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Liquid-liquid equilibria of systems containing 2-methoxyphenol or 2-ethoxyphenol and *n*-alkanes

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ABSTRACT

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

1. Introduction

Phenol derivatives are crucial intermediates to synthesize a wide variety of specialty chemicals. Phase behaviour of those product mixtures plays an important role in development of the manufacturing processes. Alkoxyphenols have a variety of applications. 2-methoxyphenol is used as an intermediate in the chemical synthesis of active pharmaceuticals, flavouring and perfumery products. For example, 2-methoxyphenol acts as an expectorant [1,2]. It serves as a precursor to flavourings such as eugenol and vanillin [3,4]. It is used as an antioxidant as well [5]. In addition to this, it is also used as an indicator in chemical reactions that produce oxygen [6]. 2-ethoxyphenol is used as an intermediate in chemical synthesis, mainly in pharmaceutical and food industries. Its derivate ethylvanillin is used for fragrance and flavouring among others as a flavourer in perfumes and in the production of chocolate [7]. Phenolic compounds are chemical pollutants that can be found in water, often due to industrial and agricultural wastewater discharge [8]. Thus, their presence in water can be a concern for public health. In this context, it is important to remove these compounds from water. A possibility is liquid-liquid extraction using 1-alkanols, such 1-pentanol or 1-octanol [8]. The corresponding design of the process needs a deep understanding of the interactions between the groups involved. At this end, the experimental characterization of phenolic compound + *n*-alkane is the first step for a further theoretical study of mixtures including phenolic compounds.

For several years, our group has been 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 an aromatic ring, as these effects are very different from those between the same groups when they belong to different molecules. For example, the upper critical solution temperature (UCST) of the system (phenol + *n*-decane) is 336.50 K [9], while the excess molar enthalpy, H^E_m, of the system (decan-1-ol + benzene) at equimolar composition and temperature $T = 298.15$ K is 1050 $J \cdot mol^{-1}$ (extrapolated value from the literature [10]). That is, intramolecular effects lead to enhanced interactions between like polar molecules, while intermolecular effects are usually more favourable in interactions between unlike molecules. For this purpose, we have studied intramolecular proximity effects in mixtures containing aromatic amines (anilines [11,12], 2-amino-1-methylbenzene [13], 1-phenylmethanamine [14,15], 2-ethoxy-benzenamine [16], 4-ethoxybenzenamine [16], 1H-pyrrole [17], quinoline [18] or imidazoles [19]); aldehydes and ketones [20–23] (phenyl methanal, 1-

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phenylethanone, 4-phenyl-2-butanone), esters [23] (benzyl ethanoate), nitriles [24] (benzonitrile, phenyl acetonitrile, 3-phenylpropionitrile), 2-phenoxy-ethanol [25] or aromatic alkanols [26–28] (phenol, phenylmethanol, 2-phenylethan-1-ol).

Alkoxyphenol molecules contain two different polar groups (—OH and —O—) attached to the phenyl ring in different positions, and intramolecular proximity effects between these two groups are also expected to exist. The case of (phenoxyethanol + *n*-alkane) systems, examined in a previous work [25], is somewhat different, as the —O— and —OH groups are placed in the same linear chain attached to the phenyl ring. As a continuation, we provide now liquid-liquid equilibrium (LLE) data for *n*-alkane systems involving 2-methoxyphenol (guaiacol) or 2-ethoxyphenol (guaethol). More precisely, we report, at pressure $p = 0.1$ MPa, the equilibrium composition and temperature of the systems: 2-methoxyphenol + *n*-decane, or + *n*-dodecane, or + *n*-tetradecane or + *n*-hexadecane; and 2-ethoxyphenol + *n*-octane, or + *n*-dodecane, or + *n*-tetradecane, or + *n*-hexadecane.

2. Materials and methods

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. The measured ρ values, listed in Table 1, show that our results are in good agreement with values from the literature. After a careful survey of literature data, no previous ρ value has been found for 2-ethoxyphenol. 2-methoxyphenol presents subcooling effect at room temperature and its purity was tested also by measuring its melting temperature. The result obtained was 301.4 K, agreeing with literature values (from 301.15 K to 301.51 K [29]).

