Article

Thermodynamics of Mixtures Containing Aromatic Alcohols. 1. Liquid−Liquid Equilibria for (Phenylmethanol + Alkane) Systems

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ABSTRACT: The liquid−liquid equilibrium (LLE) curves for (phenylmethanol + $CH_3(CH_2)_nCH_3$) mixtures (n = 5, 6, 8, 10, 12) have been obtained by the critical opalescence method using a laser scattering technique. All of the systems show an upper critical solution temperature (UCST). In addition, the LLE curves have a rather horizontal top, and their symmetry depends on the alkane size. The UCST increases almost linearly with n. For systems including a given alkane and phenol or phenylmethanol, the UCST is much higher than that of the corresponding mixtures with hexan-1-ol or heptan-1-ol. This reveals that dipolar interactions are stronger in solutions with aromatic alcohols. Preliminary DISQUAC interaction parameters for OH/aliphatic contacts in the investigated systems were obtained. It is remarkable that the coordinates of the critical points of (phenol or phenylmethanol + alkane) mixtures can be described using the same quasichemical interaction parameters for the OH/aliphatic and OH/aromatic contacts.
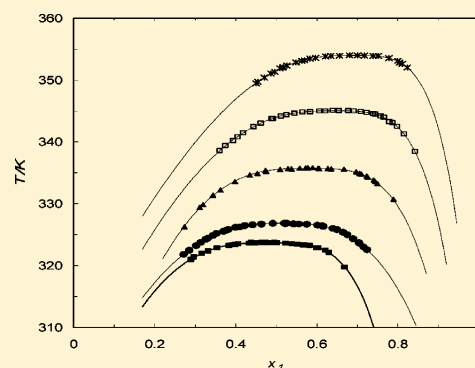
1. INTRODUCTION

Due to their complexity, the treatment of (alkanol + polar compound) mixtures is a severe test for any theoretical model. This can be ascribed to the alkanol self-association partially destroyed by the active molecules of the polar component and to the new interactions between unlike molecules created upon mixing. Up to now, we have developed detailed studies of systems of the type (alkan-1-ol + polar compound), as those containing linear ketones,[1] linear organic carbonates,[2] linear esters,[3] oxaalkanes,[4−6] thiophene, tetrahydro-, 1,1-dioxide,[7] or N,N-dialkylamides.[8,9] Now, we extend these studies by replacing the alkan-1-ol by an aromatic alcohol. The aim of this series of articles is to investigate the effect of the aromatic ring on the thermodynamic properties of the mentioned solutions to gain insight into their structure and interactions. The dipolar moment in gas phase, μ, of aromatic alcohols, for example, phenol, phenylmethanol, and 2-methylphenol, is very similar to that of alkan-1-ols ($\sim5.67\cdot10^{-30}$ C·m).[10] In addition, they have slightly higher dielectric constants than alkan-1-ols with the same number of C atoms.[11−13] Thus, strong dipolar interactions may be expected in systems with aromatic alcohols. As a first step, we present here liquid−liquid equilibrium temperatures (T_{LLE}) as a function of the mole fraction (x_1) of phenylmethanol for systems containing heptane, octane, decane, dodecane, or tetradecane as solvents. This type of data have been previously reported for the heptane solution.[14]

Aromatic alcohols show a large variety of relevant technical applications. Particularly, the properties of phenylmethanol have been the subject of considerable interest due to its versatility. For pharmaceutical aid, it is used as an antimicrobial agent.[15] In addition, it is a good solvent for gelatin, cellulose acetate, and shellac. Other applications are encountered in perfumery, veterinary science, or in microscopy as embedding material.[16] Phenylmethanol has been proposed as an additive for synthetic fuels derived from the Fischer−Tropsch process for use in ground and air vehicles.[17] It is also an additive that significantly retards the thermal degradation of jet fuels at high temperatures.[17] Its applications as a dielectric solvent for the dielectrophoretic reconfiguration of nanowires are also remarkable.[18]

