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APPLICATION OF THE UNIFAC MODEL TO ALKYLCYCLOPENTENE MIXTURES

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ABSTRACT

The UNIFAC group contribution model was tested for its ability to correlate and predict the vapour–liquid equilibria (VLE) in the binary systems 1-butylcyclopentene–*n*-nonane, 1-butylcyclopentene–isopropylbenzene, 1-butylcyclopentene–1-butanol, 1-ethylcyclopentene–*n*-heptane and 3-ethylcyclopentene–1-butanol. The initial and revised acyclic C=C group parameters taken from the literature, and those of the cyclic C=C and special cyclopentene groups obtained in this work were used in the computations. In addition, the enthalpies of mixing (H^E) of 1-ethylcyclopentene–*n*-heptane, 1-butylcyclopentene–*n*-nonane and 1-butylcyclopentene–1-butanol were predicted using the acyclic and cyclic C=C group parameters. The model represents well VLE for the hydrocarbon systems, the isothermic vapour pressure and the azeotropic data for those 1-butanols with all sets of group parameters. However, boiling-temperature predictions for the 1-butanol mixtures are considerably poorer when acyclic C=C group parameters are used. The prediction of H^E data is unacceptable although some improvement was obtained by using cyclic C=C parameters. New experimental results are reported for the boiling temperatures of the 3-ethylcyclopentene–1-butanol mixtures at 200, 400, 600 and 760 Torr.

INTRODUCTION

A survey of the literature has revealed that experimental thermodynamic data are very scarce for systems containing alkylcycloalkenes. The application of these compounds has been hampered by the lack of this kind of information. It is also necessary to elucidate the effect of the molecular structure of the alkylcycloalkenes on their thermodynamic properties. Because of limited experimental information, it is necessary to use a predictive model, such as group contribution, for this elucidation. The advantage of the latter approach is that a larger number of components may be represented by relatively few groups. A typical group model which has been widely used

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is that of UNIFAC [1]. This model has proved to be successful for a variety of mixtures, including those containing unsaturated hydrocarbons [2].

The purpose of the present study was to demonstrate how the UNIFAC model reproduces the thermodynamic properties of alkylcyclopentene mixtures with some solvents. The basis of the study was formed by our experimental VLE and H^E data and interaction group parameters both taken from the literature [1,3,4] and determined by us. When applying the UNIFAC model, no differentiation is made between the acyclic and cyclic C=C groups. In the present work, the cyclic C=C and special cyclopentene groups were introduced by correlating and predicting the VLE for the alkylcyclopentene mixtures. Using the acyclic and cyclic C=C group parameters, the enthalpies of mixing were also predicted.

EXPERIMENTAL

3-Ethylcyclopentene was synthesized [5] and fractionally distilled in a 50-plate Teflon bristle-rotor column [6] to 99% purity as detected by gas–liquid chromatography on PEG-20M and Squalane capillary columns using a hydrogen flame ionization detector. 1-Butanol ("puriss grade", Reakhim, Kharkov) was used without further purification and stored in specially devised flasks isolated from external moisture.

Boiling temperatures were measured in a semi-micro ebulliometer at fixed pressures. A detailed description of the apparatus and experimental proce-

TABLE 1

Experimental $t-x$ data for the binary system 3-ethylcyclopentene(1)–1-butanol(2) at different pressures

x_1	Boiling temperature (°C) at P (Torr) =			
	200	400	600	760
0.000	84.45	100.63	111.07	117.56
0.166	68.20	86.64	98.25	105.41
0.331	61.28	80.01	92.01	99.54
0.392	60.01	78.51	90.46	97.93
0.430	59.14	77.84	89.81	97.34
0.525	57.71	76.32	88.34	95.79
0.646	57.14	75.63	87.57	95.09
0.700	56.89	75.42	87.48	95.02
0.793	56.41	75.00	87.08	94.60
0.860	56.22	74.92	87.14	94.75
0.900	56.11	75.20	87.46	95.19
0.927	56.32	75.30	87.60	95.46
1.000	57.64	77.13	89.86	97.86

TABLE 2

Parameters of the Redlich–Kister and Wilson[a] equations

P (Torr)	Redlich–Kister			Wilson		
	b	c	d	$\Delta\lambda_{12}$	$\Delta\lambda_{21}$	t (°C)
200	1.4898	0.4974	0.2762	−0.066	7.612	60.60
400	1.3846	0.4618	0.1982	−0.219	7.124	79.12
600	1.3266	0.4234	0.1632	−0.273	6.782	91.09
760	1.2721	0.4225	0.1175	−0.298	6.486	98.58

[a] $\Delta\lambda_{ij} = \lambda_{ij} - \lambda_{ii}$ (kJ mol^{-1})

dure have been published previously [7]. The error of the temperature determination was estimated to be less than ±0.05 °C. The binary mixtures were prepared by adding the weighed amounts of components. The mole fraction error was estimated to be less than $\pm 1 \times 10^{-3}$.

