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*Helle KIRSS*\*, *Mati KUUS*\*, *Enn SIIMER*\*, and  
*Ludmilla KUDRYAVTSEVA*\***MEASUREMENT, CORRELATION, AND PREDICTION OF BINARY  
VAPOUR-LIQUID EQUILIBRIA AND EXCESS ENTHALPIES  
FOR AROMA COMPOUND MIXTURES****Introduction**

The present work, which is part of a study on aroma compounds, is concerned with collecting thermodynamic information needed for their purification. First, we present experimental vapour-liquid equilibria (VLE) and excess enthalpy ( $H^E$ ) data for binary systems containing 2-hexyn-1-ol as a starting component of *trans*-2-hexenal synthesis. Next, we examine the correlation and prediction of VLE and  $H^E$  in the systems investigated by us and other authors. These systems contain alcohols, esters, and unsaturated hydrocarbons. We focus our attention particularly on the  $H^E$  prediction by the UNIFAC group contribution model. In view of the variety of aroma compounds and possible mixtures, a large number of systems should be investigated experimentally in order to have the data needed for a practical design. Therefore, the applicability of this prediction method is of great interest.

**Experimental**

2-Hexyn-1-ol, the starting component of *trans*-2-hexenal synthesis, was prepared in our laboratory[1]. It was fractionally distilled in a Teflon bristle-rotor 50-plate column, as were 1-nonene and 1-hexanol. After distillation, the purity was 99.6%, 99.9%, and 99.6% for 2-hexyn-1-ol, 1-nonene, and 1-hexanol, respectively, as checked by capillary gas-chromatographic analysis. All the mixtures were prepared by weight. The liquid mole fractions,  $x_i$ , were evaluated to be better than 0.0002.

The experimental values of VLE for the binary systems containing 1-hexanol and 2-hexyn-1-ol were obtained using a semi-micro ebulliometer[2]. The  $H^E$  of 1-nonene—2-hexyn-1-ol mixtures were measured with a DAK-1-1 microcalorimeter. The estimated error for the  $H^E$  values was around 2%.

**Results and Discussion**

Results for the VLE of 1-hexanol—2-hexyn-1-ol mixtures are given in Table 1. For the correlation two models were used. They are a three-constant ( $b$ ,  $c$ ,  $d$ ) Redlich-Kister equation as an expression much superior to other ones in correlating VLE binary data, and that of Wilson ( $\Lambda_{12}$ ,  $\Lambda_{21}$ ), which is very useful for predicting VLE in multicomponent mixtures on the basis of binary data alone. The correlation results are presented in Table 2.

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Experimental  $T$ - $x$  data for the binary system 1-hexanol—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
0.152	401.65	407.61	412.66
0.298	399.65	405.57	410.56
0.490	397.23	403.08	407.99
0.665	395.39	401.16	406.03
0.746	394.69	400.42	405.27
0.836	394.03	399.78	404.59
0.890	393.59	399.28	404.05
1.000	392.78	398.44	403.22

Table 2

Parameters of correlation equations and the deviation of experimental pressures from calculated ones ( $\overline{\delta P}$ ) for the system 1-hexanol—2-hexyn-1-ol

$P$ (Torr)	Redlich-Kister				Wilson		
	$b$	$c$	$d$	$\overline{\delta P}$ , %	$\Lambda_{12}$	$\Lambda_{21}$	$\overline{\delta P}$ , %
200	0.0649	0.0691	-0.0214	0.096	1.7886	0.3926	0.170
250	0.0607	0.0639	-0.0173	0.130	1.7751	0.4018	0.190
300	0.0589	0.0642	-0.0152	0.106	1.7887	0.3961	0.164

Table 3

Experimental excess enthalpies,  $H^E$  (Jmol $^{-1}$ ), at 298.15 K for the binary system 1-nonene—2-hexyn-1-ol

$x_1$	$H^E$	$\delta$ , %	$x_1$	$H^E$	$\delta$ , %
0.205	529	0.8	0.503	943	2.1
0.321	813	1.4	0.561	977	0.9
0.339	838	0.8	0.634	975	1.5
0.381	886	0.1	0.668	947	0.4
0.451	932	1.3	0.789	873	0.2

