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Mati KUUS*, Helle KIRSS*, Enn SIIMER*, and
Ludmilla KUDRYAVTSEVA*APPLICATION OF THE UNIFAC MODEL TO BINARY SYSTEMS
CONTAINING AROMA COMPOUNDS

Introduction

This work was carried out as part of a general programme of studying the properties of systems containing aroma compounds or basic components of their synthesis. To solve practical problems arising in the separation processes of standard compounds, data on vapor-liquid equilibria (VLE) and enthalpy of mixing (H^E) are needed. Experimental studies on the phase behaviour in multicomponent systems and the mixing process are very time-consuming. They can be considerably simplified if prediction of the thermodynamic data by using some reliable model such as group contribution one is possible. The advantage of such an approach is that a large number of components may be represented by relatively few groups. A typical group model which has been widely applied is that of UNIFAC [1]. This model is rather easy to use and sufficiently accurate, providing the relevant group interaction parameters for VLE and lately for H^E calculation as well. Therefore, it may be used to predict VLE and H^E in the absence of experimental information for the mixtures of interest, among them ternary and multicomponent ones.

Aromas are mostly multicomponent mixtures of both simple and complex compounds. The former, such as esters, alcohols, ketones, etc., contain besides the hydrocarbon groups only one strong functional group in the molecule. There is a good deal of experimental data for them. The selection of the most suitable UNIFAC group interaction parameters from among those published seems to be a special problem for systems of such compounds. For example, there are different UNIFAC parameters for formiate (HCOO), acrylate, and benzoate (COO), as well as other esters (CCOO) [2, 3]. The alcohol groups are even more manifold: the groups (OH) [4], those containing two open-chain carbon atoms (CCOH) [5], the special group of methanol (CH₃OH) [4], and the long-chain alcohol group ([CH₂]₅OH) [6]. The last can be of special interest from the point of view of aroma compounds. The results of VLE prediction in these systems obtained with UNIFAC parameters are mostly quantitatively acceptable.

In our opinion, UNIFAC may fail to a certain extent with complex compounds which contain more than one strong functional group in a molecule. The major difficulty in the prediction is the lack of data needed and the absence of some group interaction parameters. As a group approach the UNIFAC has some limitations. For example, it

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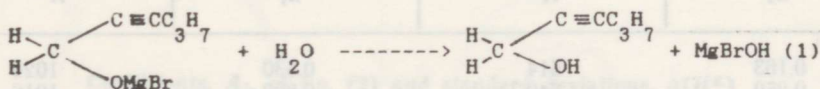
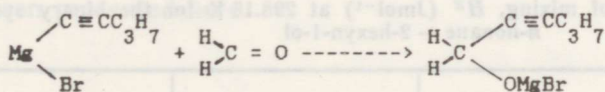
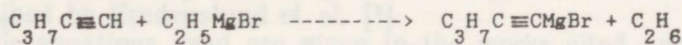
ignores the so-called proximity effects, i. e. the intramolecular influence on a group from nearby groups in the molecule, this being more considerable in complex compounds. It seems that in order to obtain a good description for complex systems, the proximity effects should be taken into account by the group specification.

The purpose of this work was to check the possibility of using the UNIFAC model for the prediction of VLE and H^E in some binary systems containing aroma compounds or the basic components of their synthesis.

The binary systems containing 2-hexyn-1-ol or benzaldehyde as one of the components and the system consisting of the derivatives of furane (furfural and furfuryl alcohol) have been selected as test systems. In order to start with this kind of investigations, the hydrocarbons were used as the second component due to their simple structure and inertness in mixture. Considering that the lack of experimental data is a continuing problem, we report here also the results of VLE and H^E measurements for the system *n*-nonane—2-hexyn-1-ol. The experimental data for all the other systems have been taken from literature.

Experimental

2-Hexyn-1-ol, the basic component of *trans*-2-hexenal synthesis [7], was obtained from 1-pentyne [8] in our laboratory* according to



It was fractionally distilled at reduced pressure in a Teflon bristle-rotor 50-plate column to 99.6% purity as found by gas chromatography on PEG-20 M capillary column using a hydrogen flame ionization detector. The physical properties of 2-hexyn-1-ol at 293.15 K were: density, d , kgm^{-3} = 893.9 and refractive index, n_D = 1.4359.

