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# DISQUAC characterization of mixtures containing alkynes and alkanes or 1-alkanols. Comparison with ERAS model

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## Abstract

Mixtures formed by alkynes and *n*-alkanes, cycloalkanes or 1-alcohols have been examined in the framework of the DISQUAC group contribution model. The corresponding interaction parameters are reported. These ones follow some simple rules: (a) the quasichemical (QUAC) interchange coefficients for the aliphatic/acetylene contacts are independent of the alkyne; (b) the dispersive (DIS) parameters for such contacts when isomeric non-terminal alkynes are involved are also independent of the alkyne; (c) in 1-alkanols + alkynes mixtures, the QUAC parameters for the hydroxyl/acetylenic contacts do not depend on the mixture compounds. Thermodynamic properties such as vapor–liquid equilibria (VLE), including coordinates of azeotropes or activity coefficients at infinite dilution ($\gamma_i^\infty$), and excess molar enthalpies ($H^E$) are correctly described by DISQUAC. The model can be applied over a wide range of temperature. 1-Alkanols + 1-alkynes, or + 3-hexyne systems have been also characterized in terms of the ERAS model. Calculations were developed neglecting the possible self-association of 1-alkynes. This is reasonable in view of the good results provided by DISQUAC (a purely physical model), and of the very low values of the equilibrium constants obtained from the ERAS model when analyzing 1-alkynes + *n*-alkanes mixtures. ERAS results on $H^E$ are improved by DISQUAC. Both models provide similar results on excess molar Gibb's energies ($G^E$) of 1-alkanols + 3-hexyne mixtures. Excess molar volumes of solutions containing 1-alkanols and 1-alkynes are represented qualitatively by ERAS. Interactions in the treated solutions are analyzed in terms of the effective dipole moment ($\bar{\mu}$). So, the higher $H^E$ of 1-alkynes + *n*-alkanes mixtures compared to that of non-terminal isomeric alkynes + *n*-alkanes solutions may be attributed to the higher $\bar{\mu}$ of 1-alkynes. Structural effects are also relevant. In 1-alkanols + 1-alkynes systems, interactions between unlike molecules become weaker with the size increase of the mixture components.

*Keywords:* Thermodynamics; Alkynes; DISQUAC; ERAS; Interactions

## 1. Introduction

It is known that unsaturated organic compounds may act as proton acceptors in hydrogen bonds [1–3]. The relative basicity of acetylene has been determined by spectroscopic methods [2,3]. On the other hand, it seems that terminal acetylenes may act also as hydrogen bonding acids [2,4–6]. So, it may be possible that 1-alkynes have both proton donating and proton accepting abilities. Consequently, association via intermolecular hydrogen bonds might take place in pure compounds. Some spectral evidence for association has been presented [2,5]. However, such hydrogen bonds are very weak, with only a very slight effect

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upon the bulk physical properties of 1-alkynes. This is supported by the fact that their Trouton's constant, $\Delta H_v/T_b$, is 21.14 cal mol$^{-1}$ K$^{-1}$ (calculated using data from [7]). This value is close to that of non-associated compounds, 22 cal mol$^{-1}$ K$^{-1}$ [8]. For, say, 1-alkanols, the Trouton's constant is 26.5 cal mol$^{-1}$ K$^{-1}$ [8].

Two preliminary studies [9,10] on mixtures containing hexynes and *n*-alkanes in terms of the DISQUAC (DQ) group contribution model [11,12] have been presented. The purpose of this work is to extend these previous treatments to any type of alkynes, reporting the interaction parameters for a number of contacts where the acetylenic group is present. Particularly, the mixtures studied are: alkynes + *n*-alkanes, + cycloalkanes, or + 1-alkanols.

The ERAS model [13], which combines the real association solution model [14–17] with a physical term, namely, the Flory's equation of state [18], has been applied to 1-alkanols + 1-alkynes systems, assuming that these acetylenes are not self-associated [19]. In exchange, more recently, 1-alkynes + *n*-alkanes mixtures have been treated using the ERAS model [20].

Under the basic assumption of neglecting the self-association of 1-alkynes, we have tried here to obtain a more meaningful variation of the ERAS parameters with the molecular structure of the solution compounds than that reported previously in the literature for 1-alkanols + 1-alkynes systems [19]. The ERAS model has also been extended to 1-alkanols + 3-hexyne mixtures.

On the other hand, no interaction parameters for solutions containing alkynes have been reported in the framework of the Dortmund UNIFAC model [21,22].

## 2. Models

### 2.1. DISQUAC

In the framework of DISQUAC, mixtures of alkynes with organic solvents are regarded as possessing three types of surfaces: (i) type a, (aliphatic: $CH_3$, $CH_2$, in *n*-alkanes, alkynes or 1-alkanols); (ii) type y (acetylenic, HC≡C in 1-alkynes, or C≡C in the remainder alkynes); (iii) type s (where type s is type c, cyclic, c-$CH_2$ in cycloalkanes; type s is type h, hydroxyl, OH, in 1-alkanols).

Table 1
Relative group increments for molecular volumes, $r_G = R_G/R_{CH_4}$, and areas, $q_G = Q_G/Q_{CH_4}$, calculated using Bondi's method [23][a]

| Group | $r_G$ | $q_G$ | Reference |
|---|---|---|---|
| $CH_3$ | 0.79848 | 0.73103 | [24] |
| $CH_2$ | 0.59755 | 0.46552 | [24] |
| c-$CH_2$[b] | 0.58645 | 0.66377–0.0385m | [39] |
| HC≡C | 1.1448 | 0.9379 | This work |
| C≡C | 0.9404 | 0.6758 | This work |
| OH | 0.46963 | 0.50345 | [25] |

[a] $R_{CH_4} = 17.12\times10^{-6}$ m$^3$ mol$^{-1}$; $Q_{CH_4} = 2.90\times10^{-5}$ m$^2$ mol$^{-1}$.
[b] Methylene group in a *m*-atom cycle.

#### 2.1.1. Assessment of geometrical parameters

When DISQUAC is applied, the total relative molecular volumes, $r_i$, surfaces, $q_i$, and the molecular surface fractions, $\alpha_{si}$ of the compounds present in the mixture are usually calculated additively on the basis of the group volumes $V_G$ and surfaces $A_G$, recommended by Bondi [23]. As volume and surface units, the volume $V_{CH_4}$ and surface $A_{CH_4}$ of methane are taken arbitrarily [24]. The geometrical parameters of the groups referred to in this work are listed in Table 1.

#### 2.1.2. Equations

The equations used to calculate $G^E$ and $H^E$ are the same as in other applications [25,26]. The interactional terms in the excess thermodynamic properties $G^E$ and $H^E$ contain a dispersive (DIS) and a quasichemical (QUAC) contribution which are calculated independently by the classical formulas and then simply added. The degree of non-randomness is thus expressed by the relative amounts of dispersive and quasichemical terms

$$G^E = G^{E,COMB} + G^{E,DIS} + G^{E,QUAC} \quad (1)$$

$$H^E = H^{E,DIS} + H^{E,QUAC} \quad (2)$$

where $G^{E,COMB}$ is the Flory–Huggins combinatorial term [24,27].

For the QUAC part, as coordination number the reference value was chosen, i.e. $z = 4$.

The temperature dependence of the interaction parameters $g_{st}$, $h_{st}$ and $c_{pst}$ has been expressed in terms of the DIS and/or QUAC interchange coefficients [25,26] $C_{st,l}^{DIS}$ and $C_{st,l}^{QUAC}$, where s and t are types a, c, h and y and $l = 1$ (Gibbs energy; $C_{\mathrm{st},1}^{\mathrm{DIS/QUAC}} = g_{\mathrm{st}}^{\mathrm{DIS/QUAC}}(T_0)/RT_0$); $l = 2$ (enthalpy; $C_{\mathrm{st},2}^{\mathrm{DIS/QUAC}} = h_{\mathrm{st}}^{\mathrm{DIS/QUAC}}(T_0)/RT_0$) and $l = 3$ (heat capacity; $C_{\mathrm{st},3}^{\mathrm{DIS/QUAC}} = c_{\mathrm{pst}}^{\mathrm{DIS/QUAC}}(T_0)/R$); $T = 298.15$ K is the scaling temperature.

