

Accepted Manuscript

Liquid-liquid equilibria for the systems 2-ethoxy-benzenamine+CH₃(CH₂)_nCH₃ (n=6,8,10,12) and 4-ethoxy-benzenamine+CH₃(CH₂)_nCH₃ (n=5,6)

Cristina Alonso Tristán, Juan Antonio González, Isaías García de la Fuente, Luis F. Sanz, José Carlos Cobos



PII: S0167-7322(18)34664-6

DOI: <https://doi.org/10.1016/j.molliq.2018.10.135>

Reference: MOLLIQ 9880

To appear in: *Journal of Molecular Liquids*

Received date: 10 September 2018

Revised date: 22 October 2018

Accepted date: 25 October 2018

Please cite this article as: Cristina Alonso Tristán, Juan Antonio González, Isaías García de la Fuente, Luis F. Sanz, José Carlos Cobos , Liquid-liquid equilibria for the systems 2-ethoxy-benzenamine+CH₃(CH₂)_nCH₃ (n=6,8,10,12) and 4-ethoxy-benzenamine+CH₃(CH₂)_nCH₃ (n=5,6). Molliq (2018), <https://doi.org/10.1016/j.molliq.2018.10.135>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**LIQUID-LIQUID EQUILIBRIA FOR THE SYSTEMS 2-ETHOXY-
BENZENAMINE + CH₃(CH₂)_nCH₃ (n =6,8,10,12) AND 4-ETHOXY-
BENZENAMINE + CH₃(CH₂)_nCH₃ (n =5,6)**

CRISTINA ALONSO TRISTÁN,⁽¹⁾ JUAN ANTONIO GONZÁLEZ,^{*(2)} ISAÍAS GARCÍA
DE LA FUENTE,⁽²⁾ LUIS F. SANZ,⁽²⁾ AND JOSÉ CARLOS COBOS⁽²⁾

⁽¹⁾ Dpto. Ingeniería Electromecánica. Escuela Politécnica Superior. Avda. Cantabria s/n.
09006 Burgos, (Spain)

⁽²⁾ G.E.T.E.F., Departamento de Física Aplicada, Facultad de Ciencias, Universidad
de Valladolid, Paseo de Belén, 7, 47011 Valladolid, Spain,

*e-mail: jagl@termo.uva.es; Fax: +34-983-423136; Tel: +34-983-423757

ABSTRACT

Liquid-liquid equilibria (LLE) phase diagrams have been determined for the systems: 2-ethoxy-benzenamine + octane, or + decane, or + dodecane, or + tetradecane and for 4-ethoxy-benzenamine + heptane, or + octane. The experimental method used is based on the observation, by mean of a laser scattering technique, of the turbidity produced on cooling when a second phase takes place. All the mixtures show an upper critical solution temperature, which increases with the alkane size. Dipolar interactions between like molecules become stronger in the sequence: 2-ethoxy-benzenamine < aniline < 4-ethoxy-benzenamine. Data available in the literature suggest that this relative variation is also valid for alkane mixtures containing other substituted anilines or phenols, characterized by having a second polar group. The dependence of the UCST values with the molecular structure of the polar aromatic compound involved is shortly discussed in terms of intramolecular and steric effects.

KEY WORDS: LLE/ phenetidine/ alkane/ substituted anilines or phenols/ intramolecular effects

1. Introduction

We are interested on the investigation of intramolecular effects between the phenyl ring (C_6H_5 – group) and a polar group, X, more or less directly attached to the aromatic ring, as these effects are very different to those between the same groups when they belong to different molecules. For example, the upper critical solution temperature (UCST) of the aniline + heptane mixture is 343.1 K [1], while the excess molar enthalpy, H_m^E , of the hexan-1-amine + benzene system at equimolar composition and 303.2 K is 627 J·mol⁻¹ [2]. That is, intramolecular effects lead to enhanced interactions between like polar molecules, while intermolecular effects make usually more favourable interactions between unlike molecules (see below). With this idea, we have studied, both experimental and theoretically, intramolecular effects, also termed proximity effects, in mixtures containing aromatic amines [3-10] (anilines, 2-amino-1-methylbenzene, 1-phenylmethanamine, 1*H*-pyrrole, quinoline or imizadoles); phenylmethanal, 1-phenylethanone, 4-phenyl-2-butanone, benzyl ethanoate [11-14], benzonitrile, phenyl-acetonitrile, 3-phenylpropionitrile [15], 2-phenoxyethanol [16], or aromatic alkanols (phenol; phenylmethanol, 2-phenylethan-1-ol) [17-19]. As a continuation, we provide now liquid-liquid equilibria data for alkane systems involving 2-ethoxy-benzenamine (*o*-phenetidine) or 4-ethoxy-benzenamine (*p*-phenetidine). Phenetidine molecules contain two different polar groups (NH₂ and –O–) attached to the phenyl ring in different points, and intramolecular effects between these two groups are also expected to exist. The case previously examined by us, phenoxyethanol + alkane systems [16], is somewhat different as the –O– and –OH groups are placed in the same linear chain attached to the phenyl ring.

Phenetidines have a variety of applications. For example, *p*-phenetidine is used as an intermediate in the dye industry or in the obtention of *p*-ethoxyacetanilide (phenatecin) or ethoxyquin which are important compounds to enhance the oxidative stability of products from food or pharmacological manufacturers [20-21]. On the other hand, poly *o*-phenetidine is useful in order to remove nitrates from water [22].

2. Experimental

2.1 Materials. All the information related to the source, purity, water content and density (ρ) of the pure compounds used in the present experimental research is collected in Table 1. The chemicals were used as received. Density measurements were conducted by means of a vibrating-tube densimeter and a sound analyser, Anton Paar model DSA-5000. The repeatability and the relative standard uncertainty of the ρ values are, respectively, $5 \cdot 10^{-3}$ kg·m⁻³, and 0.002. Density values listed in Table 1 show that our results are in good agreement with values from the literature. A careful survey of literature data showed that no ρ value has been previously reported for the *o*-phenetidine. Water contents were determined by the Karl-Fischer method. The relative standard uncertainty of the corresponding measurements is estimated to be 0.02.

2.2 Apparatus and Procedure

Small Pyrex tubes (0.009 m i.d. and about 0.04 m length; free volume of the ampoule $\approx 1.17 \cdot 10^{-6} \text{ m}^3$) were used for the preparation of the mixtures. Mixtures were prepared by mass. Weights were obtained from an analytical balance Sartorius NSU125p (weighing accuracy 10^{-8} kg). The mentioned tubes were immediately sealed by capping at 0.1 MPa and 298.15 K. Mole fractions were calculated on the basis of the relative atomic mass Table of 2015 issued by the Commission on Isotopic Abundances and Atomic Weights (IUPAC) [23].

