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LIQUID-LIQUID EQUILIBRIA FOR SYSTEMS CONTAINING 4-PHENYLBUTAN-2-ONE OR BENZYL ETHANOATE AND SELECTED ALKANES

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ABSTRACT

Liquid-liquid equilibrium (LLE) phase diagrams have been determined, by means of the critical opalescence method with a laser scattering technique, for the mixtures 4-phenylbutan-2-one + $CH_3(CH_2)_nCH_3$ (n = 10,12,14) and for benzyl ethanoate + $CH_3(CH_2)_nCH_3$ (n = 12,14). The systems are characterized by having an upper critical solution temperature (UCST), which increases with n. The corresponding LLE curves show a rather horizontal top and become skewed towards higher mole fractions of the polar compound when n is increased. Calorimetric and LLE measurements show that, for mixtures with molecules with a given functional group, interactions between aromatic molecules are stronger than those between homomorphic linear molecules (aromaticity effect). This has been ascribed to proximity effects arising from the presence of the polar group and the aromatic ring within the same molecule. Proximity effects become weaker in the sequence: 1-phenylpropan-2-one > 4-phenylbutan-2-one > 1-phenylethanone, and are more important in benzyl ethanoate than in ethyl benzoate molecules. Values of the critical compositions and temperatures calculated with the DISQUAC group contribution model are in good agreement with the experimental results. Accordingly, the shape of the LLE curves is also correctly described by DISQUAC.

Keywords: LLE, aromatic polar compound, proximity effects, DISQUAC

1. Introduction

This work is part of a series concerned with the research of mixtures involving aromatic polar compounds. Up to now, we have investigated systems with aromatic amines[1-8] [1-8] (anilines, 2-amino-1-methylbenzene, 1-phenylmethanamine, 1*H*-pyrrole, quinoline or imizadoles); aromatic alcohols[9-10] (phenol or phenylmethanol), or aromatic alkanals, ketones or alkanoates.[11-13] Now, we report LLE measurements for the mixtures 4-phenylbutan-2-one + *n*-C_{12}, or + *n*-C_{14}, or + *n*-C_{16}, and for benzyl ethanoate + *n*-C_{14}, or + *n*-C_{16}. In a previous article, we have provided LLE data for 4-phenylbutan-2-one + decane, or benzyl ethanoate + dodecane systems.[13] The presence of the C_6H_5- group and of a polar group X in the same molecule (in this investigation, X = CO, or COO) leads to the existence of proximity effects between the mentioned groups. Such effects are of intramolecular character and it is well known that may have a decisive influence on the interaction parameters of the statistical model employed for the characterization of the systems under study. For example, main groups for phenol or aniline have been defined in the framework of the UNIFAC model (Dortmund version)[14] for the improvement of the predictions of the thermodynamic properties of their mixtures. The data reported in this work are used to improve the DISQUAC[15,16] matrix of interaction parameters for contacts where the CO or COO groups participate.[11,13] On the other hand, the investigation of systems with aromatic heteroatoms is needed for a deeper understanding of the π-π interactions and of the non-conventional H-bonds.[17,18] The functional CO and COO groups are very relevant. The former is encountered in proteins and hormones. Particularly, 4-phenylbutan-2-one has been investigated as a potential fumigant or insecticide,[19] and is useful to study the rate of hydrogenation of the carbonyl group related to the ring hydrogenation.[20] The COO group attached to an aromatic ring is often employed as amine protecting group of amino acids and it is of importance in peptide synthesis.[21] Aromatic alkanoates are widely used in the manufacture of odorants and flavouring chemicals.

2. Experimental

2.1 Materials. Table 1 shows source, purity, water contents, determined by the Karl-Fischer method, and density (ρ) of the pure chemicals needed for the present experimental research. They were handled without further purification. Density values were determined using a vibrating-tube densimeter and a sound analyser, Anton Paar model DSA-5000. The repeatability of the ρ measurements is $5\cdot10^{-3}$ kg·m^{-3}, while their relative standard uncertainty is 0.002. Accordingly to the values shown in Table 1, there is a good agreement between our density results and those reported in the literature.

