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## EFFECT OF MOLECULAR STRUCTURE ON THE EXCESS ENTHALPIES OF MIXTURES WITH UNSATURATED HYDROCARBONS

(Presented by O. Eisen)

In this work excess enthalpies,  $H^E$ , for unsaturated hydrocarbon mixtures with some solvents of different polarity have been measured. We aimed at making a comparison between experimental results for the binary mixtures containing unsaturated hydrocarbons of different structure.

A survey of literature revealed that experimental data are very scarce for this class of mixtures. At present the lack of suitable experimental results hinders the interpretation and prediction of  $H^E$  for the above mixtures using the models under development.

### Experimental

The procedure using a differential microcalorimeter has been described in [1]. The errors of the observed values were lower than 2 per cent over the whole mole fraction range. For all the mixtures investigated in this work, except 2-octyne—1-octanol,  $H^E$  was measured at 298.15 K only and at atmospheric pressure. For the 2-octyne—1-octanol mixtures the results at 318.15 K have been given too.

*cis*-4-Octene, methylcyclohexene, ethylcyclopentene, butylcyclopentene and isomeric octynes were synthesized in our laboratory\* and fractionally distilled in a 50-plate Teflon bristle-rotor column [2] to 98,6 per cent and higher purity as detected by gas liquid chromatography on PEG-20M and Squalan capillary columns using H flame ionization detector. Reference should be made to earlier papers [3-5].

*n*-Heptane, *n*-nonane, 1-propanol («puriss grade») were purchased from Reakhim (USSR) and used without further purification.

Cyclohexane, 1-butanol, 2-propen-1-ol, 1-octanol, ketones and dimethyl sulphoxide («pure grade») were twice fractionally distilled with the same column to 99.8 per cent and higher estimated from their capillary chromatograms.

### Results and discussion

Table 1 presents experimental results for the molar excess enthalpies of the 24 binary systems formed by mixing methylcyclohexene and ethylcyclopentene with *n*-heptane, butylcyclopentene with *n*-nonane, *cis*-4-octene and methylcyclohexene with cyclohexane, 1-octene and 1-octyne with ethylbenzene, methylcyclohexene, 1-octene, 1-octyne and 2-octyne with methyl butyl ketone, 1-octene with methyl isobutyl ketone, 1-octene with

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Experimental excess molar enthalpies  $H^E$  (J·mol<sup>-1</sup>) at 298.15 K