The LLE curves were determined by means of the observation of the turbidity produced on cooling when a second phase takes place. A brief summary of the procedure follows. (i) The samples in the sealed Pyrex tubes are placed in a thermostat bath few hundredths of degree above the expected temperature. (ii) Mixtures are then slowly cooled at a rate of $1.2 \text{ K} \cdot \text{h}^{-1}$ under continuous stirring. Since the equilibrium times are much longer in the two-phase region than the corresponding times in the one-phase region, this method is suitable to prevent supercooling and gravity effects in mixtures at compositions far from the critical one [24,25]. (iii) A red He-Ne laser (wavelength of 635 nm) is situated on one side of the equilibrium cell, and the light beam crossing through the solution is focused on a photodiode placed at the other side of the cell. When the temperature is slowly decreased, small drops of the dispersed liquid phase start to grow and the light is dispersed during the transition. This causes a voltage variation in the mentioned photodiode, which is determined by a digital Agilent 34410A multimeter connected to a PC. Transition temperatures can be then measured. In the current investigation, the mixtures show a dark red color and the use of different lasers was tested in order to improve the technique, but no further improvement was attained. (iv) Two or three runs are usually conducted in order to get a better assessment of the equilibrium temperatures. A direct comparison between results obtained using our experimental technique and data from the literature can be encountered elsewhere [26]. The equilibrium temperatures were measured using a Pt-1000 resistance. The thermometer was calibrated according to the ITS-90 scale of temperature. The fixed points used at this end were the triple point of the water and the fusion point of Ga. The precision of the equilibrium temperature measurements is $\pm 0.001 \text{ K}$. The corresponding estimated standard uncertainty depends on the region where measurements are conducted. In the flat region of the coexistence curves (top of the curves), the uncertainty of the temperature is 0.1 K; while outside of this region (tails of the curves), it is 0.2 K. For the equilibrium mole fractions, the standard uncertainty is 0.0005. This value is determined taking into account that the more volatile component is partially evaporated to the mentioned free volume of the ampoule.

3. Experimental results

The directly measured liquid-liquid equilibrium temperatures, T , vs. x_1 , the mole fraction of the phenetidine, for the systems *o*-phenetidine + *n*-C₈, or + *n*-C₁₀, or + *n*-C₁₂, or + *n*-C₁₄ and for *p*-phenetidine + *n*-C₇, or + *n*-C₈ are collected in Table 2 (Figures 1,2). Values of UCST for the systems *o*-phenetidine + hexane (299.2 K), or + heptane (301.2 K), and *p*-phenetidine + hexane (354.2 K), or + heptane (356.2 K) are available in the literature [27]. The latter value is in good agreement with our result (355.8 K, see below). As in many systems previously investigated [5,6,11-16,18,19] the LLE curves of the mixtures under study are characterized by some typical features: (i) they show a rather flat maximum (Figures 1,2); (ii) the curves become progressively shifted towards higher x_1 values when the chain length of the alkane increases (Figure 1); (iii) the upper critical solution temperature, UCST, increases linearly with the number of C atoms of the *n*-alkane (Table 3).

The experimental (x_1, T) data of each system were correlated by means of the equation [28,29]:

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

with

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

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

In equations (1-3), m , k , α , T_c and x_{1c} stand for the parameters which must be adjusted against the experimental data. The coordinates of the critical point are denoted by (x_{1c} , T_c). It is remarkable that, when $\alpha = 1$, equation (1) is similar to [30-32]:

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

In this equation, $\Delta\lambda_1 = \lambda_1' - \lambda_2''$ is any order parameter. In other words, it is any density variable in the conjugate phase (along the present research, $\lambda_1 = x_1$). On the other hand, τ is the reduced temperature, defined as: $\tau = (T_c - T)/T_c$, β is the critical exponent related to $\Delta\lambda_1$ and B is the amplitude [32]. It is well-known that the critical exponent β depends on the theory applied to its determination.^{26,30}

The parameters m , k , α , T_c and x_{1c} were obtained from an adjustment based on a Marquardt algorithm [33] with all the points weighted equally. Final values of the parameters,

together with the standard deviations for the liquid-liquid equilibrium temperatures, $\sigma(T)$, are given in Table 3. The $\sigma(T)$ values are calculated from:

$$(\sigma(T)/K) = \left[\sum (T_{\text{exp}}/K - T_{\text{calc}}/K)^2 / (N - n) \right]^{1/2} \quad (5)$$

Here, N is the number of data points, and n , the number of adjusted parameters (= 5). Results listed in Table 3 show that equation (1) fits well the experimental results.

4. Discussion

Below, we are referring to H_m^E values at 298.15 K and equimolar composition.

4.1 Intramolecular effects in aromatic polar compound + alkane systems

Along a series of investigations, we have shown that, in alkane systems, dipolar interactions between polar molecules involving a polar group X are stronger than those between isomeric linear molecules with the same X group. For example, UCST (heptane) = 343.1 K (aniline) [1]; 327.3 (phenol) [34] while H_m^E (heptane)/J·mol⁻¹ = 962 (hexan-1-amine) [35]; 527 (hexan-1-ol) [36]; 1862 (aniline; $T = 333.15$ K); 1941 (aniline, $T = 353.15$ K) [37]. Similarly, H_m^E (heptane)/J·mol⁻¹ = 1278 (methoxybenzene) [38]; 260 (1-methoxypentane) [39]; 1492 (1-phenylethanone) [40]; 886 (heptan-2-one) [41]; 1361 (phenylmethanal) [42]; 1066 (pentanal) [43]; or H_m^E (cyclohexane)/J·mol⁻¹ = 1390 (benzonitrile) [44]; 1101 (pentanenitrile) [45]; 1654 (nitrobenzene, $T = 293.15$ K) [46]; 1225 (1-nitropentane) [47]. This behaviour has been ascribed to the existence of intramolecular effects, i.e. proximity effects, between the C₆H₅– group and the polar X group under consideration.

4.2 Intermolecular effects in linear polar compound + aromatic hydrocarbon mixtures

These effects are encountered when the aromatic ring and X do not pertain to the same molecule. They lead to increased interactions between unlike molecules, and, usually, to decreased H_m^E values. For the sake of comparison, we provide now some examples for linear polar compound + benzene mixtures. Thus, H_m^E (C₆H₆)/J·mol⁻¹ = 627 (hexan-1-amine; $T = 303.2$ K) [2]; –171 (hexan-2-one) [48]; –82 (pentanal) [49]; –112 (pentanenitrile) [50]; ≈ 205 (1-methoxypentane; $T = 293.15$ K) [51]. It is to be noted, that H_m^E values of 1-alkanol + benzene systems are higher than those of the corresponding alkane mixtures. For example, for the hexan-1-ol + benzene system, H_m^E /J·mol⁻¹ = 1141 [52]. It is clear that benzene is a much more effective

breaker of the alcohol self-association than alkanes. Taking into account the above considerations, our LLE data for phenetidine systems reveal the existence of strong dipolar interactions between these molecules, which contain three groups. In fact, the same three groups are present in the aniline + 3-oxapentane system, but in different molecules, and, at 293.15 K, the corresponding H_m^E value is $-500 \text{ J}\cdot\text{mol}^{-1}$ [53]. This remarks that intermolecular effects are predominant when the polar groups are placed in different molecules.

