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.

Keywords: Excess molar enthalpies; original UNIFAC; modified UNIFAC (Dortmund); *n*-Propanol; Acetic acid; *n*-Propyl acetate; Water

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.

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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 + H₂O, AcOH + H₂O, 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 + H₂O. 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 $T = 313.15$ K. Since the models did not give a good representation of H^E , new group interaction parameters were proposed.

2. Theoretical background

The Gibbs-Helmholtz equation

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

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

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

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

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

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 (UNIQUE Functional group Activity Coefficients) 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

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (4)$$

The combinatorial contribution to activity coefficients does not depend on temperature, only the residual part enters into the calculation of the excess molar enthalpy. The resulting expression for H^E is following:

$$H^E = -RT^2 \sum_i x_i \sum_k v_k^{(i)} \left[\left(\frac{\partial \ln \Gamma_k}{\partial T} \right)_{p,x} - \left(\frac{\partial \ln \Gamma_k^{(i)}}{\partial T} \right)_{p,x} \right], \quad (5)$$

$$\text{where } \left(\frac{\partial \ln \Gamma_k}{\partial T} \right)_{p,x} = -Q_k \sum_m \Theta_m \left[\frac{\frac{\partial \Psi_{mk}}{\partial T}}{\sum_m \Theta_m \Psi_{mk}} + \sum_n \Theta_n \frac{\Psi_{nm} \frac{\partial \Psi_{km}}{\partial T} - \Psi_{km} \frac{\partial \Psi_{nm}}{\partial T}}{\left(\sum_n \Theta_n \Psi_{nm} \right)^2} \right]. \quad (6)$$

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 . Q_k is a group parameter obtained from the van der Waals group surface areas. Parameter Q_k together with R_k (a group parameter obtained from the van der Waals group volumes) is given in the tables of UNIFAC Group Specifications. Θ_m is the area fraction of group m , and the sums are over all different groups.

Θ_m is calculates as follows:

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}, \quad (7)$$

where X_m is the mole fraction of group m in the mixture, and it is given by

$$X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n v_n^{(j)} x_j}, \quad (8)$$

where $j = 1, 2, \dots, M$ (all components); $n = 1, 2, \dots, N$ (all groups) and x_j is a mole fraction of component j .

In the original UNIFAC model the group interaction parameter Ψ_{nm} is given by

$$\Psi_{nm} = \exp \left(-\frac{U_{nm} - U_{mm}}{RT} \right) = \exp \left(-\frac{a_{nm}}{T} \right), \quad (9)$$

where U_{nm} is a measure of the energy of interaction between groups n and m , and $a_{nm} \neq a_{mn}$. Parameters a_{nm} and a_{mn} are obtained from a database using a wide range of experimental results and presented in the tables of UNIFAC interaction parameters (see, for example, [26]).

In the modified UNIFAC (Dortmund) model temperature-dependent group interaction parameters are following:

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right). \quad (10)$$

The sets of interaction parameters (a_{nm} , b_{nm} , c_{nm}) can be found in [12-15].

Thus, for the original UNIFAC model the expression (6) can be written as

$$\left(\frac{\partial \ln \Gamma_k}{\partial T}\right)_{p,x} = \frac{Q_k \sum_m \Theta_m}{T} \left[\frac{\Psi_{mk} \ln \Psi_{mk}}{\sum_m \Theta_m \Psi_{mk}} + \frac{\Psi_{km} \sum_n \Theta_n \Psi_{nm} \ln \frac{\Psi_{km}}{\Psi_{nm}}}{\left(\sum_n \Theta_n \Psi_{nm}\right)^2} \right]. \quad (11)$$

The same expression was obtained by Weidlich and Gmehling in [12] and Singh and Pathanjali in [27].

