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Prediction of vapor–liquid equilibria and enthalpy of mixing by means of UNIFAC models

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Abstract

The capabilities of the original and modified UNIFAC models in predicting the vapor–liquid equilibria (VLE) and enthalpy of mixing (H^E) in the binary systems formed by unsaturated hydrocarbons with various organic compounds are tested. Two different parameter sets of the original UNIFAC model are used. It is shown that, for the systems investigated, the modified UNIFAC (Mod. UNIFAC) often gives better quantitative VLE prediction than does the original UNIFAC. In the H^E prediction none of the models considered is clearly superior to the others.

VLE experimental results are reported for two binary systems: 1-octene–butyl acetate at pressures of 760, 600, 400 and 200 Torr, and 3-butylcyclopent-1-ene–4-methyl-2-pentanone at pressures of 600, 400 and 200 Torr. The H^E data obtained at 298.15 K and atmospheric pressure are presented for the binary mixtures 1-octene–butyl acetate and 3-butylcyclopent-1-ene–isopropylbenzene.

INTRODUCTION

The reliabilities of the well-established group-contribution UNIFAC model [1] and its modification, the Mod. UNIFAC model [2], have been compared for many binary systems, including those containing unsaturated hydrocarbons [2–4]. It was found that Mod. UNIFAC is the more suited to a simultaneous description of binary VLE and H^E data, owing to the introduction of temperature-dependent group interaction parameters.

Because of the lack of thermodynamic information, the use of group-contribution models is of importance in the design and operation of the separation and purification of unsaturated hydrocarbons.

The present paper is a continuation of our earlier studies into the thermodynamic properties of the binary mixtures formed by unsaturated hydrocarbons. The purpose of this contribution is to check the performance of the UNIFAC and Mod. UNIFAC models [1,2] by simultaneous predic-

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tion of binary VLE and H^E data. The UNIFAC computations involve use of two sets of group interaction parameters: the data published in 1982 [5] (UNIFAC 1982) and those revised and extended to the alkene and chloroalkene groups [6] (UNIFAC 1983). It was expected that, as a result of this study, a clearer picture should emerge regarding the suitability of both group models for calculation of VLE and H^E data in the system mentioned above.

EXPERIMENTAL

Methods and materials

The isobaric variation of the boiling temperature (T) with liquid-phase composition (X) in the system 1-octene–butyl acetate and 3-butylcyclopentene–4-methyl-2-pentanone was determined experimentally in a semi-micro ebulliometer [7]. The error of temperature determination was estimated to be less than ±0.05 K and those of liquid mole fraction (X) determination less than 1×10^{-3}. The experimental results are given in Table 1.

TABLE 1

Experimental $T-X$ data for the binary systems at different pressures (P)

X_1	Boiling point (K) at P (Torr)			
	200	400	600	760
1-octene (1)–butyl acetate (2)				
0.000	358.81	378.44	391.21	399.17
0.104	356.70	376.44	389.23	397.22
0.244	354.66	374.43	387.30	395.30
0.361	353.51	373.33	386.25	394.27
0.496	352.58	372.48	385.36	393.42
0.656	352.00	371.94	384.92	393.01
0.760	351.88	371.90	384.91	393.04
0.822	351.91	371.97	385.02	393.17
0.888	352.04	372.19	385.30	393.48
1.000	352.66	372.91	386.13	394.36
3-butylcylopentene (1)–4-methyl-2-pentanone (2)				
0.000	348.60	368.27	381.03	–
0.114	349.92	369.72	–	–
0.152	350.39	370.21	383.12	–
0.305	352.49	372.57	385.67	–
0.492	355.72	376.21	389.64	–
0.695	361.07	382.23	396.03	–
0.776	364.06	385.54	399.53	–
0.872	369.73	391.50	405.89	–
1.000	380.12	401.88	416.24	–

TABLE 2

Parameters of the Wilson (Λ_{12}, Λ_{21}) and Redlich–Kister (b, c, d) equations and the deviation of experimental from calculated pressures (dev. P)[a]