Nonane ("puriss grade", Reakhim, Kharkov) was used without further purification.

The isobaric variation of the boiling temperature (T) with liquid phase composition was determined in a semi-micro ebulliometer [9]. The error of temperature determination was estimated to be less than 0.05 K and that of liquid mole fractions less than 1×10^{-3} .

The mixing enthalpies were measured using a DAK-1-1A microcalorimeter. The operating procedure and the apparatus test have been described previously [10]. The estimated error for the H^E values was around 2%.

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Results and Discussion

Tables 1 and 2 summarize respectively the boiling temperature and enthalpy of mixing investigations as a function of liquid phase concentration (x_1 — mole fraction of *n*-nonane) in the binary system *n*-nonane—2-hexyn-1-ol.

Table 3 gives the results obtained in the $T-x$ binary data fit using the Redlich-Kister equation with the three parameters determined by the least squares method.

Table 1

Experimental $T - x$ data for the binary system *n*-nonane—2-hexyn-1-ol at different pressures

x_1	Boiling temperature (K) at P (Torr)		
	200	250	300
0.000	403.82	409.83	414.98
0.106	388.59	395.24	400.81
0.238	381.39	387.96	393.50
0.466	378.27	384.68	390.08
0.703	377.08	383.44	388.82
0.783	376.96	383.37	388.74
0.885	377.31	383.80	389.25
1.000	379.88	386.46	392.02

Table 2

Experimental enthalpy of mixing, H^E (Jmol⁻¹) at 298.15 K for the binary system *n*-nonane — 2-hexyn-1-ol

x_1	H^E	x_1	H^E
0.163	514	0.530	1024
0.250	740	0.609	1016
0.395	974	0.637	986
0.486	1009	0.747	914
0.528	1032	0.850	681

Table 3

Parameters (b, c, d) of the Redlich-Kister equation and the deviation of experimental pressures from calculated ones (dev, P)*

P (Torr)	b	c	d	dev. P , %
200	1.7046	0.2317	0.0746	0.394
250	1.6544	0.2209	0.0471	0.374
300	1.6151	0.2153	0.0346	0.352

* The mean absolute deviation of the experimental pressures from calculated ones relative

to the experimental pressure: $\text{dev. } P = 1/n \sum_{i=1}^n \frac{|P_{\text{exp}} - P_{\text{calc}}|_i}{P_{\text{exp}}} \times 100, \%$

The $T-P$ (P is the pressure) connections of the pure component are approximated by Antoine equations:

$$\text{for } n\text{-nonane} \quad \ln P \text{ (Torr)} = 17.01273 - \frac{3964.512}{T(K) - 41.454},$$

$$\text{for 2-hexyn-1-ol} \quad \ln P \text{ (Torr)} = 16.54571 - \frac{3351.641}{T(K) - 105.825}. \quad (2)$$

They are used to correlate and predict VLE.

A polynomial of the type

$$H^E \text{ (Jmol}^{-1}\text{)} = x_1 x_2 \sum_{i=1}^n A_i (x_1 - x_2)^{i-1} \quad (3)$$

was fitted to the experimental H^E data by the least squares method. The coefficients, A_i , are given in Table 4 along with the standard deviations, $\sigma(H^E)$.

The prediction accuracy of the binary VLE data by UNIFAC is shown in Table 5.

The VLE in the systems containing 2-hexyn-1-ol and benzaldehyde were calculated using the group interaction parameters taken from [2, 13]. The following single groups were used: for 2-hexyn-1-ol 1CH₃, 3CH₂, 1C≡C, and 1OH; for benzaldehyde 5ACH, 1AC, and 1CHO. For the system formed by furfural and furfuryl alcohol, group interaction parameters have been obtained in this work. Estimation of the latter was realized using the simplex method, the Nelder-Mead procedure, described by Fredenslund et al. [5].

The equations used are given in the works cited and have therefore not been presented here.

