

Thermodynamics of Binary Mixtures Containing Alkynes

I. Excess Enthalpies of Binary Mixtures of 1-Hexyne and 3-Hexyne With Some Hydrocarbons at 298.15 K.*

By

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With 2 Figures

(Received July 6, 1977)

Molar excess enthalpies H^E of 1-hexyne + *n*-heptane, + *n*-decane, + cyclohexane, and + benzene, and of 3-hexyne + *n*-heptane, + *n*-decane, + cyclohexane, and + benzene, at 298.15 K and atmospheric pressure were measured with a Picker type flow microcalorimeter. Generally, the 1-hexyne systems are more endothermic than the corresponding 3-hexyne systems, the increment of H_{\max}^E being of the order of 170 to 260 J/mol, which is clearly too large to be accounted for by orientational contributions to H^E due to the permanent dipole moment of 1-hexyne. It is suggested that other contributions, for example contributions resulting from different conformational behavior of the hexynes, have to be considered.

1. Introduction

Systematic investigation of thermodynamic behavior of binary liquid mixtures containing *n*-alkanes, alkenes, alicyclic and aromatic hydrocarbons has made considerable progress as evidenced by recent review articles¹ and original papers^{2, 3}. This is sharply contrasted by the scarcity of reliable data on systems containing acetylenic hydrocarbons. Aside from solubility data on several gaseous alkynes in

* Dedicated to Prof. *H. Nowotny* on the occasion of his 65th birthday. Communicated in part at the 2. Ulmer Kalorimetrietage, March 24–25, 1977, Ulm, Germany.

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liquids⁴ and some solid—liquid phase diagrams for systems alkyne + HCl⁵, only very few papers have dealt with thermodynamic properties of mixtures of alkynes with organic solvents (Copley and Holley⁶, Prausnitz et al.^{7, 8}, Desplanches et al.⁹). In particular, the almost complete absence of enthalpy of mixing data represents a major obstacle for an improved understanding of the influence exerted by a carbon—carbon triple bond upon the overall thermodynamics of binary alkyne systems.

It is well known that unsaturated organic compounds may act as proton acceptors in hydrogen bonds^{10–12}. The relative basicity of acetylenes has been determined by spectroscopic methods, that is by measuring e.g. the shift of the phenol O—H stretching frequency upon hydrogen bonding to the alkyne^{11, 12}. Conversely, terminal acetylenes may act also as hydrogen bonding acids^{11, 13–17}, as evidenced by the shift of the acetylenic C—H stretching frequency when mixed with compounds of sufficient basicity. The fact that terminal alkynes have both proton donating and proton accepting abilities suggests that association via intermolecular hydrogen bonds might take place in the pure compounds. Although some spectral evidence for association has indeed been presented^{11, 13, 14, 16, 18}, it appears however, that such hydrogen bonds are exceedingly weak, with only a very slight effect upon the gross physical properties of 1-alkynes*.

* In this context, a comparison of enthalpies of vaporization data is highly illustrative. Contrary to expectancy, ΔH_{vap} at 25 °C is smaller for 1-hexyne (32.10 kJ/mol), than for 3-hexyne (34.99 kJ/mol). These values correspond to almost equal thermal expansivities and a slightly larger molar volume of 1-hexyne (at 25 °C, $V = 115.44 \times 10^{-6} \text{ m}^3/\text{mol}$ and $\alpha = 1.41 \times 10^{-3} \text{ K}^{-1}$ for 1-hexyne, and $V = 114.16 \times 10^{-6} \text{ m}^3/\text{mol}$ and $\alpha = 1.39 \times 10^{-3} \text{ K}^{-1}$ for 3-hexyne). The respective normal boiling points are 71.3 °C vs. 81.4 °C. Enthalpies of vaporization were calculated from the Antoine equation⁹ (1-hexyne), and from the vapor pressure data reported by Hirth, Harris, and Prausnitz⁸ (3-hexyne). Real gas corrections were applied by assuming for the second virial coefficient $B = -1700 \text{ cm}^3 \text{ mol}^{-1}$ at 298.15 K in both cases. The increment in ΔH_{vap} is 2.9 kJ/mol, in agreement with the increments observed with lower homologs¹⁹. The considerably smaller cohesive energy density of 1-hexyne ascertains that other factors, such as geometrical factors involved in packing, contribute significantly more to the thermodynamic behavior of the pure 1-alkyne than intermolecular hydrogen bonding. Intuitively, this is to be expected, since 3-hexyne is a more rigid and elongated molecule as compared to 1-hexyne with its flexible "tail". A further indication as to the importance of steric factors is the influence of branching upon ΔH_{vap} . Comparison of various pentyne at their respective boiling points shows that the branched isomer 3-methyl-1-butyne possesses the lowest enthalpy of vaporization (26.15 kJ/mol at 26.34 °C) as compared to 1-pentyne (27.74 kJ/mol at 40.17 °C) and 2-pentyne (29.25 kJ/mol at 56.06 °C).