### 2.2. ERAS

This model combines the real association solution model [14–17] with Flory's equation of state [18]. The excess functions are written as

$$X^{\mathrm{E}} = X_{\mathrm{phys}}^{\mathrm{E}} + X_{\mathrm{chem}}^{\mathrm{E}} \tag{3}$$

where $X = G$ (Gibbs energy), $H$ (enthalpy), $V$ (volume). In Eq. (3), $X_{\mathrm{chem}}^{\mathrm{E}}$ is the chemical contribution, mainly due to association reactions, and $X_{\mathrm{phys}}^{\mathrm{E}}$ represents the physical contribution, consequence of the physical interactions between molecules. Correct expressions for these terms when cross-association between compounds exist are given elsewhere [19,26] for $X = H$, $V$, or $G$ and will not repeated here.

The chemical contribution to the excess properties arises from chemical interactions between the molecules, in particular hydrogen bonding. It is assumed that alkyne (B) molecules are not associated, while alcohol molecules (A) build linear chains of associated polymers

$$\mathrm{A}_n + \mathrm{A} \overset{K_{\mathrm{A}}}{\leftrightarrow} \mathrm{A}_{n+1} \tag{4}$$

where $n$ is the degree of self-association, ranging from 1 to $\infty$. The cross-association between $A$ and $B$ molecules is represented by

$$\mathrm{A}_n + \mathrm{B} \overset{K_{\mathrm{AB}}}{\leftrightarrow} A_nB \tag{5}$$

The association constants $K_i$ are assumed to be independent from the chain length. Their temperature dependence is given by

$$K_i = K_0 \exp\left[-\left(\frac{\Delta h_i^*}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{6}$$

where $K_0$ is the equilibrium constant at the standard temperature $T_0$ and $\Delta h_i^*$ the enthalpy variation for reactions (4) and (5), which corresponds to the hydrogen bonds energy. Reactions (4) and (5) are also characterized by the volume change $\Delta v_i^*$, related to the formation of the linear chains.

$X_{\mathrm{phys}}^{\mathrm{E}}$ is derived from Flory's equation of state [18], which is assumed to be valid not only for pure components but also for the mixture

$$\frac{\overline{P}_i\overline{V}_i}{\overline{T}_i} = \frac{\overline{V}_i^{1/3}}{\overline{V}_i^{4/3} - 1} - \frac{1}{\overline{V}_i\overline{T}_i} \tag{7}$$

where $i =$ A, B, M (mixture). In Eq. (7), $\overline{V}_i = V_i/V_i^*$; $\overline{P}_i = P/P_i^*$ and $\overline{T}_i = T/T_i^*$ are the reduced parameters, volume, pressure and temperature, respectively. The reduction parameters for pure components $V_i^*$, $P_i^*$, $T_i^*$ are calculated previous determination of density, thermal expansion coefficient and compressibility which can be obtained from experimental (exp) $P$–$V$–$T$ data. They also depend on $K_i$, $\Delta h_i^*$, $\Delta v_i^*$. The method is clearly explained elsewhere [28,29]. The reduction parameters for the mixture $P_{\mathrm{M}}^*$ and $T_{\mathrm{M}}^*$ are calculated via certain mixing rules [26,29], where $X_{\mathrm{AB}}$, the energetic interaction parameter characterizing the difference of dispersive intermolecular interactions between molecules A and B in the solution and in the pure components is introduced. It is the only adjustable parameter of the physical part of $H^{\mathrm{E}}$ and $V^{\mathrm{E}}$.

As in DISQUAC, the surface and volume of molecules are calculated using the Bondi's method [23].

## 3. Estimation of adjustable parameters

### 3.1. DISQUAC

The three types of surface generate three pairs of contacts: (a,y); (a,s); and (s,y), where s represents types a, c and h.

The general procedure applied in the estimation of the interaction parameters has been explained in detail elsewhere [25,26] and will not be repeated here.

#### 3.1.1. Alkynes + n-alkanes mixtures

This type of systems is characterized by a single contact: (a,y). Solutions, with 1-hexyne, have been treated previously assuming that the (a,y) contact is represented by DIS parameters [9], or by both DIS and QUAC parameters [10]. However, those mixtures involving 2-hexyne or 3-hexyne have been only studied in terms of the zeroth approximation of DISQUAC [9,10]. In this work, the (a,y) contacts

Table 2
Interchange coefficients DIS and QUAC, $C_{sy,l}^{DIS}$ and $C_{sy,l}^{QUAC}$ ($l = 1$, Gibbs energy; $l = 2$, enthalpy), for contacts (s,y)[a]

| Compound | $C_{sy,1}^{DIS}$ | $C_{sy,2}^{DIS}$ | $C_{sy,1}^{QUAC}$ | $C_{sy,2}^{QUAC}$ |
|---|---|---|---|---|
| 1-Alkynes + *n*-alkanes | | | | |
| 1-Pentyne | 0.10[b] | 0.12[b] | 1.00 | 2.75 |
| 1-Hexyne | 0.48 | 0.25 | 1.00 | 2.75 |
| ≥1-Heptyne | 1.00 | 0.37 | 1.00 | 2.75 |
| Non-terminal alkynes + *n*-alkanes | | | | |
| Pentyne | 0.80[b] | 0.90[b] | 1.00 | 2.75 |
| Hexyne | 1.15 | 1.10 | 1.00 | 2.75 |
| ≥Heptyne | 1.70[b] | 1.35 | 1.00 | 2.75 |
| 1-Alkynes + cyclopentane | | | | |
| 1-Hexyne | 0.40[b] | 0.28 | 1.00 | 2.75 |
| ≥1-Heptyne | 0.90[b] | 0.41 | 1.00 | 2.75 |
| 1-Alkynes + cyclohexane | | | | |
| 1-Pentyne | 0.10[b] | 0.25[b] | 1.00 | 2.75 |
| 1-Hexyne | 0.48[b] | 0.37 | 1.00 | 2.75 |
| ≥1-Heptyne | 0.95 | 0.46 | 1.00 | 2.75 |
| Non-terminal alkynes + cyclohexane | | | | |
| Pentyne | 0.70[b] | 0.80[b] | 1.00 | 2.75 |
| Hexyne | 1.10[b] | 0.95 | 1.00 | 2.75 |
| ≥Heptyne | 1.60[b] | 1.30[b] | 1.00 | 2.75 |
| 1-Alkynes + 1-alkanols | | | | |
| Methanol | 0.75 | −8.35 | 6.75 | 17.5 |
| Ethanol | 1.10 | −8.15 | 6.75 | 17.5 |
| ≥1-Propanol | 1.70 | −7.85 | 6.75 | 17.5 |
| 2-Alkynes + 1-alkanols | 1.65 | −6.15 | 6.75 | 17.5 |
| 3-Alkynes + 1-alkanols | 1.90 | −5.00 | 6.75 | 17.5 |

[a] Type y, HC≡C in 1-alkynes or C≡C in non-terminal alkynes; type s = a, $CH_3$, $CH_2$ in *n*-alkanes, 1-alkanols and alkynes; type s = c, c-$CH_2$ in cycloalkanes; type s = h, OH in 1-alkanols.

[b] Estimated value.

have been characterized by DIS and QUAC interaction parameters. The latter are assumed to be independent of the alkyne. A similar behavior has been encountered in other many solutions [30–37]. Final parameters are listed in Table 2.

### 3.1.2. Alkynes + cycloalkanes mixtures

This type of mixtures are characterized by three contacts: (a,c); (a,y); and (c,y). The (a,c) contacts are represented by purely dispersive parameters which are fitted to experimental data for cycloalkanes + *n*-alkanes systems [24,27,38]. However, the analysis of this type of solutions is rather difficult because cycloalkanes do not form an homologous series in terms of group contributions [38,39]. On the other hand, for a given cycloalkane, the corresponding interaction parameters change regularly with the *n*-alkane due to the so-called Patterson's effect, a positive enthalpic contribution which appears when longer *n*-alkanes are mixed with globular molecules. This is attributed to the order-destruction of the longer *n*-alkanes during the mixing process [40–42]. So, the $C_{ac,l}^{DIS}$ coefficients are only know for cyclohexane + *n*-alkanes mixtures [27]. Due to the lack of a complete set of experimental data for cyclopentane + *n*-alkanes systems, we have assumed that $C_{ac,l}^{DIS} = 0$, for such solutions. This is reasonable in view of the low values of the excess functions for those mixtures with short chain *n*-alkanes (e.g. $H^E(x_1 = 0.5; 298.15\,K) = 70\,J\,mol^{-1}$ for cyclopentane + *n*-heptane system [43].