Water mass fractions, w_{H_2O}, of the pure liquids were determined by the Karl-Fischer method with a relative standard uncertainty of 0.02. Density measurements were conducted by means of a standard vibrating-tube densimeter model Anton Paar DSA 5000 with a temperature stability of 0.001 K. The standard uncertainties of temperature and density are 0.01 K and 0.10 kg·m^{-3}, respectively. A modulated differential scanning calorimeter, model TA Instruments Q2000, was used to measure the melting temperature of 2-methoxyphenol. Tzero aluminium pans and lids purchased from TA Instruments were filled with ~7 mg of sample, and hermetically sealed. The seal prevented loss of mass from volatilization of the sample or operator error. The estimated standard uncertainty of the melting temperature is 0.3 K.

2.2. Apparatus and procedure for LLE measurements

Small Pyrex tubes (0.009 m of diameter and about 0.04 m of length; free volume of the ampoule $\approx 1.17 \cdot 10^{-6}$ m^3) were used for the preparation of the mixtures. The composition of the mixtures, given as a mole fraction of the alkoxyphenol (2-methoxyphenol or 2-ethoxyphenol), x_1, was calculated from mass measurements, performed with an analytical balance Sartorius MSU125P and correcting for buoyancy effects, with a standard uncertainty of $5 \cdot 10^{-8}$ kg. The mentioned tubes are immediately sealed by capping at pressure $p = 0.1$ MPa and temperature $T = 298.15$ K, ready to use in the LLE measurements.

Temperatures of the samples during the experiments were measured with a Pt-1000 resistance calibrated using the triple point of water and the melting point of Ga as reference standards (standard uncertainty of 0.001 K).

The LLE curves were determined by means of the observation of the turbidity produced on cooling when a second phase appears. A summary of the procedure follows. (i) The samples in the sealed Pyrex tubes are placed in a thermostatic bath few tenths of K above the expected temperature. (ii) Mixtures are then slowly cooled at a rate of 1.2 K·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 subcooling and gravity effects in mixtures at compositions far from the critical one [35,36]. (iii) A red He—Ne laser 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 (see below). 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 34410 A multimeter connected to a PC. Transition temperatures can be then measured. (iv) Two or three runs are usually conducted to get a better assessment of the equilibrium temperatures.

The measuring setup was tested by measuring the test system (methanol + heptane), obtaining deviations of the critical mole fraction lower than 0.001 and of the critical temperature lower than 0.2 K, according to reference data from literature. A direct comparison between results obtained using our experimental technique and data from the literature can be encountered elsewhere [37]. The laser used in this technique is a self-contained Helium – Neon laser from Uniphase, model Novette 1508–0. Its key specifications are a minimum output power of 0.5 mW, wavelength of 632.8 nm, beam diameter of 0.48 mm, beam divergence of 1.7 mrad and mode (TEM$_{00}$) purity greater than 95 %. The photodiode used is an integrated photodiode and transimpedance amplifier from Texas Instruments, model OPT301M. It is packaged in a hermetic TO-99 metal package with a glass window. Its key specifications are a responsivity of 0.47 A/W at 650 nm, dark errors of 2 mV, bandwidth of 4 kHz and quiescent current of 400 μA.

The expanded uncertainties U (with a coverage factor of 2) related to the LLE measurements are the following. The uncertainty of pressure is $U(p) = 10$ kPa. For the equilibrium mole fractions, the estimated uncertainty is $U(x_1) = 0.0010$; this value already takes into consideration the partial evaporation in the mentioned free volume of the ampoule.

Table 1
Properties of pure compounds at pressure $p = 0.1$ MPa and temperature $T = 298.15$ K: initial purity, density, ρ, and water mass fraction, w_{H_2O}.[a]

Compound	CAS	Source	Initial purity[b]	ρ / kg·m^{-3}		$10^6 \cdot w_{H_2O}$
				Exp.	Lit.	
2-methoxyphenol	90-05-1	Sigma-Aldrich	≥0.98	1128.50	1128.9 [29] 1129 [30]	64
2-ethoxyphenol	94-71-3	Sigma-Aldrich	≥0.98	995.93		32
n-octane	111-65-9	Sigma-Aldrich	≥0.99	698.68	698.62 [31]	38
n-decane	124-18-5	Fluka	≥0.99	726.35	726.35 [31]	20
n-dodecane	112-40-3	Fluka	≥0.98	745.51	745.31 [32]	25
n-tetradecane	629-59-4	Fluka	≥0.99	759.27	759.29 [32]	25
n-hexadecane	544-76-3	Fluka	≥0.99	770.22	770.06 [32] 770.2 [33] 770.79 [34]	33

[a] Expanded uncertainties (U) with a coverage factor of 2: $U(T) = 0.02$ K; $U(p) = 10$ kPa; $U(\rho) = 0.20$ kg·m^{-3}; $U(w_{H_2O}) = 0.04 \cdot w_{H_2O}$.