4.3 The effect of replacing an aromatic polar compound, C_6H_5-X , by its corresponding methyl derivative, $CH_3-C_6H_4-X$, in alkane systems

We note that, in mixtures with a given alkane, UCST decreases when an aromatic polar compound (aniline, phenol, nitrobenzene, $X = NH_2; OH; NO_2$) is replaced by the corresponding methyl derivative (e.g. 2-methyl-benzenamine, 4-methyl-benzenamine, 2-methyl-phenol, 4-methyl-phenol...) (Table 4). This behaviour can be ascribed to the lower aromatic surface fraction of the methyl derivatives compared to that of the C_6H_5-X molecules, which leads to weaker proximity effects between the X group and the phenyl ring. Steric effects are also present since the critical temperature of the solution with the 2-methyl derivative is lower than that of the system with the corresponding 4-methyl derivative (Table 4). The existence of the mentioned steric effects in cresols is supported by the application of the Treszcznowicz-Kehiaian model for the representation of apparent heat capacities of phenol and substituted phenols in dilute heptane [54].

4.4 The effect of replacing the CH_3 group in $CH_3-C_6H_4-X$ molecules by a second polar group, Y, in alkane systems

The Y groups under consideration are Cl, NO_2 , OCH_3 ; OCH_2CH_3 . UCST values listed in Table 4 (Figure 3) show that for heptane systems with 2-methyl-benzenamine derivatives, this magnitude changes in the order: 2-chloro-benzenamine < 2-methyl-benzenamine < 2-ethoxy-benzenamine < 2-nitro-benzenamine. For mixtures containing phenols, the corresponding UCST variation is similar: 2-chloro-phenol < 2-methyl-phenol < 2-nitro-phenol < 2-methoxyphenol. This means that dipolar interactions between the mentioned polar molecules become stronger along the indicated sequences. However, when the second polar group is attached to the aromatic ring in the *para* position, the UCST variation is somewhat different. In the case of systems with substituted anilines, such variation is as follows: 4-methyl-benzenamine < 4-chloro-benzenamine < 4-ethoxy-benzenamine. For mixtures involving substituted phenols, we also find that UCST(4-methyl-phenol) < UCST(4-chloro-phenol). We can conclude that the introduction of a second polar group (NO_2 ; OCH_3 ; OCH_2CH_3) in the 2-position may lead to stronger dipolar interactions. This is due to the existence of new interactions between the (X,Y) groups, and between the (Y, C_6H_5-) groups. Chlorinated derivatives seem to be an exception. If the Y group is situated in the 4-position, dipolar interactions become stronger, independently of the considered Y group,

compared to those existing between molecules of the 4-methyl type. An interesting point is that the UCST changes in the order: 2-ethoxy-benzenamine < aniline < 4-ethoxy-benzenamine. For example, in the case of octane systems, UCST/K = 304.1 (2-ethoxy-benzenamine); 344.9 (aniline) [55]; 358.2 (4-ethoxy-benzenamine). For phenol and its derivatives, the variation is similar (Table 4). It seems that steric effects exerted by the new Y group in the 2- position are predominant over, say, the new XY intramolecular effects and UCST decreases. In contrast, these interactions seem to be predominant when the Y group is placed in the 4- position, leading to higher values of the critical temperature. Nevertheless, for some systems containing the NO₂ group a different trend is observed. Thus, UCST(heptane)/K = 291.9 (nitrobenzene) [56]; 388.15 (1-methoxy-2-nitro-benzene) [57]. The dependence of the alkane solubility on the molecular structure of the aromatic polar compound deserves a careful experimental research, currently undertaken.

5. Conclusions

LLE phase diagrams have been obtained for the systems 2-ethoxy-benzenamine + octane, or + decane, or + dodecane, or + tetradecane, and for 4-ethoxy-benzenamine + heptane, or + octane. The mixtures are characterized by having an UCST, which increases with alkane size. Dipolar interactions between like molecules become stronger in the sequence: 2-ethoxy-benzenamine < aniline < 4-ethoxy-benzenamine. The attachment of a second polar group (different to Cl) in the *ortho* position to a molecule of the type (C₆H₅ – X; X =NH₂; OH) leads to weaker dipolar interactions. If the second polar group is attached in the *para* position, dipolar interactions become strengthened.

6. References

- (1) H. Matsuda, K. Ochi, K. Kojima. Determination and correlation of LLE and SLE data for the methanol + cyclohexane, aniline + heptane, and phenol + hexane system. *J. Chem. Eng. Data* 48 (2003) 184-189.
- (2) I. Velasco, S. Otín, C. Gutiérrez Losa. Excess enthalpies of some aliphatic amine + *n*-hexane or benzene mixtures. *J. Chim. Phys. Phys.-Chim. Biol.* 75 (1978) 706-708.
- (3) J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos. Thermodynamics of binary mixtures containing amines. IV. Systems with aniline. *Can. J. Chem.* 83 (2005) 1812-1825.
- (4) J.A. González, I. Alonso, C. Alonso-Tristán, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures containing amines. XI. Liquid + liquid equilibria and molar excess enthalpies at 298.15 K for *N*-methylaniline + hydrocarbon systems. Characterization in terms of DISQUAC and ERAS models. *J. Chem. Thermodyn.* 56 (2013) 89-98.

