novalent ions and trivalent ions were increasing in proportion to two powers of C_0.

(7) α_{Na}^M became constant although each value of x, y, C_0, and Q_0 was changed.

(8) $(\alpha_A^M Q_0^{-1})_{other}((\alpha_A^M Q_0^{-1})_{Neosepta})^{-1}$ was constant giving the average value of 0.34 between monovalent ions and bivalent ions, and $(\alpha_A^M)_{other}((\alpha_A^M)_{Neosepta})^{-1}$ was a constant value of 1.06 between monovalent ions.

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Nomenclature

a: concentration of NaOH solution (meq cm^{-3})
b: volume of NaOH solution (cm^3)
C: concentration of the total ions in solution (meq cm^{-3})
c: concentration of each ion in solution (meq cm^{-3})
E_c: exchange capacity per weight of dry membrane (meq g^{-1})
K_{Na}^M: selectivity coefficient of M^{n+} ions relative to Na$^+$ ions between membrane and solution
m: amounts of each ion (meq)
Δm: value difference between $m_{i,M}$ and m_M or $m_{i,Na}$ and m_{Na} (meq)
Q: concentration of total ions, that is, the exchange capacity per volume of dry membrane (meq cm^{-3})
q: concentration of each ion in membrane (meq cm^{-3})
v: volume of mixture solution with M^{n+} ions and Na$^+$ ions (cm^3)
W_c: water content (–)
w: weight of dry membrane (g)
x: dimensionless concentration of M^{n+} ions in solution (–)
y: dimensionless concentration of M^{n+} ions in membrane (–)

Greek Letters

α_{Na}^M: separation factor (–)
ρ: density of dry membrane (g cm^{-3})

Superscripts

M: M^{n+} ion
n: valence of M^{n+} ion
–: in the membrane

Subscripts

A: A$^+$ ion
i: initial
M: M^{n+} ion
Neosepta: Neosepta cation exchange membrane
other: Selemion or Nafion cation exchange membrane
0: total ions

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Thermodynamics of Binary Mixtures Containing Alkenes. 1. Excess Enthalpies of Some Alkenes and Polyenes + n-Heptane or Cyclohexane Mixtures[†]

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A flow microcalorimeter had been used to measure the excess enthalpies, H^E, as a function of concentration at atmospheric pressure and 298.15 K for some binary liquid mixtures containing alkenes and polyenes with n-heptane or cyclohexane. The values of H^E are small and positive: This behavior is attributed to interactions between the π electrons of the double bonds, on the analogy of π–π interactions between the aromatic hydrocarbon molecules.

Introduction

This work is part of a systematic study of the thermodynamic properties of liquid organic mixtures, the TOM-Project (1–4) with the purpose of characterizing the type and magnitude of molecular interactions in binary liquid mixtures and to improve the group contribution models currently used to predict thermodynamic excess functions.

Although there is a great industrial interest about the alkenes, their mixtures had been relatively little studied. Recently Woycicki (5), Letcher (6), and Ghassemi et al. (7) have started a more systematic study about the excess enthalpies of the mixtures containing alkenes. In order to verify and to complete the literature data and to better characterize the behavior of the C=C group, we decide to measure, in a systematic way, H^E for mixtures of alkenes: 2-hexene (cis), 2-hexene (trans), 3-hexene (trans), 1-octene, 1-decene, and 1,7-octadiene with n-heptane or cyclohexane.