Table 4

Coefficients, A_i , of Eq. (2) and standard deviations, $\sigma(H^E)$

A_0	A_1	A_2	A_3	$\sigma(H^E)$
4087.10	258.51	1322.66	2437.24	9.5

Table 5

Absolute average deviations in the vapor composition ($\overline{\Delta y}$) and total pressure, relative to the experimental values (δP , %) by UNIFAC

System	$\overline{\Delta y}$	δP , %	Source of experimental data
<i>n</i> -Nonane — 2-hexyn-1-ol	0.009*	1.4	this work
Toluene — benzaldehyde	0.022	5.1	[11]
Furfural — furfuryl alcohol	0.022	20.3	[12]

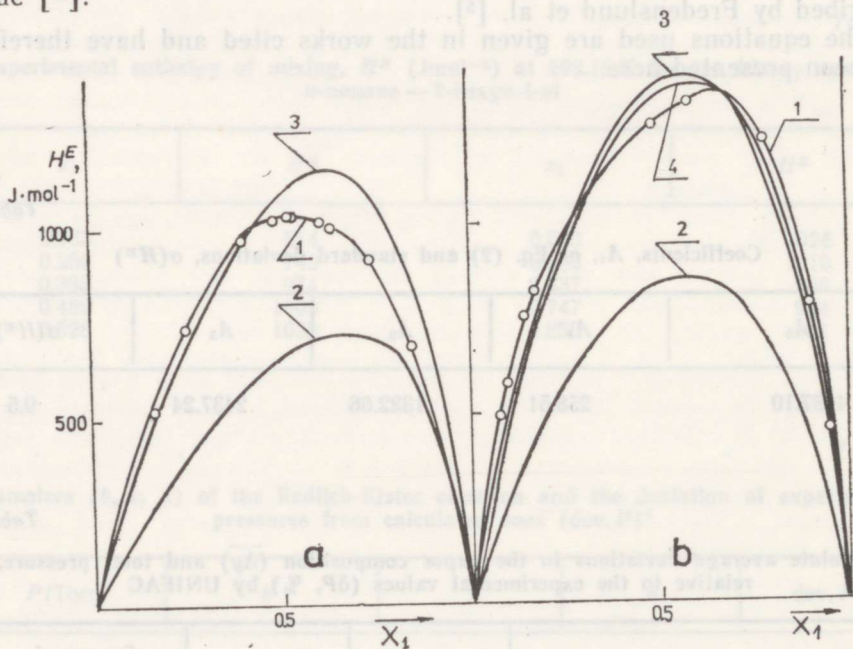
* Compared with Redlich-Kister correlation results.

Azeotropic data for the system *n*-nonane (1) — 2-hexyn-1-ol

Pressure (Torr)	<i>T</i> (K)	Composition (<i>x</i> ₁) calculated by	
		R-K	UNIFAC
200	377.0	0.80	0.81
250	383.4	0.79	0.80
300	388.7	0.78	0.79

The prediction of total pressure in the system *n*-nonane — 2-hexyn-1-ol is around four times worse than the correlations by the Redlich-Kister (R-K) equation (Table 3), whereas the vapor composition prediction can be generally considered good. This system shows positive deviations from Raoult's law and forms an azeotropic mixture. Table 6 presents results of calculating azeotropic composition at different pressures by using R-K and UNIFAC equations.

In the Figure, the H^E predictions by UNIFAC for 2-hexyn-1-ol and benzaldehyde mixtures in *n*-alkanes are compared with the experimental data taken for hexane — benzaldehyde system from literature [14]. The group interaction parameters based on VLE [2, 13] and H^E data [15, 16] are used for predictions in each system. For H^E , a satisfactory agreement with experiment is obtained using the latter parameters only. In addition, benzaldehyde was retained as a special group. The new interaction parameters, $a_{\text{benzal}/\text{CH}_2} = 16.39$ and $a_{\text{CH}_2/\text{benzal}} = 305.87$, were estimated on the experimental H^E data for the system heptane — benzaldehyde [14].



Enthalpies of mixing at 298.15 K.

a — for the system *n*-nonane(1)–2-hexyn-1-ol; o — experimental data (this work); line 1 — calculated by Eq. (3), lines 2 and 3 — predicted by UNIFAC with VLE [2, 3] and H^E [15] group interaction parameters, respectively.

b — for the system *n*-hexane(1)–benzaldehyde; o — experimental data [14]; line 1 — calculated by Eq. (3), lines 2, 3, and 4 — predicted by UNIFAC with VLE parameters [2], with H^E group interaction parameters for single groups [15], and with those for special group for benzaldehyde (this work), respectively.

As seen in the Figure, when these parameters are used for calculations, the accuracy of H^E predictions is similar to that achieved with the interaction parameters for single groups of benzaldehyde [16]. These results together with reasonable VLE predictions using single group parameters (Table 5) give evidence of the lack of any noticeable proximity effect.

