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Thermodynamics of Binary Mixtures Containing Alkynes. II[a]

Excess Enthalpies of Binary Mixtures of 1-Hexyne and 3-Hexyne With Carbon Tetrachloride, Dipropyl Ether, and Triethylamine at 298.15 K

Emmerich Wilhelm*

Institut für Physikalische Chemie, Universität Wien, A-1090 Wien, Austria

A. Inglese[b], J.-P. E. Grolier*, and H. V. Kehiaian*

Centre de Recherches de Microcalorimétrie et de Thermochimie du CNRS, Section de Thermodynamique des Alliages et des Mélanges Moléculaires, F-13003 Marseille, France

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Molar excess enthalpies H^E of 1-hexyne + carbon tetrachloride, + dipropyl ether, + triethylamine, and of 3-hexyne + carbon tetrachloride, + dipropyl ether, + triethylamine at 298.15 K and atmospheric pressure were measured with a *Picker*-type flow microcalorimeter over the whole concentration range. At equimolar concentration, H^E of 3-hexyne + carbon tetrachloride is strongly *exothermic* (— 499 J mol^{-1}), in contrast to H^E = = + 14 J mol^{-1} for the 1-hexyne system. As expected, for the ether and amine systems inverse behavior is observed: because of the active hydrogen of terminal alkynes the enthalpy of mixing at equimolar concentration is more exothermic with 1-hexyne (— 185 J mol^{-1}, dipropyl ether; — 300 J mol^{-1}, triethylamine) than with 3-hexyne (— 25 J mol^{-1}, dipropyl ether; — 92 J mol^{-1}, triethylamine). The curve H^E vs. mole fraction is considerably skewed for 3-hexyne (x_1) + triethylamine, the minimum being ca. — 197 J mol^{-1} at $x_1 \approx 0.9$.

Thermodynamik binärer Mischungen mit Alkinen als eine Komponente. II. Zusatzenthalpien binärer Mischungen von 1-Hexin und 3-Hexin mit Tetrachlorkohlenstoff, Dipropyläther und Triäthylamin bei 298,15 K

Die molaren Zusatzenthalpien H^E der sechs binären Systeme 1-Hexin + + CCl_4, + Dipropyläther, + Triäthylamin, und 3-Hexin + CCl_4, + Dipropyläther, + Triäthylamin wurden bei 298,15 K und Atmosphärendruck über den gesamten Konzentrationsbereich mit einem dynamischen Strömungsmikrokalorimeter nach *Picker* gemessen. H^E des Systems

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[b] Post-doctoral fellow from Istituto di Chimica Fisica, Universitá di Bari, Via Amendola 175, Bari, Italy.

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3-Hexin + CCl_4 ist stark *exotherm* (— 499 J mol^{-1} für $x = 0{,}5$), H^E des Systems 1-Hexin + CCl_4 endotherm (+ 14 J mol^{-1}, $x = 0{,}5$). Hingegen verhalten sich die Mischungen Hexin + Dipropyläther bzw. + Triäthylamin den Erwartungen entsprechend. Wegen des aktiven Wasserstoffs endständiger Alkine ist die Zusatzenthalpie mit 1-Hexin stärker exotherm (— 185 J mol^{-1} mit Dipropyläther und — 300 J mol^{-1} mit Triäthylamin, $x = 0{,}5$) als mit 3-Hexin (— 25 J mol^{-1} bzw. — 92 J mol^{-1}). Die molare Zusatzenthalpie des Systems 3-Hexin (x_1) + Triäthylamin ist ausgeprägt asymmetrisch mit einem Minimum von etwa — 197 J mol^{-1} bei $x_1 \approx 0{,}9$.

