

Partial molar enthalpy properties and correlation of excess molar enthalpy data of acetonitrile + diethylamine or *S*-butylamine mixtures at various temperatures and atmospheric pressure

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Abstract

Experimental data of excess molar enthalpy (H_m^E) of binary mixtures of acetonitrile + diethylamine or *S*-butylamine mixtures as a function of composition at 288.15, 293.15, 298.15 and 303.15 K at atmospheric pressure have been used to calculate excess partial molar enthalpy and partial molar enthalpy of each component as a function of composition as well as partial molar enthalpy properties at infinite dilution. The Flory and Prigogine–Flory–Patterson (PFP) theories were applied to correlate the H_m^E data. The results of the calculations as well as the influence of temperature and isomers chain on the partial molar enthalpy properties are discussed.

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1. Introduction

Excess properties, especially excess enthalpy, of binary liquid acetonitrile or amine containing mixtures [1–4] have been studied to understand the molecular interactions between the components of the mixture. In our previous work [5], experimental data of excess enthalpy of acetonitrile + diethylamine or *S*-butylamine were presented and correlated using the ERAS-model [6].

Other property of interest is the partial molar enthalpy due to its relation to other functions of interest. For instance, knowing the excess partial molar enthalpy function at infinite dilution $\bar{H}_i^{E,\infty}$ it is possible to calculate the temperature dependence of activity coefficient at infinite dilution γ_i^∞ from the equation:

$$\left(\frac{\partial \ln \gamma_i^\infty(T)}{\partial T}\right)_{p,x_i} = -\frac{\bar{H}_i^{E,\infty}(T)}{RT^2} \quad (1)$$

Literature references of volumetric partial molar properties are numerous [7–10], contrasting to references of partial molar enthalpy properties. As examples, Anderson and Olofsson [11] studied the experimental partial molar enthalpy properties of 2-butoxyethanol and 2-butanol with water and Mateolli et al. [3] the partial molar enthalpy properties of 1-heptane + primary *n*-alkyl (C_3 – C_{10}) and branched (*iso*-propyl, *sec*, *iso* and *tert*-butyl) amines. Both works emphasize the importance of the determination of these properties for the study of molecular interaction occurring in liquid mixtures.

As a continuation of our studies on excess functions of acetonitrile + amines mixtures, in this work excess molar enthalpy (H_m^E) of acetonitrile + diethylamine or *S*-butylamine mixtures have been used to calculate excess partial molar enthalpy (\bar{H}_i^E), partial molar enthalpy (\bar{H}_i) and the partial molar properties at infinite dilution \bar{H}_i^∞ as a function of composition at 288.15, 293.15, 298.15 and 303.15 K at atmospheric pressure. This work also reports the applicability of the Flory and Prigogine–Flory–Patterson theories (PFP) to correlate the H_m^E of acetonitrile + diethylamine or *S*-butylamine mixtures. A detailed description of the apparatus and the experimental procedure to obtain the excess molar enthalpy are given elsewhere [5].

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2. Theory

2.1. Partial molar enthalpy relations

The excess partial molar enthalpy has been calculated by the following equation:

$$\bar{H}_i^E = \bar{H}_i - H_i^\circ \quad (2)$$

wherein \bar{H}_i and H_i° are the partial molar enthalpy and molar enthalpy of the component i , respectively. The partial molar enthalpy values were calculated by

$$\bar{H}_1 = H_m^E + H_1^\circ - x_2 \left(\frac{\partial H_m^E}{\partial x_2} \right)_{p,T} \quad (3)$$

$$\bar{H}_2 = H_m^E + H_2^\circ + (1 - x_2) \left(\frac{\partial H_m^E}{\partial x_2} \right)_{p,T} \quad (4)$$