[b] Gas chromatography area fraction. Provided by the supplier.

The estimated uncertainty of the equilibrium temperature 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 $U(T) = 0.20$ K, while outside of this region (tails of the curves), it is $U(T) = 0.40$ K.

3. Results

The directly measured LLE temperatures, T, and mole fractions of the alkoxyphenol, x_1, at pressure $p = 0.1$ MPa of the studied systems are collected in Table 2 and represented in Figs. 1 and 2. The studied systems are: 2-methoxyphenol + n-decane, or + n-dodecane, or + n-tetradecane or + n-hexadecane; and 2-ethoxyphenol + n-octane, or + n-

Table 2

Liquid-liquid equilibrium temperature, T, and mole fraction of the alkoxyphenol, x_1, of (alkoxyphenol (1) + n-alkane (2)) systems at pressure $p = 0.1$ MPa.[a]

x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
2-methoxyphenol (1) + n-decane (2)		2-methoxyphenol (1) + n-dodecane (2)		2-methoxyphenol (1) + n-tetradecane (2)		2-methoxyphenol (1) + n-hexadecane (2)	
0.2909	311.76	0.3206	317.84	0.2953	315.26	0.3875	326.65
0.3179	314.07	0.3467	319.76	0.3498	320.46	0.4021	327.73
0.3325	315.17	0.3805	321.89	0.3849	324.30	0.4234	329.48
0.3564	316.70	0.4200	324.23	0.4125	326.33	0.4487	331.23
0.3775	317.81	0.4440	325.27	0.4413	328.24	0.4655	332.43
0.4008	319.13	0.4776	326.70	0.4551	329.10	0.4973	334.33
0.4410	320.53	0.4964	327.13	0.4850	330.57	0.5368	336.56
0.4621	321.25	0.5140	327.68	0.5086	331.63	0.5632	337.68
0.4811	321.63	0.5287	328.06	0.5455	333.32	0.5981	338.99
0.4954	321.73	0.5395	328.13	0.5596	333.49	0.6273	339.72
0.5055	321.92	0.5770	328.37	0.5940	334.49	0.6574	340.50
0.5234	322.31	0.6033	328.55	0.6049	334.88	0.6807	340.60
0.5451	322.32	0.6211	328.81	0.6271	334.81	0.7138	340.82
0.5766	322.66	0.6407	328.62	0.6511	334.99	0.7353	340.92
0.5784	322.72	0.6674	328.76	0.6542	335.17	0.7534	340.95
0.6071	322.72	0.6889	328.64	0.6653	335.40	0.7753	341.03
0.6197	322.78	0.7225	328.53	0.6789	335.18	0.7881	341.00
0.6342	322.71	0.7355	328.37	0.7100	334.97	0.8127	341.00
0.6691	322.54	0.7513	328.11	0.7111	334.91	0.8252	340.88
0.6940	322.30	0.7523	328.15	0.7138	334.96	0.8469	340.17
0.7135	322.26	0.7856	327.07	0.7163	334.92	0.8638	339.18
0.7311	321.95	0.8061	325.79	0.7404	335.02	0.8787	337.80
0.7512	321.31	0.8231	324.69	0.7468	334.99	0.8963	335.43
0.7767	320.32	0.8437	323.06	0.7647	334.84	0.9138	331.55
0.8023	318.61	0.8634	320.66	0.7892	334.66	0.9288	326.54
0.8258	316.16			0.8131	334.60	0.9469	317.80
0.8547	311.86			0.8422	333.54		
				0.8532	332.69		
				0.8690	331.43		
				0.8837	328.93		
				0.9137	323.89		
				0.9345	317.98		
2-ethoxyphenol (1) + n-octane (2)		2-ethoxyphenol (1) + n-dodecane (2)		2-ethoxyphenol (1) + n-tetradecane (2)		2-ethoxyphenol (1) + n-hexadecane (2)	
0.2653	275.49	0.2385	278.90	0.3011	286.37	0.2931	288.02
0.2931	276.82	0.2791	282.10	0.3300	288.54	0.3314	290.96
0.3224	277.70	0.3150	284.51	0.3518	289.97	0.3873	294.86
0.3506	278.29	0.3352	285.84	0.3713	291.14	0.4374	297.82
0.3789	278.69	0.3580	286.99	0.3904	292.25	0.4855	299.80
0.4094	279.00	0.3925	288.44	0.4132	293.34	0.5122	300.75
0.4446	279.15	0.4351	289.70	0.4395	294.55	0.5426	301.57
0.4701	279.18	0.4631	290.37	0.4811	295.78	0.5842	302.33
0.4963	279.27	0.4825	290.75	0.5166	296.46	0.6147	302.75
0.5301	279.21	0.5107	291.06	0.5517	296.97	0.6441	302.88
0.5560	279.18	0.5483	291.31	0.5640	297.00	0.6826	303.02
0.5872	278.98	0.5778	291.36	0.5851	297.36	0.6965	303.01
0.6168	278.83	0.6045	291.39	0.5952	297.37	0.7218	302.95
0.6180	278.81	0.6483	291.39	0.6208	297.55	0.7468	302.94
0.6415	278.49	0.6757	291.31	0.6456	297.46	0.7700	302.86
0.6423	278.53	0.6967	291.29	0.6707	297.56	0.7958	302.80
0.6750	277.75	0.7254	291.14	0.7020	297.45	0.8220	302.54
0.7046	276.88	0.7538	290.68	0.7291	297.35	0.8478	301.92
0.7368	275.57	0.7734	290.23	0.7537	297.15	0.8663	300.86
		0.8089	288.86	0.7751	296.88	0.8867	299.05
		0.8267	287.63	0.8055	296.26	0.8986	297.30
		0.8485	285.65	0.8324	295.06	0.9027	296.57
		0.8562	284.68	0.8499	294.11	0.9182	293.00
		0.8657	283.53	0.8692	292.45	0.9363	286.55
		0.8690	282.98	0.8809	291.12		
				0.8950	289.14		
				0.9064	287.21		