In view of the possible interaction in binary mixtures of the second component with the π -electron system and/or the active hydrogen in 1-alkynes, a comparative calorimetric study involving 1-hexyne and 3-hexyne is of considerable importance (*Kehiaian*¹). It is against this background that we measured the enthalpy of mixing of each of these two compounds with *n*-heptane, *n*-decane, cyclohexane and benzene, respectively. In particular, the *n*-alkanes and cyclohexane were selected to establish something like a "reference mixing behavior", since it may be safely assumed that these hydrocarbons are sufficiently inert as to preclude any specific interactions such as hydrogen bonds and charge-transfer complexes (see, for example²⁰). A paper dealing with hexyne mixtures containing more polar second components is in preparation²¹.

2. Experimental Part

All calorimetric measurements were performed with a dynamic flow microcalorimeter of the Picker type^{22, 23}. Compared to some earlier versions of the apparatus, several improvements in design and operational technique have been implemented²⁴, of which only a rather condensed outline will be presented.

In order to prevent corrosion of parts of the bent-axis rotary pumps²³, that is specifically the small Viton O-rings situated on the sliding Teflon tubings which serve as injection pistons, we utilized a new device called a *separator*. For each component this separator consists of a circular cell divided into two compartments by a thin, flexible Teflon membrane, which is carefully tested as to the absence of mechanical deficiencies. By pumping water into one of the compartments, an equal volume of substance is pushed out from the other directly into the mixing circuit of the calorimeter. The calorimeter itself was used in the *discontinuous* mode, resulting in considerably greater precision of both measured excess enthalpy and concentration as compared to the scanning mode.

The calorimeter was thermostated to ± 1 mK as checked by a Hewlett-Packard quartz thermometer, with a possible maximum absolute inaccuracy of the temperature reading of ± 5 mK. All liquids were degassed before being transferred to the separator.

Primary experimental results, that is volumetric excess enthalpy S^E at volume fraction ϕ_1 of hexyne, are easily converted to the more conventional enthalpy of mixing H^E at mole fraction x_1 by the following relations:

$$H^E = V_1 V_2 S^E / (\phi_1 V_2 + \phi_2 V_1) \quad (1)$$

$$1/x_1 = 1 - V_1/V_2 + V_1/(\phi_1 V_2) \quad (2)$$

Here, V_1 and V_2 are the molar volumes of the pure liquids. All molar quantities are based on the relative atomic mass table 1971 as issued by IUPAC²⁵. Specifically, $A_r(\text{H}) = 1.0079$, $A_r(\text{C}) = 12.011$, and $A_r(\text{Cl}) = 35.453$.

1-Hexyne and 3-hexyne (Koch Light, puriss. $\geq 99\%$ and pure, 99% by GLC), *n*-heptane, cyclohexane, benzene and CCl_4 (Fluka, puriss. $\geq 99.5\%$), and *n*-decane (Philips Research Grade) were carefully dried with

Table 1. Comparison of molar excess enthalpies H^E at 298.15 K of the system carbon tetrachloride (x_1) + benzene (x_2) with the results of Stokes, Marsh, and Tomlins²⁷. The last column contains the differences δ between their values²⁷ and ours

x_1	H^E/Jmol^{-1}		δ/Jmol^{-1}
	This work	Lit. ²⁷	
0.1558	64.12	64.57	— 0.45
0.3366	105.19	105.20	— 0.01
0.4206	114.02	113.45	0.57
0.6959	98.37	97.48	0.89
0.8367	62.49	63.47	— 0.98