P (Torr)	Λ_{12}	Λ_{21}	dev. P (%)	b	c	d	dev. P (%)
1-octene (1)–butyl acetate (2)							
200	0.9253	0.6558	0.032	0.4551	0.0380	−0.0037	0.027
400	0.9279	0.6887	0.039	0.4136	0.0306	−0.0088	0.034
600	0.9377	0.6968	0.037	0.3926	0.0281	0.0000	0.034
760	0.9321	0.7124	0.034	0.3803	0.0249	−0.0020	0.031
3-butylcyclopentene (1)–4-methyl-2-pentanone (2)							
200	0.4939	1.0055	0.35	0.5835	−0.1055	−0.0528	0.28
400	0.4773	1.1000	0.29	0.5146	−0.1125	−0.0466	0.24
600	0.4598	1.1700	0.40	0.4743	−0.1181	−0.0681	0.31

[a] The mean absolute deviation of the experimental from the calculated pressure relative to the experimental pressure.

The results obtained in a binary data fit using the Wilson and Redlich–Kister equations are given in Table 2. The binary parameters were determined by the least squares method, being non-linear for the Wilson equation.

The pure-component Antoine equations were used to correlate and predict VLE. For the liquids investigated, Table 3 lists coefficients of the Antoine equations used here in the form

$$T = \frac{B}{A - \ln P} - C \tag{1}$$

and the standard deviation of the correlated boiling temperatures, $S(T)$, from the experimental values.

The calorimeter, the operating procedure and the apparatus test have been described previously [8]. Errors in the H^{E} determination were estimated to be less than 2%. The results are reported in Table 4.

They were fitted using the equation

$$H^{\mathrm{E}} = X_1 X_2 \sum_{i=1}^{n} a_i (X_1 - X_2)^{i-1} \tag{2}$$

TABLE 3

Coefficients A, B and C of the Antoine equation and standard deviations $S(T)$

Compound	A	B	C	$S(T)$
1-Octene	15.93435	3090.319	−62.106	0.003
Butyl acetate	16.09368	3087.586	−72.800	0.006
3-Butylcyclopentene	15.12493	2821.127	−93.002	0.025
4-Methyl-2-pentanone	16.29974	3216.128	−56.267	0.008

TABLE 4

Experimental enthalpy of mixing H^E at 298.15 K for binary systems

1-Octene (1)–butyl acetate (2)		3-Butylcyclopentene (1)–isopropylbenzene (2)	
X_1	H^E	X_1	H^E
0.071	135	0.060	65
0.086	181	0.121	113
0.328	544	0.351	242
0.346	548	0.455	261
0.443	586	0.609	259
0.518	622	0.686	233
0.542	628	0.808	146
0.581	595	0.915	61
0.723	499		
0.822	362		

where the coefficients, a_i, were calculated by the method of least squares with all points weighted equally. The coefficients affording the best fit and the corresponding standard deviation $S(H^E)$ are given in Table 5.

The analytical grade 1-octene and 4-methyl-2-pentanone, and 3-butylcyclopentene synthesized in our laboratory [9], were fractionally distilled in a Teflon bristle-rotor 50-plate column. Isopropylbenzene and butyl acetate obtained from Reakhim (Kharkov, USSR) in high purity (puriss, p.a. > 99%) were used without further purification. The purity of all the sub-

TABLE 5

Coefficients, a_i, of eqn. (2) and standard deviations $S(H^E)$ (J mol^{-1}) for binary systems

System	a_1	a_2	a_3	a_4	$S(H^E)$
1-Octene (1)–butyl acetate (2)	2478.3	138.4	−256.3	–	12.3
3-Butylcyclopentene (1)–isopropylbenzene (2)	1078.6	96.7	−194.8	−435.1	4.0