So, as the parameters for the (a,c) and (a,y) contacts are known, only the (c,y) contacts must be fitted. This was done assuming that solutions formed by alkynes and *n*-alkanes, or cycloalkanes are characterized by the same QUAC coefficients $C_{ay,l}^{QUAC} = C_{cy,l}^{QUAC}$. A similar trend is observed, for example, in mixtures of oxaalkanes [44,45], chloroalkanes [46], iodoalkanes [47], ketones [48], organic carbonates [49], linear

Table 3
Pure component parameters at 298.15 K needed for ERAS model

| Compound | $P^*$ (J cm$^{-3}$) | $V^*$ (cm$^3$ mol$^{-1}$) | $V^{\mathrm{mol}}$ (cm$^3$ mol$^{-1}$) | $\Delta h$ (kJ mol$^{-1}$) | $\Delta v$ (cm$^3$ mol$^{-1}$) | $K$ |
|---|---|---|---|---|---|---|
| Methanol | 423.32[a] | 32.14[a] | 40.73[a] | −25.1[a] | −5.6[a] | 986[a] |
| Ethanol | 398.91[a] | 47.14[a] | 58.68[a] | −25.1[a] | −5.6[a] | 317[a] |
| 1-Propanol | 398.80[a] | 61.35[a] | 75.16[a] | −25.1[a] | −5.6[a] | 197[a] |
| 1-Butanol | 422.7[b] | 75.70[b] | 91.97[b] | −25.1[b] | −5.6[b] | 175[b] |
| 1-Hexyne | 506.6[a] | 87.67[a] | 115.65[a] | 0[a] | 0[a] | 0[a] |
| 1-Heptyne | 498.5[a] | 101.84[a] | 132.05[a] | 0[a] | 0[a] | 0[a] |
| 1-Octyne | 494.4[a] | 115.98[a] | 148.46[a] | 0[a] | 0[a] | 0[a] |
| 3-Hexyne | 558.0[c] | 86.32[d] | 114.16[d] | 0[e] | 0[e] | 0[e] |

[a] [19].

[b] [28].

[c] Calculated using estimated isothermal compressibility from Bondi's method [23] and thermal expansion coefficient given in [9].

[d] [9].

[e] This work.

monocarboxylic acids [50], primary [51], secondary [37], tertiary [37] and cyclic alkanols [35], phenol [52] or sulfolane [53] with *n*-alkanes or cyclohexane. Final parameters are listed in Table 2.

### 3.1.3. *Alkynes + 1-alkanols*

This type of mixtures are characterized by three contacts: (a,h); (a,y); and (h,y). The (a,h) contacts are described by DIS and QUAC interchange coefficients, obtained from data for 1-alkanols + *n*-alkanes mixtures [25,54,55]. So, due to the (a,h) and (a,y) contacts are known, only the (h,y) contacts must be fitted. As in other many alcoholic solutions, this was done assuming that the QUAC parameters are independent of the alcohol [33–37].

Final parameters are listed in Table 2.

### 3.2. *Estimation of the adjustable ERAS parameters*

The parameters adjustable to excess properties are $K_{\mathrm{A}}$, $K_{\mathrm{AB}}$, $\Delta h^*_{\mathrm{A}}$, $\Delta h^*_{\mathrm{AB}}$, $\Delta v^*_{\mathrm{A}}$, $\Delta v^*_{\mathrm{AB}}$, $X_{\mathrm{AB}}$, and $Q_{\mathrm{AB}}$ (needed to represent $G^{\mathrm{E}}$) [19,28,29,56–59]. $K_{\mathrm{A}}$, $\Delta h^*_{\mathrm{A}}$,

Table 4
Fitted parameters in the ERAS model for 1-alkanols + alkynes mixtures at 298.15 K[a]

| Alkanol | $\Delta h^*_{\mathrm{AB}}$ (kJ mol$^{-1}$) | $\Delta v^*_{\mathrm{AB}}$ (cm$^3$ mol$^{-1}$) | $K_{\mathrm{AB}}$ | $X_{\mathrm{AB}}$ (J cm$^{-3}$) | $Q_{\mathrm{AB}}$ |
|---|---|---|---|---|---|
| 1-Alkanols + 1-hexyne systems | | | | | |
| Methanol | −15.7 (−14.8) | −8.5 (−8.5) | 20 (20) | 5 (5) | |
| Ethanol | −15.4 (−15.8) | −8.4 (−7.6) | 13 (20) | 5 (4) | |
| 1-Propanol | −14.4 (−15.0) | −8.4 (−7.4) | 12 (20) | 7 (5) | |
| 1-Butanol | −14.4 | −7.6 | 11 | 13 | |
| 1-Alkanols + 1-heptyne systems | | | | | |
| Methanol | −14.8 (−12.0) | −7.6 (−7.4) | 15 (15) | 6 (5.2) | |
| Ethanol | −14.7 (−14.1) | −7.6 (−7.4) | 13 (15) | 6 (4.5) | |
| 1-Propanol | −14.3 (−13.9) | −7.6 (−5.6) | 12 (15) | 7 (4.5) | |
| 1-Alkanols + 1-octyne systems | | | | | |
| Methanol | −14.6 (−12.0) | −6.7 (−7.0) | 15 (10) | 7.5 (5.3) | |
| Ethanol | −14.5 (−14.0) | −7.4 (−6.8) | 10 (10) | 6.25 (5.0) | |
| 1-Propanol | −14.2 (−12.9) | −7.4 (−7.0) | 10 (10) | 7.5 (4.0) | |
| 1-Alkanols + 3-hexyne systems | | | | | |
| Methanol | −10.0 | −6.0 | 16 | 10 | −0.045 |
| Ethanol | −10.0 | −6.0 | 7 | 10 | −0.025 |
| 1-Butanol | −10.0 | −6.0 | 5 | 14 | 0.005 |

[a] Values in parenthesis are reported by Letcher et al. [19].

$\Delta v_{\mathrm{A}}^*$ are known for all alcohols and are fitted to $H^{\mathrm{E}}$ and $V^{\mathrm{E}}$ data of alcohol + alkane mixtures. The values used in this work are listed in Table 3. It is remarkable that $\Delta h_{\mathrm{A}}^* = -25.1$ kJ mol$^{-1}$ and $\Delta v_{\mathrm{A}}^* = -5.6$ cm$^3$ mol$^{-1}$ are values widely used (see, e.g. [26,37,56–59]).

The remaining parameters $K_{\mathrm{AB}}$, $\Delta h_{\mathrm{AB}}^*$, $\Delta v_{\mathrm{AB}}^*$, $X_{\mathrm{AB}}$ are adjusted to $H^{\mathrm{E}}$ and $V^{\mathrm{E}}$ data of 1-alkanols + 1-alkynes systems. More details are given in literature [19,28,56–59]. We must remark that we have not applied a best fitting procedure. Our final purpose

Table 5
Molar excess Gibbs energies, $G^{\mathrm{E}}$, at equimolar composition and temperature $T$ (K) of alkynes + solvents mixtures[a]