Experimental Section

The molar liquid phase molar excess enthalpy, H^E, was determined by means of a flow microcalorimeter (model 2277, LKB-Producer AB, Bromme, Sweden). The detailed description
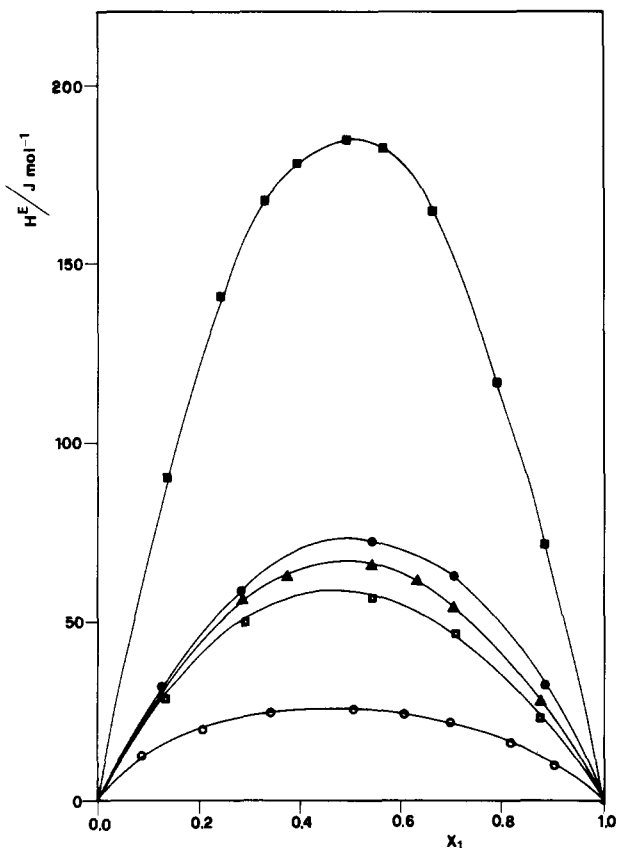
Figure 1. Molar excess enthalpies, H^E, at 298.15 K of alkenes (1) + n-heptane (2) mixtures vs x_1, the mole fraction of alkene: O, 1-decene; ●, 2-hexene (cis); ▲, 3-hexene (trans); □, 2-hexene (trans); ■, 1,7-octadiene.

of this apparatus and experimental procedure are described elsewhere (8).

Full automatic burets (ABU, from Radiometer Copenhagen) were used to pump the liquid into the LKB unit; volume of cylinder 2.5 cm³. The accuracy of the buret calibration was 0.5%.

All measurements were carried out at 298.15 ± 0.10 K. The accuracy of the LKB bath temperature is 0.1 K.

The reliabilities of the apparatus and procedure adopted were checked by performing H^E measurements on the test system benzene + cyclohexane.

Our results differed by <2% from literature data (9) over the entire composition range.

The molar excess enthalpies, H^E, evaluated from the formula

$$H^E = I^2 R(E/E_c)/\dot{n} \qquad (1)$$

where I and R are the electrical current and resistance in the electrical calibration experiment, E and E_c are the voltage readings for measurement and electrical calibration, and $\dot{n}$ is the molar flow rate of the mixture. The molar flow rate $\dot{n}_i$ of component i flowing into the mixing cell is given by

$$\dot{n}_i = \frac{\rho_i}{M_i} V_i^{\circ} F \qquad (2)$$

where ρ_i and M_i are density and molecular weight, V_i° is the molar volume of component i, and F is the actual percent of the buret flow rate selected between two references values (F values from 2.5 to 0.25 cm³ min⁻¹).

The densities were determined with a vibrating densimeter (model DMA 602 Anton Paar) within ±1.5 × 10⁻⁶ g/cm³ at 298.15 K and were found in good agreement with values published in the literature (see Table I).

Table I. Experimental Measurements of Liquid Density ρ

	$\rho/(\text{g mol}^{-1})$		
component	this work	lit.	ref
cyclohexane	0.773 89	0.773 85	13
n-heptane	0.679 46	0.679 48	13
2-hexene (cis)	0.682 43	0.687 00	13
2-hexene (trans)	0.674 96	0.677 00	13
3-hexene (trans)	0.679 03	0.677 00	13
1-octene	0.710 85	0.710 85	13
1-decene	0.736 94	0.736 93	13
1,7-octadiene	0.727 08	0.730 00	13