The case is similar for the 2-hexyn-1-ol system. As already mentioned, application of the UNIFAC model gives commonly acceptable results for mixtures of simple compounds. Both 2-hexyn-1-ol and benzaldehyde belong to this type.

The third binary system, on the contrary, consists of two complex compounds, furfural (Fald) and furfuryl alcohol (Falc), both containing two strong functional groups in a molecule. In order to reduce the proximity effects to be expected, both the components were regarded as special groups. As shown earlier [17], the definition of larger groups, including strong single ones, is a possible way to improve the UNIFAC predictions in such systems. The new interaction parameters, $a_{\text{Fald/Falc}} = -198.75$ and $a_{\text{Falc/Fald}} = 341.22$, were estimated using the VLE data obtained by Myles and Wingard at the pressure 25 Torr and presented in the collection [18, p. 744]. The total pressure correlation ($\delta P = 1.6\%$) is much better than the prediction of VLE data at 50 Torr (Table 5). It may be due to the discrepancy between the $P-T$ data for pure components obtained by different authors.

The results reported here may serve as a starting point for a further extension of the UNIFAC model which should be able to describe systems of aroma compounds correctly. From data in literature it is evident that a substantial limitation to a systematic investigation is the scantiness of experimental information. For a final selection of more suitable UNIFAC group interaction parameters, it is necessary to obtain and collect high-quality experimental data, especially for complex systems.

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MUDELI UNIFAC RAKENDAMINE AROOMAINOID SISALDAVATE BINAARSETE SÜSTEEMIDE PUHUL

On kontrollitud auru—vedeliku tasakaalu (AVT) ja segunemisentalpia (H^E) ennustamise võimalust grupimudeli UNIFAC abil binaarsete süsteemide näitel. Uuritavad süsteemid olid 2-heksüün-1-ool ja bensaldehyüd süsivesinikega ning furfurool furfuriülalkoholiga. Arvutustes on kasutatud gruppide vastastikmõju parameetreid, mis on saadud nii AVT kui ka H^E andmete alusel.

2-heksüün-1-ooli ja bensaldehyüdi sisaldavate segude AVT ning H^E ennustamisel on saadud usaldusväärseid tulemusi, kasutades nende ühendite molekulides esinevate gruppide vastastikmõju parameetreid. Furfurooli ja furfuriülalkoholi puhul on vaadeldud tervet molekuli kui gruppi, et vältida ennustustulemuste moondumist segunevate komponentide molekulides esineva kahe mittesüsivesinikgruppi vastastikuse nn. lähi-toime tõttu. Nimetatud gruppidele on määratud vastastikmõju parameetrid.

Artiklis on toodud süsteemi 2-heksüün-1-ool—*n*-nonaan katseliselt määratud isobaarilised auru—vedeliku tasakaalu andmed ja segunemisentalpia väärtused temperatuuril 298,15 K.

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ПРИМЕНЕНИЕ МОДЕЛИ УНИФАК К БИНАРНЫМ СИСТЕМАМ, СОДЕРЖАЩИМ ДУШИСТЫЕ СОЕДИНЕНИЯ

На примере бинарных систем, образованных 2-гексин-1-олом и бензальдегидом с углеводородами, а также фурфуролом с фурфуриловым спиртом, проверена возможность предсказания в них равновесия жидкость—пар (РЖП) и энтальпий смешения (H^E) с помощью групповой модели УНИФАК. В расчетах использованы параметры группового взаимодействия, полученные на основе данных как о РЖП, так и об H^E . Установлено, что для смесей 2-гексин-1-ола и бензальдегида, содержащих в молекуле по одной группе, отличной от углеводородной, модель дает надежные результаты предсказания с применением параметров взаимодействия, предложенных для отдельных групп, на которые разбиты молекулы.

Молекулы фурфурола и фурфурилового спирта рассмотрены целиком как специальные группы с целью избежать искажения результатов предсказания, обусловленного т. н. эффектом близости, взаимодействием двух неуглеводородных групп в молекулах смешиваемых компонентов. Определены параметры группового взаимодействия.

Приведены результаты измерения изобарического равновесия жидкость—пар и энтальпий смешения при 298,15 К в системе 2-гексин-1-ол—*n*-нонан.