Table 4

Coefficients  $A_i$  in Eq. (2) and an overall average deviation ( $\overline{\delta H^E}$ , %) for 1-nonene—2-hexyn-1-ol mixtures at 298.15 K

$A_0$	$A_1$	$A_2$	$A_3$	$\overline{\delta H^E}$ , %
3847.94	465.60	1290.02	3663.92	0.8

The dependence of the boiling temperature  $T$  of the pure component on the pressure  $P$  was approximated by the Antoine equations:

$$\text{for 1-hexanol: } \ln P \text{ (Torr)} = 18.11993 - \frac{4097.010}{T(K) - 73.242} ; \quad (1)$$

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

They are used for the correlation and prediction of VLE. The prediction of VLE data in the system 1-hexanol—2-hexyn-1-ol by the UNIFAC model with the interaction parameters taken from [3, 4] is good enough:

$P$ (Torr)	$\overline{\delta P}$ (%)
200	0.364
250	0.348
300	0.363

At the pressures considered this binary system is nonazeotropic.

Results for the  $H^E$  of 1-nonene—2-hexyn-1-ol mixtures are given in Table 3. For each mixture, the  $H^E$  were fitted with a smoothing function of a Redlich-Kister type

$$H^E = x_1 x_2 \sum_{i=0}^{n-1} A_i (x_1 - x_2)^i. \quad (2)$$

The coefficients  $A_i$  and the overall average deviations  $\overline{\delta H^E}$  are shown in Table 4.

The  $H^E$  is more difficult to represent with a group contribution model than VLE. In order to obtain a good  $H^E$  prediction using UNIFAC, values of group interaction parameters should be found from the experimental binary  $H^E$  data. In a recent paper [5], a matrix of such parameters is given. It has been shown [6] that the  $H^E$  prediction by UNIFAC may be considerably improved using more suitable values of group surface area parameters,  $Q_s$ . These are normalized on a methylene segment in an infinitely long, linear polymethylene molecule and determined using the data from Bondi tables [7]. Since these parameters enter into the UNIFAC expression for  $H^E$  as multipliers, we have studied the dependence of  $H^E$  correlation quality on the values of  $Q_s$ , changing the multiplication factor  $n$  in the product  $nQ_s$ , where  $Q_s$  is originally normalized.

Fig. 1 shows  $\sigma(H^E)$ , the root mean deviation between experimental and calculated  $H^E$ , as a function of  $n$  for some binary systems. They are  $n$ -alkane mixtures with alcohols (Fig. 1a), esters (Fig. 1b), and unsaturated hydrocarbons (Fig. 1c). Fig. 2 shows the effect of  $n$  values on the  $H^E$  prediction in the system 1-nonene—2-hexyn-1-ol compared with experimental results (see Table 3).

For alcohol mixtures,  $\sigma(H^E)$  changes sharply with increasing  $n$ , showing deep minimum points at  $n=0.79$ , 1.0, and 1.70 (Fig. 1a), when the alcohol groups are characterized by  $Q_{\text{COH}}=1.664$  [8],  $Q_{\text{OH}}=1.200$  [9], and  $Q_{\text{OH}}=0.584$  [8], respectively. Several minimum points for the alcohol systems considered appeared in the process of calculating interaction parameter values. This problem requires further study. For systems containing esters the optimum values of  $n$  depend on the size of the ester group, too (Fig. 1b). Only the quality of  $H^E$  description in the benzoate systems with large  $\text{C}_6\text{H}_5\text{COO}$  groups is practically independent of the  $n$  values. A similar situation is observed for 1-alkene mixtures (Fig. 1c), whereas  $\sigma(H^E) - n$  curves for terminal and internal alkyne mixtures have a steep slope before minimum shifted to  $n > 2$ , as well as a region of weak de-

pendence of  $\sigma(H^E)$  on  $n$  before and after it. The above-said is confirmed by the data presented in Table 5 together with the group interaction parameters used in this work. The  $a_{st}$  ( $a_{ts}$ ) parameters are estimated using the simplex method and the Nelder-Mead procedure described by Fredenslund et al. [8].