[a] Expanded uncertainties (U) with a coverage factor of 2: $U(p) = 10$ kPa; $U(x_1) = 0.0010$; $U(T) = 0.20$ K in the flat region of the coexistence curves; $U(T) = 0.40$ K outside the flat region.

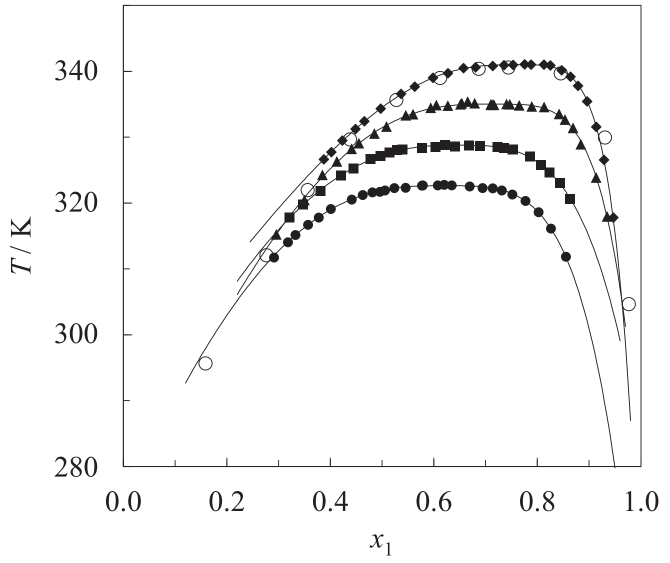

Fig. 1. Liquid-liquid equilibrium curves of (2-methoxyphenol + *n*-alkane) systems at pressure $p = 0.1$ MPa. Symbols, experimental data: (●) *n*-decane (this work); (■) *n*-dodecane (this work); (▲) *n*-tetradecane (this work); (◆) *n*-hexadecane (this work); (○) *n*-hexadecane [38]. Solid lines, calculations with Eq. (1) using the parameters listed in Table 3.

