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Thermodynamics of mixtures containing amines. XV. Liquid-liquid equilibria for benzylamine + $CH_3(CH_2)_nCH_3$ (n = 8,9,10,12,14)

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Abstract

Coexistence curves for the liquid-liquid equilibria (LLE) of 1-phenylmethanamine (benzylamine) + $CH_3(CH_2)_nCH_3$ (n = 8,9,10,12,14) have been determined using the critical opalescence method by means of a laser scattering technique. All the LLE curves show an upper critical solution temperature (UCST), which increases with n. For systems including a given n-alkane, UCST values decrease in the sequence: aniline > 2-methylaniline (o-toluidine) > benzylamine > N-methylaniline > pyridine. This means that amine-amine interactions become weaker in the same order. Most of the DISQUAC interaction parameters for the aliphatic/amine (a,n) and aromatic/amine (b,n) contacts previously determined for solutions with aniline, or o-toluidine, or N-methylaniline have been used for the representation of the LLE data. Only the first dispersive interaction parameter of the (a,n) contact has been modified. The coordinates of the critical points are correctly represented by the model.

KEYWORDS: LLE/ Benzylamine/alkanes/amine-amine interactions

1. Introduction

Benzylamine is a very interesting compound. In fact, it may be considered the main skeleton of some primary amines, such as 1-aminoadamantane, 1-adamantylethanamine or α,α-dimethylphenethylamine, which have important pharmaceutical applications.[1,2] On the other hand, at present, capture and storage of CO_2 produced by the combustion of fossil fuels is a common topic of investigation.[3-5] A standard procedure is based on the capture of CO_2 by aqueous mixtures of monoethanolamine.[4] However, the use of this amine shows some disadvantages.[5,6] For example, it reacts with NO_2 or SO_2 leading to the formation of thermally stable salts which reduces the absorption ability of the solvent.[6] Thus, new amine solvents are being considered, [4,5] and benzylamine might be important in this field. It should be mentioned that benzyl radicals may be also important when stimulating ignition in diesel and petrol engines.[7]

In this work, we provide liquid-liquid equilibrium temperatures for the mixtures benzylamine + $CH_3(CH_2)_nCH_3$ (n = 8,9,10,12,14). This type of measurements is useful to get a deeper understanding of interactions in the investigated mixtures. Previously, we have reported similar data for *o*-toluidine,[8] or *N*-methylaniline[9] + alkane systems. We have also characterized the present solutions in terms of the DISQUAC model[10,11] and the corresponding interaction parameters are reported.

2. Experimental

2.1 Materials

Information on properties of pure compounds (source, purity, water content, evaluated by the Karl-Fisher method, and density) is collected in Table 1. Densities were obtained by means of an Anton Paar DMA 602 vibrating-tube densimeter (temperature stability ± 0.01 K). Calibration details of this apparatus can be found elsewhere.[12] The resolution in density is $|\Delta\rho / \rho| = 6\ 10^{-6}$, while the accuracy is estimated to be ± $2 \cdot 10^{-2}$ kg·m^{-3}.

2.2 Apparatus and Procedure

Mixtures were prepared by mass using an analytical balance HR-202 (weighing accuracy to ± 0.00001 g), in small tubes made of Pyrex (0.9 cm i.d. and about 4 cm length). Molar quantities were calculated taking into account the relative atomic mass Table of 2006 issued by IUPAC.[13] The liquid-liquid equilibrium temperatures of the binary systems were determined by the critical opalescence procedure.[14] Temperatures were measured with a Pt-1000 resistance, calibrated on the basis of the ITS-90 scale of temperature considering the triple point of the water, and the fusion point of Ga as fixed points. The thermometer precision is ± 0.001 K and its accuracy is ± 0.05 K. Temperatures close to the UCST were reproducible to ± 0.02 K. Precision of the equilibrium composition is ca. 0.0005 in mole fraction.[14]

