



Theoretical Approach on W-Shaped Excess Heat Capacities of Some Linear and cyclic Oxaalkane-Alkane Systems.

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Abstract

The excess heat capacities, C_p^E , throughout the entire concentration range have been determined at 30 °c, 40 °c and 50 °c of linear and cyclic oxaalkane systems : 2,5,8,11,14-pentaoxapentadecane (tetraglyme) with dodecane and 1,4 dioxane with dodecane .

For all these mixtures C_p^E has a w shaped concentration dependence (two minimum speared by a maximum). By decreasing the molecular size of their component, the second minimum towards high concentration disappear at 30 °c and 40 °c but persist at 25 °c.

C_p^E behaviour correlates with degrees of non-randomness in the mixtures as quantified by the concentration-concentration correlation function S_{cc} witch is calculated using quasichemical Guggenheim-Barker-Kehiaian theory with a group-interaction model and assuming interaction between molecular surfaces [2].

The selected linear and cyclic oxaalkane-Alkane systems studied; accordingly, the influence of temperature, the size and molecular structure on the excess heat capacities has been analysed.

KEY WORDS: oxaalkane-alkane; excess heat capacity; concentration-concentration correlation function S_{cc}

1. Introduction

In this paper, measurements of the excess heat capacity in function of mole fraction and temperature of (tetraglyme + dodecane) and (1, 4 dioxane + dodecane), with a mole fraction for three temperatures: 303, 15 K; 313, 15 K and 323, 15 K. These mixtures have been selected, accordingly, the influence of the size and molecular structure. In this way, the influence of the temperature of the liquids on their excess heat capacities might be analysed.

These mixtures presented the W-shape C_p^E . Where two minimum occur separated by maximum. Components (1) and (2) of the systems apparently always differ greatly in chemical nature. For instance, component (1) can be a linear or cyclic oxaalkane. Component (2) is a normal alkane. The w-shape is suggested [1], to arise from the superposition of a positive C_p^E contribution on to a normal parabolic negative curve. The positive contribution is associated with non-randomness in the mixture, since non-randomness must disappear at the end of the molar fraction range; the positive contribution is limited to the middle of the molar fraction range giving the w-shape. Non-randomness would require the w-shape to become more pronounced with decrease of temperature. The effect of non-randomness should manifest it self toward the middle of molar fraction range transforming the normal negative parabolic C_p^E into W shape with is dramatically enhanced as the UCST is approached.

In the present work, oxalkane-alkane systems will be used to test the more specific proposal that the maximum in w-shaped C_p^E curve should correlate, in magnitude and in position in the concentration range, with the maximum in function correlation concentration – concentration S_{cc} . We justified these comportments of S_{cc} with our measurements of C_p^E .

This work is a contribution toward a more comprehensive experimental basis.

2. Results and discussion

Graphical representations of our measurements of excess heat capacities, c_p^E , of tetraglyme (1) + dodecane (2) in function of mole fraction are given in Figure 1a, in Figure 1b for 1, 4 dioxane + dodecane.

It is observed for all systems that, as the temperature increase, C_p^E decrease. This tendency is stronger at the maximum in C_p^E .