2.2 Apparatus and Procedure

Mixtures were prepared by mass in small Pyrex tubes (0.009 m i.d. and about 0.04 m length, with a free volume of the ampoule $\approx 1.17 \cdot 10^{-6}$ m^3). The tubes were immediately sealed by capping at 0.1 MPa and 298.15 K. Weights were determined by means of an analytical balance HR-202 (weighing accuracy 10^{-8} kg). Mole fractions were calculated using the relative atomic mass table of 2015 issued by the Commission on Isotopic Abundances and Atomic Weights (IUPAC)[22]

As in previous applications, the LLE phase diagrams were determined by the method of the critical opalescence. More details regarding the experimental technique can be found elsewhere.[23] The liquid-liquid equilibrium temperatures were measured by means of a Pt-1000 resistance. The thermometer calibration was conducted according to the ITS-90 scale of temperature and two fixed points were considered: the triple point of the water and the fusion point of Ga. The precision of the temperature measurements is 0.001 K. The estimated standard uncertainty is 0.1 K. The standard uncertainty of the equilibrium mole fraction is 0.0005. This value of composition uncertainty takes into account that the more volatile component is partially evaporated to the mentioned free volume of the ampoule.

3. Experimental results

Table 2 lists the directly measured liquid-liquid equilibrium temperatures, T, vs. x_1, the mole fraction of the aromatic polar compound, for the systems: 4-phenylbutan-2-one + *n*-C_{12}, or + *n*-C_{14}, or + *n*-C_{16}, and benzyl ethanoate + *n*-C_{14}, or + *n*-C_{16}. No data are available in the literature for comparison. Figures 1 and 2 show the experimental results.

We note that the LLE curves of the present systems with 4-phenylbutan-2-one or benzyl ethanoate show a rather flat maximum and become progressively skewed towards higher x_1 values when the number of C atoms of the alkane is increased. In addition, the upper critical solution temperature, UCST, of the solutions under study increases with the alkane size. These features are also encountered in many others mixtures previously investigated as those formed by alkane and 1-phenylethanone,[11] or 1-phenylpropan-2-one[13] or phenylmethanal,[12] or aromatic alcohols,[10] or aromatic amines, or linear organic carbonate, or acetic anhydride, or alkoxyethanol, or linear polyether (source of experimental data may be found in reference[13]).

The experimental (x_1,T) pairs obtained for each system were correlated with the equation:[10-13,23-25]

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

where

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

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

In equations (1)-(3), m, k, α, T_c and x_{1c} are the parameters which must be adjusted against the experimental data. Particularly, (x_{1c}, T_c) stand for the coordinates of the critical point. It should be remarked that, when α = 1, equation (1) is similar to:[26-28]

$$\Delta\lambda = B\tau^{\beta} \tag{4}$$

In equation (4), $\Delta\lambda_1 = \lambda_1' - \lambda_2''$ may be any density variable in the conjugate phase (order parameter). In this investigation, $\lambda_1 = x_1$. On the other hand, τ (= $T_c - T)/T_c$) denotes the reduced temperature and β is the critical exponent related to $\Delta\lambda_1$. The critical exponent β value depends on the theory applied to its determination.[26,29]

The adjustment of the m, k, α, T_c and x_{1c} parameters was conducted by means of the Marquardt algorithm[30] with all the points weighted equally. Final values of m, k, α, T_c and x_{1c} and of the standard deviations for LLE temperatures, $\sigma(T)$, are given in Table 3. The corresponding $\sigma(T)$ values are calculated from:

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

Here, N stands for the number of data points, and n (= 5) is the number of adjusted parameters. Equation (1) fits well the experimental measurements.