| System[b] | $T$ (K) | $N$[c] | $G^{\mathrm{E}}$ (J mol$^{-1}$) | | $\sigma_r(P)$ | | Reference |
|---|---|---|---|---|---|---|---|
| | | | Exp | DQ | Exp | DQ | |
| 1-Hexyne + $n$-$C_6$ | 328.15 | 6 | 259 | 250 | 0.004[d] | 0.005 | [67] |
| 1-Hexyne + $n$-$C_7$ | 343.15 | 6 | 257 | 237 | 0.002 | 0.01 | [68] |
| 1-Hexyne + $n$-$C_8$ | 303.15 | 5 | 265 | 279 | 0.002 | 0.008 | [69] |
| | 343.15 | 5 | 233 | 227 | 0.001 | 0.004 | [69] |
| 1-Hexyne + $n$-$C_{10}$ | 298.15 | | 276 | 258 | | | [70] |
| | 303.15 | 6 | 270 | 250 | 0.003 | 0.013 | [70] |
| | 333.15 | 6 | 224 | 202 | 0.004 | 0.015 | [70] |
| 1-Heptyne + $n$-$C_7$ | 328.15 | 9 | 307 | 308 | 0.004[d] | 0.006 | [67] |
| 1-Decyne + $C_6H_{12}$ | 298.15 | | 104 | 105 | | | [71] |
| 2-Hexyne + $n$-$C_8$ | 298.15 | 5 | 203 | 209 | 0.0004 | 0.026 | [10] |
| | 323.15 | 5 | 198 | 187 | 0.001 | 0.017 | [10] |
| 3-Hexyne + $n$-$C_8$ | 298.15 | 5 | 213 | 209 | 0.01 | 0.012 | [10] |
| | 323.15 | 5 | 207 | 187 | 0.009 | 0.012 | [10] |
| 1-Hexyne + MeOH | 263.15 | 6 | 1190 | 1106 | 0.006 | 0.049 | [72] |
| | 283.15 | 6 | 1210 | 1185 | 0.001 | 0.017 | [72] |
| | 343.15 | 5 | 1280 | 1274 | 0.003 | 0.011 | [72] |
| 1-Hexyne + EtOH | 283.35 | 6 | 1100 | 1088 | 0.003 | 0.016 | [72] |
| | 313.2 | 6 | 1130 | 1137 | 0.001 | 0.014 | [72] |
| | 353.15 | 6 | 1110 | 1113 | 0.0007 | 0.012 | [72] |
| 1-Hexyne + 1-BuOH | 263.7 | 5 | 910 | 874 | 0.001 | 0.029 | [72] |
| | 313.2 | 6 | 940 | 913 | 0.007 | 0.019 | [72] |
| | 353.1 | 6 | 843 | 842 | 0.004 | 0.006 | [72] |
| 2-Hexyne + MeOH | 263.3 | 6 | 1280 | 1232 | 0.003 | 0.031 | [73] |
| | 283.2 | 6 | 1290 | 1299 | 0.001 | 0.008 | [73] |
| | 343.2 | 6 | 1380 | 1378 | 0.0004 | 0.012 | [73] |
| 2-Hexyne + EtOH | 313.17 | 6 | 1200 | 1197 | 0.005 | 0.016 | [73] |
| | 353.2 | 6 | 1160 | 1175 | 0.004 | 0.032 | [73] |
| 2-Hexyne + 1-BuOH | 313.17 | 6 | 966 | 920 | 0.004 | 0.035 | [73] |
| | 353.2 | 6 | 869 | 858 | 0.004 | 0.019 | [73] |
| 3-Hexyne + MeOH | 263.3 | 6 | 1290 | 1267 | 0.003 | 0.027 | [74] |
| | 313.2 | 6 | 1370 | 1383 | 0.002 | 0.016 | [74] |
| | 343.2 | 6 | 1390 | 1390 | 0.002 | 0.013 | [74] |
| 3-Hexyne + EtOH | 283.2 | 6 | 1180 | 1178 | 0.006 | 0.018 | [74] |
| | 313.17 | 6 | 1210 | 1215 | 0.004 | 0.017 | [74] |
| | 353.2 | 6 | 1180 | 1183 | 0.001 | 0.015 | [74] |
| 3-Hexyne + 1-BuOH | 263.3 | 6 | 929 | 906 | 0.005 | 0.032 | [74] |
| | 313.17 | 6 | 969 | 935 | 0.006 | 0.019 | [74] |
| | 343.2 | 6 | 891 | 865 | 0.002 | 0.013 | [74] |

[a] Comparison of experimental data with DQ calculations. Standard relative deviations, $\sigma_r(P)$ defined by Eq. (8), are also given.

[b] MeOH, methanol, EtOH, ethanol; 1-BuOH, 1-butanol.

[c] Number of data points.

[d] Absolute mean deviation in mole fraction of vapor phase: $\Delta y = \sum |y_{i\,\mathrm{calc}} - y_{i\,\mathrm{exp}}|/N$.

Table 6
Comparison of experimental coordinates of azeotropes, temperatures ($T_{az}$/K); mole fraction ($x_{1az}$) and pressure ($P_{az}$/kPa), calculated from VLE measurements, with DISQUAC predictions

| System | $T_{az}$ (K) | $x_{1az}$ | | $P_{az}$ (kPa) | |
|---|---|---|---|---|---|
| | | Exp | DQ | Exp | DQ |
| 1-Heptyne+ $n$-C$_7$ | 328.15 | 0.490[a] | 0.479 | 25.41[a] | 25.42 |
| 1-Hexyne+methanol | 283.15 | 0.561[b] | 0.547 | 13.31[b] | 13.12 |
| | 343.15 | 0.420[b] | 0.402 | 174.84[b] | 175.17 |
| 1-Hexyne+ethanol | 283.35 | 0.784[b] | 0.787 | 9.81[b] | 9.69 |
| | 353.15 | 0.586[b] | 0.573 | 177.24[b] | 176.77 |
| 2-Hexyne+methanol | 283.15 | 0.561[c] | 0.547 | 13.31[c] | 13.12 |
| | 343.15 | 0.420[c] | 0.402 | 174.84[c] | 175.17 |
| 2-Hexyne+ethanol | 283.2 | 0.650[c] | 0.639 | 6.525[c] | 6.419 |
| | 343.15 | 0.500[c] | 0.455 | 147.75[c] | 149.17 |
| 3-Hexyne+methanol | 283.15 | 0.419[d] | 0.430 | 11.16[d] | 11.06 |
| | 343.15 | 0.333[d] | 0.341 | 162.6[d] | 161.4 |
| 3-Hexyne+ethanol | 283.2 | 0.686[d] | 0.671 | 7.17[d] | 7.11 |
| | 353.2 | 0.478[d] | 0.500 | 155.8[d] | 155.8 |

[a] [67].
[b] [72].
[c] [73].
[d] [74].

was to obtain a meaningful variation of the ERAS parameters with the molecular structure of the mixture compounds (Table 4) .

The parameters for 1-alkanols + 3-hexyne systems (Table 4) were obtained from $H^E$ and VLE data only, as $V^E$ measurements are not available.

## 4. Results

### 4.1. Comparison of DISQUAC with experiment

It is presented along Tables 5–8 and shown graphically, for selected systems, in Figs. 1–8.

For the sake of clarity, Table 5 includes standard relative deviations for pressures, $P$, defined as

$$\sigma_r(P) = \left\{\frac{1}{N}\sum\left[\frac{P_{exp} - P_{calc}}{P_{exp}}\right]^2\right\}^{1/2} \quad (8)$$

Table 7 also lists deviations for $H^E$ defined as

$$\mathrm{dev}(H^E) = \left\{\frac{1}{N}\sum\left[\frac{H^E_{exp} - H^E_{calc}}{H^E_{exp}(x_1 = 0.5)}\right]^2\right\}^{1/2} \quad (9)$$

In both equations, $N$ is the number of data points of each system. From this comparison, we can conclude that DISQUAC represents fairly well the thermodynamic properties of the mixtures under study. The model can be applied over a rather wide range of temperature (Tables 6 and 8).

### 4.2. ERAS results and comparison with DISQUAC

There is no practical difference between our $H^E$ results (Table 7) and those previously reported by Letcher et al. [19]. For nine systems, our averaged absolute mean deviation[1] is 63 J mol$^{-1}$, very close to their value, 59 J mol$^{-1}$.

ERAS results on $V^E(x_1 = 0.5, 298.15\,\mathrm{K})$ for 1-alkanols + 1-alkynes systems compare well with experimental data (Table 9). However, the composition dependence of the $V^E$ curves is rather poorly represented. We note the very low values of $V^E(x_1 = 0.5, 298.15\,\mathrm{K})$ and the large values of $\Delta v^*_{AB}$, which are comparable to $\Delta v^*_A = -5.6\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$, used for 1-alkanols. It remarks the importance of structural effects in these solutions [19].

DISQUAC improves ERAS results on $H^E$ (Table 7; Figs. 5 and 8). Both models represent similarly $G^E$ at 298.15 K of 1-alkanols + 3-hexyne mixtures (Fig. 3). In the case of ERAS, this is possible if $Q_{AB} \not\equiv 0$,

---

[1] Calculated as (1/number of systems)$[\sum |H^E_{exp} - H^E_{calc}|/N]$.