TABLE 6

Physical properties of compounds

Compound	$d_4{}^a$ (kg m^{-3})	$n_D{}^a$	T (K)
1-Octene	715.1	1.4087	394.36
3-Butylcyclopentene	798.7	1.4416	425.23
Isopropylbenzene	862.5	1.4910	425.62
Butyl acetate	882.5	1.3941	399.17
4-Methyl-2-pentanone	797.8	1.3962	388.98

[a] At 298.15 K.

stances used was not less than 99%, as determined by gas–liquid chromatography on PEG-20M and squalane capillary columns. They were stored under an argon atmosphere and protected from light and moisture. Table 6 presents the characteristic properties of the compounds, viz. density (d_4), refractive index (n_D) at 298.15 K and normal boiling temperature (T, K).

RESULTS AND DISCUSSION

The VLE prediction ability of the models considered is tested by means of the percent deviations, dev. P, between experimental and calculated total pressures. Table 7 compares the dev. P values with those obtained by the Wilson correlation for some binary systems. It can be seen that, in most cases, Mod. UNIFAC provides better agreement between the experimental and calculated pressures than does the original UNIFAC. In two cases only (1-butylcyclopentene–n-heptane and 1-octene–1-butanol) the Mod. UNIFAC has no advantage in VLE prediction. For these systems the best agreement is obtained by UNIFAC (1983). It seems that UNIFAC (1982) gives the best representation of the pressure data for alkene (cycloalkene) mixtures with 1-butanol using the interaction parameters for the CH_2CH_2OH alcohol groups [5]. All the prediction results for cycloalkene mixtures in this study were obtained by using the acyclic C=C group interaction parameters [1,2,6].

In the systems investigated (Table 7) the models give close prediction results for vapour composition. An example is shown in Table 8 for the system 3-butylcyclopentene–4-methyl-2-pentanone at 400 Torr.

The ability of models to predict VLE data has also been compared in obtaining azeotropic composition. The data of the present study on the 1-octene–butyl acetate system confirm the existence of a binary azeotrope marked by a minimum in boiling temperature. Azeotropic compositions and temperatures (interpolated values) at different pressures are given in Table 9.

In comparing the above results, the azeotropic compositions were estimated graphically by plotting the relative volatility calculated with different equations vs. liquid composition. Here the Wilson and UNIFAC (1982) equations afford the best representation.

The predicted H^E values are compared with experimental ones [15–21] in Fig. 1. It is clearly seen that each type of system, except examples 2, 5, 6, 11, 12 and 16, has its own most suitable model.

The H^E data have not been considered at all in the determination of parameters for UNIFAC (1982) and UNIFAC (1983). In this respect, UNIFAC (1983) performs reasonably well for the systems alkene–alkane (1), 1-octene- and octane–tetrachloroethene (7, 8) and UNIFAC (1982) for alkene (cycloalkene)–aromatic hydrocarbon (3, 4) and alkene (cycloalkene)–ketone (9, 10) systems. Replacement of the Mod. UNIFAC model

TABLE 7

Comparison between total pressure prediction of UNIFAC and Mod. UNIFAC models; correlation of Wilson equation and experimental data

System	Wilson		UNIFAC (1982)		UNIFAC (1983)		Mod. UNIFAC		Ref.
	400	600	400	600	400	600	400	600	
1-Octene–*n*-octane	0.11	0.09	0.46	0.47	0.56	0.46	0.08	0.10	7
1-Octyne–*n*-octane	0.06	0.09	0.09	0.15	–	–	–	–	10
2-Octyne–*n*-octane	0.09	0.09	1.12	1.08	–	–	–	–	10
1-Ethylcyclopentene–*n*-heptane	0.14	0.12	0.25	0.21	0.23	0.19	0.54	0.46	11
1-Octene–tetrachloroethene	0.14	0.15	3.89	4.22	1.55	1.40	–	–	12
6 1-Octene–butyl acetate	0.04	0.04	0.43	0.41	0.57	0.63	0.30	0.29	this work
3-Butylcyclopentene–4-methyl-2-pentanone	0.29	0.40	4.66	4.61	3.84	3.94	1.58	1.80	this work
1-Octene–1-butanol	0.37	0.47	1.74 1.17 [a]	2.63 0.64 [a]	1.38	2.19	1.94	2.67	12
3-Ethylcyclopentene–1-butanol	0.49	0.48	2.68 1.02 [a]	3.63 0.63 [a]	2.28	3.02	0.84	0.83	13
1-Octyne–1-butanol	0.55	0.78	1.55	0.71	–	–	–	–	14
trans-2-Octene–1-butanol	1.34	1.26	2.73 1.11 [a]	3.50 1.41 [a]	2.40	3.13	2.45	2.81	12
cis-4-Octene–1-butanol	0.40	0.50	2.17 0.29 [a]	3.00 0.92 [a]	1.80	2.59	1.88	2.33	12