Since in the modified UNIFAC (Dortmund) model the group-interaction parameter Ψ_{nm} includes interaction parameters a_{nm} , b_{nm} , and c_{nm} , the equation (6) is specialized as

$$\left(\frac{\partial \ln \Gamma_k}{\partial T}\right)_{p,x} = Q_k \sum_m \Theta_m \left[\frac{\Psi_{mk} \left[-\frac{a_{mk}}{T^2} + c_{mk} \right]}{\sum_m \Theta_m \Psi_{mk}} + \frac{\Psi_{km} \sum_n \Theta_n \Psi_{nm} \left[-\frac{a_{km} - a_{nm}}{T^2} + (c_{km} - c_{nm}) \right]}{\left(\sum_n \Theta_n \Psi_{nm}\right)^2} \right]. \quad (12)$$

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

3. Results and discussion

The predictable ability of original and modified UNIFAC methods to estimate excess molar enthalpies were tested on the binary systems n -PrOH + H₂O, AcOH + H₂O, n -PrOH + AcOH, n -PrOH + n -PrOAc, AcOH + n -PrOAc at $T = 313.15$ K. The van der Waals and interaction parameters were taken in [26] for the original UNIFAC and in [13] for the modified UNIFAC (Dortmund) and listed in Tables S1 - S4 of the Supplementary material. The experimental data were taken in [28] for n -PrOH + H₂O, [29, 30] for AcOH + H₂O, and [20] for n -PrOH + AcOH, n -PrOH + n -PrOAc, AcOH + n -PrOAc. Tables 1 – 5 and Figs. 1 – 5 show H^E prediction results using original UNIFAC (dotted lines) and modified UNIFAC (Dortmund) with

the coefficients proposed by Gmehling et al. (dashed lines). The quality of the prediction was estimated by average relative deviation ARD:

$$ARD(H^E(\%)) = \frac{100}{n} \sum_{i=1}^n \frac{|H_{\text{exp},i}^E - H_{\text{calc},i}^E|}{|H_{\text{exp},i}^E|}, \quad (13)$$

where n is the number of the data points.

As shown, the using of the modified UNIFAC (Dortmund) model with the coefficients proposed by Gmehling et al. [13] can represent data seta with greater precision than the original UNIFAC model for most of the systems, but the results are still not in a good agreement with the experimental data.

Since the temperature-dependent interaction parameters a_{nm} , b_{nm} , and c_{nm} greatly contribute to the H^E prediction by means of the modified UNIFAC (Dortmund) model, they were refit by us using multi-temperature experimental data sets of excess molar enthalpies of the binaries under study. The van der Waals volumes and surfaces of the structural groups (R_k and Q_k values) were not recalculated since R_k entered in only the combinatorial contribution to the activity coefficients, which did not depend on the temperature and, therefore, did not influence on H^E . Hence, in our calculations R_k and Q_k proposed by Gmehling et al. [13] were used. New interaction parameters were fitted for each of 5 systems under study with the method of generalized reduced coefficient the using Microsoft Excel™, for the minimization of the following objective function:

$$OF = \frac{100}{n} \sum_{i=1}^n \left[\frac{H_{\text{exp},i}^E - H_{\text{calc},i}^E}{H_{\text{exp},i}^E} \right]^2, \quad (14)$$

where n is the number of the data points. The systems and corresponding temperatures used in the fitting procedure together with average relative deviations are given in Table 6. The obtained group interaction parameters are listed in Table 8.

The van der Waals properties proposed by Gmehling et al. [13] (Table 7 or Table S3) together with interaction parameters a_{nm} , b_{nm} , and c_{nm} proposed by us (Table 8) were used to evaluate excess molar enthalpies H^E for the binary systems under study at different temperatures. The obtained results at $T = 313.15$ K are summarized in Tables 1 – 5 (last columns) and Figs. 1 – 5. The systems are described much better by modified UNIFAC (Dortmund) with proposed by us interaction parameters than with Gmehling's [13] ones. The results at all over temperatures are presented in Supplementary material, Figs. S1 - S4.

The original UNIFAC model, modified UNIFAC (Dortmund) model with the group interaction parameters proposed by Gmehling et al. [13], and modified UNIFAC (Dortmund) model with the group interaction parameters proposed by us were also tested in prediction of

VLE for 4 systems, namely n -PrOH + H₂O, AcOH + H₂O, n -PrOH + AcOH, and n -PrOH + n -PrOAc. Calculation showed that for these systems VLE was predicted in the best way with the original UNIFAC model. The modified UNIFAC (Dortmund) model with proposed by both Prof. Gmehling and us group interaction parameters showed worse results. First of all, proposed by us parameters were specially fit to perform H^E data.