- (5) M. Fernández-Regúlez, I. Mozo, J.A. González, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures containing amines. VI. Liquid-liquid equilibria of *o*-toluidine + selected alkanes. *Fluid Phase Equilib.* 259 (2007) 39-44.
- (6) C. Alonso-Tristán, J.A. González, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures containing amines. XV. Liquid-liquid equilibria for benzylamine + $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ ($n = 8,9,10,12,14$). *J. Chem. Eng. Data* 59 (2014) 2101-2105.
- (7) R. Páramo, V. Alonso, J.A. González, I. García de la Fuente, C. Casanova, J. C. Cobos. Thermodynamics of mixtures containing amines. XIV. C_{pm}^E of benzylamine with heptane at 293.15 K, or with methanol, 1-propanol, or 1-pentanol at 293.15-308.15 K. *Thermochim. Acta* 586 (2014) 75-79.
- (8) U. Domanska, M. Zawadzki, M. Królikowski, J.A. González. Phase equilibria and excess molar enthalpies study of the binary systems (pyrrole + hydrocarbon, or an alcohol) and modeling. *Fluid Phase Equilib.* 361 (2014) 116-129.
- (9) J.A. González, U. Domanska, M. Zawadzki. Thermodynamics of organic mixtures containing amines. VIII. Systems with quinoline. *J. Chem. Thermodyn.* 40 (2008) 1261-1268.
- (10) U. Domanska, M. Zawadzki, J.A. González. Thermodynamics of organic mixtures containing amines. X. Phase equilibria for binary systems formed by imidazoles and hydrocarbons: experimental data and modelling using DISQUAC. *J. Chem. Thermodyn.* 42 (2010) 545-552.
- (11) J.A. González, C. Alonso-Tristán, I. García de la Fuente, J.C. Cobos. Liquid-liquid equilibria for benzaldehyde + *n*-alkane mixtures and characterization of benzaldehyde + hydrocarbon systems in terms of DISQUAC. *Fluid Phase Equilib.* 366 (2014) 61-68.
- (12) J.A. González, C. Alonso-Tristán, I. García de la Fuente, J.C. Cobos. Liquid-liquid equilibria for acetophenone + *n*-alkane mixtures and characterization of acetophenone systems using DISQUAC. *Fluid Phase Equilib.* 391 (2015) 39-48.
- (13) J.A. González, C. Alonso-Tristán, I. García de la Fuente, J.C. Cobos. Thermodynamics of aromatic polar compound (alkanone, alkanal, alkanoate) + hydrocarbon mixtures. *Fluid Phase Equilib.* 421 (2016) 49-58.
- (14) C. Alonso-Tristán, J.A. González, F. Hevia, I. García de la Fuente, J.C. Cobos. Liquid-liquid equilibria for systems containing 4-phenylbutan-2-one or benzyl ethanoate and selected alkanes. *J. Chem. Eng. Data* 62 (2017) 988-994.
- (15) J.A. González, C. Alonso-Tristán, F. Hevia, I. García de la Fuente, L.F. Sanz. Thermodynamics of mixtures containing aromatic nitriles. *J. Chem. Thermodyn.* 116 (2017) 259-262.

- (16) V. Alonso, M. García, M. J.A. González, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures containing alkoxyethanols. XXVIII. Liquid-liquid equilibria for 2-phenoxyethanol + selected alkanes. *Thermochim. Acta* 521 (2011) 107-111.
- (17) J.A. González, I. García de la Fuente, J.C. Cobos. Application of a purely physical model (DISQUAC) to binary mixtures of phenol and organic solvents. *Ber. Bunsenges. Phys. Chem.* 100 (1996) 1746-1751.
- (18) J.A. González, C. Alonso-Tristán, I. García de la Fuente, J.C. Cobos. Thermodynamics of mixtures containing aromatic alcohols. 1. Liquid-liquid equilibria for (phenylmethanol + alkane) systems. *J. Chem. Eng. Data* 57 (2012) 1186-1191.
- (19) C. Alonso-Tristán, J.A. González, I. García de la Fuente, L.F. Sanz, J.C. Cobos. Liquid-liquid equilibria for systems containing 2-phenylethan-1-ol + alkane systems. *J. Chem. Eng. Data* 63 (2018) 429-435.
- (20) N. Haman, E. Longo, A. Schiraldi M. Sampicchio. Radical scavenging activity of lipophilic antioxidants and extra-virgin olive oil by isothermal calorimetry. *Thermochim. Acta* 658 (2017) 1-6.
- (21) F. Shahidi. Antioxidants in food and food antioxidants. Protein - lipid interactions in edible films and coatings. *Nahrung/Food* 44 (2000) 158-163.
- (22) M. H. Ausari, J.-B. Parsa, J. Arjomandi. Application of conducting polyaniline, *o*-anisidine, *o*-phenetidine and *o*-chloroaniline in removal of nitrate from water via electrically switching ion exchange: Modeling and optimization using a response surface methodology. *Sep. Purif. Tech.* 179 (2017) 104-117.
- (23) CIAAW, Atomic weights of the elements 2015, ciaaw.org/atomic-weights.htm, accessed **09/05/2015**.
- (24) S.C. Greer. Liquid-liquid critical phenomena. *Acc. Chem. Res.* 11 (1978) 427-432.
- (25) N. Nagarajan, A. Kumar, E.S.R. Kumar, S.C. Greer. Liquid-liquid critical phenomena. The coexistence curve of *n*-heptane-acetic anhydride. *J. Phys. Chem.* 84 (1980) 2883-2887.
- (26) M.A. Rubio, J.A. González, I. García De La Fuente, J.C. Cobos. Thermodynamic properties of *n*-alkoxyethanols + organic solvents mixtures VIII. Liquid-liquid equilibria of systems containing 2-methoxyethanol and alkanes (C_6H_{12} and $CH_3-(CH_2)_u-CH_3$, $u = 3,4,6,8$). *Fluid Phase Equilib.* 143 (1998) 111-123.
- (27) A.W. Francis. Solvent selectivity for hydrocarbons measured by critical solution temperature. *Ind. Eng. Chem.* 36 (1944) 764-771.
- (28) J.B. Ott, I.F. Holscher, G.M. Schneider. (Liquid-Liquid) phase equilibria in (methanol + heptane) and (methanol + octane) at pressures from 0.1 to 150 MPa. *J. Chem. Thermodyn.* 18 (1986) 815-826.