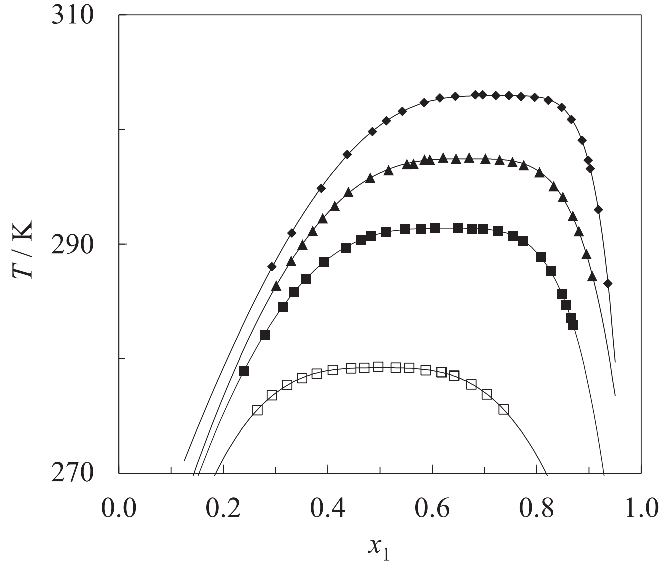

Fig. 2. Liquid-liquid equilibrium curves of (2-ethoxyphenol + *n*-alkane) systems at pressure $p = 0.1$ MPa. Full symbols, experimental data (this work): (□) *n*-octane; (■) *n*-dodecane; (▲) *n*-tetradecane; (◆) *n*-hexadecane. Solid lines, calculations with Eq. (1) using the parameters listed in Table 3.

dodecane, or + *n*-tetradecane, or + *n*-hexadecane. LLE data for comparison are not available in the literature, except for the system (2-methoxyphenol + *n*-hexadecane) [38], which are in good agreement with our results.

The experimental (x_1, T) data of each system were correlated by means of the equation [39,40]:

$$T/\mathrm{K} = T_c/\mathrm{K} + k|y - y_c|^m \tag{1}$$

where

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

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

and (x_{1c}, T_c) represent the composition and temperature of the system at the critical point. More details about subtleties of Eqs. (1)–(3) and the meaning of the parameters are included in a previous work [37]. When $\alpha = 1$, Eq. (1) is similar to the well-known Eq. [41–43]:

$$\Delta\lambda_1 = B\tau^{\beta} \tag{4}$$

In Eq. (4), $\tau = (T_c - T)/T_c$ is the reduced temperature, $\Delta\lambda_1 = \lambda_1' - \lambda_1''$ is the so-called order parameter (which can be the difference between the values λ_1' and λ_1'' in the two phases of any density variable λ_1 [42]; in our case, $\lambda_1 = x_1$) and β is a critical exponent corresponding to this order parameter (whose value depends on the theory applied to its determination [37,42]).

In Eqs. (1)–(3), the parameters *m*, *k*, α, T_c and x_{1c} are fitted to the experimental data by a Marquadt algorithm [44] with all the points weighed equally. The root-mean-square deviation of the fit to Eq. (1), $\sigma(T)$, is defined by:

$$\sigma(T) = \left[\frac{1}{N - n}\sum_{i=1}^{N}\left(T_i^{\mathrm{calc}} - T_i^{\mathrm{exp}}\right)^2\right]^{1/2} \tag{5}$$

where *N* and *n* stand for the number of data points and the number of fitted parameters, respectively; T_i^{calc} refers to the calculated values from Eq. (1) and T_i^{exp} denotes the experimental values. The values of the parameters and $\sigma(T)$ are listed in Table 3.

4. Discussion

In this section, the values of the thermophysical properties will be considered at $T = 298.15$ K and $x_1 = 0.5$ unless otherwise specified. We will denote by *n* the number of carbon atoms of the *n*-alkane.

As in many systems previously investigated [5,6,8,12–17,19,20] the LLE curves of the mixtures under study are characterized by some typical features: (i) they show a flat maximum (Figs. 1 and 2); (ii) for a given alkoxyphenol, the curves become progressively shifted toward higher x_1 values when *n* increases (Figs. 1 and 2); (iii) for a given alkoxyphenol, the upper critical solution temperature (UCST) increases roughly linearly with *n* (Table 3, Figs. 1–3). Feature (iii) is observed in mixtures formed by *n*-alkane and one of the following types of compounds: linear alkanone [45], linear organic carbonate [46], acetic anhydride [47], alkoxyethanol [37,48,49], polyether [50,51], amide [52,53], aniline [54,55], azapan-2-one [56], phenol [9,55,57,58], aromatic alcohols [27,28], phenoxyalcohol [25], benzaldehyde [20], aromatic alkanone [21–23], 2-hydroxy benzaldehyde [59] and phenetidines [16].