3. Results

Values obtained in the present work for the liquid-liquid equilibrium temperatures T vs. x_1, the mole fraction of benzylamine are collected in Table 2 (see Figure 1). All the systems show an UCST, which increases with n. As far as we know, there are no data in the literature for comparison. Data reduction was carried out as in previous works[9,14] by using the expression:

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

where

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

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

The parameters m, k, α, T_c and x_{1c} (the two latter parameters represent the coordinates of the critical points) are obtained from the fitting of the experimental data by means of eq (1), similar to:

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

when $\alpha = 1$.[15-17] In eq 4, $\Delta\lambda_1 = \lambda_1' - \lambda_2''$ is any density variable in the conjugate phase (the so-called order parameter; here, $\lambda_1 = x_1$), τ is the reduced temperature $(T_c - T)/T_c$ and β a critical exponent corresponding to the selected order parameter. The β value depends on the theory applied to its determination.[16-18]

The fitting was conducted on the basis of a Marquardt algorithm[19] with all the points weighted equally. Results are listed in Table 3, which also includes the standard deviation defined by:

$$\left(\sigma(T)/K\right) = \left[\ \sum\left(T_i^{\exp} - T_i^{cal}\right)^2 / (N - k)\right]^{1/2} \tag{5}$$

where N and k are the number of data points and the number of fitted parameters, respectively.

4. Discussion

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

Figure 2 shows UCSTs for some aromatic amine + alkane mixtures.[8,9,20-23] We note that for mixtures with a given alkane, the UCST changes in the order: aniline > *o*-toluidine > benzylamine > *N*-methylaniline > pyridine. Therefore, the strength of the amine-amine interactions becomes weaker in the order primary > secondary > tertiary. Moreover, alkylation of the aromatic ring also weakens interactions between amine molecules. This could be due to the smaller aromatic surface of the corresponding molecules. In fact, for heptane systems, H_m^E/J·mol^{-1} = 999 (benzene)[24] > 564 (toluene)[25] > 540 (ethylbenzene).[25] The same trend is encountered for mixtures including pyridines, Thus, H_m^E/J·mol^{-1} = 1729 (pyridine)[26] > 1346 (2-methylpyridine)[27] > 1046 (2,4-dimehtylpyridine)[28] > 934 (2,4,6-trimethylpyridine).[29]

An evaluation of the strength of amine-amine interactions in different aromatic molecules can be conducted in terms of the magnitude $\Delta\Delta_{vap}H_m$, defined as:[30-32]

$$\Delta\Delta_{vap}H_m = \Delta_{vap}H_m\,(\text{compound with characteristic group X}) - \Delta_{vap}H_m\,(\text{homomorphic hydrocarbon})$$

where $\Delta_{vap}H_m$ represents the standard molar enthalpy of vaporization at 298.15 K. For the aromatic amines considered, $\Delta_{vap}H_m$/kJ·mol^{-1} = 55.83 (aniline);[33] 57.8 (*o*-toluidine; T = 300 K);[34] 54.6 (benzylamine);[35] 53.1 (*N*-methylaniline);[36] 40.15 (pyridine);[33] and for the homomorphic aromatic hydrocarbons, $\Delta_{vap}H_m$/kJ·mol^{-1} = 33.71 (benzene);[33] 37.63 (toluene);[33] 41.70 (ethylbenzene);[33] 43.11 (1,2-dimethylbenzene).[33] Therefore, $\Delta\Delta_{vap}H_m$/kJ·mol^{-1} = 18.2 (aniline) > 14.6 (*o*-toluidine) > 12.9 (benzylamine) > 11.4 (*N*-methylaniline) > 6.4 (pyridine). This clearly indicates that amine-amine interactions are weakened in the same order, and confirm our previous statement based on LLE data.