Table 2. Molar excess enthalpies H^E of 1-hexyne (x_1) + hydrocarbon (x_2) and 3-hexyne (x_1) + hydrocarbon (x_2) at 298.15 K and atmospheric pressure

1-hexyne (x_1) +							
n-heptane		n-decane		cyclohexane		benzene	
x_1	H^E/Jmol^{-1}	x_1	H^E/Jmol^{-1}	x_1	H^E/Jmol^{-1}	x_1	H^E/Jmol^{-1}
0.0665	158.3	0.0864	210.9	0.0499	163.4	0.0414	26.2 ₉
0.2201	434.2	0.2726	554.1	0.1722	470.8	0.1461	81.8 ₀
0.3169	558.7	0.3813	685.5	0.2549	610.3	0.2195	107.8 ₁
0.4134	627.2	0.4835	743.5	0.3420	695.8	0.2993	125.8 ₅
0.5043	647.2	0.5747	747.3	0.4286	729.4	0.3815	134.2 ₀
0.5887	623.4	0.6554	703.9	0.5135	714.6	0.4646	133.6 ₀
0.7493	485.2	0.7989	518.1	0.6879	600.2	0.6444	110.3 ₉
0.8695	297.3	0.8985	303.1	0.8309	383.2	0.8016	70.6 ₄
0.9545	119.2	0.9654	109.7	0.9393	157.7	0.9271	27.4 ₁
3-hexyne (x_1) +							
n-heptane		n-decane		cyclohexane		benzene	
x_1	H^E/Jmol^{-1}	x_1	H^E/Jmol^{-1}	x_1	H^E/Jmol^{-1}	x_1	H^E/Jmol^{-1}
0.0672	113.1	0.1259	219.7	0.0504	102.0	0.0418	0.47
0.2220	306.5	0.3771	502.4	0.1738	300.0	0.0711	0.07
0.3193	390.4	0.5750	555.7	0.2570	386.5	0.1475	— 4.13
0.4161	439.4	0.7406	461.0	0.3445	441.7	0.2214	— 10.71
0.5071	455.3	0.8740	281.4	0.4314	466.5	0.3017	— 17.94
0.5914	439.6	0.9715	74.5	0.5163	457.9	0.3841	— 24.63
0.6715	402.9			0.6903	376.1	0.4674	— 29.54
0.7514	344.0			0.8324	238.0	0.5535	— 32.28
0.8708	210.3			0.9399	95.3	0.6470	— 32.11
0.9550	80.0					0.7422	— 28.21
						0.8033	— 24.10
						0.9279	— 11.28

molecular sieve [Union Carbide Type 4 A, 8×12 mesh (beads), from Fluka] and used directly without further purification. Densities of the pure degassed solvents were determined with a precision density meter (SODEV, Sherbrooke, Canada) and are in good agreement with reliable literature data²⁶. In particular, for the hexynes at 298.15 K we obtained $\rho_{1-H} = 711.61 \text{ kg/m}^3$ and $\rho_{3-H} = 719.58 \text{ kg/m}^3$, respectively.

3. Results and Discussion

All excess enthalpy data were subjected to least squares polynomial smoothing, i.e. they were fitted to

$$H^E/\text{J mol}^{-1} = x_1 x_2 \sum_{i=0}^{n-1} A_i (x_1 - x_2)^i. \quad (3)$$

The standard deviation σ was calculated from $\sigma^2 = \Sigma (H^E - H_{\text{calc}}^E)^2 / (N - n)$, where H_{calc}^E denotes the excess enthalpy as computed with the aid of Eq. (3) at mole fraction x_1 ; N is the total number of experimental points, and n is the number of adjustable coefficients A_i .

A routine check of the performance of the calorimeter utilizing the standard system carbon tetrachloride (x_1) + benzene (x_2) yielded results which are in excellent accord with the most reliable literature data. Our results agree with those of *Stokes, Marsh, and Tomlins*²⁷ within 1 per cent or 1 J/mol, whichever is greater (Table 1).

