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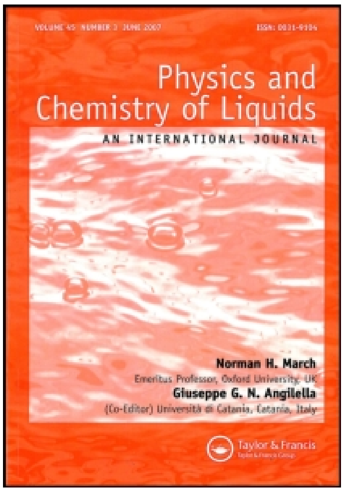

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
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To cite this Article Velasco, Inmaculada , Fernandez, Javier and Otin, Santos(1996) 'Estimation of Disquac Interchange Energy Parameters for n-Alkylamine Benzene Mixtures', Physics and Chemistry of Liquids, 31: 3, 151 — 158
To link to this Article: DOI: 10.1080/00319109608029568
URL: http://dx.doi.org/10.1080/00319109608029568

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Phys. Chem. Liq., 1996, Vol. 31, pp. 151–158
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ESTIMATION OF DISQUAC INTERCHANGE ENERGY PARAMETERS FOR n-ALKYLAMINE + BENZENE MIXTURES

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(Received 26 September 1995)

The experimental literature data on vapor-liquid equilibria (VLE), excess molar Gibbs energies (G^E_m), excess molar enthalpies (H^E_m) and activity coefficients of *n*-alkylamine + benzene mixtures are interpreted in terms of the DISQUAC group contribution model. The systems are characterized by three types of groups or contact surfaces: aliphatic (a), benzene (b) and amine (n). The interchange energies of the aliphatic/benzene and aliphatic/amine contacts were determined independently from the study of benzene + *n*-alkane and *n*-alkylamine + *n*-alkane systems, respectively. The interchange energies of the benzene/amine contact were calculated in this work from experimental G^E_m and H^E_m values. In view of the importance of the NH_2-π interaction, we have kept constant a quasichemical coefficient for the benzene-amine contact and we have only varied the dispersive coefficients with the length of the *n*-alkylamine. The model reproduces quite well the experimental data.

KEY WORDS: Thermodynamic properties, group contribution model DISQUAC.

INTRODUCTION

In a previous paper[1] we investigated the thermodynamic properties of liquid mixtures of *n*-alkylamines with *n*-alkanes. We showed that the experimental data can be correlated rather satisfactorily in terms of DISQUAC model.

Amines were regarded as consisting of two types of surfaces: type a, aliphatic (—CH_3 or —CH_2—groups), and type n, amine (—NH_2 group). *n*-Alkanes were treated as homogeneous molecules type a surface only).

The interchange-energy coefficients $C_{\mathrm{an},l}$ for contacts of type a-n were determined for the amines, and it appeared that the dispersive parameters, $C^{\mathrm{dis}}_{\mathrm{an},l}$ $(l = 1, 2)$, increase up to the *n*-butylamine and then level off for $u \geqslant 4$ (u is the number of carbon atoms in the *n*-alkylamine), where as the quasichemical coefficients, $C^{\mathrm{quac}}_{\mathrm{an},l}$ $(l = 1, 2)$, decrease up to the *n*-butylamine levelling off ($u \geqslant 4$) too (Tab. 4).

We report in this paper the results of a similar examination of the properties: excess molar Gibbs energy, G^E_m, activity coefficients at infinite dilution, γ_i^∞, and excess molar enthalpy, H^E_m, of *n*-alkylamine + benzene mixtures.

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The theoretical model used is the same as before, DISQUAC, an extended quasichemical group contribution model[2]. The thermodynamic excess functions are given in this model by the sum of two types of interactional contributions, dispersive and electrostatic, the former being treated in the random-mixing approximation of the pseudolattice model of liquid mixtures and the latter quasi-chemically.