[a] Obtained using the interaction parameters for CH_2CH_2OH alcohol groups [5].

TABLE 8

Vapour composition (y_1) in 3-butylcyclopentene (1)–4-methyl-2-pentanone (2) system at 400 Torr

X_1	y_1 calculated using the equation of				
	Wilson	Redlich–Kister	UNIFAC (1982)	UNIFAC (1983)	Mod. UNIFAC
0.114	0.062	0.061	0.072	0.071	0.065
0.152	0.079	0.080	0.093	0.091	0.084
0.305	0.147	0.149	0.170	0.165	0.160
0.492	0.239	0.238	0.256	0.250	0.252
0.695	0.367	0.381	0.373	0.373	0.386
0.776	0.478	0.473	0.443	0.448	0.465
0.872	0.632	0.633	0.574	0.586	0.608

by the original one (1982) has little influence on the H^E prediction in alkene (cycloalkene)–alkanol systems (13–15), giving good results for 1-octene–1-propanol at 298.15 K, whereas a significant improvement is observed for the H^E prediction by UNIFAC (1983) in 1-octene–1-propanol at 313.15 K and 3-ethylcyclopentene–1-butanol at 298.15 K. For the remaining six systems (2, 5, 6, 11, 12 and 16), prediction by the models considered is unacceptable; among them are three systems containing isomeric alkynes: 1-octyne–octane (5), 2-octyne–octane (6) and 1-octyne–1-butanol (16).

Parameters for $CH_2/C{\equiv}C$ interaction from UNIFAC (1982) only have been used, because Mod. UNIFAC does not give parameters for this pair of groups [2]. For VLE in octyne–octane systems (Table 7) some differences exist in the applicability of these parameters: they give better prediction for 1-octyne–octane than for 2-octyne–octane. With the alkyne–alkane systems

TABLE 9

Azeotropic parameters of the binary system 1-octene (1)–butyl acetate (2) at different pressures

Source of data	Pressure (Torr)							
	200		400		600		760	
	T (K)	X_1	T (K)	X_1	T (K)	X_1	T (K)	X_1
Ebulliometric experiment	351.85	0.781	371.89	0.742	384.90	0.715	393.0	0.697
Wilson		0.77		0.74		0.72		0.70
Redlich–Kister		0.76		0.72		0.71		0.70
UNIFAC (1982)		0.77		0.74		0.71		0.69
UNIFAC (1983)		0.74		0.70		0.68		0.67
Mod. UNIFAC		0.76		0.72		0.69		0.68