4. Conclusions

The ability of the UNIFAC models (original UNIFAC and modified UNIFAC (Dortmund)) to predict the excess molar enthalpies, H^E , was 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. As it was established, the original UNIFAC model showed bad results, for instance for the systems n -PrOH + H₂O, AcOH + H₂O, n -PrOH + AcOH the shape of concentration dependences of the excess molar enthalpies did not agree with experimental results. The differences between predicted with the original UNIFAC model excess molar enthalpies and experimental ones for the systems n -PrOH + n -PrOAc and AcOH + n -PrOAc were also huge. The modified UNIFAC (Dortmund) model with group interaction parameters proposed by Gmehling et al. showed much better results. The average relative deviation for, for example, n -PrOH + n -PrOAc was no more than 7%, but for some other systems (n -PrOH + AcOH, AcOH + n -PrOAc) it still exceeded acceptable values. Thus, since the both methods represented the H^E unsatisfactorily, new set of group interaction parameters of the UNIFAC (Dortmund) method for mentioned above compounds were proposed. The fitting procedure covered most available excess molar enthalpy data at different temperatures for mentioned above systems. In some cases the using of proposed by us interaction coefficients reduced the average relative deviation to 3%

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Table 1

Experimental and predicted excess molar enthalpies, H^E , for the binary system n -PrOH + H₂O at 313.15 K and atmospheric pressure. ^a

$x_{n\text{-PrOH}}$	H_{exp}^E [28] (J·mol ⁻¹)	H_{calc}^E (orig. UNIFAC)	H_{calc}^E (mod. UNIFAC (Dortmund), coeff. by Gmehling et al. [13])	H_{calc}^E (mod. UNIFAC (Dortmund), coeff. from this work)
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 $u_r(H_{\text{exp}}^E) = 0.02$.

Table 2

Experimental and predicted excess molar enthalpies, H^E , for the binary system AcOH + H₂O at 313.15 K and atmospheric pressure.

x_{AcOH}	H_{exp}^E [29, 30] (J·mol ⁻¹)	H_{calc}^E (orig. UNIFAC)	H_{calc}^E (mod. UNIFAC (Dortmund), coeff. by Gmehling et al. [13])	H_{calc}^E (mod. UNIFAC (Dortmund), coeff. from this work)
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	-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 [29]. The estimated relative uncertainty is $u_r(H_{\text{exp}}^E) = 0.02$.

^b The experimental data are taken from [30]. The estimated relative uncertainty is $u_r(H_{\text{exp}}^E) = 0.015$.

Table 3

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

$x_{n\text{-PrOH}}$	H_{exp}^E [19] (J·mol ⁻¹)	H_{calc}^E (orig. UNIFAC)	H_{calc}^E (mod. UNIFAC (Dortmund), coeff. by Gmehling et al. [13])	H_{calc}^E (mod. UNIFAC (Dortmund), coeff. from this work)
0.0488	122	-1.4	188	128
0.0507	126	-1.5	195	130
0.1002	218	-3.6	362	198
0.1010	219	-3.6	364	199
0.2002	338	-9.1	627	326
0.2005	338	-9.1	628	327
0.2951	389	-15.3	796	407
0.2964	390	-15.3	798	407
0.4000	408	-22.0	895	441
0.4001	409	-22.0	895	441
0.4995	393	-27.5	908	431
0.5006	392	-27.5	907	431
0.5994	358	-31.0	848	387
0.6000	359	-31.0	847	387
0.6998	307	-31.5	720	317
0.6999	307	-31.5	720	317
0.7991	237	-27.8	533	227
0.7996	236	-27.7	532	227
0.8989	137	-18.0	292	121
0.8997	136	-17.9	290	120
0.9503	73.0	-10.1	149	61.0
0.9511	69.2	-9.9	146	60.0
ARD		exceeds acceptable	exceeds acceptable	7.3%

^a Standard uncertainties u are $u(x) = 0.0002$, $u(T) = 0.05$ K, and the relative expanded standard uncertainty U_r for the excess enthalpies is $U_r(H_{\text{exp}}^E) = 0.03$ (95 % level of confidence).