A literature search reveals that thermodynamic studies of this type of mixtures are rather scarce. Only a single source of liquid-vapour equilibrium (VLE) data, by Letcher and Bayles, 1971[3], for *n*-butylamine (1) + benzene (2) (Tab. 1). As for as we know, no other isothermal VLE data have been reported in the literature for *n*-alkylamine + benzene.

Again only one data of the activity coefficients at infinite dilution, for benzene, γ_1^∞, at three temperatures, by Tiegs *et al.*, 1986[4], determined by gas-liquid chromatography with correction for vapor-phase nonideality, in the benzene (1) + *n*-hexadecylamine (2) mixture (Tab. 2).

Excess molar enthalpies, H_m^E, of *n*-alkylamines + benzene have been measured calorimetrically by four authors (Tab. 1): *n*-propylamine + benzene (Velasco *et al.*, 1978[5] and 1981[6]; Fernández *et al.*, 1990[7,8]); *n*-butylamine + benzene (Letcher and Bayles, 1971[3]; Pfestorf *et al.*, 1989[9]; Fernández *et al.*, 1990[7,8]); *n*-pentylamine + benzene (Fernández *et al.*, 1989[10] and 1990[8]); *n*-hexylamine + benzene (Velasco *et al.*, 1978[5] and 1981[6]; Pfestorf *et al.*, 1989[9]; Fernández *et al.*, 1990[7,8]); *n*-heptylamine or *n*-nonylamine or *n*-undecylamine + benzene (Fernández *et al.*, 1989[10] and 1990[8]);

Table 1 Excess molar Gibbs energies, G_m^E, and excess molar enthalpies, H_m^E, *of n*-alkylamine(1) + benzene(2) mixtures at equimolar composition ($x_1 = 0.5$) and at various temperatures T; comparison of direct experimental results (Exp.) with values calculated (Calc.) using the coefficients $C_{sn,l}^{dis}$, $C_{sn,l}^{quac}$, and $C_{ab,l}^{dis}$, from Tables 3 and 4.

n-alkylamine	*T/K*	$G_m^E(T;x_1 = 0.5)/J\,mol^{-1}$		$H_m^E(T;x_1 = 0.5)/J\,mol^{-1}$	
		Calc.	*Exp.*	*Calc.*	*Exp.*
benzene +					
$CH_3(CH_2)_2NH_2$	303.15	186	–	594	594[a,b]
	303.15	186	–	594	595[d]
$CH_3(CH_2)_3NH_2$	298.15		–	605	703[f]
	298.15		–	605	668[e]
	303.15	176	–	584	584[a,b]
	318.15		–	524	707[e]
	323.15	152	149[e]		–
	343.15	132	131[e]		–
$CH_3(CH_2)_4NH_2$	303.15	159	–	583	583[b,c]
$CH_3(CH_2)_5NH_2$	298.15		–	606	680[f]
	303.15	126	–	587	585[a,b]
	303.15	126	–	587	627[d]
$CH_3(CH_2)_6NH_2$	303.15	92	–	591	591[b,c]
$CH_3(CH_2)_7NH_2$	298.15		–	620	674[f]
	303.15	58	–	602	612[a,b]
$CH_3(CH_2)_8NH_2$	303.15	26	–	621	631[b,c]
$CH_3(CH_2)_9NH_2$	298.15		–	662	743[f]
	303.15	−2	–	646	645[a,b]
$CH_3(CH_2)_{10}NH_2$	303.15	−29	–	671	668[b,c]
$CH_3(CH_2)_{11}NH_2$	303.15	−53	–	692	686[a,b]
$CH_3(CH_2)_{14}NH_2$	313.15	−152	–	730	698[a,b]

[a] Reference 7; [b] Reference 8; [c] Reference 10; [d] Reference 5, 6; [e] Reference 3; [f] Reference 9.