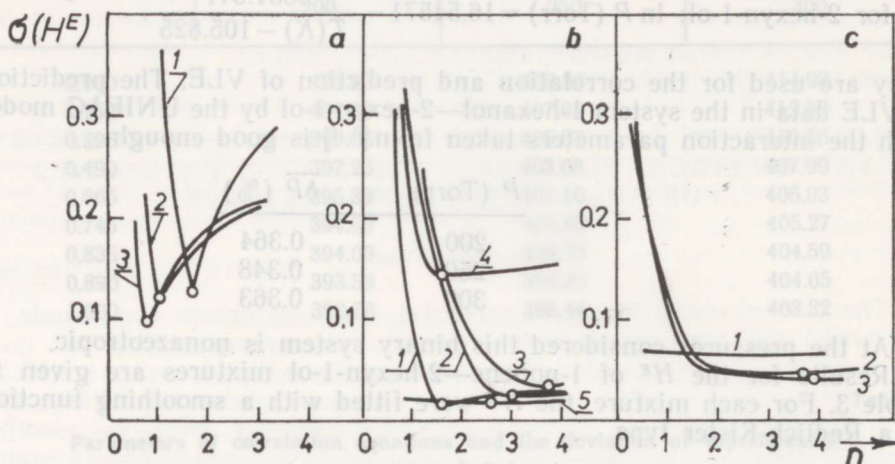


Fig. 1. The root mean deviation,  $\sigma(H^E)^*$ , between experimental excess enthalpy and that calculated by UNIFAC as a function of the multiplication factor  $n$  of group surface area parameters in binary systems of  $n$ -alkanes with other compounds.

*a* — curve 1 — alcohols (OH,  $Q_{OH}=0.584$ ), curve 2 — alcohols (OH,  $Q_{OH}=1.200$ ), curve 3 — alcohols (CCOH,  $Q_{CCOH}=1.664$ );

*b* — curve 1 — methanoates ( $HCOOCH_2$ ), curve 2 — methanoates ( $HCOO$ ), curve 3 — other alkanoates ( $COO$ ), curve 4 — other alkanoates ( $CH_2COO$ ), curve 5 — benzoates ( $C_6H_5COO$ );

*c* — curve 1 — 1-alkenes ( $CH_2=CH$ ), curve 2 — 1-alkynes ( $CH\equiv C$ ), curve 3 — *i*-alkynes ( $C\equiv C$ ); o — a minimum.

\* Relative to the experimental  $H^E$ .

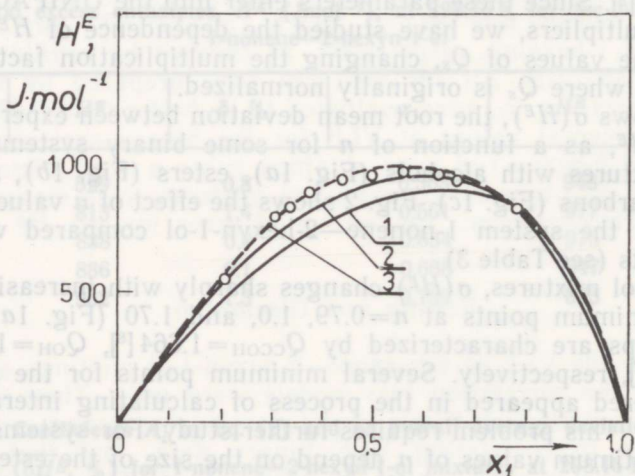


Fig. 2. Excess enthalpies of the system 1-nonene—2-hexyn-1-ol at 298.15 K plotted against the mole fraction of 1-nonene.

o — experimental results; curves 1 and 2 were calculated using UNIFAC with  $n=1$  and  $n=3$ , respectively (—), and curve 3 is calculated by Eq. (2) (-·-·-).