2. EXPERIMENTAL SECTION

2.1. Materials. Heptane (142-82-5, puriss p.a. ≥ 0.995), octane (11-65-9, puriss p.a. ≥ 0.99), decane (124-18-5, puriss p.a. ≥ 0.99), dodecane (112-40-3, puriss p.a. ≥ 0.98), and tetradecane (629-59-4, puriss p.a. ≥ 0.99) were from Fluka (purities expressed in mass fraction). Phenylmethanol (100-51-6, puriss p.a. ≥ 0.99) was from Aldrich. Prior to the measurements, the chemicals were stored over molecular sieves (Union Carbide type 0.4 nm from Fluka). The densities, ρ, measured with an Anton-Paar densimeter DMA 602 (uncertainty 0.05 kg·m^{-3}) at 298.15 K and atmospheric pressure, were in good agreement with literature values as differences between experimental and literature data are lower than 0.5 % (Table 1). The water contents, determined from the Karl Fischer method, were (in mole fraction): 0.0003, 0.00012, 0.00011, 0.00003,

Table 1. Comparison of Experimental Densities, ρ, with Literature Values for Pure Liquids at $T = 298.15$ K

compound	ρ^a/kg·m^{-3}	
	exp.	lit.
phenylmethanol	1043.53	1041.30[11]
heptane	679.71	679.46[11]
octane	698.76	698.62[11]
decane	726.43	726.35[11]
dodecane	741.54	745.18[11]
tetradecane	759.27	759.29[51]

^{a}Density uncertainty: 0.05 kg·m^{-3}.

0.00015, and 0.00002 for phenylmethanol, heptane, octane, decane, dodecane, and tetradecane, respectively.

2.2. Apparatus and Procedure. Mixtures were prepared by mass (weighing accuracy ± 0.01 kg), in small Pyrex tubes (0.009 m inner diameter (i.d.) and about 0.04 m length), immediately sealed by capping at atmospheric pressure and room temperature. The relative atomic mass table of 1995 issued by the International Union of Pure and Applied Chemistry (IUPAC) in 1996[19] was used for the conversion to molar quantities.

The liquid−liquid equilibrium curves for the investigated binary mixtures were determined by the method of the critical opalescence. Details of the experimental technique are given elsewhere.[20,21] A Pt1000 resistance was used for the measurement of the T_{LLE} values. The Pt1000 resistance was calibrated, according to the International Temperature Scale of 1990 (ITS-90) scale of temperature, against the triple point of the water

Table 2. Experimental Liquid−Liquid Equilibrium Temperatures (T_{LLE}) for (Phenylmethanol (1) + Alkane (2)) Mixtures^a

| X_1	T_{LLE}/K	x_1	T_{LLE}/K	X_1	T_{LLE}/K	x_1	T_{LLE}/K
Phenylmethanol (1) + Heptane (2)				Phenylmethanol (1) + Decane (2)			
0.2897	321.00	0.4744	323.74	0.4349	334.62	0.6971	335.14
0.2968	321.39	0.4875	323.71	0.4534	334.89	0.7051	334.88
0.3159	321.99	0.4953	323.72	0.4738	335.38	0.7095	334.84
0.3319	322.37	0.5019	323.68	0.4750	335.23	0.7229	334.45
0.3536	322.88	0.5223	323.63	0.5094	335.53	0.7255	334.32
0.3537	322.89	0.5384	323.54	0.5290	335.66	0.7404	333.80
0.3832	323.24	0.5520	323.48	0.5379	335.64	0.7441	333.57
0.3923	323.37	0.5657	323.36	0.5578	335.74	0.7495	333.23
0.3957	323.40	0.5702	323.35	0.5724	335.75	0.7888	330.71
0.3984	323.41	0.5822	323.25	0.5779	335.79		
0.4059	323.52	0.5988	322.89	Phenylmethanol (1) + Dodecane (2)			
0.4336	323.63	0.6036	322.89	0.3605	338.59	0.6395	345.09
0.4384	323.73	0.6214	322.50	0.3743	339.40	0.6544	345.04
0.4478	323.64	0.6297	322.13	0.3936	340.22	0.6780	345.05
0.4638	323.76	0.6685	319.74	0.4044	340.80	0.6904	344.99
0.4683	323.70			0.4182	341.48	0.7086	344.91
Phenylmethanol (1) + Octane (2)				0.4440	342.47	0.7229	344.77
0.2715	321.80	0.5219	326.79	0.4617	343.02	0.7387	344.57
0.2853	322.47	0.5266	326.86	0.4883	343.79	0.7442	344.48
0.3022	323.22	0.5423	326.74	0.4911	343.77	0.7576	344.21
0.3136	323.74	0.5555	326.73	0.5114	344.19	0.7656	343.99
0.3259	324.23	0.5755	326.69	0.5255	344.41	0.7786	343.29
0.3312	324.43	0.6016	326.52	0.5448	344.65	0.7865	343.12
0.3435	324.87	0.6133	326.42	0.5639	344.83	0.7980	342.51
0.3526	325.19	0.6163	326.34	0.5833	344.90	0.8151	341.29
0.3698	325.54	0.6395	325.99	0.6064	344.99	0.8420	338.47
0.3763	325.69	0.6499	325.82	0.6207	345.00		
0.3822	325.83	0.6647	325.38	Phenylmethanol (1) + Tetradecane (2)			
0.3996	326.19	0.6752	324.99	0.4502	349.47	0.6212	353.83
0.4096	326.24	0.6896	324.34	0.4544	349.71	0.6344	353.90
0.4223	326.47	0.7044	323.68	0.4702	350.39	0.6560	353.93
0.4416	326.58	0.7046	323.62	0.4863	351.06	0.6803	354.00
0.4636	326.71	0.7152	323.01	0.4965	351.31	0.7000	353.99
0.4914	326.82	0.7237	322.58	0.5091	351.861	0.7173	353.94
0.5198	326.86			0.5158	351.99	0.7386	353.89
Phenylmethanol (1) + Decane (2)				0.5170	352.09	0.7517	353.89
0.2736	326.26	0.5898	335.81	0.5265	352.31	0.7778	353.55
0.3108	329.37	0.6033	335.73	0.5485	352.85	0.7993	353.09
0.3193	329.85	0.6055	335.68	0.5631	353.08	0.8041	352.82
0.3436	331.36	0.6271	335.67	0.5695	353.19	0.8108	352.62
0.3622	332.20	0.6357	335.62	0.5832	353.47	0.8232	352.02
0.3981	333.57	0.6668	335.57	0.5966	353.60		