Table 2 Logarithm of activity coefficients at infinite dilution, ln γ_i^{∞}, in benzene(1) + *n*-hexadecylamine(2) mixtures at various temperatures *T*. Comparison of direct experimental results (Exp.), obtained by gas-liquid chromatrography (corrected for vapor-phase nonideality) with values calculated (Calc.) using the coefficients $C^{\mathrm{dis}}_{\mathrm{ab},l}$, $C^{\mathrm{dis}}_{\mathrm{sn},l}$, and $C^{\mathrm{quac}}_{\mathrm{sn},l}$ from Tables 3 and 4.

Mixture	*T/K*	$ln\gamma_1^{\infty}$		$ln\gamma_2^{\infty}$	
		Calc.	*Exp.*	*Calc.*	*Exp.*
Benzene (1) + *n*-hexadecylamine (2)	334.7	−0.29	−0.21[a]	−0.20	–
	350.1	−0.32	−0.24[a]	−0.32	–
	361.2	−0.34	−0.25[a]	−0.40	–

[a] Reference 4.

n-octylamine or *n*-decylamine + benzene (Pfestorf *et al.*, 1989[9]; Fernádez *et al.*, 1990[7,8]); *n*-dodecylamine or *n*-pentadecylamine + benzene, (Fernández *et al.*, 1990[7,8]).

THEORY

n-Alkylamine(1) + benzene(2) systems are regarded as possesing three types of surfaces: (i) type a, aliphatic (— CH_3 or — CH_2—groups, which are assumed to exert the same force field), (ii) type b, benzene (C_6H_6), and (iii) type n, amine (— NH_2 group). The three types of surface, a, b and n, generate three pairs of contacts: aliphatic-benzene (a, b), aliphatic-amine (a, n) and benzene-amine (b, n).

The relative molecular volumes r_i, the surfaces q_i, and the surface fractions α_{a1} and $\alpha_{n1} = 1 - \alpha_{a1}$ of the *n*-alkylamines have been calculated as before[1]. The solvent, benzene, is regarded as consisting of homogeneous molecule, $\alpha_{b2} = 1$, with volume r_2 and surface q_2 given in previous paper[11]: $r_2 = 2.8248$ and $q_2 = 2.0728$.

The equations used to calculate G^E_m and H^E_m are the same as in the other publications[12] and need not to be repeated here.

The temperature dependence of the interchange parameters has been expressed in terms of the dispersive (dis) and of the quasi-chemical (quac) interchange coefficients: $C_{\mathrm{ab},l}$,$C_{\mathrm{an},l}$ and $C_{\mathrm{bn},l}$ (dis or quac), where $l = 1$ (Gibbs energy) or $l = 2$ (enthalpy). Heat capacity coefficients ($l = 3$) have not been considered.

ESTIMATION OF THE INTERACTION PARAMETERS

The interchange parameters, $C^{\mathrm{dis}}_{\mathrm{an},l}$ (dispersive) and $C^{\mathrm{quac}}_{\mathrm{an},l}$ (quasi-chemical), of the aliphatic-amine (a, n) contacts have been determined previously[1] and the same values have been used in this paper (Tab. 4).

The interchange coefficients $C_{\mathrm{ab},l}$ of the aliphatic-benzene (a, b) contacts for *n*-alkylamines with benzene have been obtained from the excess functions of *n*-alkane + benzene mixtures. Average values had been proposed by Kehiaian *et al.*[11] The

Table 3 Dispersive interchange energy coefficients, $C^{\mathrm{dis}}_{\mathrm{ab},l}$, ($l = 1$, Gibbs energy; $l = 2$, enthalpy) for contact aliphatic-benzene (a, b), in the *n*-alkylamine + benzene mixtures as a function of *u*, number of C atoms in the *n*-alkylamine.