Table 1

$x_1$	$H^E$	$x_1$	$H^E$	$x_1$	$H^E$
<b>1. 1-Methylcyclohexene (1)—<i>n</i>-heptane (2)</b>					
0.104	33	0.505	163	0.152	-96
0.192	63	0.515	164	0.176	-113
0.255	64	0.576	149	0.278	-146
0.320	75	0.672	119	0.338	-159
0.417	94	0.756	89	0.387	-153
0.468	98	<b>6. 1-Octene (1)—ethylbenzene (2)</b>			
0.532	86	0.065	60	0.611	-117
0.735	80	0.136	148	0.616	-113
0.884	38	0.198	193	0.733	-87
<b>2. 1-Ethylcyclopentene (1)—<i>n</i>-heptane (2)</b>					
0.071	18	0.225	215	<b>11. 1-Octyne (1)—methyl butyl ketone (2)</b>	
0.123	30	0.340	277	0.114	76
0.173	40	0.438	297	0.178	144
0.270	54	0.469	296	0.199	152
0.370	65	0.523	299	0.244	193
0.445	74	0.602	281	0.373	267
0.498	75	0.676	253	0.609	308
0.604	73	0.680	239	0.628	303
0.605	72	0.718	231	0.694	284
0.614	73	0.814	164	0.836	190
0.670	62	0.880	110	0.886	155
0.716	58	<b>7. 1-Octyne (1)—ethylbenzene (2)</b>			
0.944	9	0.087	-15	<b>13. 1-Octyne (1)—1-propanol (2)</b>	
<b>3. 1-Butylcyclopentene (1)—<i>n</i>-nonane (2)</b>					
0.114	31	0.174	-25	0.514	909
0.146	34	0.270	-33	0.533	936
0.152	34	0.352	-38	0.595	961
0.242	50	0.481	-41	0.717	940
0.361	62	0.590	-40	<b>14. 1-Octene (1)—2-propen-1-ol (2)</b>	
0.466	68	0.674	-33	0.141	414
0.517	68	0.802	-24	0.318	577
0.654	63	0.821	-22	0.436	786
0.722	55	<b>8. 1-Octene (1)—methyl butyl ketone (2)</b>			
0.854	34	0.360	640	0.543	813
0.886	31	0.405	706	0.554	849
0.970	8	0.520	753	0.572	865
<b>4. 1-Methylcyclohexene (1)—cyclohexane (2)</b>					
0.125	63	0.543	755	0.785	782
0.216	106	<b>9. 1-Octene (1)—methyl isobutyl ketone (2)</b>			
0.363	118	0.126	298	0.866	659
0.469	134	0.176	366	<b>15. 1-Butylcyclopentene (1)—1-butanol (2)</b>	
0.552	127	0.300	565	0.055	72
0.570	120	0.322	612	0.270	378
0.750	87	0.322	612	0.401	506
0.870	45	0.556	705	0.490	581
<b>5. <i>cis</i>-4-Octene (1)—cyclohexane (2)</b>					
0.146	117	0.611	688	0.501	584
0.184	129	0.716	643	0.706	627
0.189	133	0.748	603	0.859	460
0.262	158	0.851	457	<b>16. 1-Octyne (1)—1-butanol (2)</b>	
0.403	168	<b>10. 1-Methylcyclohexene (1)—methyl butyl ketone (2)</b>			
0.411	174	0.142	250	0.112	230
0.474	168	0.225	383	0.247	524
0.490	168	0.414	573	0.395	805
<b>6. 1-Octene (1)—ethylbenzene (2)</b>					
<b>7. 1-Octyne (1)—ethylbenzene (2)</b>					
<b>8. 1-Octene (1)—methyl butyl ketone (2)</b>					
<b>9. 1-Octene (1)—methyl isobutyl ketone (2)</b>					
<b>10. 1-Methylcyclohexene (1)—methyl butyl ketone (2)</b>					
<b>11. 1-Octyne (1)—methyl butyl ketone (2)</b>					
<b>12. 2-Octyne (1)—methyl butyl ketone (2)</b>					
<b>13. 1-Octyne (1)—1-propanol (2)</b>					
<b>14. 1-Octene (1)—2-propen-1-ol (2)</b>					
<b>15. 1-Butylcyclopentene (1)—1-butanol (2)</b>					
<b>16. 1-Octyne (1)—1-butanol (2)</b>					

Table 1  
Continued

$x_1$	$H^E$	$x_1$	$H^E$	$x_1$	$H^E$
17. 2-Octyne (1)—1-butanol (2)		0.840	835	0.070	232
		0.920	650	0.111	323
0.150	374			0.233	458
0.264	632	20. 2-Octyne (1)—1-octanol (2)		0.389	472
0.468	920			0.473	469
0.576	1019	0.439	842	0.675	396
0.596	1024	0.681	1017	0.693	389
0.622	1045	$T=318.15\text{ K}$		0.794	312
0.727	1008	0.388	1047	0.852	274
0.854	952	0.507	1183	0.912	209
0.875	725	0.601	1253	0.933	169
0.898	707	0.635	1290		
		0.641	1296	23. 1-Nonyne (1)—dimethyl sulphoxide (2)	
18. 1-Octene (1)—1-octanol (2)		0.730	1277		
		0.874	1059	0.080	350
0.100	131			0.206	565
0.381	461	21. 1-Octene (1)—dimethyl sulphoxide (2)		0.403	652
0.443	526			0.647	493
0.620	601	0.029	203	0.762	373
0.640	598	0.038	210		
0.720	598	0.063	214	24. 2-Octyne (1)—dimethyl sulphoxide (2)	
0.771	591	0.335	222		
0.846	566	0.452	225	0.033	213
0.883	518	0.542	224	0.069	382
		0.779	231	0.122	658
19. 1-Octyne (1)—1-octanol (2)		0.829	234	0.158	895
		0.929	236	0.225	861
0.399	739	0.942	237	0.439	854
0.450	812	0.984	155	0.493	842
0.501	854			0.788	807
0.665	990	22. 1-Octyne (1)—dimethyl sulphoxide (2)		0.808	789
0.718	959			0.818	742
0.757	938	0.022	90	0.866	540
0.800	894	0.065	216		