- (29) U. Haarhaus, G.M. Schneider. (Liquid + liquid) phase equilibria in (methanol + butane) and (methanol + pentane) at pressures from 0.1 to 140 MPa. *J. Chem. Thermodyn.* 20 (1988) 1121-1129.
- (30) J.S. Rowlinson, F.L. Swinton. *Liquids and Liquid Mixtures*, Butterworths: London, 1982.
- (31) H.E. Stanley. *Introduction to Phase Transitions and Critical Phenomena*, Oxford University Press: New York, 1971.
- (32) J.P. Novak, J. Matous, J. Pick., *Liquid-Liquid Equilibria*, Elsevier: Amsterdam, 1987.
- (33) P.R. Bevington. *Data Reduction and Error Analysis for the Physical Sciences*, Mc-Graw-Hill: New York, 1969.
- (34) H. Matsuda, M. Fujita, K. Ochi. Measurement and correlation of mutual solubilities for high-viscosity binary systems: aniline + methylcyclohexane, phenol + heptane, phenol + octane, and glycerol + 1-pentanol. *J. Chem. Eng. Data* 48 (2003) 1076-1080.
- (35) E. Matteoli, L. Lepori, A. Spanedda. Thermodynamic study of heptane + amine mixtures: I. Excess and solvation enthalpies at 298.15 K. *Fluid Phase Equilib.* 212 (2003) 41-52.
- (36) E. Siimer, H. Kirss, M. Kuus, L. Kudryavtseva. Excess enthalpies for the systems *o*-xylene + cyclohexanol + nonane at 298.15 K and 318.15 K and 3-methylphenol + 1-hexanol + heptane at 298.15 K and for constituent binaries. *J. Chem. Eng. Data* 42 (1997) 619-622.
- (37) R. Fuchs, L. Krenzer, J. Gaube. Excess properties of binary mixtures composed of a polar component and an alkane. *Ber. Bunsenges. Phys. Chem.* 88 (1984) 642-649.
- (38) B. Marongiu, A. Piras, S. Porcedda, E. Tuveri. Excess enthalpies of aromatic ether or aromatic ketone(1) + *n*-heptane(2) mixtures. DISQUAC analysis. *J. Thermal Anal. Calorim.* 92 (2008) 137-144
- (39) K. Sosnkowska-Kehiaian, R. Hryniewicz, H.V. Kehiaian. Thermodynamics of *n*-ether - *n*-alkane mixtures. *Bull. Acad., Polon. Sci., Ser. Sci. Chem.* 17 (1969) 185-190.
- (40) O. Urdaneta, S. Haman, Y.P. Handa, G.C. Benson. Thermodynamic properties of binary mixtures containing ketones IV. Excess enthalpies of acetophenone + an *n*-alkane and phenylacetone + an *n*-alkane. *J. Chem. Thermodyn.* 11 (1979) 851-856.
- (41) O. Urdaneta, Y.P. Handa, G.C. Benson. Thermodynamic properties of binary mixtures containing ketones V. Excess enthalpies of an isomeric heptanone + *n*-heptane. *J. Chem. Thermodyn.* 11 (1979) 857-860.
- (42) I. Ferino, B. Marongiu, V. Solinas, S. Torraza. Excess enthalpies of some aromatic aldehydes in *n*-hexane, *n*-heptane and benzene. *Thermochim. Acta* 57 (1982) 147-154.
- (43) I. Ferino, B. Marongiu, V. Solinas, S. Torraza, H.V. Kehiaian. Thermodynamic properties of binary mixtures containing aldehydes. I. Excess enthalpies of some *n*-alkanal + *n*-alkane mixtures: measurement and analysis in terms of a quasi-chemical group

- contribution model and estimation of excess Gibbs energies. *Fluid Phase Equilib.* 12 (1983) 125-142.
- (44) R. Tanaka, S. Murakami, R. Fujishiro. Excess enthalpies of mixing of a polar liquid + a non-polar liquid at 298.15 K. *J. Chem. Thermodyn.* 6 (1974) 209-218.
- (45) B. Marongiu, S. Porcedda. Thermodynamics of binary mixtures containing alkanenitriles. 1. Excess enthalpies of some *n*-alkanenitrile + *n*-alkane or + cyclohexane mixtures. *J. Chem. Eng. Data* 35 (1990) 172-174.
- (46) R. Mecke, K. Zirker. Thermodynamische Mischungsgrossen des Systems Nitrobenzol-cyclohexan. *Ber. Bunsenges. Phys. Chem.* 68 (1964) 174-181.
- (47) B. Marongiu, S. Porcedda, H.V. Kehiaian. Calorimetric study of nitro group interactions in alkane solutions. Comparison with DISQUAC predictions. *Fluid Phase Equilib.* 87 (1993) 115-131.
- (48) B. Marongiu, S. Dernini, L. Lepori, E. Matteoli. Calorimetric study of molecular interactions in mixtures of substances containing carbonyl groups. *Thermochim. Acta* 149 (1989) 111-121.
- (49) B. Marongiu. Thermodynamics of binary mixtures containing aldehydes. Excess enthalpies of *n*-alkanals + benzene and + tetrachloromethane. *Thermochim. Acta* 95 (1985) 105-110.
- (50) B. Marongiu, S. Porcedda, M. Marrocu, D. Falconieri, A. Piras. Calorimetric study of nitrile group-solvent interactions and comparison with Dispersive Quasi-Chemical (DISQUAC) predictions. *J. Chem. Eng. Data* 55 (2010) 5406-5412.
- (51) H.V. Kehiaian, K. Sosnkowska-Kehiaian, R. Hryniewicz. Enthalpy of mixing of ethers with hydrocarbons at 25 °C and its analysis in terms of molecular surface interactions. *J. Chim. Phys.-Chim. Biol.* 69 (1971) 922-934.
- (52) K.-Y. Hsu, H.L. Clever. Enthalpy of mixing of some hydrocarbon-alcohol and hydrocarbon-nitroalkane mixtures at 25 °C. *J. Chem. Eng. Data* 20 (1975) 268-271.
- (53) E.J. Hartung. *Trans Faraday Soc.* 12 (1916) 66-85. (cf. 62)
- (54) S. Pérez-Casas, L.M. Trejo, M. Costas. Self-association of phenols in inert solvents. Apparent heat capacities of phenol, substituted phenols and aromatic alcohols in *n*-heptane. *J. Chem. Soc. Faraday Trans.* 87 (1991) 1733-1738.
- (55) A.F. Shepard, A.L. Henne, T. Midgley. Physical properties of the normal paraffin hydrocarbons, pentane to dodecane. *J. Am. Chem. Soc.* 53 (1931) 1948-1958.
- (56) K. Tang, C. Zhou, X. An, W. Shen. The coexistence curves of $\{x \text{ C}_6\text{H}_5\text{NO}_2 + (1-x) \text{CH}_3(\text{CH}_2)_4\text{CH}_3\}$ and $\{x \text{ C}_6\text{H}_5\text{NO}_2 + (1-x) \text{CH}_3(\text{CH}_2)_5\text{CH}_3\}$ in the critical region. *J. Chem. Thermodyn.* 31 (1999) 943-954.
- (57) A.W. Francis, *Critical Solution Temperatures*, Advances in Chemistry Series No 31: American Chemical Society, Washington DC, 1961.

- (58) C.L. Yaws. *Thermophysical properties of chemicals and hydrocarbons*, Elsevier: Amsterdam, 2014.
- (59) J.A. Riddick, W.B. Bunger, T.K. Sakano. *Organic Solvents, Techniques of Chemistry*. Weissberger, A. Ed., Wiley: New York, Vol. II, 1986.
- (60) S. Zhu, S. Shen, G.C. Benson, B.-C.Y. Lu. Excess enthalpies of (methyl 1,1-dimethylpropyl ether + an *n*-alkane) at the temperature 298.15 K. *J. Chem. Thermodyn.* 26 (1994) 35-39.
- (61) A. Ksiazczak, J.J. Kosinski. Liquid-liquid equilibria in binary polar aromatic + hydrocarbon systems. *Fluid Phase Equilib.* 59 (1990) 291-308.
- (62) J.J. Christensen, R.W. Hanks, R.M. Izatt. *Handbook of Heat of Mixing*, John Wiley, New York., 1982.