Finally, the DISQUAC model[10,11] has been applied to the present systems. The main features of the model and equations can be found elsewhere.[9,37] Benzylamine + *n*-alkane mixtures are built by three types of contacts: aliphatic/aromatic (a,b); aliphatic/amine (a,n) and aromatic/amine (b,n). The geometrical parameters of benzylamine, calculated additively on the basis of the group volumes R_G and surfaces Q_G recommended by Bondi [37-39] are: r_i (relative volume) = 3.8907; q_i (relative surface) = 2.9035; and molecular surface fractions: α_{ai} (aliphatic)

= 0.1604; α_{bi} (aromatic) = 0.6330; α_{ni} (amine) = 0.2066. The interaction parameters for the (a,b) contacts are only dispersive and are known from the investigation of aromatic hydrocarbon + *n*-alkane mixtures.[40] Interaction parameters for the (a,n) and (b,n) contacts have been determined previously for systems including aniline,[41] or *o*-toluidine,[8] or *N*-methylaniline.[9] In this work, only the first dispersive interaction parameter for the (a,n) contact has been modified (Table 4). The remainder parameters remain unchanged. As usually,[8,9,30,41-43] DISQUAC describes the coordinates of the critical points in the correct range of composition and temperature (Table 3).

5. Conclusions

LLE coexistence curves are reported for benzylamine + $CH_3(CH_2)_nCH_3$ (n = 8,9,10,12,14) mixtures. Amine-amine interactions become weaker in the order: aniline > *o*-toluidine > benzylamine > *N*-methylaniline > pyridine. DISQUAC correctly describes the coordinates of the critical points.

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Table 1

Properties of Pure Compounds at 0.1 MPa

Compound	CAS	Source	Initial mole fraction	ρ [a](298.15K)/ kg·m^{-3}		Water[b] content
				Exp.	Lit.	
Benzylamine	100-46-9	Sigma-Aldrich	≥ 0.99	978.34	981[44] 977.7[45]	680·10^{-6}
Decane	24-18-5	Fluka	≥ 0.99	726.34	726.35[46]	22·10^{-6}
Undecane	1120-21-4	Sigma-Aldrich	≥ 0.99	736.71	736.7[47]	16·10^{-6}
Dodecane	112-40-3	Fluka	≥ 0.98	745.52	745.56[48]	10·10^{-6}
Tetradecane	629-59-4	Fluka	≥ 0.99	759.32	759.29[49]	17·10^{-6}
Hexadecane	544-76-3	Fluka	≥ 0.98	770.32	770.06[49]	11·10^{-6}

[a]density, uncertainty, $u(\rho) = \pm 0.02$ kg·m^{-3}; $u(T) = \pm 0.01$ K; $u(p) = \pm 0.1$ kPa; [b]in mass fraction

Table 2

Experimental Liquid-Liquid Equilibrium Temperatures for Benzylamine(1) + $CH_3(CH_2)_nCH_3$(2) Mixtures[a] at 0.1 MPa

x_1	T/K	x_1	T/K
	$n = 8$		
0.3037	276.69	0.5913	280.07
0.3147	277.04	0.6011	280.03
0.3185	277.13	0.6263	280.05
0.3476	278.03	0.6354	280.03
0,3595	278.38	0.6497	279.99
0.3728	278.69	0.6813	279.79
0.4042	279.19	0.7061	279.53
0.4341	279.69	0.7330	279.20
0.4436	279.82	0.7436	279.02
0.4576	279.92	0.7614	278.63
0.4595	279.88	0.7691	278.41
0.4792	280.06	0.7742	278.31
0.4987	280.07	0.8024	277.34
0.5305	280.11	0.8152	276.86
0.5661	280.06	0.8374	275.83
0.5755	280.02		
	$n = 9$		
0.3501	278.83	0.6032	283.70
0.3885	280.53	0.6130	283.61
0.4070	281.22	0.6375	283.65
0.4322	282.13	0.6562	283.60
0.4336	282.14	0.6593	283.68
0.4623	282.86	0.6756	283.41
0.4847	283.14	0.6960	283.37
0.4854	283.09	0.7122	283.12
0.5075	283.23	0.7423	282.71
0.5354	283.40	0.7555	282.51
0.5724	283.69	0.7926	281.50
0.5754	283.60	0.8145	280.98
0.5972	283.67	0.8377	279.58
	$n = 10$		
0.3528	281.75	0.6236	286.87