2-propen-1-ol, 1-octyne with 1-propanol, butylcyclopentene, 1-octyne and 2-octyne with 1-butanol, 1-octene, 1-octyne and 2-octyne with 1-octanol, 1-octene, 1-octyne, 2-octyne and 1-nonyne with dimethyl sulphoxide (DMS). In all cases  $x_1$  denotes the mole fraction of unsaturated hydrocarbon in the binary.

The results were fitted with the following equation

$$H^E (\text{J}\cdot\text{mol}^{-1}) = x_1 x_2 \sum_{p=1}^n A_p (x_1 - x_2)^{p-1} \quad (1)$$

The values of the coefficients  $A_p$ , determined by the least squares method, and standard deviation  $\sigma$  are summarized in Table 2. Smooth representations of the results and experimental points for systems with cyclohexane, ketones, alkanols and DMS are also presented in Figs 1—4 together with the curves and points taken from our previous works [6, 7] (Figs 1 and 3b).

In our earlier work we have measured the excess enthalpies of  $n$ -alkane mixtures with  $n$ -alkenes and  $n$ -alkynes [1, 8, 9]. The excess enthalpies of the alkyl cyclene mixtures with  $n$ -alkane (Table 1, Nos 1—3) with a given number of carbon atoms are higher than those of  $n$ -alkene mixtures ( $H^E_{x=0.5} = 49 \text{ J}\cdot\text{mol}^{-1}$  for 1-heptene— $n$ -heptane [9]) and much lower than those of  $n$ -alkyne mixtures ( $H^E_{x=0.5} = 555 \text{ J}\cdot\text{mol}^{-1}$  for 1-heptyne— $n$ -heptane [8]). In such systems, with increasing number of carbon atoms in the cyclene molecule the  $H^E$  increases. The opposite is observed with the cyclene alkyl length.

Parameters  $A_p$  of equation (1) and standard deviations  $\sigma^*$ 

System	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma$
1-Methylcyclohexene (1)— <i>n</i> -heptane (2)	380.0	49.6	-12.0	-73.6	6.5
1-Ethylcyclopentene (1)— <i>n</i> -heptane (2)	301.9	4.1	-95.2	-72.2	2.9
1-Butylcyclopentene (1)— <i>n</i> -nonane (2)	271.2	31.6	20.9	-60.7	1.9
1-Methylcyclohexene (1)—cyclohexane (2)	520.1	124.0	-34.0	3.7	7.1
<i>cis</i> -4-Octene (1)—cyclohexane (2)	658.2	-277.2	-31.4	-231.8	2.4
1-Octene (1)—ethylbenzene (2)	1213.6	-230.8	-195.1	316.9	6.8
1-Octyne (1)—ethylbenzene (2)	-162.6	10.8	3.7	24.2	1.1
1-Octene (1)—methyl isobutyl ketone (2)	2801.3	385.5	640.0	601.8	13.7
1-Methylcyclohexene (1)—methyl butyl ketone (2)	2444.0	670.5	642.0	601.4	20.9
1-Octyne (1)—methyl butyl ketone (2)	-564.1	410.3	-125.1	-445.7	3.0
2-Octyne (1)—methyl butyl ketone (2)	1243.7	188.8	-167.6	470.5	6.2
1-Butylcyclopentene (1)—1-butanol (2)	2345.3	1185.8	712.3	651.5	5.7
1-Octene (1)—1-octanol (2)	2141.1	678.8	1855.6	2625.5	20.5
1-Octyne (1)—1-butanol (2)	3743.1	2085.0	986.8	872.9	5.9
2-Octyne (1)—1-butanol (2)	3808.5	1822.4	2225.7	1972.4	49.5
1-Octyne (1)—dimethyl sulphoxide (2)	1747.2	581.6	1860.1	3.5	12.8
2-Octyne (1)—dimethyl sulphoxide (2)	5268.8	-1874.1	876.5	1811.0	33.4**