Table 1

Properties of pure compounds at 0.1 MPa and 298.15 K^a

Compound	CAS	Source	Initial mole ^b fraction	ρ /kg·m ⁻³	Water Content ^c
----------	-----	--------	---------------------------------------	----------------------------	-------------------------------

				Exp.	Lit.	
2-ethoxy- benzenamine	90-70-2	Sigma- Aldrich	≥ 99.4%	1045.74		123·10 ⁻⁴
4-ethoxy- benzenamine	156-43-4	Sigma- Aldrich	≥ 99.1%	1056.76	1057 ⁵⁸	700·10 ⁻⁴
Heptane	142-82-5	Fluka	≥ 99.5%	679.51	679.46 ⁵⁹	8·10 ⁻⁴
Octane	111-65-9	Sigma- Aldrich	≥ 99.4%	698.68	698.62 ⁵⁹	15·10 ⁻⁴
Decane	24-18-5	Fluka	≥ 99.8%	726.35	726.35 ⁵⁹	12·10 ⁻⁴
Dodecane	112-40-3	Fluka	≥ 99.7%	745.51	745.32 ⁶⁰	7·10 ⁻⁴
Tetradecane	629-59-4	Fluka	≥ 99.5%	759.27	759.32 ⁶⁰	9·10 ⁻⁴

^astandard uncertainties are: $u(T) = 0.01$ K; $u(P) = 0.5$ kPa; the relative standard uncertainty for density is $u_r(\rho) = 0.002$ and 0.02 for water content; ^bprovided by the supplier by gas chromatography; ^cin mass fraction.

Table 2

Experimental liquid-liquid equilibrium temperatures for 2-ethoxy-benzenamine (1), or 4-ethoxy-benzenamine (1) + *n*-alkane(2) mixtures^a at 0.1 MPa.

x_1	T/K	x_1	T/K
2-ethoxy-benzenamine (1) + octane (2)			
0.1755	295.8	0.4505	304.1
0.1923	297.4	0.4615	304.1
0.2055	298.1	0.4915	304.0
0.2191	299.5	0.5285	303.9
0.2338	300.4	0.5594	303.7
0.2452	301.0	0.5749	303.6
0.2650	301.8	0.5980	303.2
0.2863	302.6	0.6140	303.1
0.3094	303.0	0.6524	302.4
0.3217	303.3	0.6641	302.1
0.3485	303.7	0.6850	301.3
0.3955	304.1	0.7067	300.6
0.4202	304.2		
2-ethoxy-benzenamine (1) + decane (2)			
0.2691	305.2	0.4586	310.5
0.2826	306.0	0.4718	310.5
0.300	307.1	0.4983	310.6
0.3273	307.9	0.5230	310.7
0.3625	308.9	0.5607	310.6
0.3928	309.5	0.5871	310.7
0.4277	310.3	0.6219	310.4
0.4432	310.4		
2-ethoxy-benzenamine (1) + dodecane (2)			
0.2191	304.1	0.5317	317.8
0.2492	306.7	0.5552	317.8
0.2741	309.5	0.5762	317.8
0.2954	311.7	0.6081	317.7
0.3189	313.2	0.6204	317.7
0.3474	314.3	0.6435	317.6
Table 2 (continued)			
0.3646	315.0	0.6966	317.5
0.3876	315.8	0.6984	317.3
0.4188	316.7	0.7341	316.9

0.4417	317.0	0.7437	316.7
0.4855	317.7	0.7800	315.2
0.5169	317.8		
2-ethoxy-benzenamine (1) + tetradecane (2)			
0.2545	310.3	0.5510	324.6
0.2591	310.9	0.5806	324.9
0.2757	312.5	0.6154	324.8
0.3002	314.9	0.6517	324.7
0.3387	317.8	0.6724	324.6
0.3525	318.5	0.6740	324.5
0.3963	320.9	0.7050	324.5
0.4354	322.3	0.7240	324.4
0.4833	323.7	0.7552	324.0
0.5209	324.3		
4-ethoxy-benzenamine (1) + heptane (2)			
0.0988	333.0	0.3367	355.4
0.1156	337.6	0.3702	356.0
0.1323	340.8	0.3779	356.0
0.1733	347.2	0.4070	356.0
0.2103	350.7	0.4635	356.0
0.2318	352.2	0.4736	355.9
0.2691	354.1	0.4930	356.0
0.2906	354.5	0.5290	355.6
0.3115	355.0	0.5418	355.5
0.3340	355.4	0.5657	355.3
4-ethoxy-benzenamine (1) + octane (2)			
0.1414	341.9	0.3750	357.9
0.1602	344.6	0.4198	358.2
0.1919	349.1	0.4497	358.2
0.2007	349.9	0.4682	358.3
0.2391	353.3	0.5086	358.2
Table 2 (continued)			
0.2811	355.7	0.5403	358.1
0.2963	356.3	0.5447	358.2
0.3234	357.0	0.5779	358.0

0.3489

357.9

^astandard uncertainties are: $u(x_1) = 0.0005$; $u(p) = 1$ kPa; the combined expanded uncertainty (0.95 level of confidence) for temperature is $U_c(T) = 0.2$ K in the flat region of the curves and 0.4 K outside this region

ACCEPTED MANUSCRIPT

Table 3

Coefficients in eq. (1) for the fitting of the (x_1, T) pairs listed in Table 2 for 2-ethoxy-benzenamine, or 4-ethoxy-benzenamine (1) + n -alkane(2) Mixtures; $\sigma(T)$ is the standard deviation defined by eq. (5).

N^a	m	k	α	T_c/K	x_{1c}	$\sigma(T)/K$
2-ethoxy-benzenamine(1) + octane(2)						
25	2.944	-262	1.529	304.1	0.450	0.09
2-ethoxy-benzenamine (1) + decane(2)						
15	3.216	-824	0.475	310.6	0.540	0.09
2-ethoxy-benzenamine(1) + dodecane(2)						
23	3.546	-620	0.744	317.7	0.587	0.08
2-ethoxy-benzenamine(1) + tetradecane(2)						
19	3.286	-418	0.683	324.7	0.639	0.11
4-ethoxy-benzenamine(1) + heptane(2)						
20	3.929	-2086	0.852	355.8	0.440	0.17
4-ethoxy-benzenamine(1) + octane(2)						
18	3.417	-615	1.080	358.2	0.478	0.11

^a number of experimental data points

Table 4

Upper critical solution temperatures (UCST) for aromatic polar compound^a + *n*-alkane mixtures.