Introduction

Deviations from ideal behavior of liquid mixtures are generally interpreted in terms of various types of intermolecular forces operating within the mixtures, the most convenient distinction being that of strongly attractive "chemical" interactions and weakly attractive (nonspecific) "physical" interactions. However, there is no sharp boundary and this classification is to be taken as a mere heuristic convenience. In the preceding paper[1] we reported the excess enthalpy H^E for several mixtures of 1-hexyne and 3-hexyne each with *n*-heptane, *n*-decane, cyclohexane, and benzene as second component. Specifically, the first three hydrocarbons have been selected to establish something like a "reference mixing behavior", since one may safely assume that these substances are sufficiently inert as to preclude specific interactions with the acetylenic compound, such as charge transfer complexes and hydrogen bonds[2]. The present work is a continuation of our efforts to secure high precision thermodynamic data for binary liquid mixtures containing alkynes, and deals with somewhat more complex substances as second components, that is carbon tetrachloride, dipropyl ether, and triethylamine. With increasing basicity, the influence of the acidic hydrogen in 1-hexyne should become clearly discernible, and eventually predominant, thus contributing to our understanding of the influence of the position of the carbon-carbon triple bond upon the overall thermodynamics of binary alkyne systems. With accumulating data a more detailed quantitative treatment of this topic is projected[3]. Steps in this direction have been reported by *Prausnitz* and collaborators, who have discussed the solubility of acetylene in various organic solvents[4] and several selected systems with hexyne and strongly polar solvents[5, 6], and more recently by *Desplanches et al.*[7] who have studied vapor-liquid equilibria of 1-hexyne + acetonitrile, and 1-heptyne + acetonitrile.

Experimental

All calorimetric measurements were performed with a dynamic flow microcalorimeter of the *Picker* type[8–11] operating in the discontinuous mode[1, 12, 13]. Improvements in design and operational technique have

been discussed in detail in Refs.[1, 12, 13]. Test runs with standard systems like benzene + carbon tetrachloride, or benzene + cyclohexane were in excellent agreement with the very best literature data[14], that is well within 1 per cent or 1 J mol^{-1}, whichever is greater.

The calorimeter was thermostated to $\pm$ 1 mK as checked by a calibrated *Hewlett-Packard* quartz thermometer (model 2801 A), with the possible maximum absolute inaccuracy of the temperature reading being less than $\pm$ 5 mK. All liquids were degassed prior to the actual measurement.

Primary experimental results, that is volumetric excess enthalpy $\mathfrak{H}^E$ at volume fraction ϕ_1 of hexyne as obtained from the XY-recorder traces and the calibration *Joule* effect (via *Zener* diode), are easily converted to the more conventional molar excess enthalpy H^E at mole fraction x_1 by the following relations (where V_1 and V_2 denote the molar volumes of the pure liquids):

$$H^E = V_1 V_2 \, \mathfrak{H}^E / (\phi_1 V_2 + \phi_2 V_1) \tag{1}$$

$$1/x_1 = 1 - V_1/V_2 + V_1/(\phi_1 V_2). \tag{2}$$

All molar quantities are based on the relative atomic mass table 1975 as issued by IUPAC[15] [A_r (H) = 1.0079, A_r (C) = 12.011, A_r(N) = 14.0067, A_r (O) = 15.9994, and A_r (Cl) = 35.453].

1-Hexyne and 3-hexyne (Koch Light Laboratories Ltd., puriss. $\geqslant$ 99%, and pure $\geqslant$ 99%, by GLC), carbon tetrachloride (Fluka, puriss. $\geqslant$ 99.5%), and dipropyl ether (Fluka, puriss. $\geqslant$ 99.5%) were carefully dried with molecular sieve [Union Carbide Type 4 A, 8 $\times$ 12 mesh (beads), from Fluka] and used directly without further purification. Triethylamine (Fluka, puriss. p.a., $\geqslant$ 99.5%) was distilled twice in a 25-plate column (reflux ratio 20 : 1) and stored in the dark with the vapor phase being in contact with anhydrous magnesium perchlorate. The refractive index was in accord with reliable literature values[16, 17], i.e. $n_D^{20} = 1.40030$.