Table 7
Molar excess enthalpies, $H^E$, at equimolar composition and temperature $T$ (K) of alkynes + solvents mixtures[a]

| System[b] | $T$ (K) | $N$[c] | $H^E$ (J mol$^{-1}$) | | Dev ($H^E$) | | | Reference |
|---|---|---|---|---|---|---|---|---|
| | | | Exp | DQ | Exp | DQ | ERAS | |
| 1-Hexyne + $n$-$C_6$ | 298.15 | 20 | 594 | 606 | 0.004 | 0.013 | | [75] |
| 1-Hexyne + $n$-$C_7$ | 298.15 | 9 | 645 | 648 | 0.006 | 0.008 | | [9] |
| 1-Hexyne + $n$-$C_8$ | 303.15 | 14 | 677 | 683 | 0.004 | 0.022 | | [10] |
| 1-Hexyne + $n$-$C_{10}$ | 298.15 | 9 | 748 | 748 | 0.003 | 0.011 | | [9] |
| 1-Heptyne + $n$-$C_6$ | 298.15 | 7 | 518 | 522 | 0.002 | 0.008 | | [76] |
| 1-Heptyne + $n$-$C_7$ | 298.15 | 22 | 561 | 561 | 0.005 | 0.005 | | [9] |
| | | 15 | 556 | | 0.013 | 0.038 | | [77] |
| | 318.15 | 17 | 523 | 552 | 0.011 | 0.057 | | [78] |
| 1-Octyne + $n$-$C_8$ | 298.15 | 14 | 517 | 508 | 0.017 | 0.019 | | [77] |
| | 318.15 | 16 | 480 | 497 | 0.010 | 0.033 | | [77] |
| 1-Nonyne + $n$-$C_9$ | 298.15 | 14 | 469 | 464 | 0.014 | 0.017 | | [77] |
| 2-Hexyne + $n$-$C_8$ | 303.15 | 14 | 407 | 472 | 0.005 | 0.14 | | [10] |
| 2-Octyne + $n$-$C_8$ | 298.15 | 15 | 370 | 353 | 0.010 | 0.038 | | [78] |
| | 318.15 | 12 | 340 | 344 | 0.015 | 0.025 | | [78] |
| 3-Hexyne + $n$-$C_6$ | 298.15 | 23 | 409 | 421 | 0.019 | 0.039 | | [75] |
| 3-Hexyne + $n$-$C_7$ | 298.15 | 10 | 453 | 450 | 0.003 | 0.006 | | [9] |
| 3-Hexyne + $n$-$C_8$ | 303.15 | 9 | 482 | 472 | 0.008 | 0.027 | | [10] |
| 3-Hexyne + $n$-$C_{10}$ | 298.15 | 6 | 554 | 517 | 0.007 | 0.045 | | [9] |
| 3-Octyne + $n$-$C_8$ | 298.15 | 13 | 362 | 353 | 0.011 | 0.025 | | [78] |
| | 318.15 | 12 | 330 | 344 | 0.009 | 0.042 | | [78] |
| 4-Octyne + $n$-$C_8$ | 298.15 | 14 | 367 | 353 | 0.009 | 0.033 | | [78] |
| | 318.15 | 14 | 329 | 344 | 0.011 | 0.039 | | [78] |
| 1-Hexyne + $C_5H_{10}$ | 298.15 | 13 | 518 | 513 | 0.004 | 0.017 | | [79] |
| 1-Heptyne + $C_5H_{10}$ | 298.15 | 13 | 430 | 444 | 0.007 | 0.035 | | [79] |
| 1-Octyne + $C_5H_{10}$ | 298.15 | 14 | 383 | 374 | 0.008 | 0.026 | | [79] |
| 1-Hexyne + $C_6H_{12}$ | 298.15 | 9 | 726 | 738 | 0.006 | 0.010 | | [9] |
| 1-Heptyne + $C_6H_{12}$ | 298.15 | 12 | 647 | 664 | 0.005 | 0.022 | | [79] |
| 1-Octyne + $C_6H_{12}$ | 298.15 | 13 | 603 | 613 | 0.006 | 0.017 | | [79] |
| 1-Decyne + $C_6H_{12}$ | 298.15 | 20 | 563 | 556 | 0.009 | 0.018 | | [80] |
| 3-Hexyne + $C_6H_{12}$ | 298.15 | 9 | 463 | 474 | 0.004 | 0.014 | | [9] |
| 1-Hexyne + MeOH | 298.15 | 14 | 512 | 504 | 0.011 | 0.102 | 0.15 | [66] |
| | 298.15 | 16 | 538 | | 0.014 | 0.073 | | [72] |
| 1-Heptyne + MeOH | 298.15 | 11 | 579 | 579 | 0.008 | 0.062 | 0.20 | [66] |
| 1-Octyne + MeOH | 298.15 | 11 | 611 | 651 | 0.009 | 0.095 | 0.106 | [66] |
| 1-Hexyne + EtOH | 298.15 | 12 | 622 | 638 | 0.008 | 0.022 | 0.103 | [66] |
| 1-Heptyne + EtOH | 298.15 | 11 | 723 | 683 | 0.007 | 0.067 | 0.115 | [66] |
| 1-Octyne + EtOH | 298.15 | 12 | 676 | 732 | 0.007 | 0.064 | 0.106 | [66] |
| 1-Hexyne + 1-PrOH | 298.15 | 17 | 805 | 797 | 0.006 | 0.026 | 0.066 | [81] |
| 1-Heptyne + 1-PrOH | 298.15 | 17 | 835 | 820 | 0.009 | 0.027 | 0.080 | [81] |
| 1-Octyne + 1-PrOH | 298.15 | 17 | 859 | 849 | 0.008 | 0.014 | 0.089 | [81] |
| | | | 909[d] | | | | | [82] |
| 1-Nonyne + 1-PrOH | 298.15 | 15 | 996 | 884 | 0.010 | 0.056 | | [83] |
| | 313.15 | 19 | 1199 | 1203 | 0.013 | 0.022 | | [83] |
| 1-Hexyne + 1-BuOH | 298.15 | 15 | 882 | 851 | 0.007 | 0.035 | 0.055 | [72] |
| 1-Octyne + 1-BuOH | 298.15 | 9 | 940 | 874 | 0.020 | 0.046 | | [83] |
| 1-Nonyne + 1-BuOH | 298.15 | 16 | 953 | 897 | 0.009 | 0.040 | | [82] |
| 1-Octyne + 1-OcOH | 298.15 | | 886 | 851 | | | | [82] |
| 2-Hexyne + MeOH | 303.15 | 8 | 731 | 772 | 0.003 | 0.042 | | [73] |
| 2-Hexyne + EtOH | 303.15 | 9 | 835 | 810 | 0.002 | 0.027 | | [73] |
| 2-Hexyne + 1-BuOH | 303.15 | 9 | 893 | 894 | 0.002 | 0.026 | | [73] |
| 2-Octyne + 1-BuOH | 298.15 | 10 | 955 | 848 | 0.051 | 0.105 | | [82] |

Table 7 (*Continued*)

| System[b] | $T$ (K) | $N$[c] | $H^E$ (J mol$^{-1}$) |  | Dev ($H^E$) |  |  | Reference |
|---|---|---|---|---|---|---|---|---|
|  |  |  | Exp | DQ | Exp | DQ | ERAS |  |
| 2-Octyne + 1-OcOH | 298.15 |  | 842[e] | 726 |  |  |  | [82] |
|  | 318.15 | 7 | 1187 | 1074 | 0.017 | 0.11 |  | [82] |
| 3-Hexyne + MeOH | 298.15 | 10 | 792 | 809 | 0.002 | 0.032 | 0.082 | [74] |
| 3-Hexyne + EtOH | 298.15 | 9 | 854 | 832 | 0.001 | 0.041 | 0.047 | [74] |
| 3-Hexyne + 1-BuOH | 298.15 | 10 | 953 | 902 | 0.003 | 0.037 | 0.042 | [74] |

[a] Comparison of experimental data with DQ and ERAS calculations. Deviations (dev($H^E$)), defined by Eq. (9), are also given.

[b] For symbols, see Table 5. 1-PrOH, 1-Propanol; and 1-OcOH, 1-octanol.

[c] Number of data points.

[d] $x_1 = 0.486$.

[e] $x_1 = 0.439$.