\* For alkanol systems for  $x_1=0$  to 0.9 only.

\*\* For homogeneous region only.

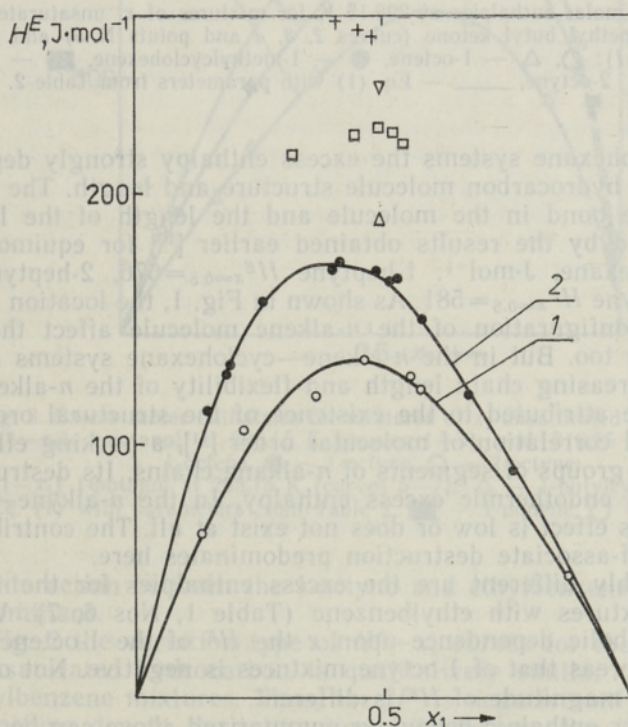


Fig. 1. Excess molar enthalpies at 298.15 K for mixtures of  $x_1$  unsaturated hydrocarbons with  $(1-x_1)$  cyclohexane: ● — *cis*-4-octene (curve 2), ○ — 1-methylcyclohexene (curve 1), △ — *trans*-4-octene [6], □ — 1-heptene [6], △ — 1-octene [6], + — 1-nonen [9], — — Eq. (1) with parameters from Table 2.