The experimental results for the boiling temperatures of the 3-ethylcyclopentene(**1**)–1-butanol(**2**) mixtures are given in Table 1. The detailed results obtained in a binary data fit using the Wilson and three-parameter Redlich–Kister equations are given in Tables 2 and 3, respectively. The binary parameters (Table 2) were determined by the method of least squares, being non-linear for the Wilson equation. In Table 3 the absolute average deviation between the experimental and calculated pressure

$$(P)a \equiv \Delta P = 1/n \sum_{n} |P_{\text{exp}} - P_{\text{calc}}|$$

are presented along with the relative error observed

$$r \equiv \delta P = \frac{\sum_{n} |\Delta P|}{n P_{\text{exp}}} 100\%$$

where n is the number of experimental points.

TABLE 3

Absolute average (a) and relative (r) deviations between experimental pressures and those calculated using the Redlich–Kister and Wilson equations

P (Torr)	Redlich–Kister		Wilson	
	a (Torr)	r (%)	a (Torr)	r (%)
200	1.1	0.6	1.0	0.5
400	1.0	0.2	2.0	0.5
600	1.2	0.2	2.9	0.5
760	2.2	0.3	4.0	0.5

The pure component Antoine equations

$$\ln(P_1) = 6.75827 - \frac{1198.569}{t + 211.262} \tag{1}$$

$$\ln(P_2) = 7.28926 - \frac{1255.686}{t + 167.277} \tag{2}$$

were used to correlate VLE with the Redlich–Kister and Wilson equations (P_1, P_2 in Torr; t in °C).

At all the pressures studied, except 200 Torr, the Redlich–Kister equation describes the pressure better than the Wilson one. At 200 Torr, both equations are fitted similarly.

RESULTS AND DISCUSSION

The classification of the groups and their corresponding volumes R_k and surface areas Q_k are given in Table 4. Table 5 contains the group interaction parameters (α_{mn}) used in this work; i.e. the interaction parameters taken from three literature sources [1,3,4] and estimated by us for the cyclic C=C and special cyclopentene groups.

TABLE 4

Group-volume (R_k) and surface-area (Q_k) parameters (k = m, n)

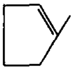
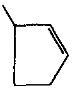
Main group	Subgroup, k	R_k	Q_k
CH_2	CH_3	0.9011	0.848
	CH_2	0.6744	0.540
	CH	0.4469	0.228
C=C	CH=CH	1.1167	0.867
	CH=C	0.8886	0.676
Cyclopentene		2.9118	2.296
		2.9121	2.175
ACH	ACH	0.5313	0.400
ACH_2	ACH_2	0.8121	0.348
CCOH	CH_2CH_2OH	1.8788	1.664
OH	OH	1.0000	1.200

TABLE 5

UNIFAC group interaction parameters (α_{mn}) used in this work

m	n							
	CH_2	Acyclic C=C	Cyclic C=C	Cyclo- pentene	ACH	$ACCH_2$	CCOH	OH
CH_2	0	-200.0^{a} 86.02^{c}	-122.54^{d} 107.54^{e}	-304.9^{d} -60.6^{e}	61.13^{a}	76.50^{a}	737.5^{a}	986.5^{b}
Acyclic C=C	2520^{a} -35.36^{c}	0	–	–	340.7^{a} 38.81^{c}	4102^{a} 74.15^{c}	535.2^{a}	693.9^{b} 524.1^{c}
Cyclic C=C	2729^{d} -6.31^{e}	–	0	–	–	–	–	342.86^{e}
Cyclo- pentene	2625^{d} 78.0^{e}	–	–	0	–	–	–	577.65^{e}
ACH	-11.12^{e}	-94.78^{a} 3.446^{c}	–	–	0	167.0^{a}	–	–
$ACCH_2$	-69.70^{a}	-269.7^{a} -113.6^{c}	–	–	-146.8^{a}	0	–	–
CCOH	-87.93^{a}	121.5^{a}	–	–	–	–	0	–
OH	156.4^{b}	8694^{b} 457^{c}	325.29^{e}	270.41^{e}	–	–	–	0

[a] Ref. 1. [b] Ref. 3. [c] Ref. 4. [d] Obtained in this work using initial values from ref. 11. [e] Obtained in this work using initial values from ref. 4.