4. Discussion

Below, we'll refer to H_m^E values at 298.15 K and x_1 = 0.5. Firstly, we remark that H_m^E values of binary systems formed by one alkane and one aromatic polar compound are larger than those of mixtures where the polar group is situated within a linear chain. For example, H_m^E(n-C_7)/J•mol^{-1} = 1492 (1-phenylethanone);[31] 886 (heptan-2-one);[32] 1361 (phenylmethanal);[33] 1066 (pentanal);[34] 1154 (ethyl benzoate);[35] 528 (ethyl hexanoate).[36] Therefore, it is possible to conclude that interactions between like molecules are stronger in systems containing aromatic polar compounds. The existence of miscibility gaps for such mixtures at temperatures not far from 298.15 K confirms this point (Figure 3).[11,13] The observed

behaviour can be ascribed to the existence of proximity effects (intramolecular effects) between the aromatic ring and the polar group within the same molecule. In contrast, intermolecular effects are present in systems of the type linear polar compound + benzene, where the aromatic ring and polar group belong to different molecules. These intermolecular effects lead to H_m^E(linear polar compound + benzene) < H_m^E(aromatic polar compound + heptane), as it is indicated by the following examples (see above): H_m^E(benzene)/J·mol^{-1} = 138 (2-propanone);[37] −171 (2-hexanone);[38] 54 (propanal);[39] −82 (pentanal);[39] 84 (ethyl ethanoate).[35]

The variation of proximity effects with the separation between the polar group and the aromatic ring strongly depends on the polar group under consideration. In the case of aromatic alkanones, the mentioned effects become weaker in the sequence: 1-phenylpropan-2-one > 4-phenylbutan-2-one > 1-phenylethanone, as for mixtures with a given alkane, the corresponding values of UCST (Figure 3) and of H_m^E decrease in the same order. Thus, H_m^E(n-C$_7$)/J·mol^{-1} = 1680 (1-phenylpropan-2-one)[31] > 1604 (4-phenylbutan-2-one)[40] > 1480 (1-phenylethanone).[31] This set of experimental data allows conclude that alkanone-alkanone interactions become weakened in the same sequence. Interactions between aromatic esters are also stronger in benzyl ethanoate systems than in those with ethyl benzoate, as H_m^E(n-C$_7$)/ J·mol^{-1} = 1783 (benzyl ethanoate);[41] 1154 (ethyl benzoate).[35] An inversion of this behaviour is encountered in mixtures containing heptane and phenol (UCST = 327.3 K)[42] or phenylmethanol (323.7 K).[10]

Now, we compare results for mixtures with isomeric polar molecules and an alkane. Here, we remark the rather large difference between the UCST values of heptane mixtures involving methyl 2-phenylacetate (278.7 K) or benzyl acetate (263.0 K),[43] what clearly indicates that interactions between polar molecules are stronger in 2-phenylacetate systems. On the other hand, Figure 3 shows that the UCST values of 1-phenylpropan-2-one mixtures are higher than those of benzyl acetate systems. Therefore, one can conclude that interactions between like polar molecules are weaker in the latter solutions. However, the H_m^E(n-C$_7$)/J·mol^{-1} values change in the opposite way: 1783 (benzyl ethanoate)[41] > 1680 (1-phenylpropan-2-one).[31] This suggests that interactions related to dispersive forces are more important in mixtures with the ester.

In previous works,[11,13] we have characterized aromatic alkanone or alkanoate + alkane systems by means of DISQUAC,[15,16] providing the needed interaction parameters. Here, we have explored the validity of the mentioned parameters for the representation of the LLE curves of the studied solutions. Details on DISQUAC, equations and fitting procedure, can be found elsewhere.[44,45] We merely remark that the functional dependence of the interaction parameters with the temperature is expressed in terms of the DIS (dispersive) and QUAC (quasichemical)

