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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:

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

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 $\bar{H}_i^\infty$ 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:

$$\bar{H}_i^E = \bar{H}_i - H_i^\circ \tag{2}$$

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

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

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

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

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

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 $\bar{H}_2$:

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

$$\times \sum_{j=0}^{j=n} A_j (j-1)[1 - 2(1 - x_2)]^{(j-2)} \tag{6}$$

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

$$\times \sum_{j=0}^{j=n} A_j (j-1)[1 - 2(1 - x_2)]^{(j-2)} \tag{7}$$

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

$$\Delta H_f^\circ(T) = \Delta H_f^\circ(T_0) + \int_{T_0}^{T} \sum_i \nu_i Cp_i^0 \, dT \tag{8}$$

Cp_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 $Cp^0 = 174 \, \text{J mol}^{-1} \, \text{K}^{-1}$ [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	S-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:

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

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

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

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.

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

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

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

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

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

2.2. Flory and PFP equations

In the Flory model the excess molar enthalpy is given by

$$H_m^E \text{ (Flory)} = x_1 P_1^* V_1^* \left(\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}} \right)$$

$$+ x_2 P_2^* V_2^* \left(\frac{1}{\tilde{V}_2} - \frac{1}{\tilde{V}} \right) + \frac{x_1 V_1^* \theta_2}{\tilde{V}} \chi_{12} \tag{14}$$

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

$$\tilde{V} = \tilde{V}^0 + \tilde{V}^E \tag{15}$$

in which the ideal reduced volume for the mixture

$$\tilde{V}^0 = \phi_1 \tilde{V}_1 + \phi_2 \tilde{V}_2 \tag{16}$$

with the segment and site fractions given by

$$\phi_1 = 1 - \phi_2 = \frac{x_1 V_1^*}{x_1 V_1^* + x_2 V_2^*} \tag{17}$$

$$\theta_1 = 1 - \theta_2 = \frac{x_1 V_1^*(S_1/S_2)}{x_1 V_1^*(S_1/S_2) + x_2 V_2^*} \tag{18}$$

wherein

$$S_1/S_2 = \left(\frac{V_1^*}{V_2^*}\right)^{-1/3}$$

The χ_{12} is the Flory interaction parameter. The development of this theory is presented elsewhere [15–23]. Patterson proposed to substitute the segment fraction term used in the Flory theory for the contact energy fraction term ψ represented by

$$\psi_1 = 1 - \psi_2 = \frac{\phi_1 P_1^*}{\phi_1 P_1^* + \phi_2 P_2^*} \tag{19}$$

Another modification is related to the mixing functions: Patterson proposed a mathematical approximation procedure, using several liquid models based on the cell partition function. For more details, see [24–27]. The PFP theory gives the following expression for the excess molar enthalpy:

$$H_m^E(PFP) = H_m^E(f.v.) + H_m^E(int) \tag{20}$$

The first term in the right side is the free volume contribution to the excess molar enthalpy, given by

$$H_m^E(f.v.) = (x_1 U_1^* + x_2 U_2^*)\tilde{C}p(\tilde{T}_U)(\psi_1 \tilde{T}_1 + \psi_2 \tilde{T}_2 - \tilde{T}_U) \tag{21}$$

and the second term is the interaction contribution to the excess molar enthalpy given by

$$H_m^E(int) = (x_1 U_1^* + x_2 U_2^*)[\tilde{T}_U \tilde{C}p(\tilde{T}_U) - \tilde{U}(\tilde{T}_U)]\frac{\chi_{12}\psi_1\theta_2}{P_1^*} \tag{22}$$

The terms x_i, P_i^*, V_i^*, $\tilde{V}_i$, $\tilde{V}$, θ_2 and χ_{12} represented in Eqs. (21) and (22) have the same significance as those Eq. (14); U_i^* is the configurational characteristic energy of the pure components and $\tilde{U}(\tilde{T}_U)$ is the configurational reduced energy of the mixture; $\tilde{T}_i$ is the reduced temperature of the pure components and $\tilde{T}_U$ is the reduced temperature of the mixture; $\tilde{C}p(\tilde{T}_U)$ is the reduced heat capacity of the mixture and ψ_1 is the contact energy fraction of the component 1. The expressions to obtain the values of the terms in Eqs. (21) and (22) are presented elsewhere [28,29].