The parameter-estimating program was based on Marquardt's optimization algorithm [8]. The procedure comprised minimization of the function F

$$F = \sum_{i=1}^{NP} \left(1 - P^{\text{calc}}/P^{\text{exp}}\right)^2 \tag{3}$$

The summation over i included all NP experimental points in the binary systems. The parameters of the binary-group contribution cyclic C=C/CH_2 and cyclopentene/CH_2 were obtained from VLE data on the 1-butylcyclopentene–*n*-nonane system at 400 and 600 Torr [9], for the cyclic C=C/OH and cyclopentene/OH pairs from those on the 1-butylcyclopentene–1-butanol system at 400 and 600 Torr [10] and from the data reported here. The different initial values, from [1] and [4], used in the parameter-estimating procedure yielded different results corresponding to the equal minimum quantity.

Tables 6–9 and Figs. 1 and 2 show the calculated results obtained with new parameters. For comparison, they also show values predicted by the UNIFAC model without adjusting parameters to the new data.

For the boiling temperatures of the 1-butylcyclopentene–*n*-nonane systems, the differences between the calculated results obtained with various

TABLE 6

Absolute average ($\overline{\Delta t}$) and maximum ($\Delta t_{\max}$) deviations for the boiling temperature measurements [9] of 1-butylcyclopentene–*n*-nonane mixtures at different pressures

P (Torr)	From ref. 1		From ref. 4		This work				Cyclopentene [b]	
					Cyclic C=C [a]		Cyclic C=C [b]			
	$\overline{\Delta t}$	$\Delta t_{\max}$	$\overline{\Delta t}$	$\Delta t_{\max}$	$\overline{\Delta t}$	$\Delta t_{\max}$	$\overline{\Delta t}$	$\Delta t_{\max}$	$\overline{\Delta t}$	$\Delta t_{\max}$
600	0.08	−0.14	0.08	−0.15	0.06	0.14	0.06	0.13	0.06	0.14
400	0.11	−0.23	0.11	−0.23	0.05	−0.15	0.07	−0.15	0.06	−0.15
200			0.15	−0.30	0.09	−0.19	0.08	−0.17		

[a] α_{mn} estimated using the initial values from ref. 1.

[b] α_{mn} estimated using the initial values from ref. 4.

TABLE 7

Absolute average ($\overline{\Delta t}$) and maximum ($\Delta t_{\max}$) deviations for boiling-temperature measurements [10] of alkylcyclopentene mixtures with 1-butanol at 400 Torr

Alkylcyclopentene	From ref. 1		From ref. 3		From ref. 4		This work [a]			
							Cyclic C=C		Cyclopentene	
	$\overline{\Delta t}$	$\Delta t_{\max}$	$\overline{\Delta t}$	$\Delta t_{\max}$	$\overline{\Delta t}$	$\Delta t_{\max}$	$\overline{\Delta t}$	$\Delta t_{\max}$	$\overline{\Delta t}$	$\Delta t_{\max}$
1-Butylcyclopentene	1.38	5.9	2.19	8.54	2.11	7.78	0.82	3.90	0.51	2.55
3-Ethylcyclopentene [b]	–	–	0.94	2.54	0.76	2.32	0.96	−1.14	0.88	−1.30

[a] α_{mn} estimated using initial values from ref. 4.

[b] Measurement results given in this paper.