Table 2 (continued)

0.3677	282.45	0.6364	286.79
0.3746	282.79	0.6667	286.70
0.3813	283.15	0.6926	286.62
0.4022	283.67	0.6973	286.66
0.4509	285.53	0.7373	286.38
0.4658	285.85	0.7418	286.38
0.4838	286.16	0.7597	286.26
0.4916	286.28	0.7853	285.85
0.5041	286.47	0.7954	285.52
0.5249	286.55	0.7969	285.55
0.5423	286.75	0.8240	284.55
0.5617	286.86	0.8336	284.15
0.5658	286.81	0.8496	283.15
0.5804	286.88	0.8506	283.03
0.5921	286.87	0.8560	282.67
0.5983	286.86	0.8654	282.24
0.6072	286.84		
	$n = 12$		
0.3783	285.88	0.7009	291.93
0.3895	286.23	0.7203	292.01
0.3924	286.52	0.7372	291.97
0.4311	288.14	0.7588	291.86
0.4656	289.30	0.8037	291.56
0.4835	289.89	0.8151	291.42
0.5201	290.68	0.8401	290.63
0.5373	290.94	0.8565	289.96
0.5619	291.40	0.8743	288.53
0.6025	291.98	0.8843	287.87
0.6424	291.98	0.8987	286.12
0.6614	291.97	0.9320	279.35
0.6797	291.92		
	$n = 14$		
0.4124	288.97	0.7156	298.33
0.4372	290.54	0.7334	298.30
0.4705	292.06	0.7533	298.34

Table 2 (continued)

0.4913	293.11	0.7656	298.32
0.4950	293.22	0.7733	298.23
0.5212	294.52	0.8002	297.97
0.5644	295.99	0.8092	297.88
0.5728	296.26	0.8373	297.67
0.5851	296.48	0.8383	297.49
0.6037	297.22	0.8484	297.16
0.6591	298.26	0.8806	296.02
0.6774	298.25	0.8952	294.76
0.7026	298.37	0.9120	292.89

[a] uncertainties, u are; $u(x_1) = 0.0005$; $u(T) = 0.05$ K; $u(p) = \pm 0.1$ kPa

Table 3

Coefficients in Eq. (1) for the Fitting of the (x_1, T) Pairs given in Table 2 for Benzylamine(1) + $CH_3(CH_2)_nCH_3$(2) Mixtures; σ is the Standard Deviation defined by eq 5.

N[a]	m	k	α	T_c/K	x_{1c}	σ/K
			$n = 8$			
31	3.10	−224	0.91	280.09 (283.2)[b]	0.569 (0.493)[b]	0.05
			$n = 9$			
26	2.89	−257	0.99	283.63 (287.1)[b]	0.603 (0.530)[b]	0.09
			$n = 10$			
35	3.34	−395	0.75	286.82 (291.4)[b]	0.632 (0.560)[b]	0.10
			$n = 12$			
25	3.59	−505	0.389	291.96 (296.1)[b]	0.707 (0.615)[b]	0.09
			$n = 14$			
26	2.89	−248	0.411	298.33 (300.9)[b]	0.745 (0.669)[b]	0.15

[a] number of experimental measurements; [b]DISQUAC value

Table 4

Dispersive (DIS) and Quasichemical (QUAC) Interchange Coefficients[a] for (s,n) Contacts in Benzylamine Mixtures.