3. Results and discussion

The calculated results for the excess partial molar enthalpy and partial molar enthalpy of the studied systems are presented in Supplementary Tables 2a and b and 3a and b and the partial molar enthalpy properties at infinite dilution are listed in Table 2a and b. The excess partial molar enthalpy data at infinite dilution are positive and increase with the temperature. The

Table 2
Partial molar properties at infinite dilution of acetonitrile + diethylamine and acetonitrile + S-butylamine systems

Components	T (K)	$\bar{H}_i^{E,\infty}$ (kJ mol^{-1})	$\bar{H}_i^{\infty}$ (kJ mol^{-1})
(a)Acetonitrile + diethylamine			
Acetonitrile	288.15	2.02	55.76
	293.15	2.16	55.79
	298.15	2.32	55.89
	303.15	2.40	55.90
Diethylamine	288.15	2.95	−101.13
	293.15	2.96	−100.93
	298.15	2.97	−100.77
	303.15	3.01	−100.46
(b)Acetonitrile + S-butylamine			
Acetonitrile	288.15	2.07	55.81
	293.15	2.41	56.07
	298.15	2.62	56.20
	303.15	2.77	56.24
S-butylamine	288.15	2.26	−135.58
	293.15	2.39	−135.28
	298.15	2.62	−134.88
	303.15	2.74	−134.56

variation of these quantities with the temperature is greater in acetonitrile + S-butylamine system. For diethylamine is $\bar{H}_i^{E,\infty}$ almost temperature independent.

We note that the partial molar enthalpy at infinite dilution and the excess partial molar enthalpy of acetonitrile are almost independent of solvent (diethylamine or S-butylamine). This probably means that acetonitrile—amine interactions are very similar in both systems. This is not surprisingly, since both amines are isomers. On the other hand, partial molar enthalpy values at infinite dilution for both components are similar to the corresponding molar values. This probably means that specific interactions (self-association, cross-association) are present in the mixtures [5]. As showed in [30], the isomers of these amines are self-associated to different degrees in the liquid state and acetonitrile is a polar liquid with a proton acceptor nitrogen atom and as determined by spectroscopy, the amine and acetonitrile liquid mixtures form hydrogen-bonded complexes.

Figs. 1 and 2 show the composition dependence of H_m^E data, free volume and interaction contributions as well as the PFP theory calculations. The interaction contribution to the excess molar enthalpy is positive and predominant in all systems and increase with the temperature. The free volume contribution, which is a measure of the molecular geometrical accommodation, is always negative, increases in absolute values with temperature and it seems to have little significance for the systems studied.

The parameters of pure components needed in the Flory and PFP theories for estimating the H_m^E of binary mixtures are given in [5]. The interaction parameter calculated from Eqs. (21) and (22), as well as the values of standard deviations, calculated from equation:

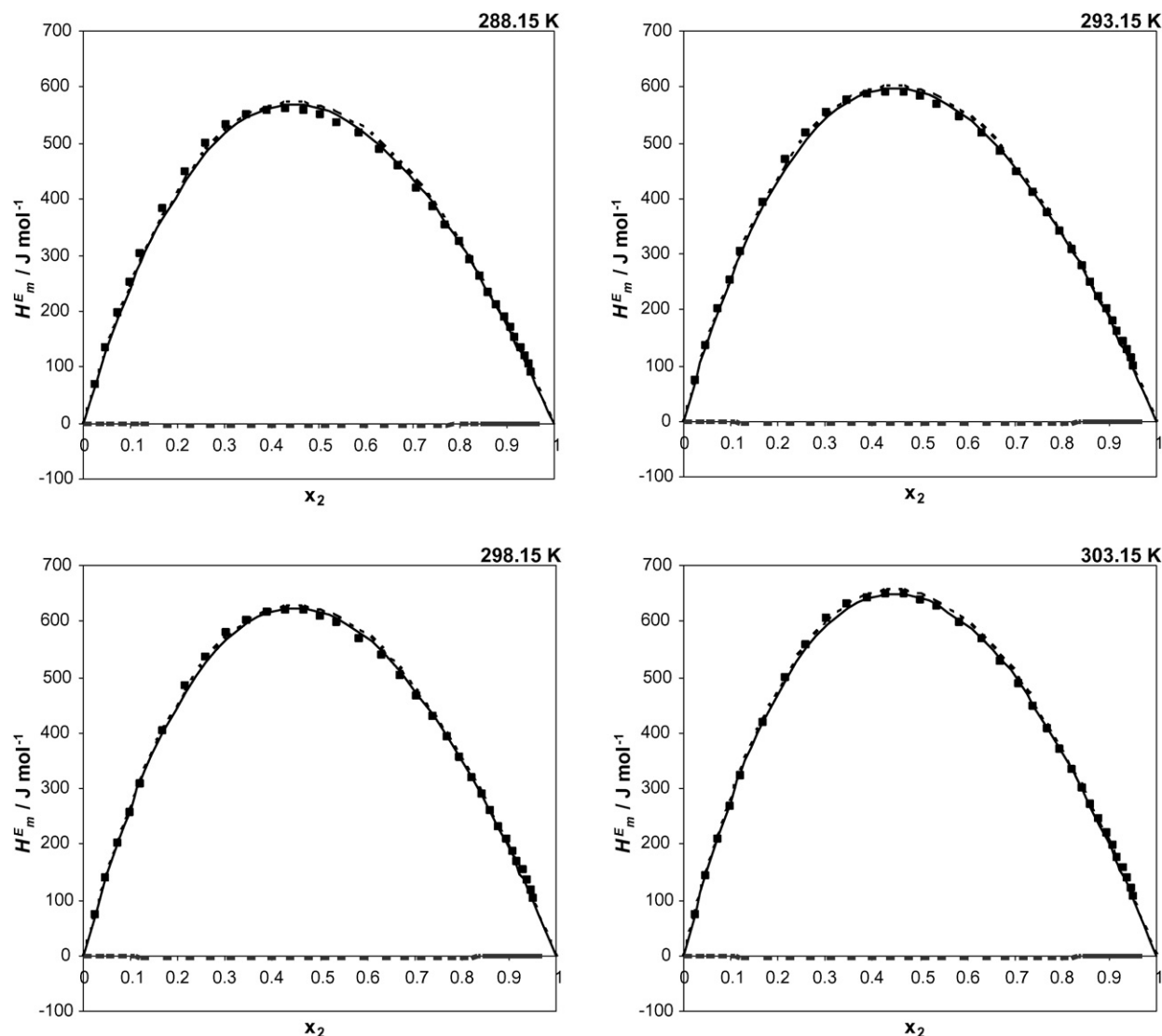$$\sigma = \left[\sum \frac{(H_{m_{exper}}^E - H_{m_{calc}}^E)^2}{N - k}\right]^{1/2} \tag{23}$$

Fig. 1. Values of H_m^E as a function of the mole fraction of amine (x_2) of (acetonitrile + diethylamine) mixtures at 288.15, 293.15, 298.15 and 303.15 K, respectively. (■) Experimental; (—) PFP-model; (- - -) free volume contribution; (···) interaction contribution.

in which N is the number of data points and k is the number of adjustable parameters in Eq. (5), are given in Table 3. By comparing the standard deviations values, it is possible to conclude that the PFP theory is more adequate to correlate the H_m^E data than the Flory's theory.

Although Flory's and PFP theories do not consider all the possible interactions existent in the binary mixtures studied and by using only one fitted parameter adjusted to H_m^E data, the agreement between calculated values and experimental values is satisfactory for both models at all temperatures.