Table 5

UNIFAC group interaction parameters,  $a_{st}$  and  $a_{ts}$ , based on the binary  $H^E$  data, root mean,  $\sigma(H^E)$ , and relative average,  $\bar{\delta}$ , deviations between  $H^E$  experimental and calculated values;  $n$  is the multiplication factor of group surface area parameters,  $Q_s$ , originally normalized<sup>a</sup>

$s$	$t$	$n$	$a_{st}$	$a_{ts}$	$\sigma(H^E)$	$\bar{\delta}$ , %	Number of data sets
CH <sub>2</sub>	CH <sub>2</sub> =CH	1	45.48	24.09	0.068	4.6	6
		2	25.71	8.78	0.068	4.6	
		3	18.39	4.65	0.068	4.6	
CH <sub>2</sub>	CH≡C	1	456.64	181.46	0.094	7.0	10
		2	250.85	142.08	0.048	3.1	
		3	197.41	19.37	0.046	3.0	
CH <sub>2</sub>	C≡C	1	501.16	166.83	0.102	8.2	7
		2	298.13	118.91	0.049	4.1	
		3	239.64	4.24	0.046	3.9	
CH <sub>2</sub>	OH	1	981.13	190.98	0.110	8.4	10
		2	549.93	-158.61	0.195	15.3	
		3	459.84	-169.83	0.214	16.4	
CH <sub>2</sub>	COO	1	686.32	175.16	0.388	35.8	12
		2	432.51	184.23	0.104	8.4	
		3	297.86	194.63	0.038	2.9	
CH <sub>2</sub>	HCOO	1	656.90	182.43	0.441	42.2	7
		2	446.34	192.85	0.061	4.6	
		3	315.67	566.93	0.024	1.7	
CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> COO	1	200.18	93.42	0.041	2.9	4
		2	127.77	2.83	0.039	3.0	
		3	105.68	-17.90	0.039	3.0	
CH <sub>2</sub> =C	OH	1	827.44	359.69	0.135	10.4	6
		2	2609.60	1.48	0.178	15.0	
		3	471.02	-137.87	0.193	15.4	
C≡C	OH	1	690.81	612.74	0.194	15.9	3
		2	903.49	389.06	0.157	12.3	
		3	1007.80	106.96	0.146	11.8	
OH	COO	1	581.89	554.40	0.219	20.3	4
		2	452.78	1409.51	0.065	5.1	
		3	203.07	372.95	0.074	6.0	
OH	HCOO	1	542.42	541.76	0.188	17.1	4
		3	205.17	494.40	0.025	2.0	
ACH	COO	1	128.01	-22.68	0.091	5.4	1
		3	80.25	111.77	0.088	6.0	
CH <sub>2</sub> =CH	C≡C	1	145.08	104.31	0.071	5.5	2
		3	149.26	-69.24	0.074	5.5	

<sup>a</sup> The alcohol groups OH are characterized by  $Q_{OH}=1.200$  [9] when  $n=1$ .

The  $H^E$  prediction is characterized by data given in Table 6.

Many observations can be made concerning the prediction results of this work. Firstly, in 1-alkene systems (Nos. 1–3) the deviations between experimental and predicted data increase with increasing molecule length, due probably to the molecular orientation<sup>[15]</sup>. Secondly, for the best  $H^E$  prediction the group specification selected here has to be taken into account; ignoring that it would lead to a failure in  $H^E$  prediction (systems

Table 6

Estimation of  $H^E$  prediction quality using the UNIFAC model with  $H^E$  data fitted parameters.  $n$  is the multiplication factor of group surface area parameters,  $Q_s$ , originally normalized