System	Contact (s,n)[b]	$C_{sn,1}^{DIS}$	$C_{sn,2}^{DIS}$	$C_{sn,3}^{DIS}$	$C_{sn,1}^{QUAC}$	$C_{sn,2}^{QUAC}$	$C_{sn,3}^{QUAC}$
Benzylamine + *n*-alkane	(a,n)	0.97	0.65		6	11.5	
Benzylamine + benzene	(b,n)	3.7	−2.8	−4	1.25	10	4

[a](l = 1, Gibbs energy; l = 2, enthalpy, l = 3, heat capacity); [b]s = a, CH_3 or CH_2 in *n*-alkanes, or benzylamine; s = b, C_6H_5 in benzylamine or benzene; s = n, NH_2 in benzylamine

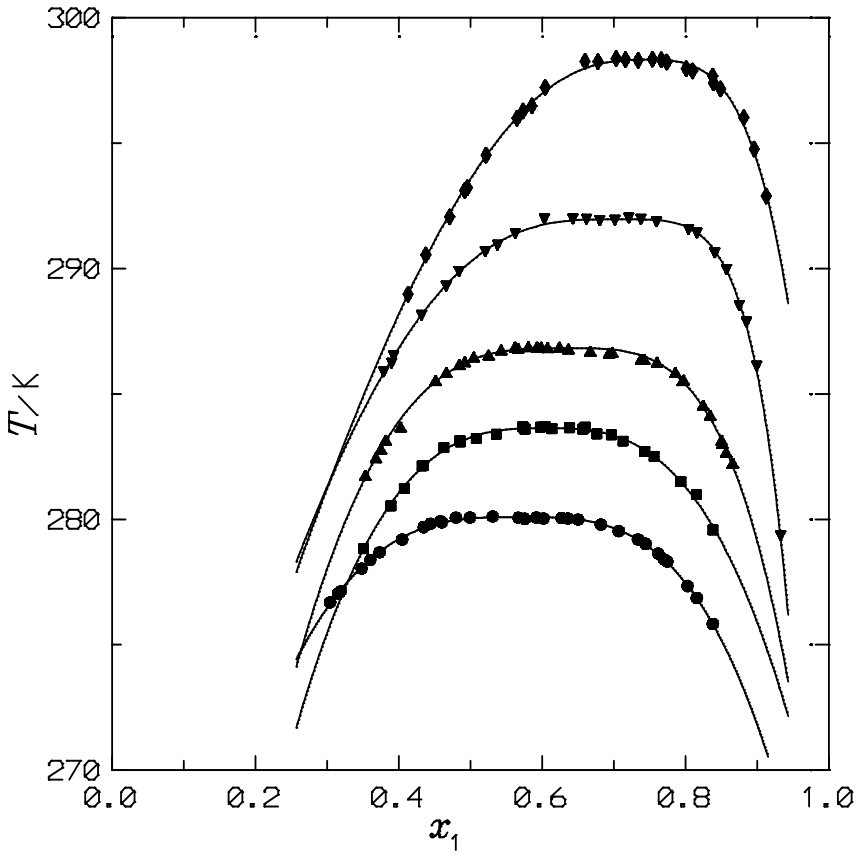

Figure 1. LLE for bezylamine(1) + $CH_3(CH_2)_nCH_3$(2) mixtures. Points, experimental results (this work): (●), n = 8; (■), n = 9; (▲), n = 10; (▼), n = 12; (◆), n = 14. Solid lines, results from eq. (1) using parameters from Table 3.

