Application of the UNIFAC models for prediction and description of excess molar enthalpies for binary mixtures of n-propanol, acetic acid, n-propyl acetate, and water

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ABSTRACT

In this paper the ability of the UNIFAC methods (original UNIFAC and modified UNIFAC (Dortmund)) to predict the excess molar enthalpies, H^E, is considered. The predicted and the obtained earlier experimental values of the excess molar enthalpies for 5 binary systems of n-propanol, acetic acid, n-propyl acetate, and water were compared. Since the both methods represent the H^E unsatisfactorily, new set of group interaction parameters of the UNIFAC (Dortmund) method for mentioned above compounds was evaluated.

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1. Introduction

Coupled processes are the processes of simultaneous chemical reaction and mass exchange between some coexisting phases. These processes are applied in a lot of modern technological schemes, being one of the most perspective ways of development of energy- and resource-saving environment-friendly technologies.

The coupled processes researches are mostly focused on phase equilibrium compositions, vapor pressure data, etc. [1–6], while thermochemical investigations are scarce. Excess molar enthalpies and other thermochemical parameters give an opportunity to extend one-temperature data on a wide temperature range thermodynamically correctly, for instance to determine equilibrium properties at temperatures close to boiling point.

Thermochemical investigations are time-consuming and experimentally complicated. It makes the researchers to create and develop theoretical models and approaches to estimate

thermochemical values. One of the best and promising approaches is UNIFAC model, applicable to predict both the parameters of the phase equilibria and thermochemical properties of systems of different physico-chemical types (see for example, recent works of Gmehling and co-authors [7–10]).

In our research we considered the ability of an original UNIFAC model [11] and a modified UNIFAC (Dortmund) model [12–15] to predict excess molar enthalpies for some binary systems, namely n-PrOH + H$_2$O, AcOH + H$_2$O, n-PrOH + AcOH, n-PrOH + n-PrOAc, AcOH + n-PrOAc. The study of thermochemical properties of these systems is carried out within the complex investigation of a quaternary system n-PrOH + AcOH + n-PrOAc + H$_2$O. Solubility, liquid-liquid and vapor-liquid phase equilibria, chemical equilibrium of this system and its subsystems were studied by our scientific group earlier [1,2,16–19]. The excess molar enthalpies of the binary and ternary constituent subsystems were studied at different temperatures [20–22], but there is no a uniform database with multi-temperature data [23–25]. In our research we compare the excess molar enthalpies of the mentioned above binary systems predicted with the origin UNIFAC model and the modified UNIFAC (Dortmund) model with the obtained experimentally at

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Table 1
Experimental and predicted excess molar enthalpies, H^E, for the binary system n-PrOH + H_2O at 313.15 K and atmospheric pressure.[a]

$x_{n\text{-PrOH}}$	H^E_{exp} [28]	H^E_{calc} (Orig. UNIFAC)	H^E_{calc} (Mod. UNIFAC (Dortmund), coeff. by Gmehling et al. [13])	H^E_{calc} (Mod. UNIFAC (Dortmund), coeff. from this work)
	(J mol^{-1})			
0.05	−160.7	92.5	−64.7	−147.8
0.1	−95.3	128.5	−76.6	−133.1
0.15	0.0	131.1	−57.1	−62.3
0.2	55.4	113.4	−19.9	25.7
0.3	195.4	46.7	74.1	195.4
0.4	300.3	−33.4	162.6	322.1
0.5	400.5	−106.1	225.9	394.0
0.6	415.8	−157.4	255.2	410.8
0.7	377.7	−176.5	247.0	375.6
0.8	280.4	−155.4	200.9	292.6
0.9	155.3	−91.6	117.9	166.0
0.95	80.1	−47.0	63.2	87.7
ARD		Exceeds Acceptable	42.8%	12.1%

[a] The estimated relative uncertainty is $u_r (H^E_{exp}) = 0.02$.

2. Theoretical background

The Gibbs-Helmholtz equation

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

and the equation for the excess Gibbs energy, G^E,

$$G^E = RT \sum_i x_i \ln \gamma_i \qquad (2)$$

permit to relate the excess enthalpy, H^E, as follows:

$T = 313.15$ K. Since the models did not give a good representation of H^E, new group interaction parameters were proposed.

$$H^E = -RT^2 \sum_i x_i \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{p,x}. \qquad (3)$$

Thus the task of H^E calculations is reduced to the differentiation of the expression for the activity coefficient of component i. The most successful methods used for calculation of activity coefficients in the liquid phase are the group contribution methods, in which the liquid phase is considered to be a mixture of structural groups. The best-known and most successful of the group contribution methods in the UNIFAC (**UNI**QUAC **F**unctional group **A**ctivity **Co**efficients) model [11] and its modifications [12–15].

The UNIFAC models split up the activity coefficient for each species in the system into two parts, a combinatorial part γ_i^C and a residual part γ_i^R. In a multicomponent mixture, the UNIFAC equation for the activity coefficient of (molecular) component i is

Table 2
Experimental and predicted excess molar enthalpies, H^E, for the binary system AcOH + H_2O at 313.15 K and atmospheric pressure.

x_{AcOH}	H^E_{exp} [29,30]	H^E_{calc} (Orig. UNIFAC)	H^E_{calc} (Mod. UNIFAC (Dortmund), coeff. by Gmehling et al. [13])	H^E_{calc} (Mod. UNIFAC (Dortmund), coeff. from this work)
	(J mol^{-1})			
0.021	−5.0[a]	−1.0	−1.7	−3.4
0.037	−6.3[a]	−2.7	0.7	−2.6
0.049	−0.4[a]	−4.5	4.4	−0.3
0.2	142[a]	−48.9	131	102
0.3	222[a]	−86.2	240	195
0.386	285[a]	−115	323	265
0.416	301[a]	−124	348	285
0.52	364[a]	−145	407	330
0.546	372[a]	−148	414	334
0.6	381[a]	−151	421	335
0.733	364[a]	−137	375	282
0.814	305[a]	−112	302	216
0.918	155[a]	−58.7	156	101
0.932	194[b]	−50	132	84
0.876	280[b]	−83	222	150
0.755	370[b]	−132	358	267
0.612	377[b]	−151	420	333
0.542	359[b]	−148	413	334
0.437	309[b]	−129	363	297
0.335	240[b]	−99	276	226
0.24	158[b]	−64	175	139
0.118	43[b]	−21	49	34
ARD		Exceeds Acceptable	70.5%	21.6%

[a] The experimental data are taken from Ref. [29]. The estimated relative uncertainty is $u_r (H^E_{exp}) = 0.02$.
[b] The experimental data are taken from Ref. [30]. The estimated relative uncertainty is $u_r (H^E_{exp}) = 0.015$.