UCST

Alkane	X	C ₆ H ₅ -X	Y	2-Y-C ₆ H ₄ -X	4-Y-C ₆ H ₄ -X
Heptane	NH ₂	343.1 ¹	CH ₃	292.9 ⁵	305.6 ^{b,57}
			Cl	286.2 ²⁷	353.2 ²⁷
			OCH ₂ CH ₃	304.1 ²⁷	358.2 ^c
			NO ₂	479.2 ²⁷	
Heptane	OH	327.1 ³⁴	CH ₃	282.1 ²⁷	285.2 ²⁷
			Cl	279.0 ²⁷	340.2 ²⁷
			NO ₂	316.2 ²⁷	373.0 ²⁷
hexadecane	OH	360.7 ⁶¹	CH ₃	299.2 ⁵⁷	315.2 ⁵⁷
			NO ₂	334.6 ⁶¹	
			OCH ₃	340.5 ⁶¹	
			Cl		359.5 ⁶¹
Heptane	NO ₂	291.9 ⁵⁶	CH ₃	272.1 ²⁷	
			OCH ₃	388.2 ⁵⁷	

^athe polar compounds considered are: aniline, phenol, or nitrobenzene (polar group X = NH₂; OH, NO₂) and the derivatives including the Y group (CH₃; Cl; OCH₃; OCH₂CH₃) in the 2- or 4-positions; ^bmixture with 2-methylpentane; ^cthis work

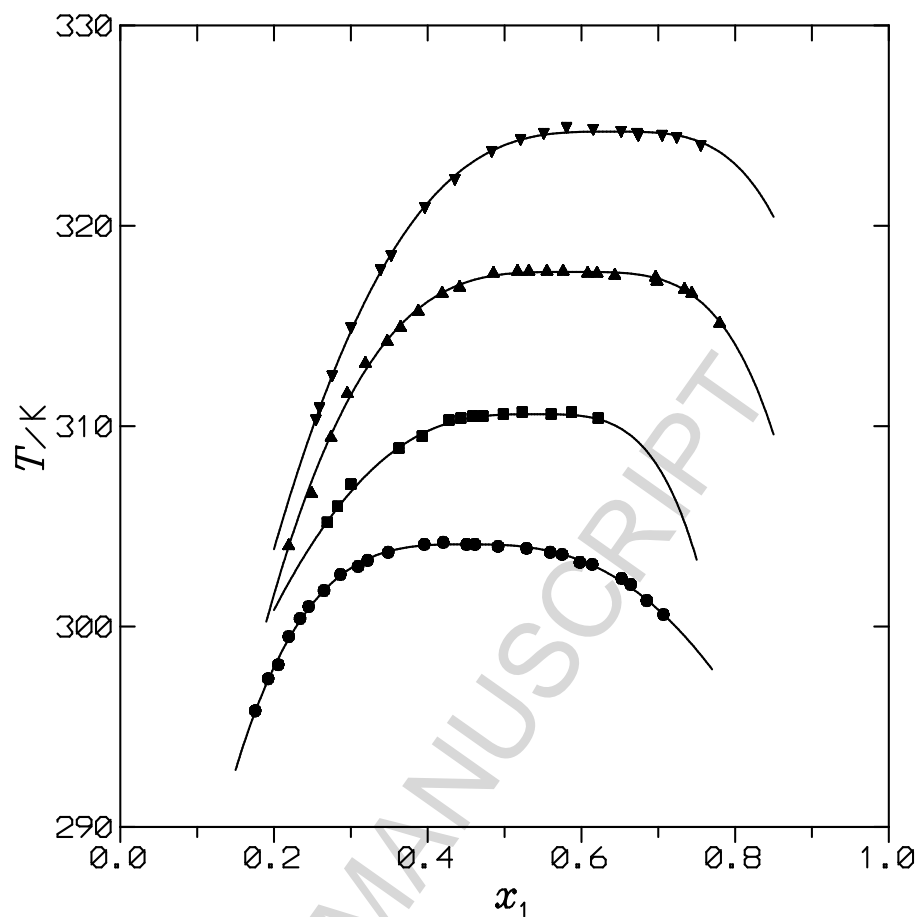


Figure 1. LLE for 2-ethoxy-benzenamine(1) + octane(2) (●); + decane(2) (■); + dodecane(2) (▲); + tetradecane(2) (▼) systems. Points, experimental results (this work); solid lines, calculations with equation 1 using the parameters listed in Table 3.

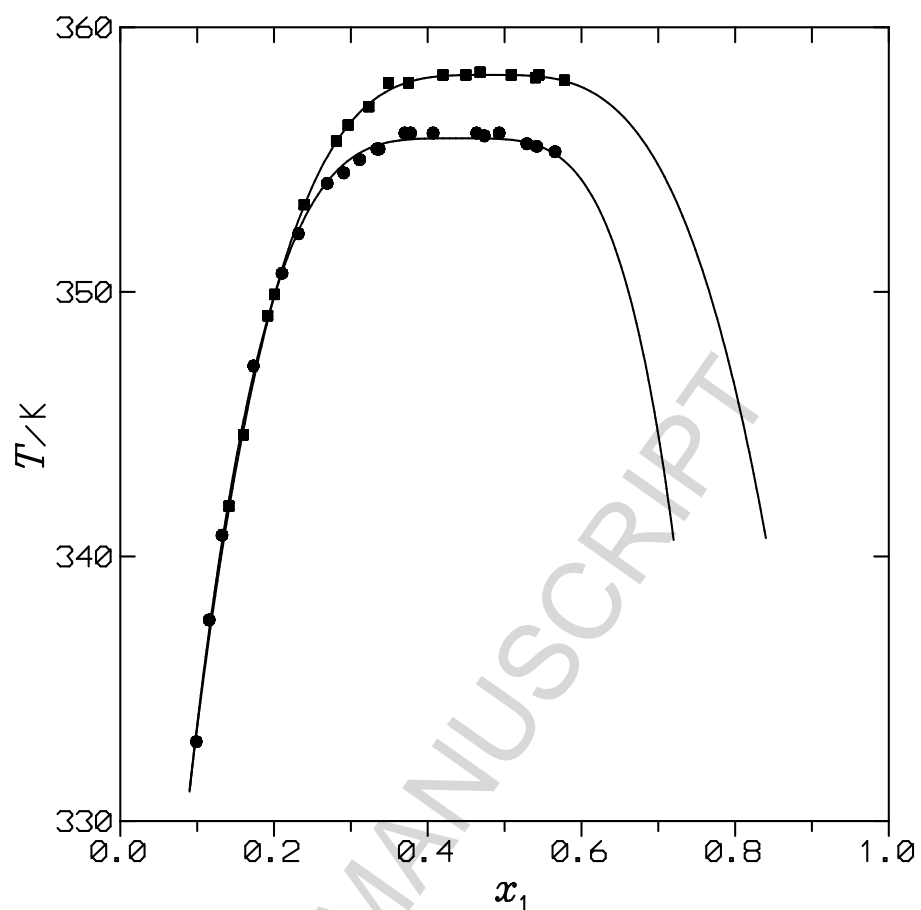


Figure 2. LLE for 4-ethoxy-benzenamine(1) + heptane(2) (●); + octane(2) (■) systems. Points, experimental results (this work); solid lines, calculations with equation 1 using the parameters listed in Table 3.