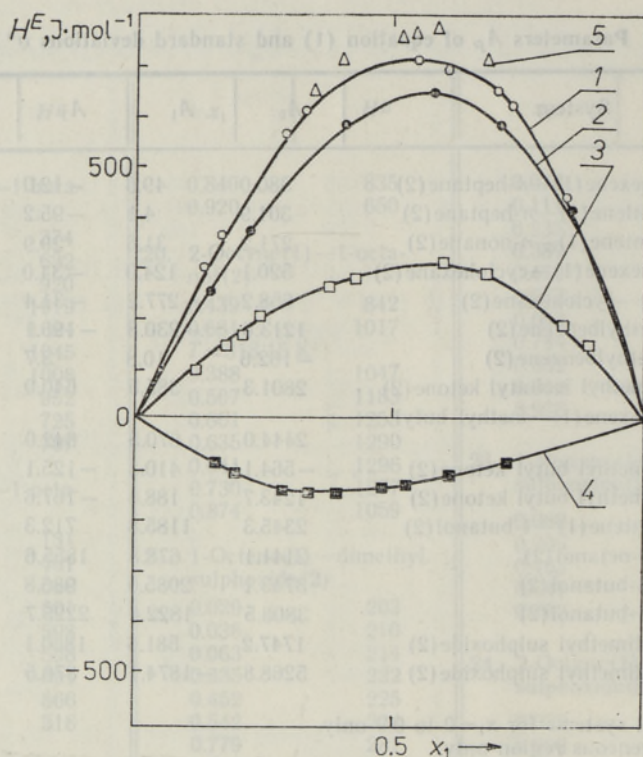


Fig. 2. Excess molar enthalpies at 298.15 K for mixtures of  $x_1$  unsaturated hydrocarbons with  $(1-x_1)$  methyl butyl ketone (curves 2, 3, 4 and points N 5) and methyl isobutyl ketone (curve 1):  $\circ$ ,  $\Delta$  — 1-octene,  $\bullet$  — 1-methylcyclohexene,  $\blacksquare$  — 1-octyne,  $\square$  — 2-octyne, — — Eq. (1) with parameters from Table 2.

For cyclohexane systems the excess enthalpy strongly depends on the unsaturated hydrocarbon molecule structure and length. The strong effect of the triple bond in the molecule and the length of the latter can be demonstrated by the results obtained earlier [10] for equimolar mixtures with cyclohexane,  $\text{J}\cdot\text{mol}^{-1}$ : 1-heptyne  $H^E_{x=0.5} = 676$ , 2-heptyne  $H^E_{x=0.5} = 515$ , 1-octyne  $H^E_{x=0.5} = 581$ . As shown in Fig. 1, the location of the double bond and configuration of the  $n$ -alkene molecule affect the  $H^E$  values significantly too. But in the  $n$ -alkene—cyclohexane systems  $H^E$  increases with the increasing chain length and flexibility of the  $n$ -alkene molecule. This may be attributed to the existence of the structural ordering effect, the so-called correlation of molecular order [11], a packing effect favoured between the groups of segments of  $n$ -alkane chains. Its destruction contributes to the endothermic excess enthalpy. In the  $n$ -alkyne—cyclohexane mixtures this effect is low or does not exist at all. The contribution of the  $n$ -alkyne self-associate destruction predominates here.

Remarkably different are the excess enthalpies for the 1-octene and 1-octyne mixtures with ethylbenzene (Table 1, Nos 6, 7). With a more or less parabolic dependence upon  $x$  the  $H^E$  of the 1-octene mixtures is positive, whereas that of 1-octyne mixtures is negative. Not only the sign but also the magnitude of  $H^E$  is different.

The excess enthalpic behaviour summarized above can be qualitatively explained by postulating that  $H^E$  is the resultant of two opposing effects: the breaking of self-associates and structural order leads to endothermic contribution and the exothermic one arises from interactions between unlike molecules. In the 1-octyne—ethylbenzene system the contribution