interchange coefficients,[44] $C_{st,l}^{DIS}; C_{st,l}^{QUAC}$ where s ≠ t denote two contact surfaces present in the mixture and l = 1 (Gibbs energy); l = 2 (enthalpy); l = 3 (heat capacity). The systems under consideration are built by the three following surfaces: type a, aliphatic (CH_3, CH_2, in alkanes or aromatic polar compounds), type b, aromatic (C_6H_5 in aromatic polar compound) and type k (CO in aromatic alkanone, or COO in aromatic alkanoate). Therefore, in these solutions, we have three contacts: (a,b); (a,k) and (b,k). The interchange coefficients of the (a,b) contacts are purely dispersive and can be encountered in the literature.[46] The (b,k) contacts in aromatic alkanoate systems are also represented by DIS parameters only, while the remainder contacts are described by both DIS and QUAC interchange coefficients.[13] The $C_{bk,l}^{DIS/QUAC}$ (l =1,2,3) coefficients have been used without modification.[13] However, as in other previous DISQUAC studies as those on mixtures including *N,N*-dialkylamides,[44] or pyridine[47] or phenylmethanol,[10] or 1-phenylethanone,[11] calculations show that the $C_{ak,l}^{DIS}$ coefficients must be assumed to be dependent on the alkane size (Table 4) in order to provide correct values of (x_{1c}, T_c) (Table 3). This can be explained taking into account that DISQUAC is a mean field theory and that, therefore, theoretical calculations on LLE are developed under the assumption that G_m^E (molar excess Gibbs energy) is an analytical function close to the critical point. However, it is well known that, at temperatures close to the critical one, thermodynamic functions are expressed in terms of scaling laws with universal critical exponents and universal scaling functions.[26] This also leads to the theoretical LLE curves are more rounded than the experimental ones at temperatures not far from the UCST (Figures 1,2). Moreover, the calculated critical temperatures are higher than the experimental values at UCST and lower than the experimental results at the LCST[26] (lower critical solution temperature). In spite of these shortcoming of mean field theories, an important result obtained here is that DISQUAC correctly describes the change in the symmetry of the LLE curves for the benzyl ethanoate mixtures when the alkane size is increased (Figure 2).

5. Conclusions

LLE curves have been experimentally obtained for the mixtures 4-phenylbutan-2-one + dodecane, or + tetradecane, or + hexadecane and benzyl ethanoate + tetradecane, or + hexadecane. All the curves show an UCST, which increases with the alkane size. Alkanone-alkanone interactions become weaker in the order: 1-phenylpropan-2-one > 4-phenylbutan-2-one > 1-phenylethanone and proximity effects between the C_6H_5- ring and the CO group become also weaker in the same sequence. Proximity effects are also more relevant in benzyl ethanoate than in ethyl benzoate. DISQUAC provides rather accurate results for (x_{1c}, T_c) and

represents correctly the shape of the LLE curves by means of dispersive Gibbs energy parameters dependent on the alkane for the CH_2/X (X =CO, or COO) contacts.

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Table1

Properties of Pure Compounds at 0.1 MPa and 298.15 K[a]

Compound	CAS	Source	Initial mole fraction	ρ [a]/kg·m^{-3}		water[b] content
				Exp.	Lit.	
4-phenylbutan-2-one	2550-26-7	Sigma-Aldrich	≥98%	984.742	982.95[48] 984.34[40]	700
Benzyl ethanoate	140-11-4	Sigma-Aldrich	≥99%	1051.10	1051.13[49]	350
Dodecane	112-40-3	Fluka	≥98%	745.508	745.32[50]	25
Tetradecane	629-59-4	Fluka	≥99%	759.275	759.316[50]	25
Hexadecane	544-76-3	Fluka	≥99%	770.221	770.316[50]	33

[a]standard uncertainties are: $u(T) = 0.01$ K; $u(P) = 1$ kPa; the relative standard uncertainty for density is $u_r(\rho)$ = 0.002 and 0.02 for water content; [b]in mass fraction (ppm)

Table 2

Experimental Liquid-Liquid Equilibrium Temperatures for 4-Phenylbutan-2-one (1) or Benzyl Ethanoate(1) + *n*-Alkane(2) Mixtures[a] at 0.1 MPa.