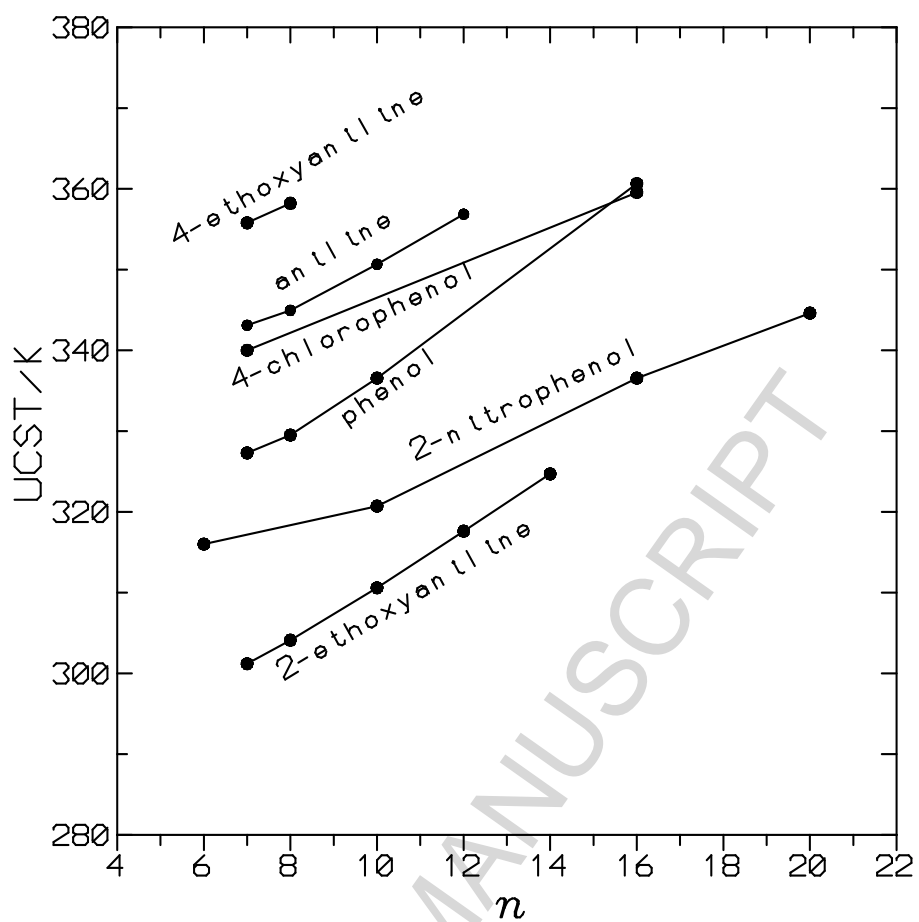
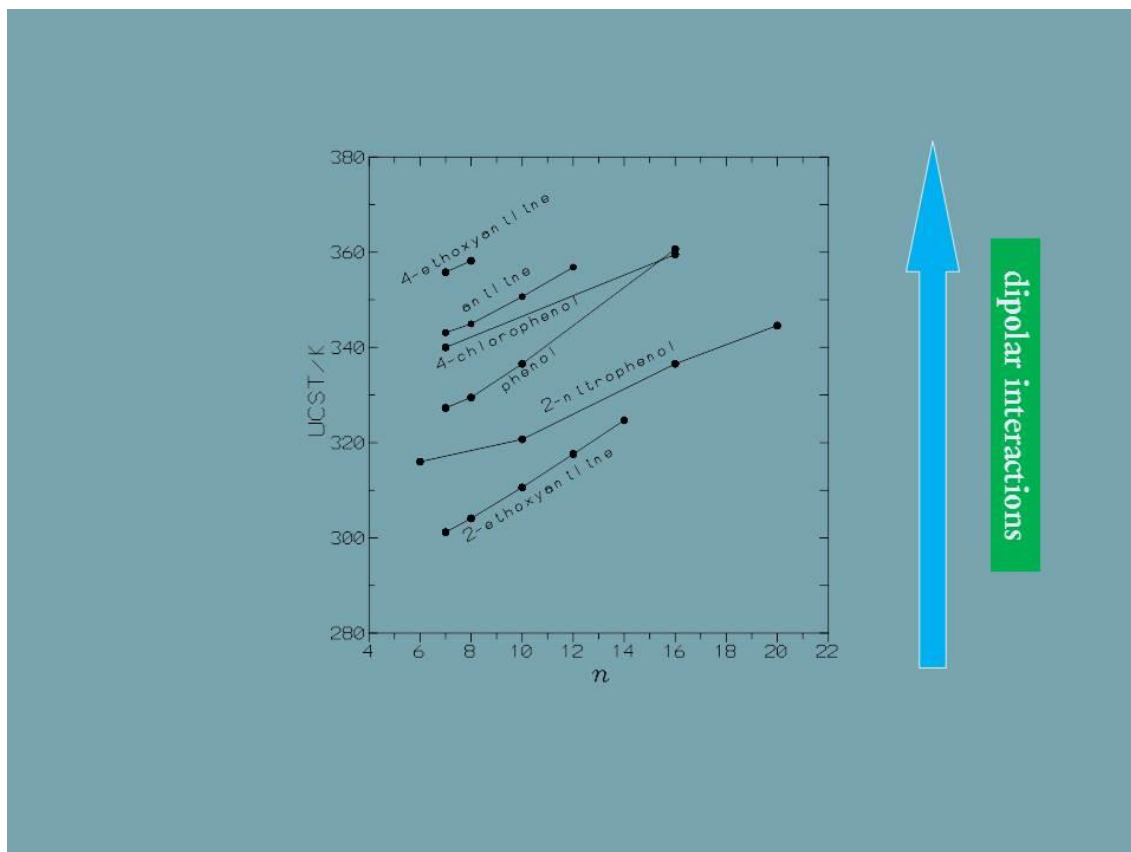


Figure 3. UCST for aromatic polar compound + n -alkane mixtures vs. n , the number of C atoms in the alkane (for references of experimental data, see Table 4)

GRAPHICAL ABSTRACT



Upper Critical Solution Temperatures for aromatic polar compound + *n*-alkane mixtures vs. *n*, the number of C atoms in the *n*-alkane

Highlight

- ➔ LLE diagrams are determined for *o*-phenetidine, or *p*-phenetidine + *n*-alkane systems
- ➔ All the mixtures show an UCST, which increases with the alkane size
- ➔ Amine-amine dipolar interactions change as follows: *o*-phenetidine < aniline < *p*-phenetidine
- ➔ Interactions between other anilines/phenols with a second polar group are examined
- ➔ Steric effects in *ortho* or *para* anilines/phenols with a second polar group are discussed

ACCEPTED MANUSCRIPT