



Liquid–liquid equilibria for acetophenone + *n*-alkane mixtures and characterization of acetophenone systems using DISQUAC



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ABSTRACT

Liquid–liquid equilibrium (LLE) temperatures have been determined for acetophenone + CH₃(CH₂)_{*n*}CH₃ (*n* = 8, 10, 12, 14) mixtures by means of the opalescence method using a laser scattering technique. All the solutions show an upper critical solution temperature (UCST), which increases almost linearly with *n*. Acetophenone + benzene, or +alkane, or +1-alkanol mixtures have been treated by means of the DISQUAC model. The corresponding dispersive and quasi-chemical interaction parameters for the contacts CO/aromatic; CO/aliphatic; CO/*c*-CH₂ and CO/hydroxyl are reported. The model correctly describes LLE diagrams and excess molar enthalpies, H_m^E , of the investigated solutions, over a wide range of temperature using the same set of interaction parameters. Mixtures with alkanes are mainly characterized by dipolar interactions. From the analysis of molar excess functions: H_m^E , volumes, V_m^E , and internal energies at constant volume, U_m^E , and on LLE for such systems, it is shown that interactions between acetophenone molecules are stronger than those between 2-hexanone or 2-octanone molecules and that they are similar to acetone–acetone interactions. Thus, the phenyl ring in acetophenone leads to strengthened interactions between alkanone molecules. Dipolar interactions are also important in mixtures containing 1-alkanols, and become more relevant in solutions with longer 1-alkanols. The enthalpy of the alcohol–acetophenone interactions, ΔH_{OH-CO} , were determined. This magnitude increases with the alkanol size and remains practically constant from 1-butanol.

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1. Introduction

Acetophenone is a precursor to resins which are components of coatings and inks. Moreover, it is widely used as an ingredient in fragrances. Acetophenone derivatives have medical applications as, e.g., new agents for potential application in Alzheimer's disease [1]. On the other hand, the study of mixtures containing an aromatic compound with a polar functional group allows investigate a number of effects such as intramolecular interactions between the phenyl ring and a polar functional group (*n*– π interactions). In this framework, we have reported liquid–liquid equilibrium (LLE) phase diagrams for 2-phenoxyethanol [2], *N*-methylaniline [3], benzylamine [4] or benzaldehyde [5] +alkane mixtures and isobaric excess molar heat capacities for benzylamine +heptane, or +1-alkanol systems [6]. As continuation, we provide now LLE measurements for acetophenone + decane,

+dodecane, +tetradecane, or +hexadecane mixtures, and we extend the DISQUAC group contribution model [7] to solutions containing this aromatic ketone and *n*-alkanes, cyclohexane, benzene or 1-alkanols. DISQUAC treatments for *n*-alkanone +alkane [8], +aromatic hydrocarbons [9,10], or +1-alkanol [11] systems are available in the literature. It should be also mentioned that some acetophenone +*n*-alkane mixtures have been investigated using DISQUAC under the assumption that the interaction parameters of the carbonyl/aliphatic contacts are the same as in the corresponding mixtures with 2-alkanones [12].

2. Experimental

2.1. Materials

Table 1 shows the main characteristics of pure compounds used in the present work including source, purity, water contents, determined by the Karl-Fischer method, and density (ρ). The chemicals were used without further purification. Densities were measured by means of a vibrating-tube densimeter and a sound

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Nomenclature

| | |
|-------------------------|---|
| C | Interchange coefficient |
| C_p | Heat capacity at constant pressure |
| G | Gibbs energy |
| H | Enthalpy |
| ΔH_{vap} | Standard enthalpy of vaporization at 298.15 K |
| k | Adjustable parameter (Eq. (1)) |
| m | Adjustable parameter (Eq. (1)) |
| T | Temperature |
| V | Volume |
| x | Mole fraction in liquid phase |
| y | Magnitude defined by Eq. (2) |

Greek letters

| | |
|-------------|------------------------------------|
| α | Adjustable parameter (Eq. (2)) |
| μ | Dipole moment |
| $\bar{\mu}$ | Effective dipole moment (Eq. (10)) |
| ρ | Density |

Superscripts

| | |
|------|--------------------------------|
| COMB | Combinatorial term |
| DIS | Dispersive term |
| E | Excess property |
| m | Adjustable parameter (Eq. (1)) |
| QUAC | Quasichemical term |

Subscripts

| | |
|--------|---|
| ij | Compound in the mixture, ($i, j = 1, 2$) |
| l | Order of the interchange coefficient ($l = 1$, Gibbs energy; $l = 2$, enthalpy; $l = 3$, heat capacity) |
| m | Molar property |
| c | Critical point |
| s, t | Type of contact surface in DISQUAC ($s \neq t = a$ (CH ₃ ; CH ₂); b (C ₆ H ₆ ; C ₆ H ₅); c (c-CH ₂); k (CO); h (OH)) |

analyzer, Anton Paar model DSA-5000. The resolution in density is $|\Delta\rho/\rho| = 6 \times 10^{-6}$, and the corresponding accuracy is estimated to be $\pm 2 \times 10^{-2} \text{ kg m}^{-3}$. The ρ values of the pure liquids are in good agreement with those from the literature (Table 1).