x_1	T/K	x_1	T/K
4-Phenylbutan-2-one (1) + dodecane(2)			
0.2232	279.3	0.5673	292.4
0.2653	285.2	0.5993	292.3
0.2833	286.4	0.6316	292.2
0.2929	287.1	0.6521	292.2
0.3250	288.9	0.6695	291.9
0.3431	289.6	0.6939	291.6
0.3688	290.6	0.7211	291.0
0.4059	291.4	0.7534	289.9
0.4605	292.3	0.7684	289.1
0.4775	292.4	0.7997	286.8
0.4844	292.5	0.8176	285.5
0.4853	292.5	0.8341	283.2
0.5528	292.4	0.8683	278.3
4-Phenylbutan-2-one (1) + tetradecane(2)			
0.2262	285.8	0.5949	300.0
0.2421	287.3	0.6374	299.9
0.2911	291.6	0.6873	299.8
0.3173	293.4	0.7021	299.7
0.3346	294.7	0.7183	299.4
0.3524	295.5	0.7218	299.4
0.3731	296.4	0.7475	298.9

Table 2 (continued)

0.3958	297.4	0.7740	297.1
0.4479	299.0	0.7958	295.6
0.4610	299.3	0.8233	293.6
0.5040	299.9	0.8566	289.9
0.5259	300.1	0.8629	289.0
0.5511	300.1	0.8920	285.6
0.5826	300.0		
4-Phenylbutan-2-one (1) + hexadecane(2)			
0.2459	290.2	0.5920	307.0
0.2521	290.8	0.6483	307.0
0.2903	295.3	0.6709	306.9
0.3035	296.2	0.7028	306.7
0.3438	299.1	0.7288	306.5
0.3533	299.8	0.7457	306.4
0.3862	301.8	0.7760	306.0
0.4053	302.9	0.7991	305.3
0.4257	303.6	0.8161	304.4
0.4397	304.1	0.8521	302.0
0.4676	305.7	0.8714	299.3
0.5174	306.4	0.8981	294.5
0.5433	306.8		
Benzyl ethanoate(1) + tetradecane(2)			
0.3480	280.0	0.6619	288.2
0.3762	281.8	0.6909	288.2
0.4014	283.2	0.7069	288.1

Table 2 (continued)

0.4429	285.1	0.7088	288.1
0.4452	285.1	0.7198	288.1
0.4756	286.2	0.7213	288.0
0.5098	287.0	0.7619	287.6
0.5244	287.3	0.7887	287.1
0.5582	287.8	0.7958	286.9
0.5780	287.9	0.8243	285.6
0.5898	288.0	0.8476	283.2
0.6211	288.1	0.8721	280.2
0.6501	288.31		
Benzyl ethanoate(1) + hexadecane(2)			
0.3915	287.8	0.6463	295.1
0.4011	288.1	0.6695	295.1
0.4319	289.4	0.6952	295.1
0.4512	290.5	0.7127	295.0
0.4616	290.8	0.7487	295.0
0.4634	290.9	0.7671	294.9
0.5110	292.8	0.8052	294.3
0.5289	293.4	0.8184	293.6
0.5609	294.0	0.8390	293.2
0.5745	294.3	0.8676	291.2
0.6006	294.7	0.8917	288.1
0.6235	295.0	0.9109	285.3

[a] standard 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

Table 3

Coefficients in eq. (1) for the Fitting of the (x_1, T) Pairs Listed in Table 2 for 4-Phenylbutan-2-one (1) or Benzyl Ethanoate(1) + *n*-Alkane(2) Mixtures; σ(T) is the Standard Deviation Defined by eq. (5).