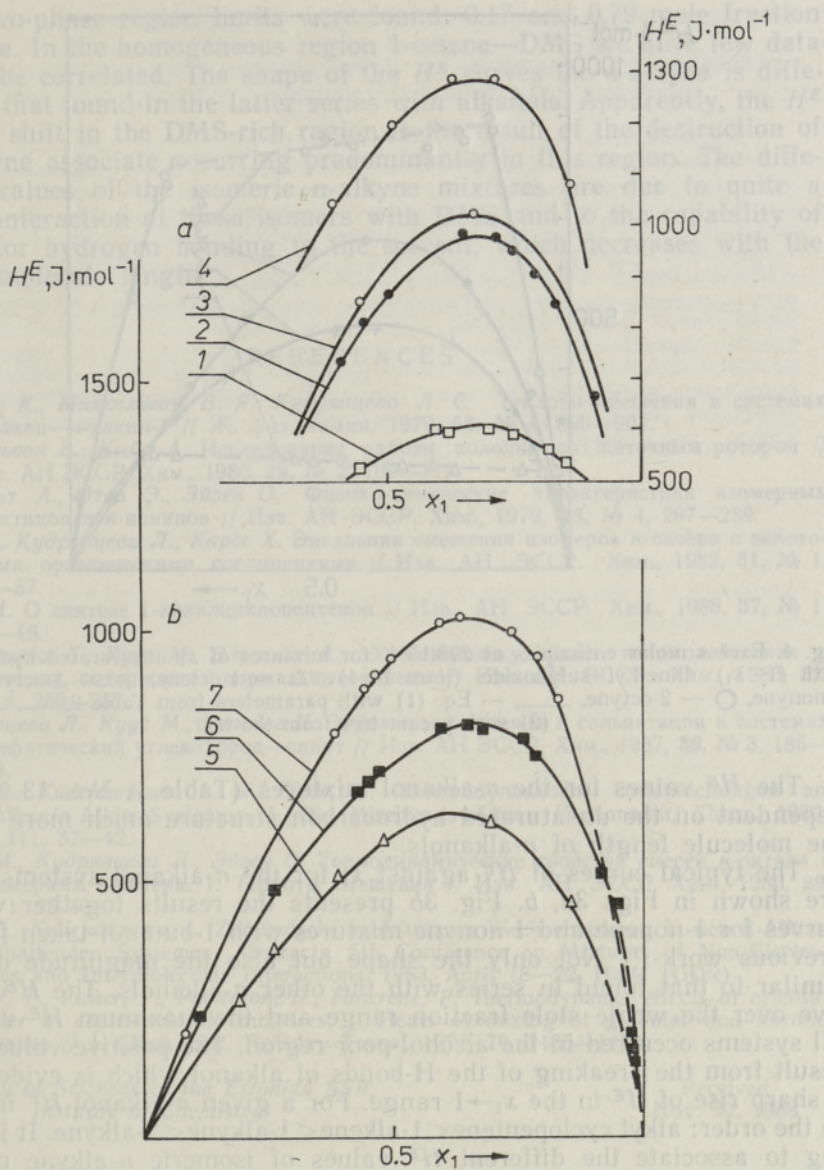


Fig. 3. Excess molar enthalpies for mixtures of  $x_1$  unsaturated hydrocarbons  
 a) with  $(1-x_1)$  1-octanol at 298.15 K (curves 1–3) and 318.15 K (curve 4):  $\square$  —  
 1-octene,  $\bullet$  — 1-octyne,  $\circ$  — 2-octyne;  
 b) with  $(1-x_1)$  1-butanol at 298.15 K (curves 5–7):  $\triangle$  — 1-butylcyclopentene, — —  
 Eq. (1) with parameters from Table 2,  $\blacksquare$  — 1-nonene,  $\circ$  — 1-nonyne.

of the interaction between the 1-octyne and ethylbenzene molecules to  $H^E$  is predominant.

In Fig. 2 the variation type of  $H^E-x_1$  curves for the ketone mixtures with unsaturated hydrocarbon is qualitatively similar to that found for the ethylbenzene mixtures. Thus, the  $H^E$  is negative only for the mixture with 1-octyne due to the interaction with ketone. For the mixtures with other components the  $H^E$  is positive, decreasing in the order 1-octene > methylcyclohexene > 2-octyne. The positive values of  $H^E$  in the 2-octyne mixtures result from the breaking of associates which predominates over the whole concentration range.