l	$C^{\mathrm{dis}}_{\mathrm{ab},l}$							
	$u \leqslant 7$	*8*	*9*	*10*	*11*	*12*	*15*	*16*
1	0.251	0.251	0.252	0.256	0.260	0.265	0.279	0.284
2	0.560	0.561	0.564	0.570	0.575	0.577	0.581	0.583

random-mixing approximation reproduces quite well the shape of the experimental curves, i.e. we can assume that G^E_m and H^E_m are given by the dispersive terms only, $C^{\mathrm{dis}}_{\mathrm{ab},l}$, with $C^{\mathrm{quac}}_{\mathrm{ab},l} = 0$, in accord with the non-polar nature of the groups. A more careful examination[13] has showed that the $C^{\mathrm{dis}}_{\mathrm{ab},l}$ parameters increase with the chain length of the *n*-alkane. This increase was attributed to conformational changes[14] (or changes in molecular order) occurring when *n*-alkanes are mixed with a globular molecule such as C_6H_{12}, C_6H_6 and CCl_4. The study of long-chain *n*-alkylamines + short-chain alkanes[1] showed that similar effects also occur in *n*-alkylamine mixtures. In order to calculate accurately H^E_m of long-chain *n*-alkylamines we proceeded in principle using chain-length dependent $C^{\mathrm{dis}}_{\mathrm{ab},l}$ parameters[15]. We assumed that $C^{\mathrm{dis}}_{\mathrm{ab},l}$ of a *n*-alkylamine with *m* heavy atoms (carbon + nitrogen) equals $C^{\mathrm{dis}}_{\mathrm{ab},l}$ of the *n*-alkane with *m* carbon atoms. The experimental values of H^E_m for the benzene mixtures containing long-chain *n*-alkylamines are lower than those predicted by the DISQUAC model using these above mentioned $C^{\mathrm{dis}}_{\mathrm{ab},l}$ parameters. This fact reveals a smaller orientational order in long *n*-alkylamines that in the corresponding *n*-alkanes, probably due to the existence of association in amines. The dispersive coefficients aliphatic-benzene (a, b) in *n*-alkylamine + benzene mixtures are listed in Table 3.

The interchange parameters of the (a, b) (Tab. 3) and (a, n) (Tab. 4) contacts being known, the representation of G^E_m and H^E_m of *n*-alkylamine + benzene mixtures required only the adjustment of the benzene-amine (b, n) parameters. In view of the importance of the NH_2-π interaction[16], and following a similar way that in previous studies[17] involving *n*-alkanols + benzene, we have kept constant a quasichemical coefficient, $C^{\mathrm{quac}}_{\mathrm{bn},l}$ ($l = 1, 2$), for the benzene-amine contact and have only varied the dispersive coefficients, $C^{\mathrm{dis}}_{\mathrm{bn},l}$ ($l = 1, 2$), with the length of the *n*-alkylamine, From the experimental results for G^E_m and for H^E_m for *n*-butylamine + benzene mixture[3,7,8], and using the already known parameters for the aliphatic-amine and aliphatic-benzene contacts, we have calculated both the dispersive and quasichemical benzene-amine coefficients for this system. For the other *n*-alkylamines, we have kept constant the quasichemical coefficients, $C^{\mathrm{quac}}_{\mathrm{bn},l}$ ($l = 1, 2$), and we have obtained the dispersive ones, $C^{\mathrm{dis}}_{\mathrm{bn},2}$ (enthalpy), from H^E_m experimental data for *n*-alkylamine + benzene mixtures[7,8,10]. The dispersive coefficients, $C^{\mathrm{dis}}_{\mathrm{bn},1}$ (Gibbs energy), were estimated proposing a variation similar to $C^{\mathrm{dis}}_{\mathrm{bn},2}$ (enthalpy). Figure 1 and Table 4 show the variation of the dispersive coefficients, $C^{\mathrm{dis}}_{\mathrm{bn},l}$ ($l = 1, 2$), with the length of the aliphatic chain in the *n*-alkylamine.