N[a]	M	k	α	T_c/K	x_{1c}	σ(T)/K
			4-Phenylbutan-2-one(1)+ dodecane(2)			
26	3.792	– 949	0.906	292.3	0.552	0.22
				(296.4)[b]	(0.563)[b]	
			4-Phenylbutan-2-one(1) + tetradecane(2)			
27	2.899	– 333	0.723	300.2	0.593	0.24
				(304.2)[b]	(0.613)[b]	
			4-Phenylbutan-2-one(1) + hexadecane(2)			
25	3.488	– 627	0.532	306.9	0.653	0.23
				(310.2)[b]	(0.658)[b]	
			Benzyl ethanoate(1) + tetradecane(2)			
25	3.372	– 589	0.445	288.2	0.668	0.09
				(291.3)[b]	(0.656)[b]	
			Benzyl ethanoate(1) + hexadecane(2)			
24	2.728	– 223	0.476	295.2	0.698	0.15
				(298.3)[b]	(0.702)[b]	

[a] number of experimental data points; [b]DISQUAC value obtained using interchange coefficients listed in Table 4

Table 4

Dispersive (DIS) and Quasichemical (QUAC) Interchange Coefficients, $C_{ak,l}^{DIS}$ and $C_{sk,l}^{QUAC}$ (*l* = 1, Gibbs energy; *l* = 2, Enthalpy; *l* = 3, Heat Capacity) for (a,k) Contacts[a] in 4-Phenylbutan-2-one or Benzyl Ethanoate + *n*-Alkane Mixtures.

C_nH_{2n+2}	$C_{ak,1}^{DIS}$	$C_{ak,2}^{DIS}$	$C_{ak,3}^{DIS}$	$C_{ak,1}^{QUAC}$	$C_{ak,2}^{QUAC}$	$C_{ak,3}^{QUAC}$
4-phenylbutan-2-one						
$n = 10$	2.33	1.5	2	5.75	5.75	2
$n = 12$	2.17	1.5	2	5.75	5.75	2
$n = 14$	2.07	1.5	2	5.75	5.75	2
$n = 16$	1.98	1.5	2	5.75	5.75	2
Benzyl ethanoate						
$n < 10$	− 1.65	0.21		2.8	2.25	
$n \geq 10$	− 2	0.21		2.8	2.25	

[a]type a, CH_3, CH_2 in *n*-alkanes, or in aromatic polar compounds considered; type k, CO in 4-phenylbutan-2-one, or COO in benzyl ethanoate