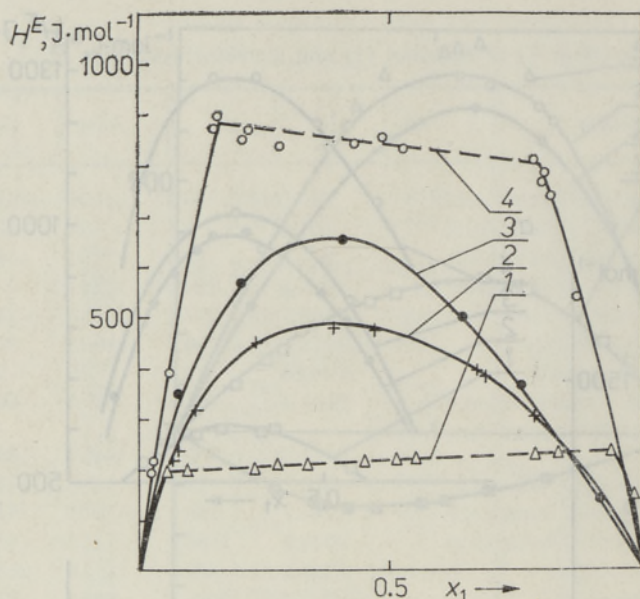


Fig. 4. Excess molar enthalpies at 298.15 K for mixtures of  $x_1$  unsaturated hydrocarbons with  $(1-x_1)$  dimethyl sulphoxide (lines 1–4):  $\Delta$  — 1-octene, + — 1-octyne,  $\bullet$  — 1-nonyne,  $\circ$  — 2-octyne, — — — Eq. (1) with parameters from Table 2, — — — Eq. (2) with parameters from the text.

The  $H^E$  values for the  $n$ -alkanol mixtures (Table 1, Nos 13–20) are dependent on the unsaturated hydrocarbon structure much more than on the molecule length of  $n$ -alkanols.

The typical curves of  $H^E$  against  $x_1$  for the  $n$ -alkanol systems studied are shown in Figs 3a, b. Fig. 3b presents the results together with the curves for 1-nonene and 1-nonyne mixtures with 1-butanol taken from our previous work [7]. Not only the shape but also the magnitude of  $H^E$  is similar to that found in series with the other  $n$ -alkanols. The  $H^E$  is positive over the whole mole fraction range and the maximum  $H^E$  value for all systems occurred in the alcohol-poor region. The positive values of  $H^E$  result from the breaking of the H-bonds of alkanol which is evident from a sharp rise of  $H^E$  in the  $x_1 \rightarrow 1$  range. For a given  $n$ -alkanol  $H^E$  increases in the order: alkyl cyclopentene < 1-alkene < 1-alkyne < 2-alkyne. It is tempting to associate the different  $H^E$  values of isomeric  $n$ -alkyne mixtures with the different interactions of these isomers with  $n$ -alkanol, taking into account the change in  $H^E$  in the cyclohexane series.

As noted for the other unsaturated hydrocarbon—alkanol mixtures [7], equation (1) does not represent the experimental results of  $H^E$  very closely for  $x_1$  values higher than 0.9. In the present work each set of results was fitted using equation (1) only in the  $x_1 = 0.0$ –0.9 range. Data on  $H^E$  were few for 1-octyne—1-propanol and 2-octyne—1-octanol to be fitted.

In the DMS series (Table 1, Nos 21–24) the  $H^E$  is positive for all the mixtures and as it can be seen in Fig. 4, the systems containing 1-octene and 2-octyne have a central immiscibility gap. The results in this two-phase region are represented by the linear form

$$H^E (\text{J}\cdot\text{mol}^{-1}) = b_0 + b_1 x_1, \quad (2)$$

where  $b_0 = 207.3$ ,  $b_1 = 31.6$ ,  $\sigma = 2.2$  and  $b_0 = 919.8$ ,  $b_1 = -178.1$ ,  $\sigma = 20.7$  for 1-octene and 2-octyne mixtures with DMS respectively. The results for the two homogeneous regions of 2-octyne—DMS were combined and fitted by a smoothing function (1). By simultaneous solution of equations (1) and

(2) the two-phase region limits were found: 0.17 and 0.79 mole fraction of 2-octyne. In the homogeneous region 1-octene—DMS we have few data on  $H^E$  to be correlated. The shape of the  $H^E$  curves for  $n$ -alkyne is different from that found in the latter series with alkanols. Apparently, the  $H^E$  maximum shift in the DMS-rich region is the result of the destruction of the  $n$ -alkyne associate occurring predominantly in this region. The different  $H^E$  values of the isomeric  $n$ -alkyne mixtures are due to quite a different interaction of these isomers with DMS and to the capability of 1-alkyne for hydrogen bonding to the solvent, which decreases with the  $n$ -alkyne molecule length.