Table II. Experimental Molar Excess Enthalpies, H^E, at 298.15 K for Binary Mixtures of Alkenes or Polyenes + n-Heptane or Cyclohexane

x_1	$H^E/(\text{J mol}^{-1})$	x_1	$H^E/(\text{J mol}^{-1})$	x_1	$H^E/(\text{J mol}^{-1})$
		x_1 2-Hexene (cis) + x_2 n-Heptane			
0.1304	32.8	0.5454	72.7	0.8781	32.5
0.2856	59.2	0.7058	62.7		
		x_1 2-Hexene (trans) + x_2 n-Heptane			
0.1294	30.0	0.5432	56.6	0.8771	24.1
0.2838	50.7	0.7040	47.1		
		x_1 3-Hexene (trans) + x_2 n-Heptane			
0.1292	32.7	0.5427	65.7	0.7036	54.7
0.2835	57.2	0.6403	61.7	0.8769	28.7
0.3724	63.1				
		x_1 1-Decene + x_2 n-Heptane			
0.1144	13.2	0.3406	24.7	0.6992	23.0
0.2053	19.6	0.5081	26.7	0.8230	16.7
0.2053	20.2	0.6078	25.0	0.9029	9.9
		x_1 1,7-Octadiene + x_2 n-Heptane			
0.1401	91.3	0.3945	178.6	0.6616	164.7
0.2457	141.9	0.4955	185.6	0.7963	117.3
0.3283	168.4	0.5670	182.8	0.8866	72.2
		x_1 2-Hexene (cis) + x_2 Cyclohexane			
0.0993	87.1	0.3981	193.0	0.7015	135.4
0.3060	182.3	0.4684	191.1	0.7710	105.2
		x_1 2-Hexene (trans) + x_2 Cyclohexane			
0.0988	97.0	0.3047	198.1	0.7004	143.4
0.2261	174.0	0.4671	208.6	0.7761	110.0
		x_1 3-Hexene (trans) + x_2 Cyclohexane			
0.0986	78.3	0.3043	160.3	0.7000	117.8
0.2258	140.2	0.4667	165.2	0.8400	61.7
		x_1 1-Octene + x_2 Cyclohexane			
0.1030	131.7	0.4079	257.4	0.6739	195.8
0.1867	198.1	0.4887	254.0	0.8052	133.2
0.3147	250.4	0.5794	231.1	0.8921	81.7
		x_1 1,7-Octadiene + x_2 Cyclohexane			
0.1073	150.4	0.4187	333.3	0.6937	255.7
0.1938	235.5	0.4899	331.7	0.8192	165.6
0.3246	311.5	0.6016	300.9	0.8966	98.4

All liquids were of the best quality available from Fluka (AG, puriss. grade). The estimated purities as determined by liquid chromatographic analysis were better than 99.5% for cyclohexane, n-heptane, 1-octene, 1-decene, and 1,7-octadiene and better than 98% for 2-hexene (cis), 2-hexene (trans), and 3-hexene (trans).

The experimental H^E values reported in Table II were fitted to the smoothing equation

$$H^E_{\text{calc}}/(\text{J mol}^{-1}) = x_1 x_2 \sum a_i (x_1 - x_2)^i \qquad (3)$$

where x_1 is the mole fraction of alkene and x_2 the mole fraction of n-alkane or cyclohexane.