Table 4 Interchange energy coefficients, dispersive $C^{\text{dis}}_{\text{sn}}, l$ and quasi-chemical $C^{\text{quac}}_{\text{sn},l}$, ($l$ = 1 Gibbs energy; l = 2, enthalpy) for contact (s, n) (s = a, aliphatic; s = b, benzene; n = $-\text{NH}_2$); u is the number of C atoms in the n-alkylamine.

u	$C^{\text{dis}}_{\text{sn},1}$	$C^{\text{dis}}_{\text{sn},2}$	$C^{\text{quac}}_{\text{sn},1}$	$C^{\text{quac}}_{\text{sn},2}$
n-alkane (s = a)				
3	0.923	1.900	3.549	7.269
⩾4	1.200	2.400	3.510	7.200
benzene (s = b)				
3	1.05[a]	2.047	1.621	2.950
4	1.293	2.516	1.621	2.950
5	1.34[a]	2.580	1.621	2.950
⩾6	1.34[a]	2.610	1.621	2.950

[a] Estimated value.

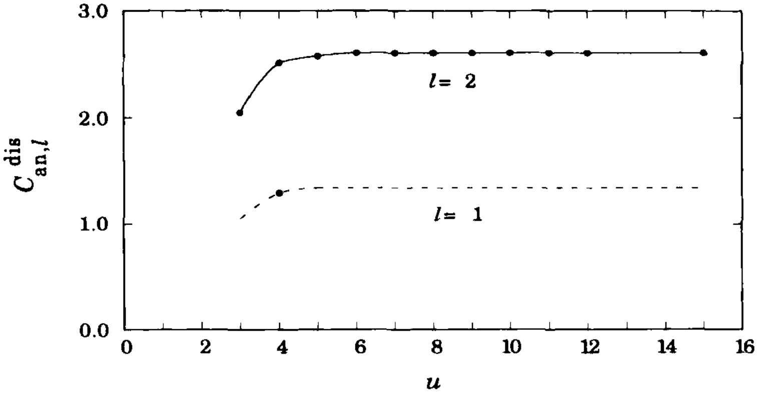

Figure 1 Dispersive interchange energy coefficients, $C^{\text{dis}}_{\text{bn},l}$ (l = 1, Gibbs energy; l = 2, enthalpy) for contact (b, n) (b = benzene, C_6H_6; n = amine, $-\text{NH}_2$) plotted against u, the number of C atoms in the n-alkylamine.

COMPARISON WITH EXPERIMENT AND DISCUSSION

This type of associate solute + polarizable solvent mixtures, although endothermic, shows however an important exothermic contribution due to the specific interaction NH_2-π. If we use constant quasichemical coefficients and other dispersive ones which vary with the chain length of amine, the DISQUAC reproduces quite satisfactorily the H^E_m curves from Velasco *et al.*[5,6] and Fernández *et al.*[7,8,10] (Tab. 1, Fig. 2). Pfestorf *et al.*[9] results are always higher (from 9% to 17% at $x_1 = 0, 5$), and their paper does not say anything about purification of amines. Letcher and Bayles[3] results for n-butylamine + benzene are also higher than DISQUAC predictions (10% at 298.15 K and 13% at 318.15 K, $x_1 = 0, 5$), and they report than H^E_m increases when temperature