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#### MOLEKULI STRUKTUURI MÕJU KÜLLASTUMATUID SÜSIVESINIKKE SISALDAVATE SEGUDE LIIGENTALPIATELE

Mikrokalorimeetris DAK-1-1 on määratud temperatuuril 298,15 K liigentalpiad  $H^E$  24 binaarse süsteemi jaoks:  $n$ -heptaan 1-metüülsüklohekseeni ja 1-etüülsüklopenteeni;  $n$ -nonaan 1-butüülsüklopenteeni; tsükloheksaan 1-metüülsüklohekseeni ja *cis*-4-okteeni; etüülbenseen 1-okteeni ja 1-oktüüniga; metüülbutüülketoon 1-metüülsüklohekseeni, 1-okteeni, 1-oktüüni ja 2-oktüüniga; metüülisobutüülketoon 1-okteeniga; 2-propeen-1-ool 1-okteeniga; 1-propanool 1-oktüüniga; 1-butanool 1-butüülsüklopenteeni, 1-oktüüni ja 2-oktüüniga; 1-oktanool 1-okteeni, 1-oktüüni ja 2-oktüüniga; dimetüülsulfoksiid 1-okteeni, 1-oktüüni, 2-oktüüni ja 1-nonüüniga. Süsteemides dimetüülsulfoksiid—1-okteen ja dimetüülsulfoksiid—2-oktüün on vedel faas kihistunud. Homogeensete lahuste  $H^E$  sõltuvus kontsentratsioonist on aproksimeeritud Redlichi-Kisteri võrandiga, heterogeenses piirkonnas aga sirge võrandiga. On näidatud, et iga lahusti puhul sõltuvad liigentalpiad küllastumatute süsivesinike molekulide kujust ja suurusest, küllastumuse astmest ja kordse sideme asukohast molekulis.



### ВЛИЯНИЕ МОЛЕКУЛЯРНОЙ СТРУКТУРЫ НА ИЗБЫТОЧНЫЕ ЭНТАЛЬПИИ СМЕСЕЙ С НЕНАСЫЩЕННЫМИ УГЛЕВОДОРОДАМИ

В микрокалориметре ДАК-1-1 при 298,15 К определены энтальпии смешения,  $H_E$ , в 24 бинарных системах, образованных 1-метилциклогексеном и 1-этилциклопентеном с *n*-гептаном, 1-бутилциклопентеном с *n*-нонаном, 1-метилциклогексеном и *цис*-4-октенем с циклогексаном, 1-октенем и 1-октином с этилбензолом, 1-метилциклогексеном, 1-октенем, 1-октином и 2-октином с метилбутилкетонем, 1-октенем с метилизобутилкетонем, 1-октенем с 2-пропен-1-олом, 1-октином с 1-пропанолом, 1-бутилциклопентеном, 1-октином и 2-октином с 1-бутанолом, 1-октенем, 1-октином, 2-октином с 1-октанолом, 1-октенем, 1-октином, 2-октином и 1-нонином с диметилсульфоксидом (ДМС). В системах, образованных ДМС с 1-октенем и 2-октином, жидкая фаза расслаивается. Концентрационная зависимость  $H_E$  гомогенных растворов аппроксимирована уравнением Редлиха—Кистера, гетерогенной области — уравнением прямой линии. Показано, что избыточные энтальпии смесей данного растворителя с ненасыщенными углеводородами зависят от формы и величины молекул последних, их степени ненасыщенности и поло-жения в них кратной связи.