^{a}Uncertainties, u are; $u(x_1) = 0.0005$; $u(T_{LLE}) = 0.05$ K.

and the fusion point of Ga. The precision of the equilibrium temperature measurements is $\pm$ 0.001 K, with an estimated uncertainty of $\pm$ 0.05 K. The mentioned temperatures were reproducible to $\pm$ 0.02 K for those values close to the UCST. For the equilibrium composition measurements, the uncertainty of the mole fraction is better than 0.0005. As a matter of fact, the precision of the weighing technique is 0.0001 in mole fraction, but because the more volatile component is partially evaporated to the free volume of the ampule ($\approx 1.17 \cdot 10^{-6}$ m^3), this value is slightly reduced.

3. RESULTS

Table 2 lists the directly measured T_{LLE} values obtained in this work versus x_1 for (phenylmethanol + heptane, + octane, + decane, + dodecane, or + tetradecane) mixtures (see Figures 1 to 3).
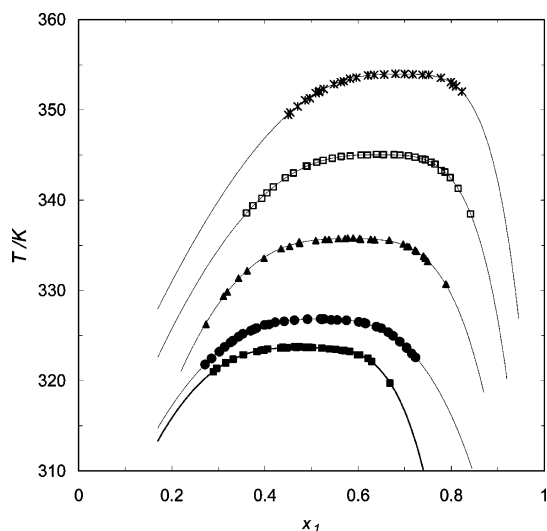