Table 3. Values of coefficients A_i in Eq. (3) determined by method of least squares, and standard deviation σ , all at 298.15 K

System	A_0	A_1	A_2	A_3	$\frac{\sigma}{\text{Jmol}^{-1}}$
1-hexyne (x_1) + <i>n</i> -heptane (x_2)	2581.0	38.5			3.78
+ <i>n</i> -decane (x_2)	2991.9	401.7			1.96
+ cyclohexane (x_2)	2903.7	— 446.4	295.0		4.87
+ benzene (x_2)		527.9	— 162.0	27.5	0.77
3-hexyne (x_1) + <i>n</i> -heptane (x_2)	1814.6	53.0			1.46
+ <i>n</i> -decane (x_2)	2216.5	357.0	99.4		1.96
+ cyclohexane (x_2)	1853.6	— 291.2	101.8		1.92
+ benzene (x_2)	— 123.62	— 68.38	55.7	— 39	0.14

Table 2 contains experimental excess enthalpies at 298.15 K and atmospheric pressure for the eight binary mixtures 1-hexyne (x_1) + *n*-heptane, + *n*-decane, + cyclohexane, + benzene, and 3-hexyne (x_1) + *n*-heptane, + *n*-decane, + cyclohexane, + benzene. All the parameters A_i of the fitting equations are given in Table 3, together

with the standard deviation of the fit in each case. The internal inconsistency as characterized by σ is in general considerably less than ± 1 per cent of the maximum value H_{\max}^E . As an example, a graphical representation of the experimental results in the systems 1-hexyne (x_1) + benzene, and 3-hexyne (x_1) + benzene is given in Fig. 1.

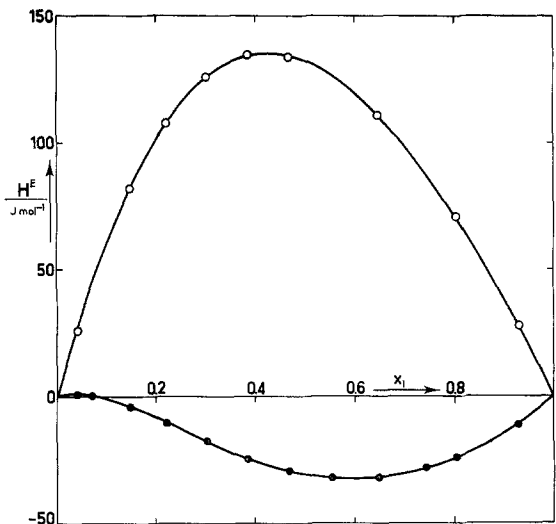


Fig. 1. Experimental values of the molar excess enthalpy H^E at 298.15 K for 1-hexyne (x_1) + benzene (○), and of 3-hexyne (x_1) + benzene (●). The curves are calculated from Eq. (3) with coefficients from Table 3

On the basis of the group contributinal approach of *Kehiaian et al.*² excess enthalpies for the alkane systems have been calculated:

$$H^E = x_1 x_2 \frac{q_1 q_2}{q_1 x_1 + q_2 x_2} h^*, \quad (4)$$

with q_i ($i = 1$ or 2) being suitably reduced molecular surfaces. Generally, the enthalpic interaction parameter h^* is given by

$$h^* = -\frac{1}{2} \sum_s \sum_t (\alpha_{1s} - \alpha_{2s}) (\alpha_{1t} - \alpha_{2t}) h_{st}^*, \quad (5)$$

where h_{st}^* denotes the molar interchange enthalpy, and α_{is} and α_{it} represent the "surface fraction" of type s and type t surfaces on molecule i , respectively, that is $\alpha_{is} = q_{is}/q_i$ etc. For the systems hexyne (1) + n -alkane (2), Eq. (5) simplifies to

$$h^* = \alpha_{1t}^2 h_{at}^*, \quad (6)$$

where α_{1i} is the fraction of molecular surface occupied by an acetylenic bond ($-\text{C}\equiv\text{C}-$ or $\text{CH}\equiv\text{C}-$), and h_{at}^* is the aliphatic (*a*)—acetylenic (*t*) interchange enthalpy*. As can be seen from Fig. 2, agreement with experiment is good, the experimental curves showing a somewhat higher symmetry than the calculated curves.