The values of the coefficients a_i and the standard deviation $\sigma(H^E)$

$$\sigma(H^E) = [\sum (H^E_{\text{calc}} - H^E)^2/(N - n)]^{1/2} \qquad (4)$$
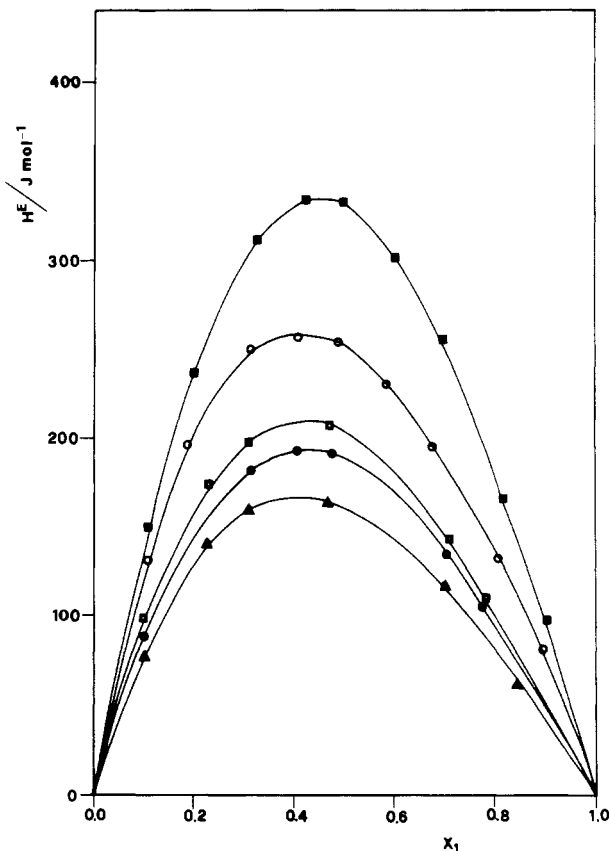
Figure 2. Molar excess enthalpies, H^E, at 298.15 K of alkenes (1) + cyclohexane (2) mixtures vs x_1, the mole fraction of alkene: ▲, 3-hexene (trans); ●, 2-hexene (cis); □, 2-hexene (trans); ○, 1-octene; ■, 1,7-octadiene.

where N is the number of experimental points and n the number of coefficients a_i, determined by a least-squares fit, are reported in Table III.

Discussion

As shown in Figures 1 and 2 the values of H^E are positive and small. The relatively small values of H^E for the mixtures containing 1-alkenes added to n-heptane compared with those of benzene added to n-alkanes, can be explained partly by the conjugated double bonds in benzene. The interest in this study of the polyenes is to determine with cumulated, conjugated, and isolated double bonds.

We think that more positive values H^E of 2-alkenes (cis) than 1-alkanes are due to the inductive effect of the CH_3 on the electronic density of the double bond.

The smaller values of H^E *ans*-2-alkenes compared with 1-alkanes are explained by the steric effect; in fact the π–π interactions will take place more easly between two isomers

Table III. Values of Coefficients a_i in Equation 3 and Standard Deviations $\sigma(H^E)$ (Equation 4) of Experimental Molar Excess Enthalpies H^E for Alkenes or Polyenes (1) + n-Heptane or Cyclohexane (2)

component 1	component 2	a_0	a_1	a_2	$\sigma(H^E)/(J\ mol^{-1})$
2-hexene (cis)	heptane	295	11		0.5
2-hexene (cis)	cyclohexane	754	−264		0.8
2-hexene (trans)	heptane	236	−30		1.0
2-hexene (trans)	cyclohexane	814	−327		1.0
3-hexene (trans)	heptane	270	−17		1.0
3-hexene (trans)	cyclohexane	654	−266		2.1
1-octene	cyclohexane	997	−364	209	1.1
1-decene	heptane	111	−7		1.1
1,7-octadiene	heptane	745	−33		1.1
1,7-octadiene	cyclohexane	1319	−309		0.9

cis than trans. The inductive effect is indicated by the ionized potential of the alkenes (*10*, *11*):

$$I/eV \quad 10.62 \qquad 9.72 \qquad 9.26$$

$$9.27 \qquad 8.89 \qquad 8.53$$
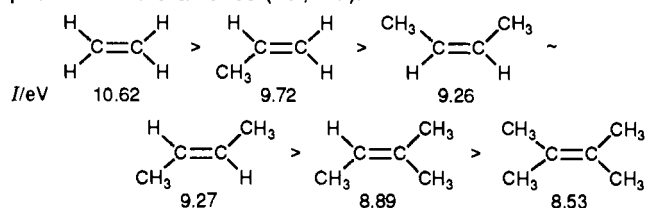
Similar conclusions can be reached for cyclohexane mixtures with the alkenes. H^E is higher by about 100 J mol^{-1} at the maximum than the corresponding values for n-heptane. That may be attributed to dispersive aliphatic–cycloaliphatic interactions. In this connection, it is worth remembering that, for n-heptane + cyclohexane, H^E (x_1 = 0.5) at 298.15 K is about 240 J mol^{-1} (*12*).

A detailed interpretation of these results in terms of the DISQUAC group contribution model (*4*) will be presented separately.

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