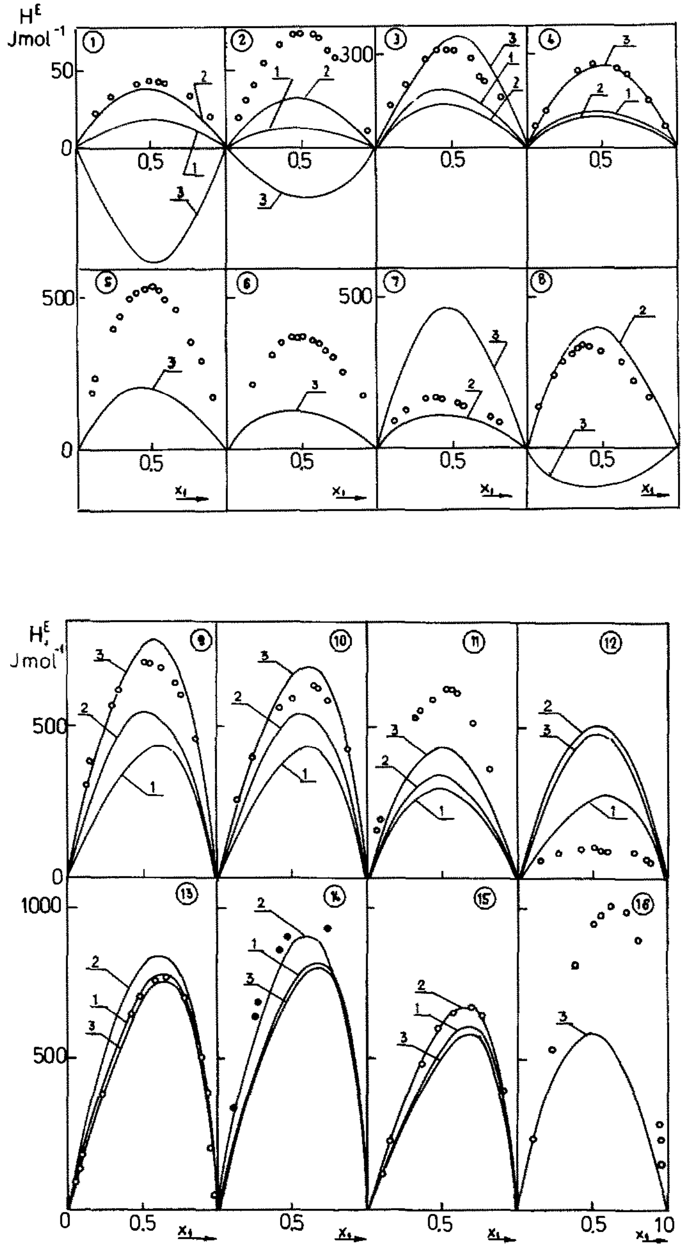

Fig. 1. Excess enthalpies for various mixtures containing unsaturated hydrocarbons predicted using Mod. UNIFAC (curve 1) compared with the original UNIFAC (curves (2) and (3) obtained with group parameters [6] and [5] respectively). Experimental, (○) at 298.15 K, (●) at 313.15 K. (1) 1-Octene–octane; (2) 1-methylcyclohexene–heptane; (3) 1-octene–toluene; (4) 3-butylcyclopentene–isopropylbenzene; (5) 1-octyne–octane; (6) 2-octyne–octane; (7) 1-octene–tetrachloroethene; (8) octane–tetrachloroethene; (9) 1-octene–4-methyl-2-pentanone; (10) 1-methylcyclohexene–2-hexanone; (11) 1-octene–butyl acetate; (12) 1-octene–dibutyl ether; (13), (14) 1-octene–1-propanol; (15) 3-ethylcyclopentene–1-butanol; (16) 1-octyne–1-butanol.

the advantage of differentiating the terminal and internal triple bond groups has been confirmed earlier [10].

It should be noted that the first run using the original UNIFAC model employed the parameter values for HC≡C/OH ($a_{CH\equiv C/OH} = 577.1$; $a_{OH/CH\equiv C} = 107.7$) in our earlier papers [14,22]. These parameters have been obtained from limited information (VLE data of the 1-octyne–1-propanol system at 400 and 600 Torr [14]), and this may be one of the reasons for the disagreement between the calculated and experimental H^E data. In our opinion, the H^E prediction may be improved if the triple bond position in the alkyne molecules is taken into account. Work on VLE and H^E measurements is now in progress to extend group-contribution models to the systems containing isomeric alkynes.

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