TABLE 8

Vapour pressure (Torr) of the binary systems at 25 ° C

1-Ethylcyclopentene (**1**)–*n*-heptane(**2**)				1-Butanol(**1**)–1-butylcyclopentene(**2**)						
x_1	Exp. [a]	Predicted		x_1	Exp. [a]	Predicted				
		From ref. 1	Cyclic C=C [b]			[1]	[3]	[4]	Cyclic C=C [b]	
0.302	42.2	41.8	42.1	0.089	5.6	6.0	6.1	5.9	5.4	
0.433	40.5	40.1	40.5	0.172	6.1	6.5	6.6	6.1	6.0	
0.499	40.1	39.2	39.7	0.268	6.8	6.7	6.8	6.8	6.4	
0.522	39.7	38.9	39.4	0.407	6.9	6.8	6.9	6.9	6.7	
0.701	37.5	36.6	37.0	0.549	7.0	6.9	6.9	7.0	6.8	
				0.700	7.3	6.8	7.0	7.0	6.8	
				0.799	7.0	6.7	6.8	6.9	6.7	
				0.898	6.5	6.4	6.5	6.6	6.4	
				0.947	6.2	6.2	6.2	6.2	6.2	

[a] Obtained using isobaric data [10,12] and extrapolation to 25 ° C.

[b] α_{mn} estimated using initial values from ref. 4.

TABLE 9

Binary azeotrope 3-ethylcyclopentene(1)–1-butanol(2) calculated for different pressures using the Redlich–Kister (RK) and Wilson (W) correlations

P (Torr)	t exp. (°C)	x_1		From ref. 3		From ref. 4		This work [a]			
		RK	W	t (°C)	x_1	t (°C)	x_1	Cyclic C=C		Cyclopentene	
								t (°C)	x_1	t (°C)	x_1
200	56.2	0.89	0.90	56.3	0.89	56.5	0.89	57.2	0.94	57.1	0.93
400	74.9	0.85	0.86	74.6	0.84	74.9	0.84	76.0	0.87	75.9	0.87
600	87.0	0.82	0.83	86.4	0.80	86.6	0.80	88.0	0.83	87.9	0.82
760	94.5	0.81	0.82	93.6	0.78	93.9	0.78	95.4	0.80	95.4	0.80

[a] α_{mn} estimated using initial values from ref. 4.

parameter sets and reported in Table 6 are relatively small, especially at 600 Torr. The predictions are considered satisfactory, although they are a little poorer than the correlations.

Satisfactory prediction results were also obtained for the isopropylbenzene system [11]. The boiling-temperature calculations using the acyclic C=C group parameters are summarized in Table 10. The data indicate that the "old" parameters [1] give better results than do the re-estimated ones [4].

In the 1-butanol mixtures, being far from ideal, the boiling temperatures are poorly predicted when the acyclic C=C group parameters were used. The data in Table 7 show that the mean and maximum temperature errors are reduced by using the cyclic C=C parameters, while with the parameters of the special cyclopentene group the model produces the lowest mean errors. The largest deviations were obtained in the alkylcyclopentene rich region, corresponding to the large differences in calculated activity coefficients just in this region (Fig. 1).

Prediction reliability with respect to the vapour pressure at 25 °C [10,12] is demonstrated by the data in Table 8. An examination of the pressure errors shows maximum relative errors of 2% and 7% for 1-ethylcyclopentene–n-heptane and 1-butylcyclopentene–1-butanol, respectively.

TABLE 10

Absolute average ($\overline{\Delta t}$) and maximum ($\Delta t_{\max}$) deviations for boiling-temperature measurements [11] of 1-butylcyclopentene–isopropylbenzene mixtures

P (Torr)	From ref. 1		From ref. 4	
	$\overline{\Delta t}$	$\Delta t_{\max}$	$\overline{\Delta t}$	$\Delta t_{\max}$
600	0.11	0.20	0.37	0.58
400	0.09	−0.15	0.25	0.43
200	0.07	0.12	0.17	0.31