From Figure 1 (a) and (b), it can be inferred that the maximum of mole fraction

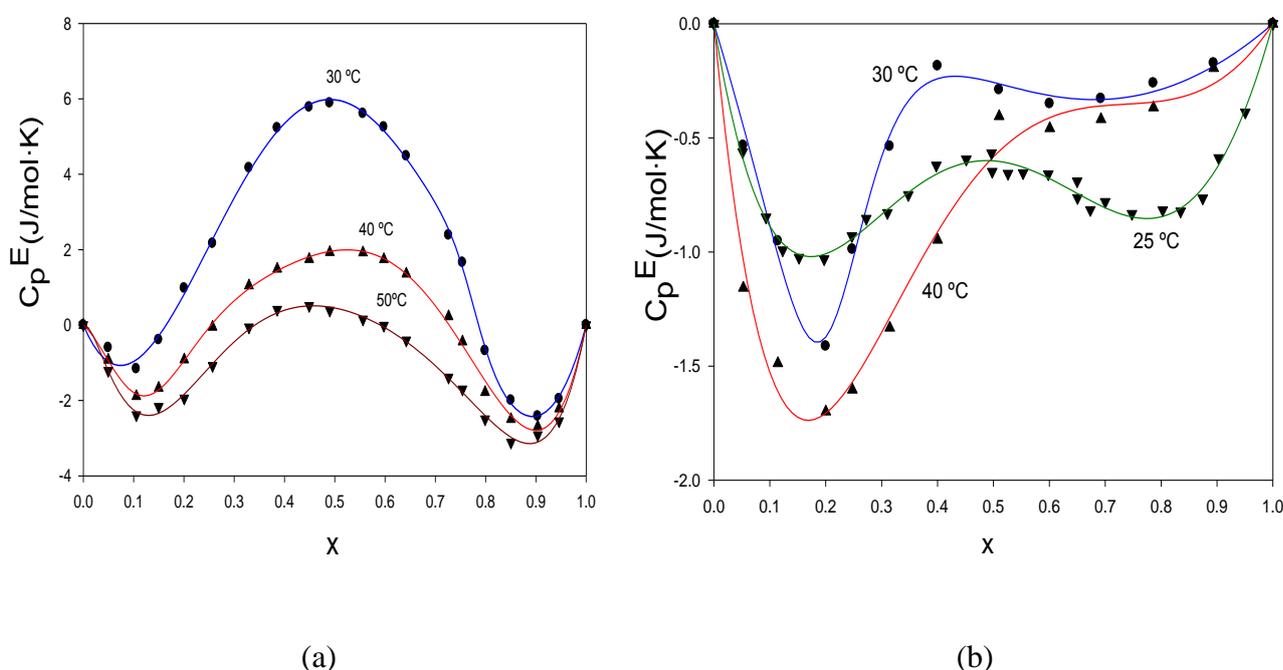


Figure 1: Excess heat capacities C_p^E against oxalkane mole fraction at 30 °c, 40 °c and 50 °c for tetraglyme-dodécane (a) and 1,4 dioxane-n-dodécane at 25 °c, 30 °c and 40 °c (b).

dependent excess heat capacities of linear oxalkane-Alkane systems, increase as the temperature decrease, or/and the alkyl chain length increase [5]. In this regard, it can be concluded that the maximum of c_p^E disappear when the alkyl chain is under twelve carbon atoms. Moreover, this behaviour is similar for all the temperatures. For cyclic oxalkane –alkane systems the maximum of c_p^E is small and the W shape of c_p^E disappear when the longer chains is under twelve carbon atoms. These comportments, indicating the greater influence of the temperature and the alkyl groups on the excess heat capacities.

3. GUGGENHEIM-BARKER-KEHIAIAN Treatment of S_{cc} .

From equations given the excess function free enthalpy g^E of Guggenheim– Barker – Kehiaian theory, induced in the equation given S_{cc}^{-1} , we concluded by simple calculation the expression of this function S_{cc} :

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$$S_{cc}^{-1} = [x_1 \cdot x_2]^{-1} + \left[\frac{(r-1)}{(x_1 + r \cdot x_2)} \right]^2 - \frac{2 \cdot g_{12} \cdot v_1 \cdot r^2}{RT(x_1 + r \cdot x_2)^3} \quad (1)$$

Where $r = \frac{r_2}{r_1}$. In this equation, the function S_{cc}^{-1} is the some of three terms:

- The one term is the ideal combinatorial. It's positive and stabilize the solution.
- The second term is the non ideal combinatorial. It's small, positive and stabilise either the solution.
- The third term interactionnel, negatif and favorise the deformation , increasing the function S_{cc} .
 The value of S_{cc} .

For each temperature and binary mixture, we represented the function $S_{cc}(x)$.