Table 8

Activity coefficients at infinite dilution, $\gamma_i^\infty$, and at temperature $T$ for alkynes(1) + $n$-alkanes(2) mixtures[a]

| System | $T$ (K) | $\gamma_1^\infty$ |  | $\gamma_2^\infty$ |  | Reference |
|---|---|---|---|---|---|---|
|  |  | Exp | DQ | Exp | DQ |  |
| 1-Hexyne+$n$-C$_6$ | 328.15 | 1.41[b] | 1.44 | 1.48[b] | 1.45 | [67] |
| 1-Hexyne+$n$-C$_7$ | 343.15 | 1.31[c] | 1.36 | 1.56[c] | 1.44 | [68] |
| 1-Hexyne+$n$-C$_8$ | 298.15 | 1.42[c] | 1.48 | 1.55[c] | 1.67 | [69] |
|  | 343.15 | 1.28[c] | 1.32 | 1.38[c] | 1.45 | [69] |
| 1-Hexyne+$n$-C$_{10}$ | 298.15 | 1.68[c] | 1.40 | 1.62[c] | 1.73 | [70] |
|  | 343.15 | 1.25[c] | 1.23 | 1.48[c] | 1.43 | [70] |
| 1-Heptyne+$n$-C$_7$ | 328.15 | 1.51[b] | 1.56 | 1.64[b] | 1.59 | [67] |
|  | 373 |  | 1.42 | 1.25[d] | 1.44 | [84] |
| 1-Octyne+$n$-C$_8$ | 358 |  | 1.40 | 1.28[d] | 1.42 | [85] |
|  | 377.29 | 1.19[d] | 1.35 |  | 1.37 | [85] |
|  | 390.6 | 1.22[d] | 1.30 |  | 1.34 | [85] |
|  | 399.4 |  | 1.31 | 1.20[d] | 1.33 | [85] |
| 1-Nonyne+$n$-C$_9$ | 380.4 | 1.20[d] | 1.30 | 1.19[d] | 1.32 | [85] |
|  | 401.6 | 1.18[d] | 1.27 | 1.20[d] | 1.28 | [85] |
|  | 423.9 | 1.15[d] | 1.24 | 1.15[d] | 1.25 | [85] |
| 3-Nonyne+$n$-C$_9$ | 380.1 | 1.17[d] | 1.21 |  | 1.22 | [85] |
|  | 421.24 |  | 1.17 | 1.07[d] | 1.17 | [85] |

[a] Comparison between experimental data values and DQ calculations.

[b] From $x$–$y$ measurements.

[c] From $P$–$x$ measurements.

[d] From $T$–$x$ measurements.

and the same occurs for 1-alkanols + triethylamine systems [37]. In exchange, VLE and liquid–liquid equilibria of 1-alkanols + $n$-alkanes mixtures have described simultaneously with $Q_{AB} = 0$ [56].

The main advantage of ERAS is, of course, its ability to provide information on $V^E$. However, it can be only applied to those systems where association is expected, and it is quite difficult to use over a wide range of temperature [26,37].

## 5. Discussion

Thermodynamic properties of mixtures can be examined taking into account differences in molecular size, shape, anisotropy, dispersion forces and so forth. To investigate the impact of polarity on bulk properties, the effective dipole moment, $\overline{\mu}$, can be used ([26,37,60–65], see Appendix A). A large $\overline{\mu}$ does not always mean strong interactions between unlike

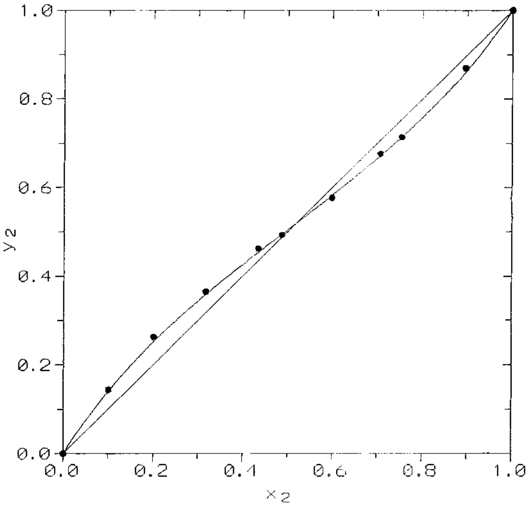

Fig. 1. VLE phase diagram for 1-heptyne (1) + $n$-heptane (2) system at 328.15 K. Points, experimental results [67]; solid line, DISQUAC calculation.

molecules because the strength of these interactions depends on those between molecules in pure liquids, what can be analyzed in terms of the differences between the standard enthalpy of vaporization of a given compound with a characteristic group $Z$ and that of the homomorphic alkane [44,60,61].

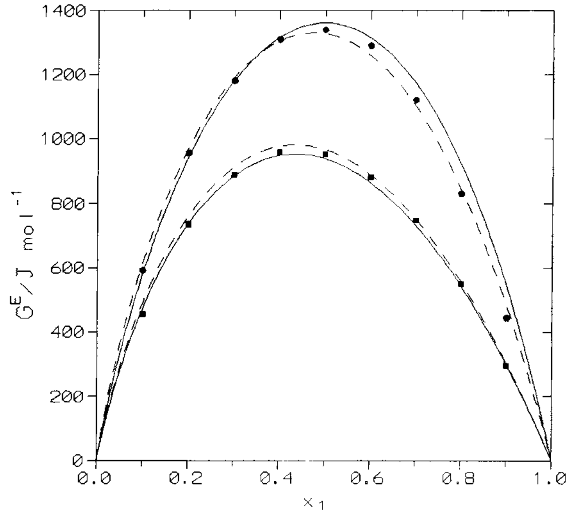

Fig. 3. $G^E$ at 298.15 K for 1-alkanols (1) + 3-hexyne (2) mixtures. Points, experimental results [74]; (●) methanol; (■) 1-butanol; solid lines, DISQUAC calculations; dashed lines, ERAS results.

### 5.1. Alkynes + alkanes mixtures

In systems with 1-alkynes, for a fixed $n$-alkane, $H^E(x_1 = 0.5;\ 298.15\ K)$ decreases with the chain length of the polar component (Table 7). It may be attributed to the lower endothermic contribution to $H^E$

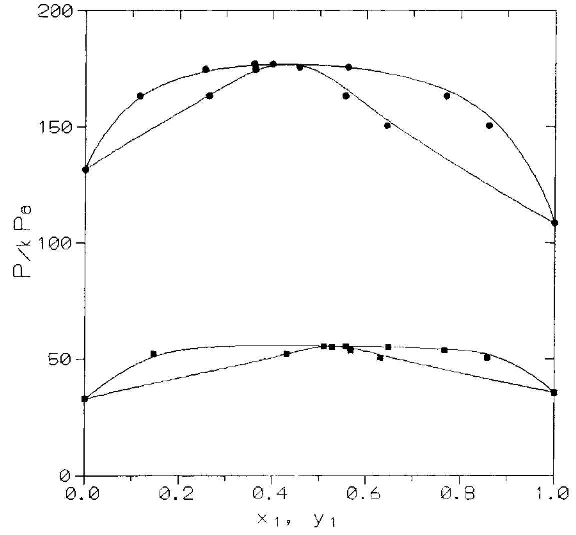

Fig. 2. VLE phase diagrams for 1-alkanols (1) + 1-hexyne (2) mixtures. Points, experimental results [72]; (■) methanol; $T = 313.15$ K; (●) ethanol, $T = 353.15$ K; solid lines, DISQUAC calculations.

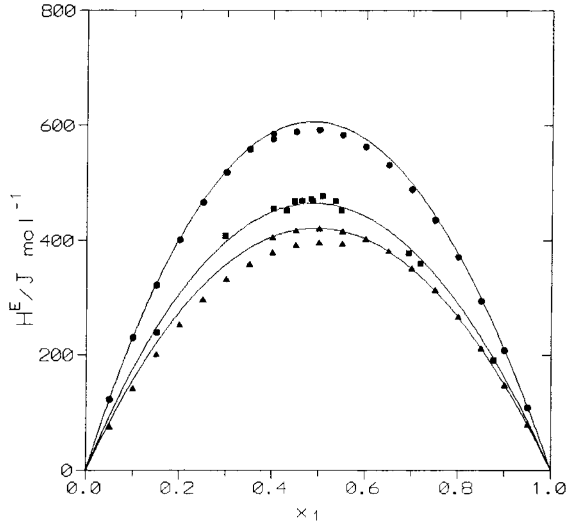

Fig. 4. $H^E$ at 298.15 K for alkyne(1) + $n$-alkanes(2) mixtures. Points, experimental results; (●) 1-hexyne (1) + $n$-hexane (2) [75]; (■) 1-nonyne (1) + $n$-nonane (2) [77]; (▲) 3-hexyne (1) + $n$-hexane (2) [75]; solid lines, DISQUAC calculations.