A convenient starting point for further discussion is the difference in excess enthalpy between two corresponding hexyne systems. With

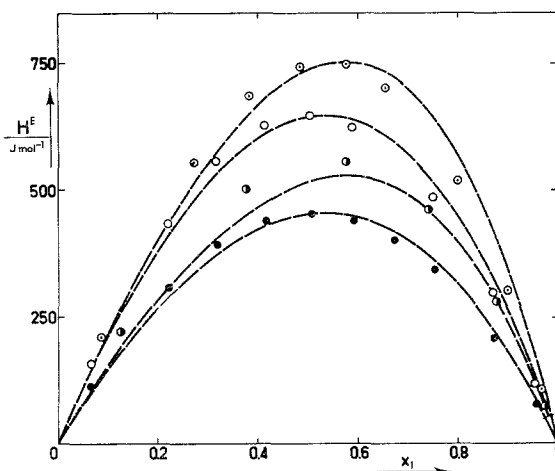


Fig. 2. Comparison of theory with experiment for the molar excess enthalpy of 1-hexyne (x_1) + *n*-heptane (○), + *n*-decane (◐), and of 3-hexyne (x_1) + *n*-heptane (●), + *n*-decane (◑).

Broken lines signify calculated results, points denote experimental values

all four hydrocarbons, $\Delta = H_{\text{max}}^E$ (1-hexyne system) — H_{max}^E (3-hexyne system) is rather large and positive, i.e. ca. 170 to 260 J/mol. Since the position of the acetylenic bond results in a zero dipole moment ($\vec{\mu}_3 = 0$) of 3-hexyne, in contrast to $\vec{\mu}_1 = 0.83$ D for 1-hexyne²⁸, these differences might be attributed, as a first guess, to the

* Following the simple geometrical arguments of Ref.², we assumed $q(\text{CH}\equiv\text{C}-) = 1.125$, and $q(-\text{C}\equiv\text{C}-) = 1.0$, as compared to $q(\text{CH}_3-) = 0.875$ and $q(-\text{CH}_2-) = 0.750$. Consequently, for 1-hexyne $\alpha_{1t} = 0.2647$ is obtained, and for 3-hexyne $\alpha_{1t} = 0.2353$. This information suffices to fix the interchange enthalpy parameter h_{at}^* by utilizing the experimental results, say, at $x_1 = 0.5$ of 1-hexyne (x_1) + *n*-heptane (x_2), in conjunction with the theoretical expressions Eq. (4) and (6). Such a parameter should then be applicable within the homologous series 1-hexyne + *n*-alkane. For the two hexyne series we obtained $h_{at}^*(1\text{-hexyne}) = 7650$ J/mol, and $h_{at}^*(3\text{-hexyne}) = 6800$ J/mol.

difference in polarity. Thus, deviations are expected to be less endothermic in 3-hexyne systems than in 1-hexyne systems. In order to obtain some crude estimate of the orientational effect we adopted the simple approach of *Pople*²⁹, which, despite all its shortcomings, will serve our present purpose. The excess free energy of mixing may be written as the sum of two contributions $F^E = F_{\text{cent}}^E + F_{\text{or}}^E$, where F_{cent}^E is the excess free energy arising from interaction via central forces, and F_{or}^E is the additional free energy resulting from orientational forces. If only one of the components is polar, and moments other than dipole moments are neglected, we obtain as a first approximation

$$H_{\text{or}}^E/RT \approx 2 F_{\text{or}}^E/RT \approx 2.4 x_1 (1 - x_1) (N_A \bar{\mu}_1^2/VkT)^2. \quad (7)$$

For the system 1-hexyne (x_1) + *n*-heptane (x_2) at equimolar concentration, H_{or}^E amounts to 9 J/mol, which is clearly much too small to account for the observed differences. Hence, the greatest part of the increments Δ must be due to other contributions, such as different conformational behaviour of the hexynes (geometrical contributions, see above) and/or different multipole interaction.

If the absolute values of H^E are considered, the benzene systems differ significantly from the other hydrocarbon mixtures, in that H_{max}^E is rather small for 1-hexyne (135 J/mol) and even negative for 3-hexyne (−33 J/mol). This behaviour can be rationalized with the aid of the NMR investigation of *Hatton* and *Richards*¹⁵. Their data suggest weak association in alkyne/benzene systems, favoring collisions in which the axis of the solute is parallel to the plane of the aromatic ring. This configuration should be easier attainable for 3-hexyne than for 1-hexyne (see above).

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