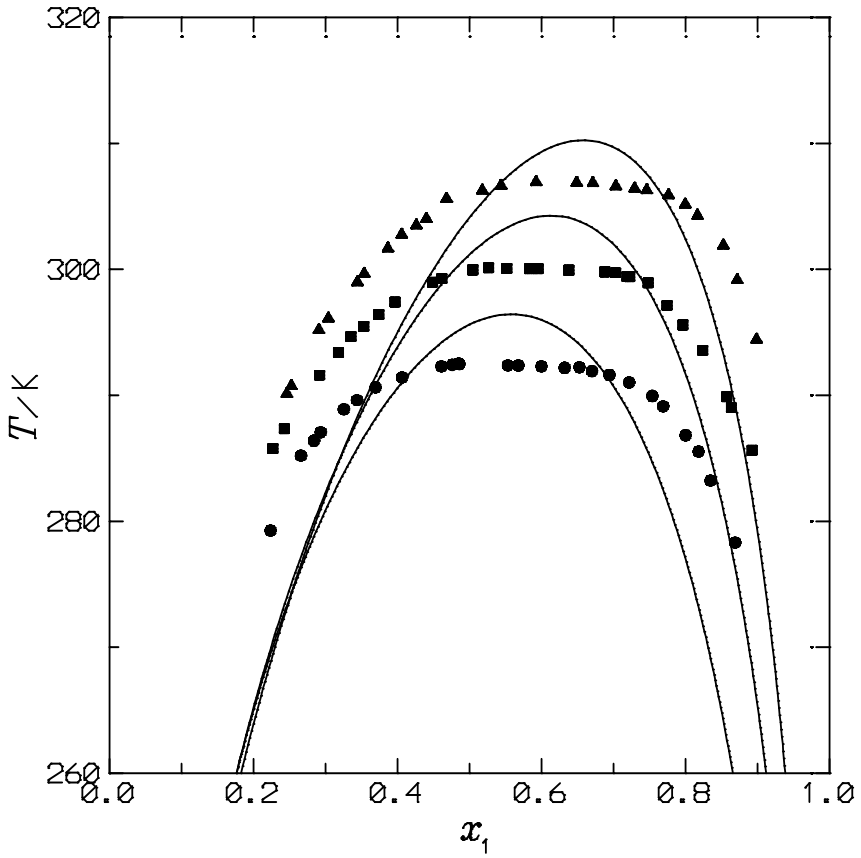

Figure 1. LLE for 4-phenylbutna-2-one(1) + dodecane(2) (●); + tetradecane(2) (■); + hexadecane(2) (▲) systems. Point, experimental results (this work); solid lines, DISQUAC calculations using interchange coefficients listed in Table 4.

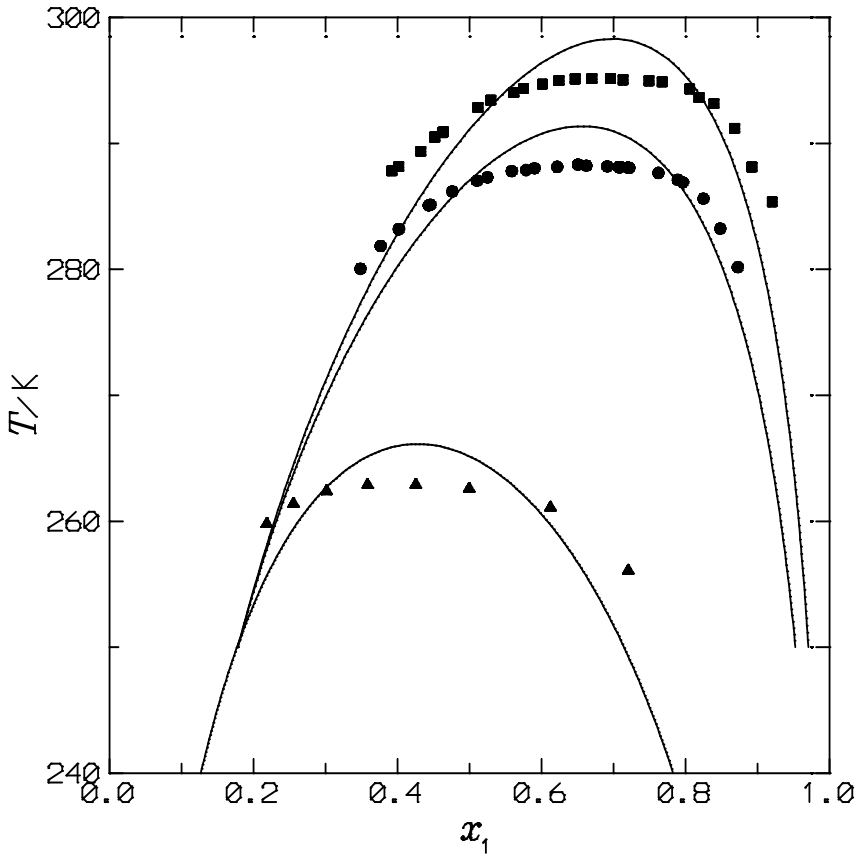

Figure 2. LLE for benzyl ethanoate(1) + heptane(2)[43] (▲); + tetradecane(2) (●); + hexadecane(2) (■) (this work). Points, experimental results; solid lines, DISQUAC calculations with interchange coefficients listed in Table 4.