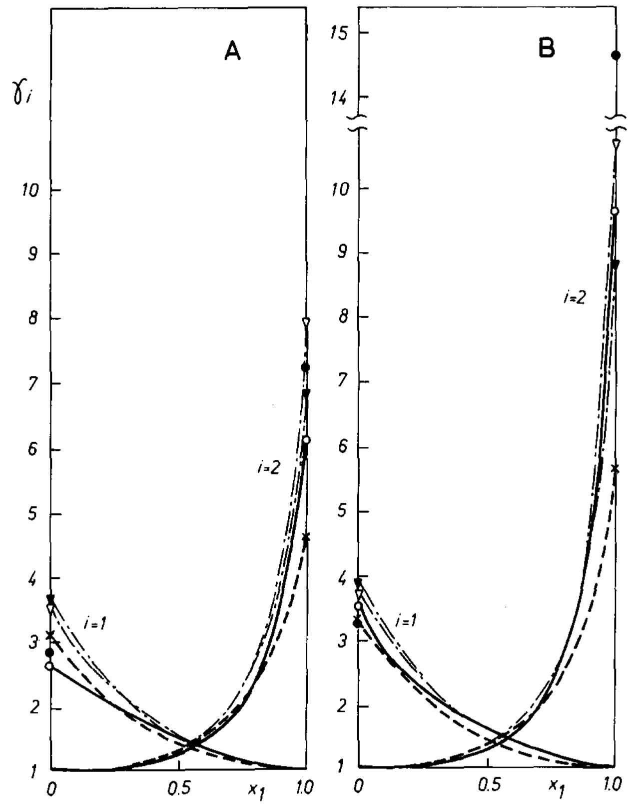


Fig. 1. Calculated γ_i data for 3-ethylcyclopentene(1)–1-butanol(2) at (A) 760 and (B) 200 Torr. The lines represent calculations of the Redlich–Kister (o) and Wilson (●) equations and the UNIFAC model ones with acyclic C=C [3] (▼), [4] (▽) and cyclic C=C (×) and special cyclopentene (×) group parameters.

The binary systems containing 1-butanol show a temperature minimum at the pressures considered. The binary azeotropes are clearly predicted with all sets of group interaction parameters. The quality of prediction characterizes the data on the 3-ethylcyclopentene–1-butanol azeotrope (Table 9).

Finally, Fig. 2 shows the excess enthalpies of the alkylcyclopentene mixtures with the *n*-alkanes and 1-butanol. Agreement between the experimental H^E values and the calculated ones is poor for all parameter sets, although the asymmetry of the H^E–x curve for the alcohol system is represented satisfactorily. In this system, the errors in H^E prediction with two sets of parameters, those from ref. 3 and those estimated using the initial values in ref. 4, are of the same order as those of the modified UNIFAC for hydrocarbon–alcohol systems [15]. The hydrocarbon system H^E values calculated using the acyclic C=C group parameters differ from the experimental both in magnitude and in sign.

The results of the present study demonstrate that the UNIFAC model is a reliable method for estimating the VLE of alkylcyclopentene mixtures. For

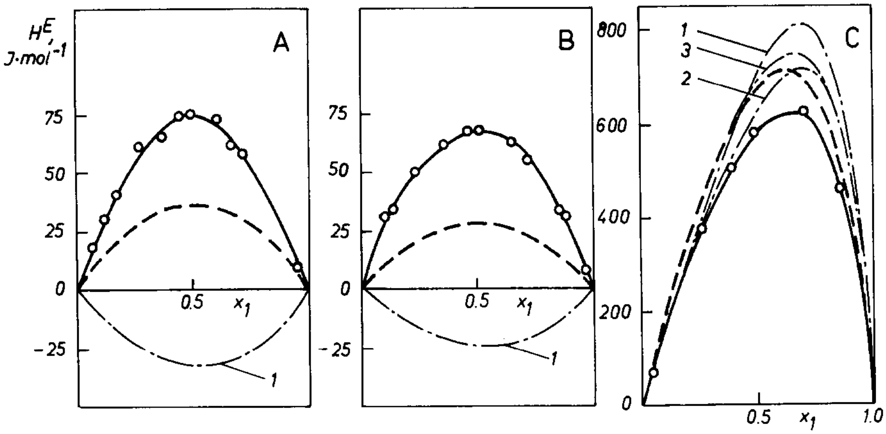


Fig. 2. Experimental and calculated H^E data for the systems: (A) 1-ethylcyclopentene (**1**) −*n*-heptane(**2**); (B) 1-butylcyclopentene(**1**) −*n*-nonane(**2**); (C) 1-butylcyclopentene(**1**) −1-butanol(**2**). Points: experimental data at 298.15 K [13,14]. The lines represent the Redlich–Kister correlations (solid line without a number) and predictions using the UNIFAC model with acyclic C=C (curves: 1 [1], 2 [3], 3 [4]) and cyclic C=C group parameters (dashed line).

appreciably non-ideal systems somewhat better results can be obtained by including the interaction parameters of the cyclic C=C or special cyclopentene groups. Although the predictions of H^E are quantitatively unacceptable, use of the cyclic C=C parameters yields qualitatively reasonable H^E values. The study reported here may serve as a starting point for further extension of the UNIFAC model which should be able to describe correctly other alkylcyclene systems.

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