Results and Discussion

Excess enthalpy data H^E at 298.15 K and atmospheric pressure for all six alkyne systems, covering the whole concentration range, are recorded in Tables 1 a, b. Each series was subjected to least squares polynomial smoothing, i.e. the (x_1, H^E)-data were fitted according to

$$H^E/\mathrm{J\ mol^{-1}} = x_1 x_2 \sum_{i=0}^{n-1} A_i (x_1 - x_2)^i, \tag{3}$$

where n is the number of adjustable coefficients A_i. However, no satisfactory representation with a reasonable number of *Redlich-Kister* constants, say $n \leqslant 5$ could be obtained for the triethylamine systems. In view of the rather unusual form of the curve H^E vs. x_1, in particular for 3-hexyne (x_1) + triethylamine (x_2), this is not surprising. Thus, in order to circumvent the difficulties associated with too large a number

Table 1a. *Molar Excess Enthalpies H^E of 1-Hexyne + Carbon Tetrachloride, + Dipropyl Ether, and + Triethylamine at 298.15 K and Atmospheric Pressure*

1-Hexyne (x_1) + CCl_4		1-Hexyne (x_1) + $(C_3H_7)_2O$		1-Hexyne (x_1) + $(C_2H_5)_3N$	
x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.0448	4.10	0.0624	— 32.0	0.0633	— 55.6
0.0759	7.62	0.1044	— 53.1	0.2112	— 173.8
0.1567	16.57	0.2085	— 104.6	0.3057	— 233.0
0.2340	19.90	0.3023	— 143.6	0.4008	— 276.1
0.3169	20.23	0.3969	— 171.5	0.4912	— 300.4
0.4011	18.42	0.4872	— 185.2	0.5760	— 304.6
0.4852	14.72	0.5721	— 184.7	0.6574	— 296.0
0.5710	10.58	0.6538	— 169.1	0.7394	— 272.7
0.6631	5.92	0.7363	— 151.0	0.8167	— 243.1
0.7556	1.76	0.8143	— 111.1	0.8634	— 202.0
0.8143	— 0.10	0.8615	— 88.6	0.9522	— 114.4
0.9325	— 2.06	0.9514	— 36.0		

Table 1b. *Molar Excess Enthalpies H^E of 3-Hexyne + Carbon Tetrachloride, + Dipropyl Ether, and + Triethylamine at 298.15 K and Atmospheric Pressure*

3-Hexyne (x_1) + CCl_4		3-Hexyne (x_1) + $(C_3H_7)_2O$		3-Hexyne (x_1) + $(C_2H_5)_3N$	
x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
0.0453	— 77.1	0.0630	— 4.19	0.0933	— 13.3
0.0767	— 132.4	0.1054	— 6.61	0.1973	— 29.8
0.1581	— 265.7	0.2104	— 12.64	0.3020	— 49.1
0.2360	— 368.4	0.3046	— 17.40	0.4030	— 68.9
0.3193	— 445.2	0.3996	— 21.45	0.5829	— 112.5
0.4038	— 489.4	0.4900	— 24.55	0.6710	— 139.1
0.4879	— 499.2	0.5748	— 26.60	0.7529	— 163.4
0.5737	— 480.5	0.6563	— 27.50	0.8320	— 186.4
0.6656	— 430.2	0.8160	— 24.50	0.8721	— 193.8
0.7576	— 345.7	0.8629	— 21.68	0.9605	— 172.4
0.8160	— 282.5	0.9520	— 11.30		
0.9332	— 116.9				

of parameters, we adopted a somewhat more flexible generalized representation of the form[18]

$$H^E/\text{J mol}^{-1} = x_1 x_2 \sum_{i=0}^{n'-1} A_i (x_1 - x_2)^i \Big/ \sum_{j=0}^{n''-1} B_j (x_1 - x_2)^j \qquad (4)$$

with $B_0 = 1$. When B_2, B_3 *etc.* $= 0$ this equation reduces to the *Myers* and *Scott*[19] equation, where B_1 is known as the skewing factor. Here, the total number of adjustable parameters is $n = n' + n'' - 1$. The terms

of the denominator in Eq. (4) are constrained in such a way as not to yield a pole within the range $0 \leqslant x_1 \leqslant 1$.