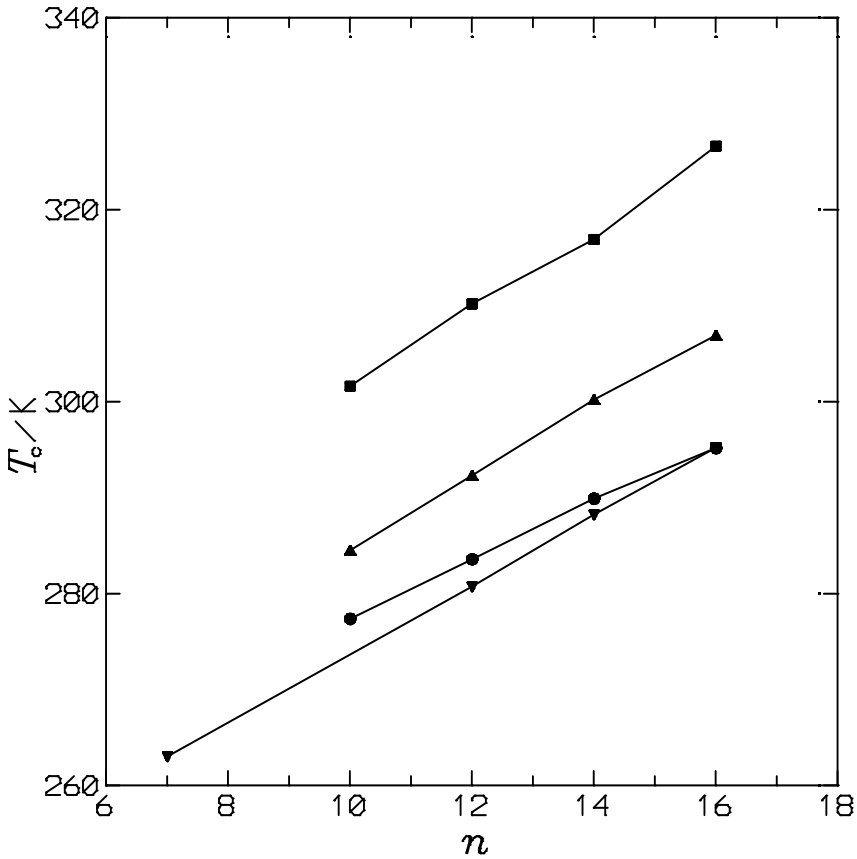

Figure 3. Upper critical solution temperatures, T_c, vs. n, the number of C atoms in the n-alkane for aromatic polar compound + n-alkane mixtures: (●), 1-phenylethanone;[11] (▲), 4-phenylbutan-2-one (this work);[13] (■), 1-phenylpropan-2-one;[13] (▼), benzyl ethanoate (this work).[43]

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LIQUID-LIQUID EQUILIBRIA FOR SYSTEMS CONTAINING 4-PHENYLBUTAN-2-ONE OR BENZYL ETHANOATE AND SELECTED ALKANES

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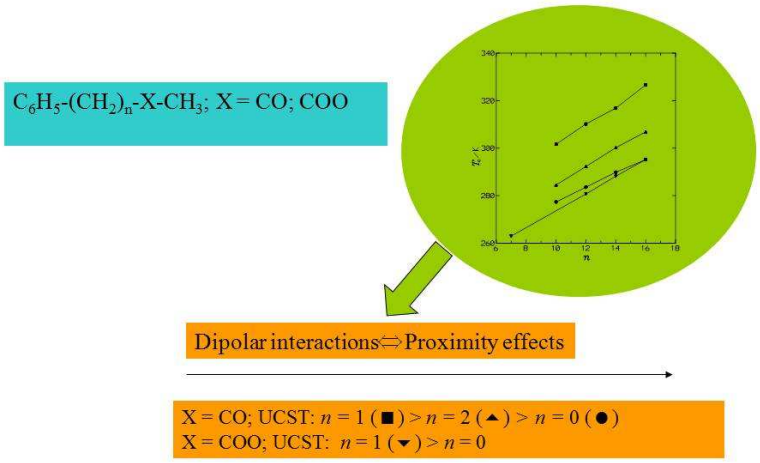
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