No.	$n$	$\sigma(H^E)$	$\bar{\delta}$ , %	
1	3	<i>n</i> -Hexane–1-heptene [10]	2.8	
		0.039		
2	3	<i>n</i> -Decane–1-decene [5]	4.0	
		0.054		
3	3	<i>n</i> -Dodecane–1-heptene [5]	19.4	
		0.257		
4	3	<i>n</i> -Hexane–1-heptyne [10]	2.8	
		0.036		
5	1	<i>n</i> -Decane–1-hexyne [14]	12.8	
			2	1.0
			3	1.1
6	3	<i>n</i> -Decane–3-hexyne [14]	7.0	
			0.088	
7	2.16	<i>n</i> -Octane–2-octyne [12]	52.3 <sup>a</sup>	
			0.562 <sup>a</sup>	
8	3	<i>n</i> -Alkane–alkyl benzoate (4 data sets [13])	52.5 <sup>b</sup>	
			0.536 <sup>b</sup>	
9	1	<i>n</i> -Nonane–2-hexyn-1-ol [1]	11.2	
			2	11.0
			3	9.9
10	1	1-Nonene–2-hexyn-1-ol	10.7	
			3	5.3
11	1	1-Octyne–ethanol [14]	16.0	
			2	12.6
			3	19.1
12	1	Butyl methanoate–1-butanol [10]	10.8	
			3	5.0
13	1	Butyl methanoate–1-pentanol [10]	11.7	
			3	4.4

<sup>a</sup> Results of  $H^E$  calculation are obtained with HC≡C/CH<sub>2</sub> group interaction parameters.

<sup>b</sup> Results of  $H^E$  calculation are obtained with COO/CH<sub>2</sub> group interaction parameters.

7 and 8). Thirdly, for most systems considered reasonable results are obtained using the group interaction parameters corresponding to the treble values of  $Q_s$  originally normalized. And fourthly, the  $H^E$  prediction results are obtained for systems containing both one pair of groups (Nos. 1—7) and several pairs of them (Nos. 8—13). The extension of  $H^E$  model calculations to components other than alkanes is important and of interest as the first step to obtain reasonable results by using interaction parameters of arbitrary group pairs.

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**AURU-VEDELIKU TASAKAALU JA SEGUNEMISENTALPIATE MÖÖTMINE, KORRELATSIOON JA ENNUSTAMINE AROOMAINEID SISALDAVATES BINAARSETES SÜSTEEMIDES**

On toodud isobaarilise auru-vedeliku tasakaalu (AVT) ja segunemisentalpiate ( $H^E$ ) eksperimentaalse uurimise tulemused 298,15 K juures binaarsetes süsteemides 1-heksool—2-heksüün-1-ool ja 1-noneen—2-heksüün-1-ool ning nende korrelatsioon Redlichi-Kisteri (AVT ja  $H^E$ ) ja Wilsoni (AVT) võrrandiga. On näidatud, et UNIFAC'i grupimudeli abil saab usaldusväärset ennustada alkohole, estreid ja küllastumata süsivesinikke sisaldavate süsteemide  $H^E$  väärtusi, kui kasutada eksperimentaalse segunemisentalpiate alusel arvutatud vastastikmõju parameetreid ning arvestada sobivaimaid gruppide pinnaparameetreite väärtusi.

Хелле КИРСС, Мати КУУС, Энн СИИМЕР, Людмила КУДРЯВЦЕВА

**ИЗМЕРЕНИЕ, КОРРЕЛЯЦИЯ И ПРЕДСКАЗАНИЕ РАВНОВЕСИЯ ЖИДКОСТЬ—ПАР И ЭНТАЛЬПИЙ СМЕШЕНИЯ В БИНАРНЫХ СИСТЕМАХ ДУШИСТЫХ ВЕЩЕСТВ**

Приведены результаты экспериментального исследования изобарического равновесия жидкость—пар (РЖП) и энтальпий смешения ( $H^E$ ) при 298,15 К в бинарных системах 1-гексанол—2-гексин-1-ол и 1-нонен—2-гексин-1-ол и их корреляции с помощью уравнений Редлиха—Кистера (РЖП и  $H^E$ ) и Вильсона (РЖП). Показана возможность надежного предсказания  $H^E$  в системах, содержащих спирты, сложные эфиры и ненасыщенные углеводороды, с помощью групповой модели УНИФАК, параметры взаимодействия которой определены по данным об энтальпиях смешения с учетом наиболее пригодных значений поверхностных параметров групп.