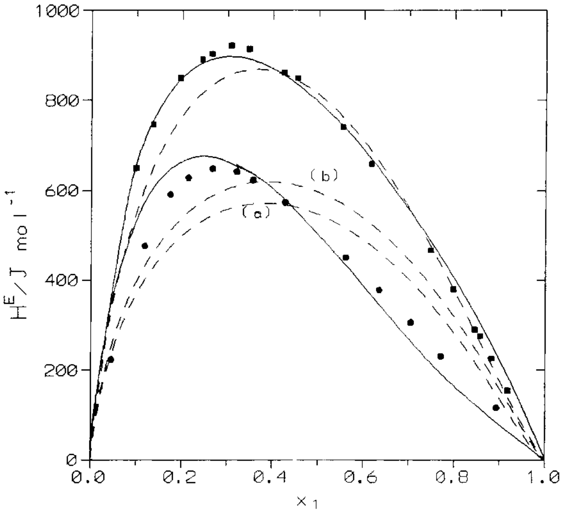

Fig. 5. $H^E$ at 298.15 K for 1-alkanols (1) + 1-hexyne (2) mixtures. Points, experimental results [66]; (●) methanol; (■) ethanol; solid lines, DISQUAC calculations; dashed lines, ERAS results: (a), methanol (1) + 1-hexyne (2) with parameters from Table 4; (b), methanol (1) + 1-hexyne (2) with parameters from [19].

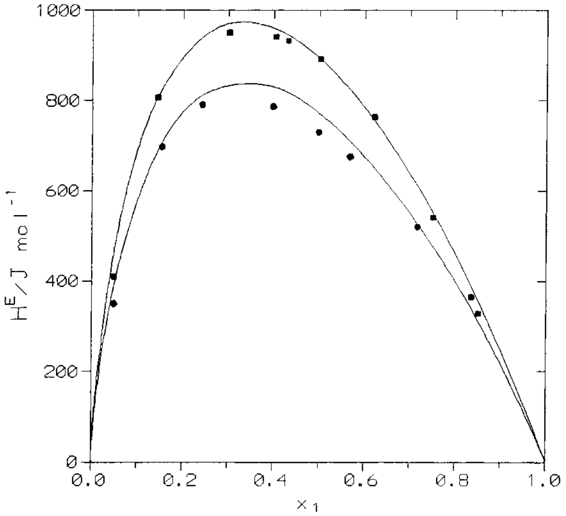

Fig. 7. $H^E$ at 303.15 K for 1-alkanols (1) + 2-hexyne (2) mixtures. Points, experimental results [74]: (●) methanol; (■) 1-butanol; solid lines, DISQUAC calculations.

from the disruption of the dipole-dipole interactions between 1-alkyne molecules, as $\overline{\mu}$ decreases with their size (Table 10).

On the other hand, solutions involving non-terminal alkynes (say, 2-hexyne or 3-hexyne) show lower $H^E(x_1 = 0.5;\ 298.15\ \mathrm{K})$ than those with the isomeric 1-alkyne. Probably, this is due to $\overline{\mu}$(non-terminal alkyne) < $\overline{\mu}$(isomeric 1-alkyne) (Table 10). Structural effects also play a role of the major importance in comparison to the possible self-association of 1-alkynes [9].

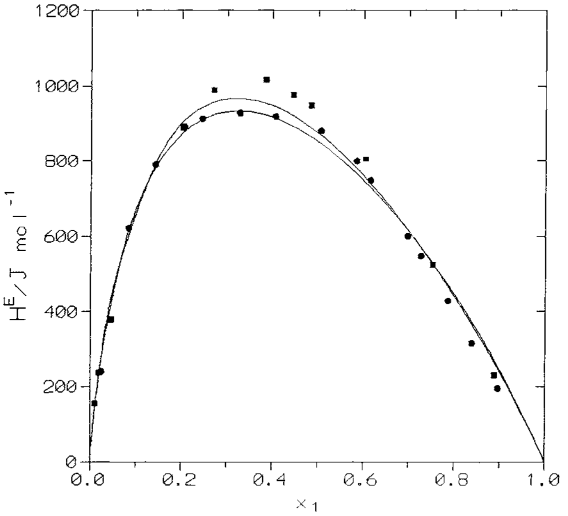

Fig. 6. $H^E$ at 298.15 K for 1-butanol (1) + 1-alkynes (2) mixtures. Points, experimental results: (●) 1-hexyne [72]; (■) 1-octyne [83]; solid lines, DISQUAC calculations.

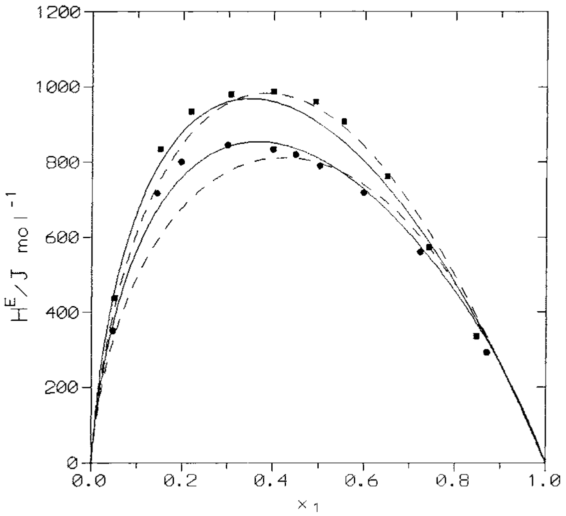

Fig. 8. $H^E$ at 298.15 K for 1-alkanols (1) + 3-hexyne (2) mixtures. Points, experimental results [73]: (●) methanol; (■) 1-butanol; solid lines, DISQUAC calculations; dashed lines, ERAS results.

Table 9
Excess molar volumes, $V^E$, at equimolar composition and 298.15 K for alkynes + 1-alkanols mixtures[a]

| System | $V^E$ (cm$^3$ mol$^{-1}$) | | Reference |
|---|---|---|---|
| | Exp | ERAS | |
| 1-Hexyne + methanol | −0.131 | −0.133 | [66] |
| 1-Heptyne + methanol | −0.029 | −0.034 | [66] |
| 1-Octyne + methanol | 0.027 | 0.025 | [66] |
| 1-Hexyne + ethanol | −0.095 | −0.093 | [66] |
| 1-Heptyne + ethanol | −0.014 | −0.015 | [66] |
| 1-Octyne + ethanol | 0.048 | 0.032 | [66] |
| 1-Hexyne + 1-propanol | −0.085 | −0.085 | [81] |
| 1-Heptyne + 1-propanol | 0.007 | 0.017 | [81] |
| 1-Octyne + 1-propanol | 0.049 | 0.058 | [81] |

[a] Comparison of experimental data with ERAS calculations.

Solutions formed by 2-octyne, 3-octyne or 4-octyne and *n*-octane present similar $H^E$ (Table 7). It is interesting to note that the enthalpy of vaporization and boiling point of these alkynes are very close (2-octyne: $\Delta H_v/\mathrm{J\,mol^{-1}} = 37.26$, $T_b/\mathrm{K} = 410.7$; 3-octyne: $\Delta H_v/\mathrm{J\,mol^{-1}} = 36.94$, $T_b/\mathrm{K} = 406.3$; 4-octyne: $\Delta H_v/\mathrm{J\,mol^{-1}} = 36.0$, $T_b/\mathrm{K} = 404.7$ [7]). So, in terms of DISQUAC, we have merely made distinction between 1-alkynes and non-terminal alkynes.

The $C^{\mathrm{DIS}}_{\mathrm{ay},2}$ coefficient increases with the chain length of the alkyne and is constant from 1-heptyne (Table 2), what has been typically attributed to an increasing of inductive effects [48]. On the other hand, $C^{\mathrm{DIS}}_{\mathrm{ay},2}$ (non-terminal alkyne) $>$ $C^{\mathrm{DIS}}_{\mathrm{ay},2}$ (isomeric 1-alkyne) (Table 2). It under line, the more relevant weight of other effects than those related to orientational forces in non-terminal alkynes.