Figure 1. LLE of (phenylmethanol (1) + alkane (2)) mixtures. Points, experimental results: $\blacksquare$, heptane; $\bullet$, octane; $\blacktriangle$, decane; $\square$, dodecane; $*$, tetradecane. Solid lines, results from the fitting eq 1.
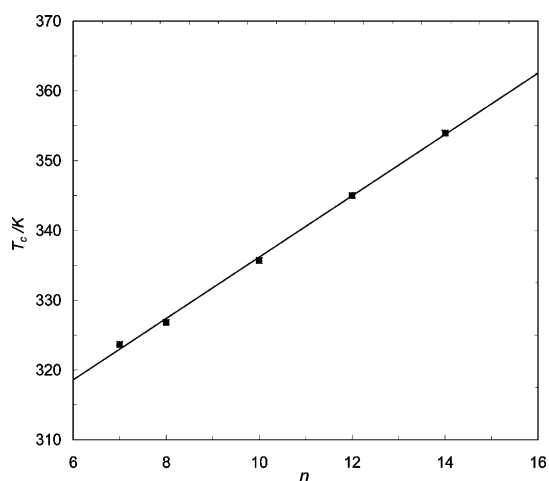
Figure 2. Upper critical solution temperatures T_c, vs n, the number of carbon atoms of the alkane, for (phenylmethanol + alkane) mixtures.

All of the systems show an UCST. Note that the LLE curves have a flat maximum and that their symmetry depends on the alkane size (Figure 1).
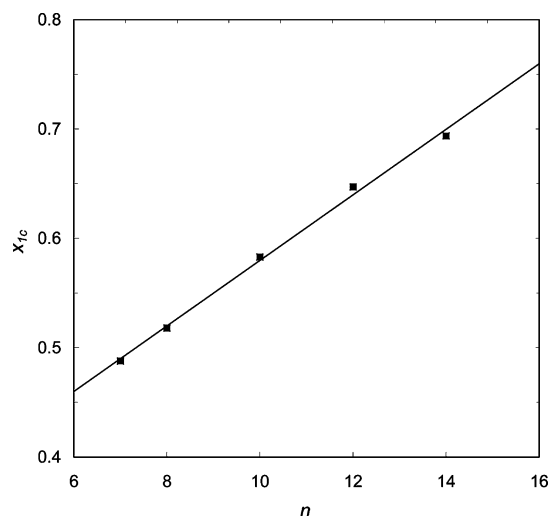
Figure 3. Upper critical solution composition, x_{1c}, vs n, the number of carbon atoms of the alkane, for (phenylmethanol + alkane) mixtures.

Table 3 lists the composition (x_{1c}) and temperature (T_c) of the critical points obtained by reducing the experimental measurements using the equation[22,23]

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

being

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

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

In eqs 1 to 3, m, k, α, T_c, and x_{1c} are the parameters to be fitted against the experimental data. For $\alpha = 1$, eq 1 is similar to:[24-26]

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

where $\Delta \lambda_1 = \lambda_1' - \lambda_2''$ is the so-called order parameter, which is any density variable in the conjugate phase (in the present case, $\lambda_1 = x_1$), τ ($= T_c - T)/T_c$) is the reduced temperature, and β denotes the critical exponent connected to $\Delta \lambda_1$. The β value depends on the theory applied to its determination.[24-26] More details can be encountered elsewhere.[27]

The adjustment of the parameters involved in eq 1 was performed on the basis of the Marquardt algorithm[28] with all the points weighted equally. Values of the fitted m, k, α, T_c, and x_{1c} parameters are collected in Table 3, which also contains the standard deviations for temperatures calculated according to:

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

Here, N and n are, respectively, the number of data points and the number of fitted parameters. Equation 1 fits the experimental measurements well. Our coordinates for the critical point of the heptane solution are close to literature values ($x_{1c} = 0.4866$; $T_c = 324.65$ K).[14]

4. DISCUSSION

The UCST of the studied systems increases with the number of C atoms in the chain length of the alkane (Figure 2, Table 3). The same behavior is observed in mixtures formed by alkane with, azapan-2-one,[20] linear alkanone,[29] linear organic carbonate,[30]

Table 3. Coefficients in eq 1 for the Fitting of the (x_1, T_{LLE}) Pairs Given in Table 2 for (Phenylmethanol (1) + Alkane (2)) Mixtures; σ Is the Standard Deviation Defined by eq 5

N^a	m	K	α	T_c/K	x_{1c}	σ/K
			Phenylmethanol (1) + Heptane (2)			
31	3.305	−1065	0.564	323.67 (327.0)^b	0.487 (0.377)^b	0.07
			Phenylmethanol (1) + Octane (2)			
35	2.740	−283	0.768	326.85 (331.3)^b	0.518 (0.421)^b	0.07
			Phenylmethanol (1) + Decane (2)			
31	3.248	−583	0.652	335.71 (341.1)^b	0.583 (0.507)^b	0.07
			Phenylmethanol (1) + Dodecane (2)			
31	3.190	−528	0.460	345.03 (349.9)^b	0.647 (0.589)^b	0.04
			Phenylmethanol (1) + Tetradecane (2)			
27	3.190	−501	0.39128	353.97 (358.2)^b	0.694 (0.647)^b	0.015