For a fixed *n*-alkane, we note that UCST changes in the order: 2-methoxyphenol >2-ethoxyphenol. We have shown along a series of investigations that, in *n*-alkane systems, dipolar interactions between aromatic polar molecules involving a polar group X are stronger than those between isomeric linear molecules with the same X group. For example, UCST(phenol + *n*-heptane) = 327.3 K [58], while (hexan-1-ol + *n*-heptane) show no miscibility gap at $T = 298.15$ K and H_m^E(hexan-1-ol + *n*-heptane) = 527 J mol^{-1} [62]. This behaviour has been ascribed to the existence of intramolecular proximity effects between the C_6H_5- group and the polar X group under consideration.

When the aromatic ring and the polar group X are not in the same molecule, i.e., in a mixture of the form (polar compound + aromatic compound), the intermolecular effects that appear between the polar compound and the aromatic compound can be relevant compared to the corresponding (polar compound + *n*-alkane) systems. In fact, the H_m^E values of (alkan-1-ol + benzene) systems are higher than those of the corresponding *n*-alkane mixtures. For example, H_m^E(hexan-1-ol + benzene) = 1141 J mol^{-1} [63] > H_m^E(hexan-1-ol + *n*-hexane) = 461 J mol^{-1}

Table 3

Parameters (m, k, α, T_c, x_{1c}) of Eq. (1) and root-mean-square deviation ($\sigma(T)$, Eq. (5)) of the fit of the liquid-liquid equilibrium temperature (T) as a function of the alkoxyphenol mole fraction (x_1), for 2-methoxyphenol, or 2-ethoxyphenol (1) + n-alkane (2) mixtures at pressure $p = 0.1$ MPa. N is the number of experimental points used for the fit, T_c is the upper critical solution temperature and x_{1c} is the critical composition.

System	N	m	k	α	T_c/K	x_{1c}	$\sigma(T)$/K
2-methoxyphenol (1) + n-decane (2)	27	3.2225	−585.32	0.5182	322.63	0.6252	0.07
2-methoxyphenol (1) + n-dodecane (2)	25	2.9390	−377.98	0.5389	328.75	0.6523	0.13
2-methoxyphenol (1) + n-tetradecane (2)	32	3.3945	−627.75	0.4050	335.02	0.7169	0.13
2-methoxyphenol (1) + n-hexadecane (2)	26	3.3648	−692.23	0.2676	340.99	0.7614	0.06
2-ethoxyphenol (1) + n-octane (2)	19	3.1438	−343.54	1.0112	279.20	0.5006	0.04
2-ethoxyphenol (1) + n-dodecane (2)	25	3.4908	−557.07	0.5428	291.37	0.6320	0.04
2-ethoxyphenol (1) + n-tetradecane (2)	27	3.3927	−476.88	0.5091	297.43	0.6713	0.06
2-ethoxyphenol (1) + n-hexadecane (2)	24	3.9204	−917.07	0.3246	302.95	0.7311	0.05

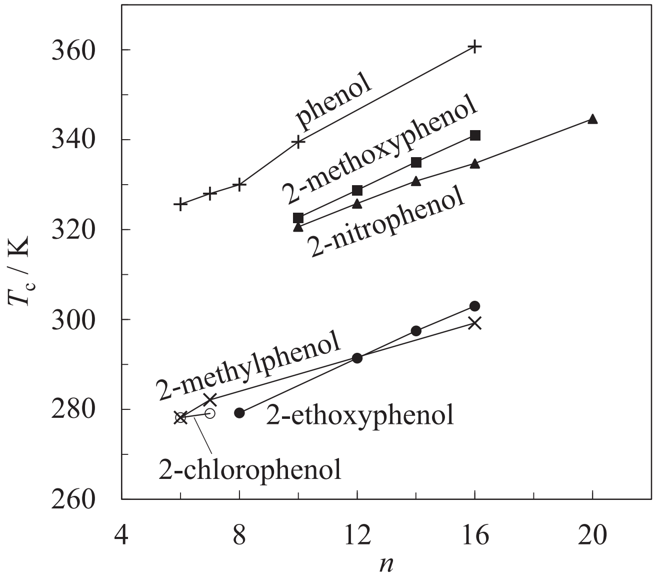

Fig. 3. Upper critical solution temperatures (T_c) of (aromatic polar compound + n-alkane) systems at pressure $p = 0.1$ MPa as a function of the number of carbon atoms of the n-alkane (n): (+) phenol [9,38,55,58]; (■) 2-methoxyphenol (this work, [38]); (▲) 2-nitrophenol [38,60]; (●) 2-ethoxyphenol (this work); (x) 2-methylphenol [60,61]; (○) 2-chlorophenol [60]. See also Table 4.