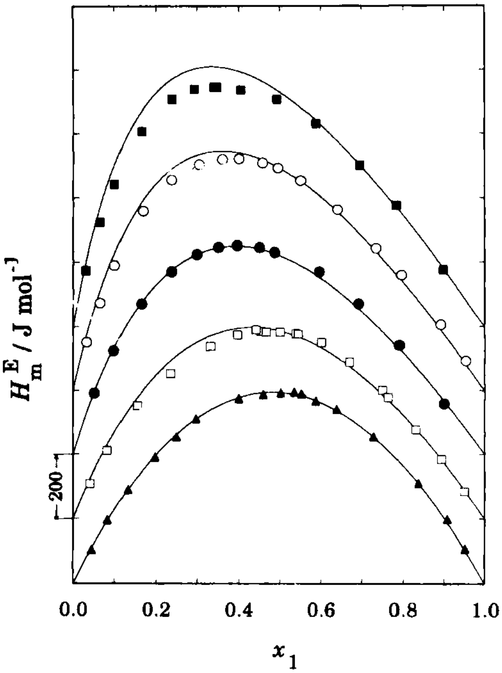

Figure 2 Comparison of theory with experiment for the excess molar enthalpy, H^E_m, at 303.15 K, of *n*-alkylamine(1) + benzene(2) mixtures versus x_1, the mole fraction of *n*-alkylamine. Full lines, predicted values; points, experimental H^E_m results (Fernández *et al.*[7,8,10]): , $u = 3$; , $u = 6$; , $u = 9$; O, $u = 12$; ι, $u = 15$ ($T = 313.15$ K); *u* represents the number of C atoms in the *n*-alkylamine.

increases (Tab. 1); Velasco[18] obtains a opposite variation of H^E_m with temperature for *n*-propylamine + benzene and *n*-hexylamine + benzene mixtures, in agreement with DISQUAC predictions.

The coefficients calculated in this way from VLE measurements reproduce also well both the magnitude and symmetry of the Letcher and Bayles[3] G^E_m-composition curves for *n*-butylamine + benzene at two temperatures (Tab. 1, Fig. 3), and the activity coefficients at infinite dilution for benzene in benzene + *n*-hexadecylamine (Tab. 2) obtained by Tiegs *et al.*[4] from GLC with corrected vapor phase.

The calculated values for G^E_m diminish with increasing number of carbon atoms in the *n*-alkylamine, quite like as happens by *n*-haloalkane + benzene[19,20,21] and by *n*-alcohol + benzene[22,23] mixtures. Regarding the intensity of the concerned interactions, the systems studied by us could be placed about halfway between those containg either a haloderivative or an alcohol.

From H^E_m at infinite dilution of *n*-alkylamine + benzene[16] and of *n*-alkane + benzene[24], we have found for the specific NH_2-π interaction (exothermic) in the *n*-alkylamine + benzene mixtures a value of -6.5 ± 0.1 kJ mol^{-1}. This is in agreement with the introduction of a quasichemical coefficient, $C^{\text{quac}}_{\text{bn},l}$ ($l = 1, 2$), for the amine-benzene contact.

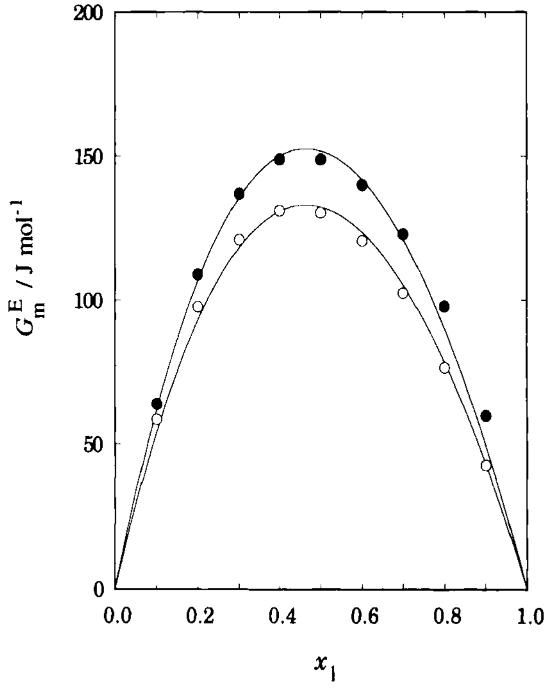

Figure 3 Comparison of theory with experiment for the excess molar Gibbs energy, G_m^E, at 323.15 K () and 343.15 K (O), of *n*-butylamine(1) + benzene(2) mixture versus x_1, the mole fraction of *n*-butylamine. Full lines, predicted values; points, experimental G_m^E results (Letcher and Bayles[3]).

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