Table 4

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

$x_{n\text{-PrOH}}$	H_{exp}^E [19] (J·mol ⁻¹)	H_{calc}^E (orig. UNIFAC)	H_{calc}^E (mod. UNIFAC (Dortmund), coeff. by Gmehling et al. [13])	H_{calc}^E (mod. UNIFAC (Dortmund), coeff. from this work)
0.0500	333	158	313	323
0.0518	349	163	324	334
0.0995	622	294	581	602
0.1030	633	303	598	621
0.1982	1048	511	995	1044
0.2005	1042	515	1003	1053
0.3012	1303	663	1274	1352
0.3013	1313	663	1275	1353
0.4002	1447	744	1410	1512
0.4041	1447	746	1413	1515
0.5000	1468	764	1427	1544
0.5004	1482	764	1426	1544
0.5996	1395	726	1333	1456
0.7005	1216	629	1136	1251
0.7006	1208	629	1135	1251
0.7995	931	478	847	941
0.7998	938	477	846	940
0.8997	529	268	466	521
0.9010	527	265	461	516
0.9496	282	142	245	275
0.9506	278	140	240	270
ARD		49.7%	6.5%	2.9%

^a Standard uncertainties u are $u(x) = 0.0002$, $u(T) = 0.05$ K, and the relative expanded standard uncertainty U_r for the excess enthalpies is $U_r(H_{\text{exp}}^E) = 0.03$ (95 % level of confidence).

Table 5

Experimental and predicted excess molar enthalpies, H^E , for the binary system AcOH + *n*-PrOAc at 313.15 K and atmospheric pressure. ^a

x_{AcOH}	H_{exp}^E [19] (J·mol ⁻¹)	H_{calc}^E (orig. UNIFAC)	H_{calc}^E (mod. UNIFAC (Dortmund), coeff. by Gmehling et al. [13])	H_{calc}^E (mod. UNIFAC (Dortmund), coeff. from this work)
0.0503	17.4	44.3	11.8	13.8
0.0504	18.4	44.3	11.8	13.8
0.1022	29.1	44.7	19.4	24.1
0.1030	28.0	44.4	19.5	24.3
0.1994	40.8	-23.2	23.9	34.5
0.2001	40.5	-23.9	23.8	34.5
0.2008	40.6	-24.6	23.8	34.6
0.3000	39.4	-130	18.1	35.2
0.3001	38.8	-130	18.0	35.2
0.3001	39.1	-130	18.0	35.2
0.3997	27.4	-233	5.4	28.1
0.4002	27.0	-233	5.3	28.0
0.4996	13.8	-310	-11.0	15.3
0.5003	13.9	-310	-11.1	15.2
0.5993	-0.7	-347	-27.6	-1.0
0.6004	-1.0	-348	-27.8	-1.2
0.7001	-16.6	-339	-41.0	-18.2
0.7004	-16.0	-339	-41.0	-18.2
0.8001	-26.2	-279	-45.9	-31.0
0.8001	-26.3	-279	-45.9	-31.0
0.8997	-23.9	-167	-35.9	-28.3
0.8998	-24.1	-167	-35.8	-28.3
0.9487	-15.7	-92.3	-22.5	-14.1
0.9498	-15.6	-90.6	-22.1	-13.7
ARD		exceeds acceptable	exceeds acceptable	14.6%

^a Standard uncertainties u are $u(x) = 0.0002$, $u(T) = 0.05$ K, and the relative expanded standard uncertainty U_r for the excess enthalpies is $U_r(H_{\text{exp}}^E) = 0.03$ (95 % level of confidence).

Table 6

Excess enthalpy data used to determine group interaction parameters

System	T (K)	Number of data points	$U_r(H_{\text{exp}}^E)^a$	ARD (%)
<i>n</i> -PrOH + H ₂ O	298.15	22	0.02	13.1
	300.15	20	0.02	9.9
	313.15	12	0.02	12.1
	316.59	19	0.03	10.5
	323.15	22	0.01	13.6
	333.15	12	0.015	16.9
	348.15	17	0.01	10.6
	353.15	12	0.02	16.1
AcOH + H ₂ O	298.15	25	0.02	43.5
	303.15	9	0.02	26.4
	308.15	9	0.02	22.1
	313.15	22	0.015-0.02	21.6
	328.15	9	0.02	26.3
	333.15	8	0.02	30.6
	353.15	10	0.02	35.3
<i>n</i> -PrOH + AcOH	298.15	13	0.03	3.5
	313.15	22	0.03	7.3
<i>n</i> -PrOH + <i>n</i> -PrOAc	300.15	8	0.02	3.0
	313.15	21	0.03	2.9
	323.15	7	0.02	3.3
	348.15	7	0.02	2.2
AcOH + <i>n</i> -PrOAc	313.15	24	0.03	14.6

^a The relative expanded standard uncertainty U_r for the excess enthalpies, $U_r(H_{\text{exp}}^E)$, (95 % level of confidence).