[64]. From these values, it is clear that benzene is a much more effective breaker of the alcohol self-association than n-alkanes. However, when the aromatic ring and the polar group are in the same molecule, the intramolecular proximity effects can lead to enhanced intermolecular interactions between like molecules. This is the case of the (alkoxyphenol + n-alkane) solutions, where there are 3 coupled functional groups in the same molecule (aromatic ring, —OH and methoxy or ethoxy group). The significantly enhanced alkoxyethanol-alkoxyethanol interactions lead to miscibility gaps, as demonstrated by our LLE data.

In mixtures with a given n-alkane, UCSTs decrease when the aromatic polar compound (phenol, X = OH) is replaced by the corresponding 2-methyl, 2-cloro, 2-nitro, 2-methoxy or 2-ethoxy derivative (2-methylphenol, 2-clorophenol, 2-nitrophenol, 2-methoxyphenol or 2-ethoxyphenol) (Table 4, Fig. 3). This behaviour can be ascribed to the lower aromatic surface fraction of the phenol derivatives compared to phenol, which leads to weaker proximity effects between the —OH group and the phenyl ring.

In the analogous case of solutions containing 2-ethoxy-benzenamine or 4-ethoxy-benzenamine and n-alkanes [16], it is observed that the UCSTs of 2-ethoxy-benzenamine mixtures are lower than that of the systems with 4-ethoxy-benzenamine, due to the proximity between the amine group and the ethoxyl group in 2-ethoxy-benzenamine, which hinders the amine group and weakens interactions between like molecules. This suggests that a similar steric effect should be present in (alkoxyphenol + n-alkane) mixtures.

Let us examine the effect on the UCST of the replacement of the nonpolar CH$_3$ group in a 2-methylphenol molecule by a polar group Y = Cl, NO$_2$, OCH$_3$, OCH$_2$CH$_3$, (having then two polar groups in the molecule), in n-alkane systems. For that purpose, let us compare the UCSTs of n-alkane systems containing 2-methylphenol with the corresponding systems with 2-clorophenol, 2-nitrophenol, 2-methoxyphenol or 2-ethoxyphenol (Table 4, Fig. 3). For n-hexadecane systems, UCST values change in the order: 2-methylphenol $<$ 2-ethoxyphenol $<$ 2-nitrophenol $<$ 2-methoxyphenol. In contrast, for n-hexane and n-heptane systems, the UCSTs vary as: 2-clorophenol $\le$ 2-methylphenol. Consequently, dipolar interactions among polar molecules of the same species become stronger in the sequence: 2-clorophenol $<$ 2-methylphenol $<$ 2-ethoxyphenol $<$ 2-nitrophenol $<$ 2-methoxyphenol. This variation can be ascribed to the existence of new intramolecular interactions between the (X, Y) groups, and between the (Y, C$_6$H$_5$-) groups. This proximity effect seems to reduce the strength of the dipolar interactions in 2-clorophenol compared to 2-methylphenol, whereas it enhances them in 2-ethoxyphenol, 2-nitrophenol and 2-methoxyphenol.

An interesting point is that the UCST of n-hexadecane systems

Table 4

Upper critical solution temperatures (T_c) for (aromatic polar compound + n-alkane) mixtures. The polar compounds considered are phenol (C$_6$H$_5$-X, polar group X = OH), 2-methylphenol and its derivatives including the Y group in the 2-position (2-Y-C$_6$H$_4$-X, for Y = CH$_3$, Cl, NO$_2$, OCH$_3$, OCH$_2$CH$_3$). Non-referenced values are experimental measurements from the present work.

