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Thermodynamics of mixtures containing amines: XIII. Application of the ERAS model to cyclic amine + alkane mixtures

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ABSTRACT

Primary or secondary cyclic amine + alkane mixtures have been investigated in the framework of the ERAS (Extended Real Associated Solution) model. The corresponding ERAS parameters are reported. All the amines considered have the same equilibrium constant ($K_A = 0.75$). Cyclopropylamine, cyclopentylamine, cyclohexylamine and pyrrolidine are characterized by the same enthalpy of self-association ($\Delta h_A^* = -15\,\mathrm{kJ\,mol^{-1}}$). Piperidine and hexamethyleneimine show a less negative Δh_A^* value ($-13\,\mathrm{kJ\,mol^{-1}}$). Experimental data on excess enthalpies, H_m^E, volumes, V_m^E, and isobaric heat capacities, C_{pm}^E, reveal the existence of physical interactions and structural effects in the studied solutions. The latter lead to values of self-association of pure amines, Δv_A^*, which may depend on the solvent in systems with a given amine. Although the model overestimates the Δh_A^* values, the relatively high values of the physical parameters X_{AB} remark the importance of physical interactions. ERAS describes correctly the excess functions H_m^E, V_m^E, C_{pm}^E and G_m^E (molar Gibbs energy), and the enthalpy of vaporization of pure amines. Nevertheless, discrepancies with experimental data are found for the concentration dependence of V_m^E and G_m^E of some mixtures including cyclic primary amines.

1. Introduction

Amines are substances of biological interest. In fact, many neurotransmitters, as histadine, are amines; the breakdown of amino acids gives amines, and the amine group is present in proteins. The treatment of pyridine systems is necessary for a better understanding of the pyrrole ring, specially important to model binding sites on proteins [1] Spectroscopic studies show that amino acids and proteins behave like n-electron donors similarly to aliphatic amines [2]. Hydrogen bonding between water and the protein and within the protein itself plays a relevant role on protein folding and stability [3,4].

The theoretical analysis of amine + alkane mixtures is a first step needed for the investigation of alcohol + amine mixtures, which are of importance in complex biological solutions. The DISQUAC model [5] has been used for the characterization of systems including primary [6] and secondary linear amines [7]. An association theory which includes a chemical contribution described by an athermal association model and a physical term represented by the Flory theory [8] has been applied to the study of linear amine + alkane mixtures [9]. The Mecke–Kempter [10] or the athermal monomer–dimer [11] association models coupled with a physical contribution, described by the Scatchard–Hildebrand equation [12], have been used for the prediction of vapor–liquid equilibria (VLE) of amine + alkane systems [13]. The model monomer concept [14], together with perturbed hard-chain theory [15] to take into account equation of state effects, has been applied to describe VLE and excess molar volumes, V_m^E, of propylamine, butylamine, hexylamine or diethylamine + alkane mixtures [16]. Cyclic amine + alkane mixtures have been also investigated [17] in terms of DISQUAC and of the Kirkwood–Buff formalism [18]. As continuation, these systems are now studied in the framework of ERAS [19]. Previously, we have presented a full treatment of linear secondary amine [20], aniline [21] or *N*-methylaniline [22,23] + alkane mixtures in terms of such model. In contrast, self-association of linear primary amines has been merely characterized by means of ERAS as part of more general studies of 1-alkanol + amine solutions [24–27].

2. ERAS model

In this model, the excess functions are split into two additive terms, which arise from hydrogen-bonding effects (the chemical contribution, $X_{m,chem}^E$) and non-polar van der Waals' interactions

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Table 1
ERAS parameters[a] for pure compounds at 298.15 K.

Compound	V_i (cm^3 mol^{-1})	α_{Pi} (10^{-3} K^{-1})	κ_{Ti} (10^{-12} Pa^{-1})	V_i^* (cm^3 mol^{-1})	P_i^* (J cm^{-3})	K_i	Δh_i^* (kJ mol^{-1})	Δv_i^* (cm^3 mol^{-1})
Cyclopropylamine	70.44[b]	1.65[b]	1426[c]	51.93	610.2	0.75	−15	−1
Cyclopentylamine	98.17[b]	1.15[b]	870[c]	79.29	511.6	0.75	−15	−4.6
Cyclohexylamine	115.02[d]	1.05[d]	764[e]	95.29	480.3	0.75	−15	−6.8
Pyrrolidine	83.24[f]	1.13[f]	824[g]	67.28	534	0.75	−13	−3.6
Piperidine	99.37[h]	0.96[j]	782[k]	82.19	463.2	0.75	−13	−4
Hexamethyleneimine	113.02[b]	1[b]	700[l]	93.67	520.2	0.75	−13	−6.2
Cyclohexane	108.75[f]	1.22[f]	1140[f]	84.22	531.9			

[a] V_i, molar volume; α_{Pi}, isobaric thermal expansion coefficient; κ_{Ti}, isothermal compressibility; K_i, equilibrium constant; V_i^* and P_i^*, reduction parameters for volume and pressure, respectively; Δh_i^*, hydrogen bonding enthalpy; Δv_i^*, self-association volume.

