of curves as shown in Figs. 1 and 2. It has been observed that the absolute per cent errors calculated for the system isopropylbenzene-ethyl acetate are 10.33% with the ASOG model, 34.48% with the UNIFAC model and 15.83% with the UNIFAC-II model. Similarly, it has been calculated that the absolute per cent errors for the system of isopropylbenzene-butyl acetate are 15.05% with the ASOG model, 37.77% with the UNIFAC model and 12.13% with the UNIFAC-II model. The experimental

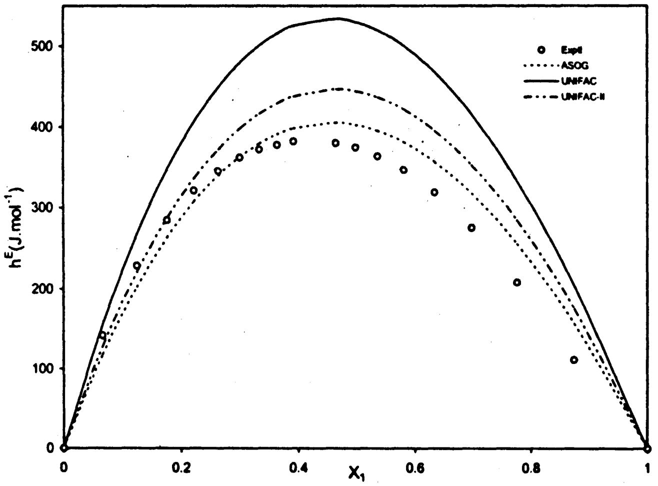

Fig. 1: Excess enthalpies of mixing of isopropylbenzene (1)+ethylacetate (2) at 298.15 K.

Fig. 1. Excess enthalpies of mixing of isopropylbenzene (1) + ethylacetate (2) at 298.15 K

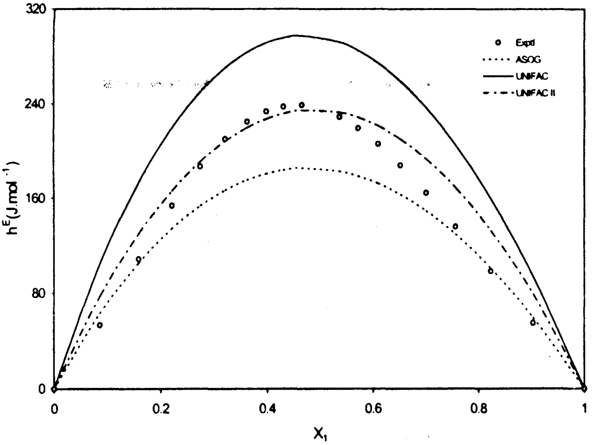

Fig. 2: Excess enthalpies of mixing of isopropylbenzene (1)+butylacetate (2) at 298.15 K.

Fig. 2. Excess enthalpies of mixing of isopropylbenzene (1) + butylacetate (2) at 298.15 K

values of ethyl acetate system are higher than that of butyl acetate system which is also predicted similarly by all the three models used. This also shows that as the alkyl chain length of ester increases, the excess enthalpy decreases.

For both the systems of isopropylbenzene with ethyl acetate and butyl acetate, the ASOG model and UNIFAC-II model give errors within 15% which is quite satisfactory. The UNIFAC model predicts higher values of enthalpies of mixing as compared to those predicted by the ASOG and the UNIFAC-II models. The ASOG model gives the least errors for both the systems. There is still further scope for improvement of interaction parameters used in these models by increasing the experimental data base so that the models can be made more accurate.

Nomenclature

A_{j-1} = constant in eqn. (1)
A_{jk} = interaction parameter of groups j and k
a_{mn} = UNIFAC parameter
B_{jk} = group interaction parameter, K
b_{kj}, c_{kj} = ASOG parameters
H_K = excess enthalpy of group k, J
H^*_{ki} = excess enthalpy of group k in a reference solution containing only molecules of type I, J
h_i^- = partial molar excess enthalpy of component, I, J/mol
h^E = excess enthalpy of mixing, J/mol
h^E (expt) = experimental excess enthalpy of mixing, J/mol

h^E (ASOG/UNIFAC/UNIFAC II) = excess enthalpy of mixing predicted using ASOG/UNIFAC/UNIFAC-II model, J/mol
N_{mi}, N_{ki} = number of groups of type m, k in component i
R = universal gas constant
S = average per cent absolute error
T = absolute temperature
X_j = liquid phase group fraction
x_i = mole fraction of component i
Z = lattice co-ordination number
θ_m = area fraction of group m
ψ_{mk}, ψ_{mn} = UNIFAC group interaction parameters
σ = standard deviation

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