n-alkane	T_c(C$_6$H$_5$-X + n-alkane)/K	Y	2-Y-C$_6$H$_4$-X	T_c(2-Y-C$_6$H$_4$-X + n-alkane)/K
n-hexane	325.6 [55]	CH$_3$	2-methylphenol	278.1 [60]
		Cl	2-clorophenol	278.1 [60]
n-heptane	327.3 [58]	CH$_3$	2-methylphenol	282.1 [60]
		Cl	2-clorophenol	279.1 [60]
		NO$_2$	2-nitrophenol	316.2 [60]
n-octane	329.5 [58]	OCH$_2$CH$_3$	2-ethoxyphenol	279.2
n-decane	336.5 [9]	OCH$_3$	2-methoxyphenol	322.6
n-hexadecane	360.7 [38]	CH$_3$	2-methylphenol	299.2 [61]
		OCH$_3$	2-methoxyphenol	340.5 [38], 341.0
		OCH$_2$CH$_3$	2-ethoxyphenol	302.9
		NO$_2$	2-nitrophenol	334.6 [38]

changes in the order: 2-ethoxyphenol $<$ 2-methoxyphenol $<$ phenol. In other words, dipolar interactions between the polar molecules are smaller when the new Y group in the 2-position gets larger. This suggests that steric hindrance due to the size of the new Y group in the 2-position are predominant over the X-Y proximity effects.

Also, from this study it can be seen that the most stable conformations for these systems are mainly determined by the balance of two antagonistic phenomena: (i) electron conjugation effects involving the aromatic ring and the π-electron donor methoxyl or ethoxyl group (these interactions are favoured by the coplanarity between the substituents and the ring), and (ii) steric repulsions between ortho groups which force the methoxyl or ethoxyl group to adopt an out of plane conformation relative to the ring. The H atom of the hydroxyl group points toward the ortho methoxyl substituent, a preference that results in further stabilization, since an intramolecular hydrogen bond interaction presumably comes into play with the oxygen on the methoxyl group, the acceptor for the hydroxyl hydrogen donor. For 2-methoxyphenol, the $H\cdots O(CH_3)$ distance is found to be 2.086 Å [65]. This value, which is lower than the sum of the Van der Waals radii of oxygen (1.4 Å) and hydrogen (1.2 Å), supports the presence of an intramolecular hydrogen bond in 2-methoxyphenol. Also, other experimental (nuclear magnetic resonance [66,67], gas electron diffraction [68], core X-ray photoelectron spectroscopy [69], infrared spectroscopy [67,70,71], thermochemical [71] and quantum-chemical calculation [68,69,71]) studies further support it and compare the effect with the case of 3-methoxyphenol and 4-methoxyphenol [69–71]. Unfortunately, to the best of our knowledge no similar information is available in the literature for phenols with more than one methoxyl substituent, particularly for 2-ethoxyethanol. When an additional methylene group is added to the methoxyl group of 2-methoxyphenol to become 2-ethoxyphenol, the final methyl group of 2-ethoxyphenol should be in gauche position with respect to the benzene ring, however according to two-dimensional Infrared Vibrational Echo Spectroscopy [72], the methyl group is below the plane of benzene ring, i.e., the methyl group is in the anti-position relative to the benzene ring. This addition of a methylene group to the methoxyl group, i.e. to form 2-ethoxyphenol, hinders the formation of the intramolecular hydrogen bond, causing the UCST to decrease.

5. Conclusions

LLE phase diagrams have been obtained for systems 2-methoxyphenol + *n*-decane, or + *n*-dodecane, or + *n*-tetradecane or + *n*-hexadecane; and 2-ethoxyphenol + *n*-octane, or + *n*-dodecane, or + *n*-tetradecane, or + *n*-hexadecane. The liquid-liquid equilibrium temperature data have been correlated to Eq. (1) as a function of the alkoxyphenol mole fraction, obtaining root-mean-square deviations of less than 0.1 K for all the mixtures studied.

In this work, intramolecular effects in alkoxyphenol systems have been analyzed and compared with other phenol derivatives. For a given alkoxyphenol, the mixtures are characterized by having UCSTs which increase with the *n*-alkane size. For a given *n*-alkane, the UCST is higher for mixtures containing 2-methoxyphenol. Dipolar interactions between like molecules become stronger in the sequence: 2-ethoxyphenol $<$ 2-methoxyphenol $<$ phenol. The attachment of a second polar group in the ortho position to a phenol leads to weaker dipolar interactions.

CRediT authorship contribution statement

Cristina Alonso Tristán: Writing – original draft, Investigation, Formal analysis, Data curation. **João Victor Alves-Laurentino:** Writing – review & editing, Investigation. **Fatemeh Pazoki:** Writing – review & editing, Investigation. **Susana Villa:** Writing – review & editing, Validation, Formal analysis. **Daniel Lozano-Martín:** Writing – review & editing, Supervision, Funding acquisition. **Fernando Hevia:** Writing – review & editing, Writing – original draft, Funding acquisition, Formal analysis.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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