Table 10
Critical temperatures, ($T_c$), pressures ($P_c$), dipole moments in vapor phase ($\mu$), effective dipole moments ($\overline{\mu}$; Eq. (A.4)) and reduced dipole moments ($\mu^*$; Eq. (A.3)) in liquid phase for some of the compounds considered in this work

| Compound | $T_c$ (K) | $P_c$ (bars) | $\mu$ (D) | $\overline{\mu}$ | $\mu^*$ |
|---|---|---|---|---|---|
| Methanol | 512.64[a] | 80.92[a] | 1.7[c] | 1.023 | 0.216 |
| Ethanol | 513.92[a] | 61.32[a] | 1.7[c] | 0.849 | 0.188 |
| 1-Propanol | 536.78[a] | 51.68[a] | 1.7[c] | 0.750 | 0.165 |
| 1-Butanol | 563.05[a] | 44.23[a] | 1.66[c] | 0.662 | 0.142 |
| 1-Decanol | 689[a] | 24.10[a] | 1.6[c] | 0.443 | 0.083 |
| 1-Hexyne | 502[b] | 37[b] | 0.88[d] | 0.313 | 0.077 |
| 3-Hexyne | 535[b] | 37.4[b] | 0[e] | 0 | 0 |
| 1-Heptyne | 525[b] | 33[b] | 0.87[d] | 0.290 | 0.069 |
| 1-Octyne | 547[b] | 29.6[b] | 0.96[d] | 0.301 | 0.069 |

[a] [86].

[b] From Joback's method [87].

[c] [87].

[d] [88].

[e] [9].

1-Alkynes + *n*-alkanes mixtures have been treated in the framework of the ERAS model [20]. Although, $\Delta h_i^*$ and $\Delta v_i^*$ are quite large in absolute value, the corresponding equilibrium constants are very low 0.2, 0.1 and 0.05 for 1-hexyne, 1-heptyne and 1-octyne, respectively. This justifies the use of a purely physical model (DISQUAC) to characterize alkyne–alkyne interactions.

### 5.2. Alkynes + 1-alkanols mixtures

Here, $H^E$ arises from different contributions: (a) a positive contribution from the breaking of H-bonds of alcohols upon mixing, which decreases with the chain length of the alcohol. Note that, in this case, $\overline{\mu}$ also decreases (Table 10) and, consequently, also the alkanol–alkanol interactions in the condensed phase [26,37]; (b) a positive contribution from the disruption of the alkyne–alkyne interactions during the mixing process, which is higher of 1-alkynes than for other alkynes (see above); (c) a negative contribution from interactions between unlike molecules, which decreases when the $\overline{\mu}$ of the system components decrease. As $H^E$s are positive, it means that interactions between equal molecules predominate.

The higher ability of alkynes to break the self-association of alcohols it is remarked by $H^E$(1-alkanols + *n*-alkanes) $<$ $H^E$ (1-alkanols + isomeric alkynes). So, methanol + alkynes systems do not show miscibility gaps. The set of interactions present in the analyzed solutions leads to more asymmetrical $H^E$ curves than those of 1-alkanols + *n*-alkanes mixtures [66].

The relative variation of $\Delta h^*_{\mathrm{AB}}$, $\Delta v^*_{\mathrm{AB}}$ and $K_{\mathrm{AB}}$ with the molecular structure in 1-alkanols + 1-alkynes systems (Table 4) remarks that interactions between unlike molecules become weaker when the size of the mixture compounds increase. In terms of DISQUAC, the interchange coefficients do not depend on the 1-alkyne. Only the $C^{\mathrm{DIS}}_{\mathrm{hy},l}(l = 1, 2)$ coefficients increase with the size of the 1-alkanol, but are constant from 1-propanol (Table 2). A similar behavior is observed, e.g. in solutions of 1-alkanols with benzene [33], $CCl_4$

[34], triethylamine [37], or of sec-alkanols with benzene or $n$-alkanones [37].

On the other hand, $H^{\mathrm{E}}$ (1-alkanols + 1-hexyne) $< H^{\mathrm{E}}$ (1-alkanols + 3-hexyne). It may be attributed to cross-association is stronger in solutions with 1-hexyne. This is supported by the larger values of $\Delta h^*_{\mathrm{AB}}$, $\Delta v^*_{\mathrm{AB}}$ and $K_{\mathrm{AB}}$ of 1-alkanols + 3-hexyne systems (Table 4). In the framework of DISQUAC, $C^{\mathrm{DIS}}_{\mathrm{hy},2}$ (1-alkanols + 3-hexyne) $> C^{\mathrm{DIS}}_{\mathrm{hy},2}$ (1-alkanols + 1-hexyne) (Table 2), as orientational forces are less important in solutions with 3-hexyne.

Finally, it should be mentioned that the adjustable parameters in both models vary with the molecular structure similarly for 1-alkanols + 3-hexyne mixtures (Tables 2 and 4).

## 6. Conclusions

Mixtures of alkynes with $n$-alkanes, cycloalkanes or 1-alcohols have been characterized in terms of DISQUAC. The determined $C^{\mathrm{DIS}}_{\mathrm{sy},l}$ and $C^{\mathrm{QUAC}}_{sy,l}$ coefficients follow rather sinmple rules: (a) $C^{\mathrm{QUAC}}_{\mathrm{ay},l}$ coefficients are independent of the alkyne; (b) $C^{\mathrm{DIS}}_{\mathrm{ay},l}$ coefficients do not depend on the isomeric non-terminal alkyne considered; (c) $C^{\mathrm{QUAC}}_{\mathrm{hy},l}$ are independent of the 1-alkanol and alkyne present in the system.

The model represents fairly well, over a wide range of temperature, a whole set of thermodynamic properties: VLE, coordinates of azeotropes, $\gamma_i^\infty$ and $H^{\mathrm{E}}$.

1-Alkanols + 1-alkynes, or + 3-hexyne mixtures have been also examined in the framework of the ERAS model. DISQUAC improves ERAS results on $H^{\mathrm{E}}$. The $V^{\mathrm{E}}$ of 1-alkanols + 1-alkynes systems are qualitatively described by ERAS.

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## Appendix A

For the purpose of characterizing the effective polarity of a molecule with dipole moment in gas phase $\overline{\mu}$, and to examine the impact of the polarity on thermodynamic properties of pure liquids and liquid mixtures, one may define a reduced dipole moment according to [62–65]

$$\hat{\mu} = \left[\frac{\mu^2}{4\pi\varepsilon_0\sigma^3\varepsilon}\right]^{1/2} \tag{A.1}$$

where $\varepsilon_0$ is the permittivity of the vacuum, $\sigma$ an appropriate molecular size parameter and $\varepsilon$ the corresponding interaction energy parameter. This expression may advantageously be transformed by virtue of the corresponding states principle to

$$\mu^* = \left[\frac{\mu^2 N_{\mathrm{A}}}{4\pi\varepsilon_0 V_{\mathrm{c}} k_{\mathrm{B}} T_{\mathrm{c}}}\right]^{1/2} \tag{A.2}$$

or equivalently to

$$(\mu^*)' = \left[\frac{\mu^2 P_{\mathrm{c}}}{4\pi\varepsilon_0 k_{\mathrm{B}}^2 T_{\mathrm{c}}^2}\right]^{1/2} \tag{A.3}$$

where $V_{\mathrm{c}}$, $T_{\mathrm{c}}$ and $P_{\mathrm{c}}$ are, the critical molar volume, the critical temperature and the critical pressure, respectively. $N_{\mathrm{A}}$ is the Avogadro's constant, and $k_{\mathrm{B}}$ the Boltzmann's constant [63,64], $\hat{\mu}$, $\mu^*$ and $(\mu^*)'$ refer to a single, isolated molecule. However, if the focus is on the impact of polarity on bulk properties, the appropriate quantity to be used is [64]

$$\overline{\mu} = \left[\frac{\mu^2 N_{\mathrm{A}}}{4\pi\varepsilon_0 V^{\mathrm{mol}} k_{\mathrm{B}} T}\right]^{1/2} \tag{A.4}$$

which may be called the effective dipole moment.

While for a given series, say 1-alkanols, $\mu$ varies only slightly with the chain length, by necessity the reduced dipole moments $\hat{\mu}$ or $\mu^*$ show much greater variation. For a given temperature, the magnitude of $\overline{\mu}$ evidently depends on if one discusses, e.g. a low-density gaseous system or a dense liquid phase.

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