^{a}Number of experimental data points. ^{b}DISQUAC value calculated with the interchange coefficients listed in Table 4.

acetic anhydride,[31] alkoxyethanol,[27,32,33] polyether,[34,35] or phenol.[36−40] Figure 3 shows that the LLE curves are progressively shifted to higher x_1 values when the number of C atoms of the alkane increases. A similar trend is encountered for many other mixtures.[27,31−40]

It is remarkable that mixtures involving phenylmethanol or phenol and a given alkane are characterized by close UCST values. Thus, for heptane systems, UCST(phenol) = 326.05 K[36] or 327.3;[38] UCST(phenylmethanol) = 323.67 K, for mixtures with octane, UCST(phenol)[39] = 329.54 K; UCST(phenylmethanol) = 326.85 K; and for solutions containing decane, UCST(phenol)[39] = 336.50 K; UCST(phenylmethanol) = 335.71 K. This reveals that in such mixtures interactions between like molecules are rather similar. In contrast, UCSTs of systems involving phenol or phenylmethanol are much higher than those of mixtures with hexan-1-ol or heptan-1-ol, as these alcohols are miscible with alkanes at 298.15 K at any composition.[41,42] This indicates that alkanol−alkanol interactions are enhanced by the aromatic ring of phenol or phenylmethanol. A similar behavior is observed, for example, for (1-hexanamine or aniline + a given alkane) systems. Thus, at equimolar composition and 298.15 K, for (1-hexanamine + heptane),[44] the molar excess enthalpy is 1064 J·mol^{-1}, while UCST(aniline + heptane)[37] = 343.11 K.

It is known that the impact of polarity on bulk properties may be characterized by using the effective dipole moment, $\bar{\mu}$.[24,44,45] This magnitude is defined by:

$$\bar{\mu} = \left[\frac{\mu^2 N_A}{4\pi\varepsilon_o V k_B T} \right]^{1/2} \quad (6)$$

where N_A is Avogadro's number; k_B, the Boltzmann constant; V, the molar volume; and ε_0, the permittivity of the vacuum. For a given homologous series (e.g., alkan-1-ols) at temperature T, the application of eq 6 leads to a much higher variation with compound size of $\bar{\mu}$ compared to that observed for μ.[45] Thus at 298.15 K, $\bar{\mu}$ (methanol) = 1.023 > $\bar{\mu}$ (ethanol) = 0.852 > $\bar{\mu}$ (butan-1-ol) = 0.664 > $\bar{\mu}$ (hexan-1-ol) = 0.580 > $\bar{\mu}$ (heptan-1-ol) = 0.547 > $\bar{\mu}$ (decan-1-ol) = 0.443. For phenylmethanol, $\bar{\mu}$ = 0.639 (value calculated using the density listed in Table 1 and μ= 5.67·10^{-30} C·m[10]). For phenol, $\bar{\mu}$ = 0.647 (value obtained at 318.15 K using density reported in the literature[11] and μ = 5.50·10^{-30} C·m[10]). The difference for $\bar{\mu}$ values of these aromatic alcohols with those of hexan-1-ol and heptan-1-ol may explain the lower solubility of the former in alkanes.

Finally, we have explored the possibility of representing the (x_{1c}, T_c) values of the phenylmethanol solutions considered here