The term H_m^E in the Eqs. (3) and (4) was calculated by the Redlich–Kister equation:

$$H_m^E = x_2(1 - x_2) \sum_{i=0}^4 A_j (1 - 2x_2)^i \quad (5)$$

The parameters A_j were obtained from experimental data of excess molar enthalpy of the studied systems and are given in [5]. Differentiation of Eq. (5) with respect to x_2 and combination of the results of differentiation with Eqs. (3) and (4) leads to the followings equations for the partial molar enthalpy of acetonitrile \bar{H}_1 and amines \bar{H}_2 :

$$\begin{aligned} \bar{H}_1 = H_1^\circ + x_2^2 \sum_{j=0}^{j=n} A_j [1 - 2(1 - x_2)]^{(j-1)} - 2(1 - x_2)x_2^2 \\ \times \sum_{j=0}^{j=n} A_j (j - 1) [1 - 2(1 - x_2)]^{(j-2)} \end{aligned} \quad (6)$$

$$\begin{aligned} \bar{H}_2 = H_2^\circ + (1 - x_2)^2 \sum_{j=0}^{j=n} A_j [1 - 2(1 - x_2)]^{(j-1)} + 2(1 - x_2)^2 x_2 \\ \times \sum_{j=0}^{j=n} A_j (j - 1) [1 - 2(1 - x_2)]^{(j-2)} \end{aligned} \quad (7)$$

For H_i° values standard molar enthalpy of formation ΔH_f° was used. The temperature dependence was calculated by the Kirchhoff equation:

$$\Delta H_f^\circ(T) = \Delta H_f^\circ(T_0) + \int_{T_0}^T \sum_i v_i C p_i^0 dT \quad (8)$$

$C p_i^0$ was considered constant and the data at 298.15 K were obtained from [12]. The results of calculations are showed in Table 1. For *S*-butylamine was adopted the value $C p^0 = 174 \text{ J mol}^{-1} \text{ K}^{-1}$ [13]. By setting $x_2 = 1$ and $x_1 = 0$, the

Table 1

Standard molar enthalpy of formation ΔH_f° of pure components (kJ mol^{-1})

T (K)	Acetonitrile	Diethylamine	<i>S</i> -Butylamine
288.15	53.74 ^a	−104.09 ^a	−137.84 ^a
293.15	53.66 ^a	−103.89 ^a	−137.67 ^a
298.15	53.58 ^b	−103.70 ^c	−137.50 ^c
303.15	53.50 ^a	−103.51 ^a	−137.33 ^a

^a Calculated from Eq. (8).

^b From [12].

^c From [14].

Eq. (6) becomes:

$$\bar{H}_1^\infty = H_1^\circ + \sum_{j=0}^{j=n} A_j \quad (9)$$

and by setting $x_2 = 0$ and $x_1 = 1$, the Eq. (7) becomes:

$$\bar{H}_2^\infty = H_2^\circ + \sum_{j=0}^{j=n} A_j (-1)^{j-1} \quad (10)$$

Eqs. (9) and (10) represent the partial molar enthalpy of acetonitrile and amines at infinite dilution, respectively. The excess partial molar enthalpy at infinite dilution has been obtained using the Eq. (2) at infinite dilution condition, i.e.

$$\bar{H}_i^{E,\infty} = \bar{H}_i^\infty - H_i^\circ \quad (11)$$

Substituting the Eq. (9) in (11) the excess partial molar enthalpy at infinite dilution of the acetonitrile (1) in amines (2) (diethylamine or *S*-butylamine) is given by

$$\bar{H}_1^{E,\infty} = \sum_{j=0}^{j=n} A_j \quad (12)$$

and substituting the Eqs. (10) in (11), the excess partial molar enthalpy at infinite dilution of the amines (2) in acetonitrile (1) is represented by

$$\bar{H}_2^{E,\infty} = \sum_{j=0}^{j=n} A_j (-1)^{j-1} \quad (13)$$

2.2. Flory and PFP equations

In the Flory model the excess molar enthalpy is given by

$$\begin{aligned} H_m^E(\text{Flory}) = x_1 P_1^* V_1^* \left(\frac{1}{\bar{V}_1} - \frac{1}{\bar{V}} \right) \\ + x_2 P_2^* V_2^* \left(\frac{1}{\bar{V}_2} - \frac{1}{\bar{V}} \right) + \frac{x_1 V_1^* \theta_2}{\bar{V}} \chi_{12} \end{aligned} \quad (14)$$

wherein x_i , P_i^* , V_i^* are the molar fraction, characteristic pressure and characteristic volume of the pure components, respectively. \bar{V}_i is the reduced volume of the pure components and \bar{V} the reduced volume of the mixture given by

$$\bar{V} = \bar{V}^0 + \bar{V}^E \quad (15)$$

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