Table 7

Main groups, subgroups and the corresponding van der Waals parameters for the modified UNIFAC (Dortmund) model used in present research

Group Numbers		Name	Volume R_k	Surface Area Q_k
Main	Secondary			
1	1	CH ₃	0.6325	1.0608
	2	CH ₂	0.6325	0.7081
5	14	OH	1.2302	0.8927
7	16	H ₂ O	1.7334	2.4561
11	21	CH ₃ COO	1.2700	1.6286
20	42	COOH	0.8000	0.9215

Table 8

Proposed modified UNIFAC (Dortmund) model group interaction parameters.

Main group	m=1	5	7	11	20
a_{nm} (K)					
n=1	0.0	3304.21	1500.12	79.63	1026.35
5	618.87	0.0	-1121.24	1136.09	-1075.47
7	-153.99	2999.9	0.0	-	-1028.52
11	92.28	69.41	-	0.0	2.67
20	2616.67	1778.83	763.95	20.59	0.0
b_{nm}					
n=1	0.0	-9.8033	-3.734	0.2906	-3.5222
5	-5.6081	0.0	5.1291	-1.8475	3.3348
7	0.5392	-13.1315	0.0	-	6.922
11	-3.0587	1.35	-	0.0	-1.4908
20	-9.6307	-3.8267	-4.6897	-1.1989	0.0
c_{nm} (K ⁻¹)					
n=1	0.0	$2.083 \cdot 10^{-3}$	$7.93 \cdot 10^{-4}$	$-5.71 \cdot 10^{-3}$	$7.346 \cdot 10^{-3}$
5	$2.031 \cdot 10^{-3}$	0.0	$-9.65 \cdot 10^{-3}$	$1.1577 \cdot 10^{-2}$	$-7.31 \cdot 10^{-3}$
7	$1.76 \cdot 10^{-4}$	$1.4098 \cdot 10^{-2}$	0.0	-	$-5.81 \cdot 10^{-3}$
11	$1.75 \cdot 10^{-3}$	$-1.04 \cdot 10^{-3}$	-	0.0	$-2.67 \cdot 10^{-3}$
20	$1.0131 \cdot 10^{-2}$	$-5.64 \cdot 10^{-5}$	$5.339 \cdot 10^{-3}$	$-5.26 \cdot 10^{-3}$	0.0

Fig. 1. Excess molar enthalpies, H^E , for the binary system n -PrOH + H₂O at 313.15 K: • are experimental values [28]; dotted line is results of original UNIFAC calculations; dashed line is results of modified UNIFAC (Dortmund) calculations; solid line is result of modified UNIFAC (Dortmund) calculations with the coefficients evaluated in this work.

Fig. 2. Excess molar enthalpies, H^E , for the binary system AcOH + H₂O at 313.15 K: ● and ◆ are experimental values [29, 30]; dotted line is results of original UNIFAC calculations; dashed line is results of modified UNIFAC (Dortmund) calculations; solid line is result of modified UNIFAC (Dortmund) calculations with the coefficients evaluated in this work.

Fig. 3. Excess molar enthalpies, H^E , for the binary system n -PrOH + AcOH at 313.15 K: • are experimental values [20]; dotted line is results of original UNIFAC calculations; dashed line is results of modified UNIFAC (Dortmund) calculations; solid line is result of modified UNIFAC (Dortmund) calculations with the coefficients evaluated in this work.

Fig. 4. Excess molar enthalpies, H^E , for the binary system n -PrOH + n -PrOAc at 313.15 K: • are experimental values [20]; dotted line is results of original UNIFAC calculations; dashed line is results of modified UNIFAC (Dortmund) calculations; solid line is result of modified UNIFAC (Dortmund) calculations with the coefficients evaluated in this work.

Fig. 5. Excess molar enthalpies, H^E , for the binary system AcOH + *n*-PrOAc at 313.15 K: ● are experimental values [20]; dotted line is results of original UNIFAC calculations; dashed line is results of modified UNIFAC (Dortmund) calculations; solid line is result of modified UNIFAC (Dortmund) calculations with the coefficients evaluated in this work.