Table 2 contains the constants of the fitting equations, together with the standard deviation σ:

$$\sigma = [\sum (H^E - H^E_{\text{calc}})^2/(N - n)]^{1/2}, \tag{5}$$

where H^E_{calc} denotes the excess enthalpy as computed via Eq. (3) or (4);

Table 2. *Values of Coefficients A_i and B_1 of Eqs. (3) and (4) as Determined by the Method of Least Squares, and Standard Deviation σ, all at 298.15 K. Eq. (4) Was Used Only for the Two Triethylamine Systems*

System	A_0	A_1	A_2	A_3	A_4	B_1	σ/J mol^{-1}
-Hexyne (x_1)							
+ carbon tetrachloride	55.5$_2$	— 102.0	41.0	21.7	— 86		0.5
+ dipropyl ether	— 741.6	— 102.4	137.8				2.0
+ triethylamine	— 1200.4	849.5	154.5			— 0.9714	1.8
-Hexyne (x_1)							
+ carbon tetrachloride	— 1995.3	223.3	54.9	— 301.4	171		1.4
+ dipropyl ether	— 98.3$_8$	— 54.3	— 56.6	— 43.8			0.5
+ triethylamine	— 366.5	— 145.3	— 52.5			— 0.9555	0.6

N is the total number of experimental points. In general, the internal inconsistency as characterized by σ is less than 1 per cent of the maximum value of H^E, except for the very small enthalpies of mixing, where it is somewhat larger.

In Figs. 1 and 2 the calculated curves and experimental points provide a graphical representation of the overall behavior in both hexyne series.

Several particularly interesting aspects can be noted:

First, the excess enthalpy for 1-hexyne + CCl_4 is substantially smaller than in 1-hexyne + alkane systems, and *a fortiori* this is the case for 3-hexyne + CCl_4, when compared to 3-hexyne + alkane.

Thus, second, the increment (at equimolar concentration)

$\Delta_{CCl_4} = H^E$(1-hexyne system) — H^E(3-hexyne system) ≈ 513 J mol^{-1} is about three times larger than the corresponding quantity for the alkane mixtures. It is intuitively appealing to associate the exothermic contribution to H^E with specific interaction between CCl_4 and the carbon—carbon triple bond of hexyne, say of n-π type[20–22]. However, as yet we do not have sufficient information to provide a detailed picture on a molecular level. In particular, we are quite ignorant about the influence of geometry (i.e. of packing) connected with the

more rigid 3-hexyne as compared to 1-hexyne, an aspect which was discussed in part I of this series[1]. To a much smaller extent a somewhat similar behavior was reported by *Wóycicki*[21] and by *Ghassemi, Grolier*, and *Kehiaian*[22] for alkene systems: the interaction involving internal carbon—carbon double bonds is stronger than with terminal double bonds, although the magnitude of the effect in the alkyne systems is rather surprising.