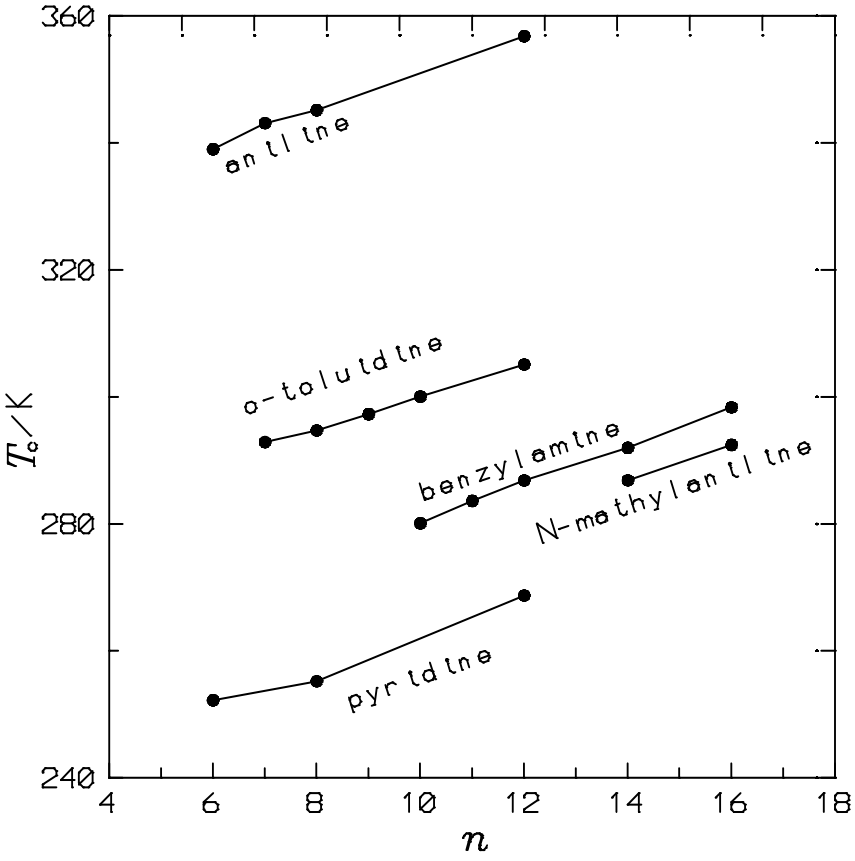

Figure 2 T_c, vs. n, the number of C atoms in the n-alkane for aromatic amine + n-alkane systems (see references in text).

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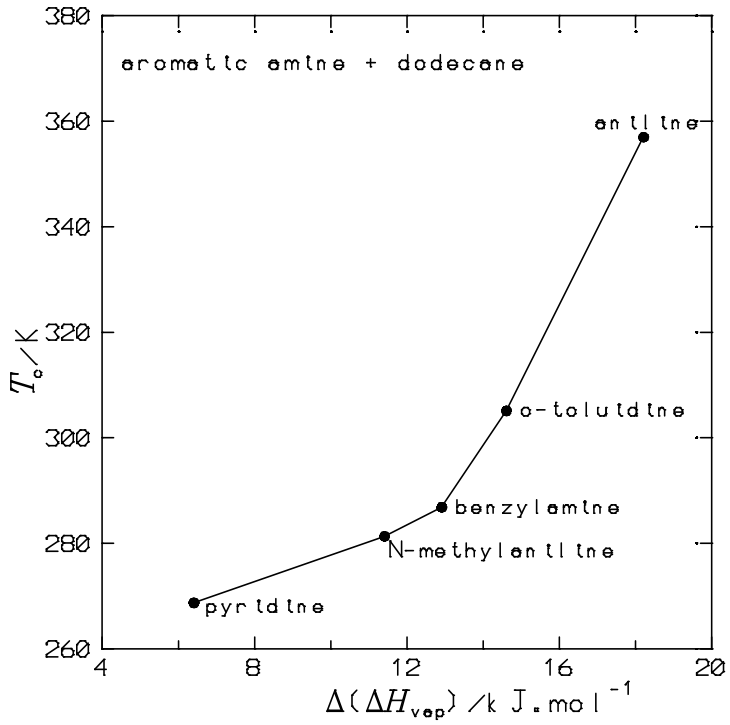

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