Table 3
Optimized model parameters in the temperature range studied

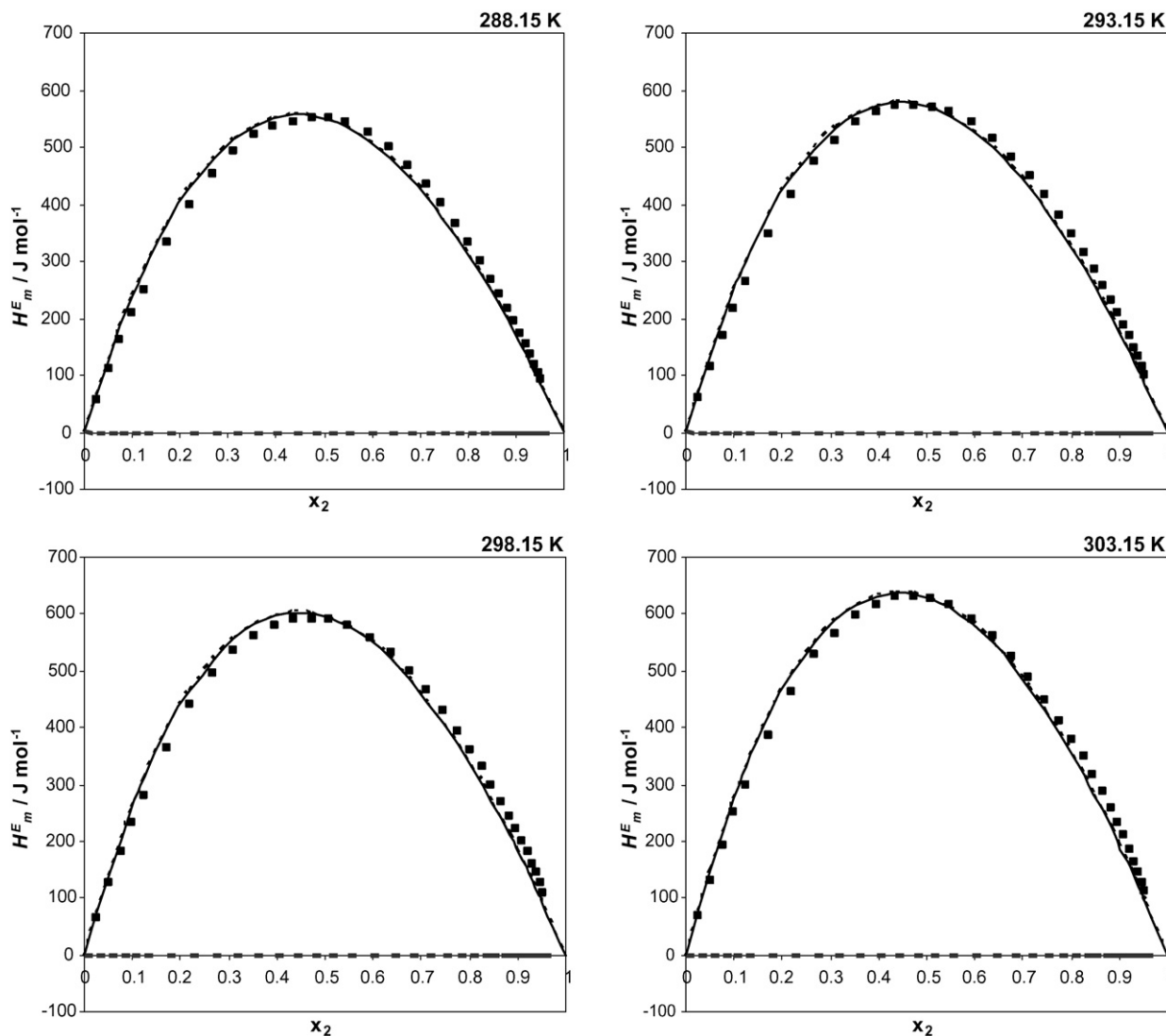| System	T (K)	PFP theory		Flory theory	
		χ_{12} (J cm^{-3})	σ (J mol^{-1})	χ_{12} (J cm^{-3})	σ (J mol^{-1})
	288.15	35.10	8.62	53.70	12.45
	293.15	36.70	6.95	56.50	15.74
$(1-x_2)CH_3CN + x_2(C_2H_5)_2NH$	298.15	38.22	7.14	59.18	17.92
	303.15	39.60	6.78	61.80	19.45
	288.15	34.60	20.53	52.30	33.24
	293.15	35.50	24.14	54.50	36.00
$(1-x_2)CH_3CN + x_2(C_2H_5)CH(NH_2)CH_3$	298.15	36.80	24.83	56.80	36.66
	303.15	38.70	24.30	60.00	36.84

Fig. 2. Values of H_m^E as a function of the mole fraction of amine (x_2) of (acetonitrile + *S*-butylamine) mixtures at 288.15, 293.15, 298.15 and 303.15 K, respectively. (■) Experimental; (—) PFP-model; (- - -) free volume contribution; (···) interaction contribution.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.09.012.

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