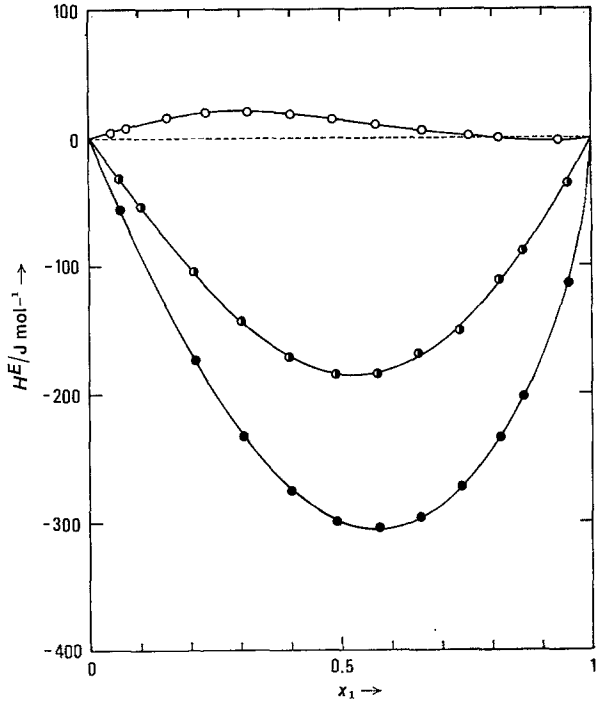

Fig. 1. Experimental molar excess enthalpy H^E vs. mole fraction x_1 for the systems 1-hexyne (x_1) + carbon tetrachloride (◯), + dipropyl ether (◑), and + triethylamine (●) at 298.15 K and atmospheric pressure. The full curves correspond to the least squares representation either by Eq. (3) or Eq. (4) utilizing the constants given in Table 2

Third, the negative sign of the quantity Δ (at $x_1 = 0.5$) for the ether ($\Delta_{(C_3H_7)_2O} \approx -160$ J mol^{-1}) and amine mixtures ($\Delta_{(C_2H_5)_3N} \approx$ ≈ -208 J mol^{-1}) is consistent with the increase in basicity and therefore in hydrogen-bond forming ability of oxygen and nitrogen in dipropyl ether and triethylamine, respectively. In these cases the acidic hydrogen of the terminal alkyne is the determining factor, although its influence is

superimposed on the n-π interactions between the lone pair electrons of nitrogen or oxygen and the triple bond, which effect is present in both types of hexynes. At the present moment we cannot offer any explanation of the unusual, highly skewed curve H^E vs. x_1 for 3-hexyne(x_1) + triethylamine.

In conclusion, it is clear that much more systematic experimental results on binary alkyne systems are needed to secure a firm basis for a

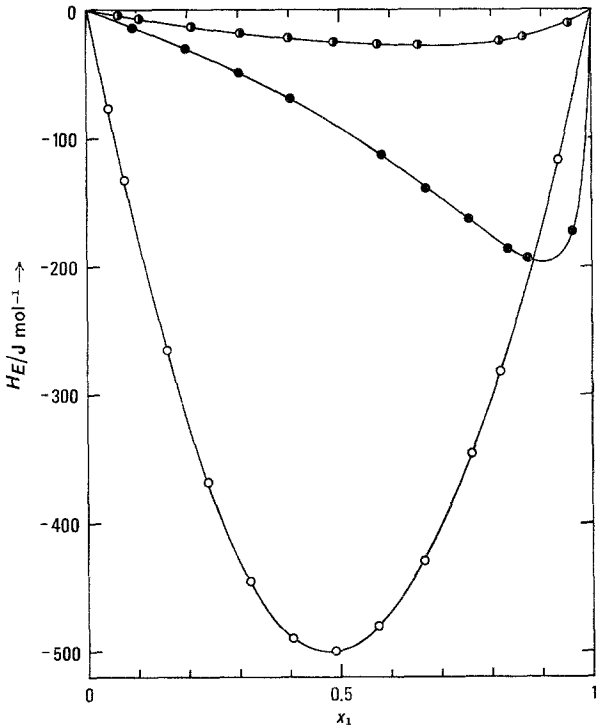

Fig. 2. Experimental molar excess enthalpy H^E vs. mole fraction x_1 for the systems 3-hexyne (x_1) + carbon tetrachloride (○), + dipropyl ether (◑), and + triethylamine (●) at 298.15 K and atmospheric pressure. The full curves correspond to the least squares representation either by Eq. (3) or Eq. (4) utilizing the constants given in Table 2

more detailed discussion. Results pertaining to selected additional systems will be communicated in forthcoming publications.

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