[b] Ref. [36].

[c] Estimated using the method given in [32] (see text).

[d] Ref. [47].

[e] From adiabatic compressibility reported in [68] ($\kappa_T = \kappa_S + (TV\alpha_p^2/C_p)$); C_p is estimated to be 200 J mol^{-1} K^{-1}.

[f] Ref. [69].

[g] From adiabatic compressibility reported in [70], with C_p = 160.2 kJ mol^{-1}[71]

[h] Ref. [60].

[j] Ref. [72].

[k] From adiabatic compressibility given in [70] with C_p = 177.41 kJ mol^{-1} [60]; [l]estimated from values of pyrrolidine and piperidine.

including free volume effects (physical contribution, $X^E_{m,phys}$). The excess functions are written as:

$$X^E_m = X^E_{m,phys} + X^E_{m,chem} \quad (1)$$

where $X^E_m = H^E_m, C^E_{pm}, V^E_m, G^E_m$. Expressions for these functions are given elsewhere [28]. In addition, it is assumed that only consecutive linear association occurs, which is described by a chemical equilibrium constant (K_A) independent of the chain length of the associated species (cyclic amines), according to the equation:

$$A_m + A \leftrightarrow A_{m+1} \quad (2)$$

with m ranging from 1 to ∞. There is no cross-association between self-associated species A_m and a non self-associated compound B (alkanes in the present work). Eq. (2) is characterized by Δh_A^*, the enthalpy of the reaction that corresponds to the hydrogen-bonding energy, and by the volume change (Δv_A^*) related to the formation of the linear chains.

$X^E_{m,phys}$ is derived from the Flory's equation of state [29], which is assumed to be valid not only for pure compounds but also for the mixture [26,27].

$$\frac{\bar{P}_i\bar{V}_i}{\bar{T}_i} = \frac{\bar{V}_i^{1/3}}{\bar{V}_i^{1/3}-1} - \frac{1}{\bar{V}_i\bar{T}_i} \quad (3)$$

where i = A, B or M (mixture). In Eq. (3), $\bar{V}_i = V_i/V_i^*$; $\bar{P}_i = P/P_i^*$; $\bar{T}_i = T/T_i^*$ are the reduced volume, pressure and temperature respectively. The pure component reduction parameters V_i^*, P_i^*, T_i^* are determined from P–V–T data (density, ρ, isobaric expansion coefficient, α_p, and isothermal compressibility, κ_T), and association parameters [26,27]. The reduction parameters for the mixture P_M^* and T_M^* are calculated from mixing rules [26,27]. The total relative molecular volumes and surfaces of the compounds were calculated additively on basis the group volumes and surfaces, recommended by Bondi [30].

2.1. Adjustment of ERAS parameters

Values of V_i, α_{pi}, and κ_{Ti}, V_i^* and P_i^* of pure amines and cyclohexane at T = 298.15 K, needed for calculations, are listed in Table 1.

Table 2
ERAS paremeters[a] for pure amines and for mixtures used in the calculation of molar excess functions of cyclic amine + alkane mixtures at temperature T.

System	T/K	Δv_A^* (cm^3 mol^{-1})	X_{AB} (J cm^{-3})	(dX_{AB}/dT) (J cm^{-3} K^{-1})	Q_{AB} (J cm^{-3} K^{-1})
Cyclopropylamine + n-C_7	298.15	−1	20		−0.040
Cyclopentylamine + n-C_7	298.15	−4.6	14.2		
Cyclohexylamine + n-C_7	298.15	−6.8	16		0.020
	303.15	−6.8	16.4		
Cyclohexylamine + n-C_8	303.15	−6.8	17		
Cyclohexylamine + n-C_{10}	303.15	−6.8	17.2		
Cyclohexylamine + C_6H_{12}	298.15	−3.5	9.2		
Pyrrolidine + n-C_7	298.15	−3.6	17		
Pyrrolidine + C_6H_{12}	298.15	−2	17		−0.004
Piperidine + n-C_7	298.15	−4	17.7	0.057	
	303.15	−4	18		
Piperidine + n-C_8	298.15	−4	18	0.037	
	303.15	−4	18.2		
Piperidine + n-C_{10}	298.15	−4.4	18	0.016	
	303.15	−4.4	18.08		
Piperidine + n-C_{12}	298.15	−4.9	18	−0.01	
Piperidine + n-C_{14}	298.15	−5.2	18	−0.045	
Piperidine + C_6H_{12}	298.15	−2	9	0.052	0.013
Hexamethyleneimine + n-C_7	298.15	−6.2	14.9		
Hexamethyleneimine + + C_6H_{12}	298.15	−3	7		0.020

[a] Δv_A^*, self-association volume of pure amine; X_{AB}, physical parameter; (dX_{AB}/dT), variation of the physical parameter with temperature; Q_{AB}, parameter for representing the entropic contribution of the non-polar interactions to G^E_m.