by means of the group contribution model DISQUAC[44,45] on the basis of our previous study on phenol systems.[46] Details on DISQUAC have been reported elsewhere.[44,45] The geometrical parameters of the groups referred to in this work (see below) are available in the literature.[46] The variation with the temperature of the interaction parameters is expressed in terms of the DIS (dispersive) and QUAC (quasichemical) interchange coefficients,[44,45] $C_{st,l}^{DIS}$; $C_{st,l}^{QUAC}$ where s ≠ t are two contact surfaces present in the mixture and l = 1 (Gibbs energy); l = 2 (enthalpy); l = 3 (heat capacity). The investigated mixtures are built by three surfaces: type a, aliphatic (CH_3, CH_2, in alkanes, or phenylmethanol); type b, aromatic (C_6H_5 in phenylmethanol) and type h, hydroxyl (OH in phenylmethanol). Thus, (phenylmethanol + alkane) mixtures are built by three types of contact: (a,b), (a,h), and (b,h). The interaction parameters are entirely dispersive for the (a,b) contact and are known from the study of (alkylbenzene + alkane) mixtures.[47] The (a,h) and (b,h) contacts are characterized by DIS and QUAC interchange coefficients. The values for $C_{bh,l}^{DIS}$, $C_{sh,l}^{DIS}$ (s = a,b; l = 2,3), and for $C_{sh,l}^{QUAC}$ (s = a,b and l = 1,2,3) are assumed to be the same as in phenol mixtures. Therefore, only the coefficients $C_{ah,l}^{DIS}$ have been fitted to represent the data. Values of the final interchange coefficients are given in Table 4. DISQUAC results for the coordinates

Table 4. Dispersive (DIS) and Quasichemical (QUAC) Interchange Coefficients, $C_{st,l}^{DIS}$ and $C_{st,l}^{QUAC}$, for (s,t) Contacts in (Phenylmethanol + Alkane) Mixtures (l = 1, Gibbs Energy; l = 2, Enthalpy; l = 3, Heat Capacity)

contact^a (s,t)	$C_{st,1}^{DIS}$	$C_{st,2}^{DIS}$	$C_{st,3}^{DIS}$	$C_{st,1}^{QUAC}$	$C_{st,2}^{QUAC}$	$C_{st,3}^{QUAC}$
(b,h)	4.80	−2.65		5.70	13	
(a,h) $n \leq 7^b$	3.42	0.50	−5	11.25	16	12
(a,h) $n = 8^b$	3.32	0.50	−5	11.25	16	12
(a,h) $n > 8^b$	3.32	0.50	5	11.25	16	30

^{a}a, aliphatic in alkane, or phenylmethanol; b, C_6H_5 in phenylmethanol; h, OH, in phenylmethanol; $^b n$ is the number of C atoms in the alkane

of the critical points are listed in Table 3. It is remarkable that they are correctly represented (Table 3), as differences between calculated and experimental UCST do not exceed 5.5 K, and for x_{1c} such differences are 0.1 or lower. Discrepancies between experimental and calculated results, as well as the variation of the $C_{ah,l}^{DIS}$ (l = 1,3) coefficients with the size of the alkane, can be explained as follows. DISQUAC is a mean field theory, and in this type of theories, excess functions are assumed to be analytical close to the critical points, in such a way that calculations are developed under this basic (and erroneous) assumption. In fact,

thermodynamic properties, in the proximity of the critical point, follow scaling laws with universal critical exponents and universal scaling functions.[24] According to the critical exponents theory,[24] DISQUAC provides LLE curves which are: (i) more rounded than the experimental ones at temperatures near to the UCST; (ii) too high at the UCST and too low at the LCST[24] (lower critical solution temperature). Thus, the $C_{ah,l}^{DIS}$ (l = 1,3) coefficients must be kept between certain limits to provide not very high calculated values of UCSTs. The same occurs in other applications as those on systems including thiophene, tetrahydro-, 1,1-dioxide,[7] alkoxyethanol,[48] amide,[8] or pyridine[49] and alkane. The theoretical results obtained here suggest that systems with phenol or phenylmethanol can be described using the same QUAC interaction parameters for the OH/aliphatic and OH/aromatic contacts. A similar behavior is encountered for (aniline[50] or 2-methylaniline[21] + alkane) solutions.

5. CONCLUSIONS

Liquid−liquid equilibrium curves were determined for mixtures of phenylmethanol with heptane, octane, decane, dodecane, and tetradecane. For systems with a given alkane and phenol or phenylmethanol, the UCST is much higher than that of the corresponding mixtures with hexan-1-ol or heptan-1-ol, which reveals that dipolar interactions are stronger in solutions with aromatic alcohols. Preliminary DISQUAC interaction parameters for the OH/aliphatic contacts in the investigated systems were obtained. The $C_{sh,l}^{QUAC}$ (s = a,b; l = 1, 2, 3) coefficients are the same as in phenol + alkane mixtures.

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Notes

The authors declare no competing financial interest.

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