2.2. Apparatus and procedure

Mixtures were prepared by mass using an analytical balance HR-202 (weighing accuracy $\pm 10^{-5} \text{ g}$), in small Pyrex tubes (0.009 m i.d. and about 0.04 m length), immediately sealed by capping at atmospheric pressure and room temperature. The

relative atomic mass table of 2006 issued by IUPAC [13] was used for the conversion to molar quantities.

The liquid–liquid equilibrium curves were determined by the method of the critical opalescence. Details of the experimental technique are given elsewhere [2]. Equilibrium temperatures were measured using a Pt-1000 resistance, calibrated, according to the ITS-90 scale of temperature, against the triple point of the water and the fusion point of Ga. The precision of the equilibrium temperature measurements is $\pm 0.001 \text{ K}$, with an estimated uncertainty of $\pm 0.05 \text{ K}$. The mentioned temperatures were reproducible to $\pm 0.02 \text{ K}$ for those values close to the UCST. For the equilibrium composition measurements, the uncertainty of the mole fraction is better than 0.0005. The precision of the weighing technique is 0.0001 in mole fraction, but, due to the more volatile component is partially evaporated to the free volume of the ampoule ($\approx 1.17 \times 10^{-6} \text{ m}^3$), this value is slightly reduced.

3. Experimental results

Table 2 lists the directly measured liquid–liquid equilibrium temperatures, T , vs. the mole fraction of acetophenone, x_1 , for mixtures containing decane, or dodecane, or tetradecane, or hexadecane. A few data corresponding to solid–liquid equilibrium (SLE) measurements are also included. No data have been encountered in the literature for comparison. All the systems show an UCST, which increases almost linearly with the chain length of the alkane. In addition, the LLE curves have a flat maximum, and their symmetry depends on the alkane size (Fig. 1). LLE phase diagrams of many other systems as those containing linear organic carbonate [14], acetic anhydride [15], alkoxyethanol [2,16–18], linear polyether [19,20], aromatic alcohol [21–23], amide [24,25] or benzaldehyde [5] and alkane show similar trends.

Table 3 lists the composition (x_{1c}) and temperature (T_c) of the critical points obtained by reducing the experimental measurements with the equation [26,27]:

$$T/K = T_c/K + k|y - y_c|^m \quad (1)$$

where

$$y = \frac{\alpha x_1}{1 + x_1(\alpha - 1)} \quad (2)$$

$$y_c = \frac{\alpha x_{1c}}{1 + x_{1c}(\alpha - 1)} \quad (3)$$

In these equations, m , k , α , T_c and x_{1c} are the parameters which must be fitted against the experimental data. For $\alpha = 1$, Eq. (1) is similar to [28–30]:

$$\Delta\lambda = B\tau^\beta \quad (4)$$

Table 1

Properties of pure compounds at 0.1 MPa and 298.15 K.

| Compound | CAS | Source | Initial mole fraction | $\rho^a/\text{kg m}^{-3}$ | | Water ^b content |
|--------------|----------|--------|-----------------------|---------------------------|---|----------------------------|
| | | | | Exp. | Lit. | |
| Acetophenone | 98-86-2 | Fluka | ≥ 0.99 | 1023.048 | 1023.82 ^c 1023.1 ^d | 230×10^{-6} |
| Decane | 24-18-5 | Fluka | ≥ 0.99 | 726.347 | 726.337 ^c | 35×10^{-6} |
| Dodecane | 112-40-3 | Fluka | ≥ 0.98 | 741.523 | 745.52 ^e | 21×10^{-6} |
| Tetradecane | 629-59-4 | Fluka | ≥ 0.99 | 759.275 | 759.316 ^f | 32×10^{-6} |
| Hexadecane | 544-76-3 | Fluka | ≥ 0.99 | 770.221 | 770.316 ^f | 41×10^{-6} |

^a Density, uncertainty, $u(\rho) = \pm 0.02 \text{ kg mg}^{-3}$; $u(T) = \pm 0.01 \text{ K}$; $u(P) = \pm 0.01 \text{ kPa}$.

^b In mass fraction.

^c [65].

^d [99].

^e [100].

^f [101].

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