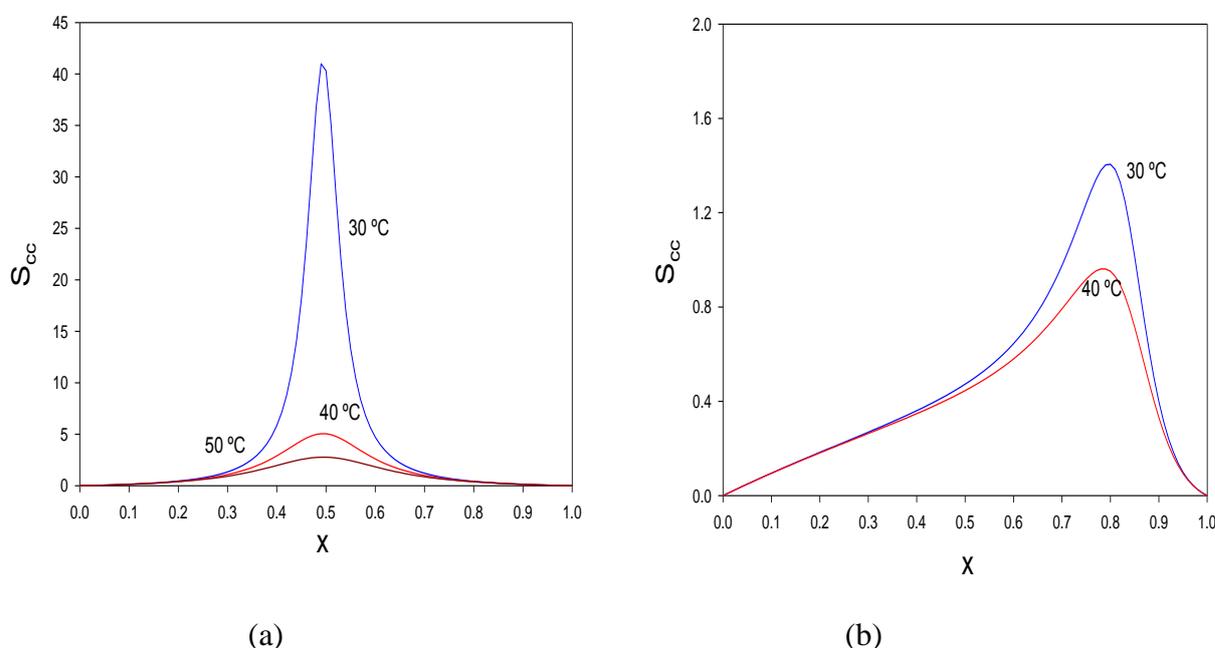


Figure2: Function S_{cc} against oxaalkane mole fraction for tetraglyme + dodécane (a) at 30 °c, 40 °c and 50 °c and (b) for 1,4 dioxane + dodecane at 30 °c and 40 °c calculated using the quasichemical theory (Guggenheim-Barker-Kehiain).

Fig.2(a) and (b) shows a plot of S_{cc} against oxaalkane mol fraction at 30 °c, 40 °c and 50 °c for oxaalkane + n-alkane mixtures. For clarity, the w shape character should be more intense when the molecular size of the components is increased. These predictions are clearly corroborated in fig 1a,1b, where S_{cc} and cp^E are apparently similar functions of the concentration. With the largest oxaalkane, tetraglyme, when we increasing alkane carbon number, i.e increasing q_i or molecular surface, we increasing S_{cc} or non randomness and in fig 1a, 1b an increasing positive maximum in Cp^E . The diglyme +nC7 have a maximum calculated S_{cc} value of 0.83 which lies just above the value of 0.7 suggested [4] as a threshold value for the appearance of the w shape. The S_{cc} calculation fig 2a, 2b, where the maximum in S_{cc} for 1,4 dioxane + n-C12 is 1 at $T = 40$ °c , bigger than the threshold of 0.7, more specially the difference in S_{cc} are due to different α_o values , the fraction of the molecular surface of the oxaalkane which is of oxygen character. On going from 1,4 dioxane to G4 (tetraglyme), α_o increases producing an increase in S_{cc} and the appearance of w shaped Cp^E . These results in fig 1a, 1b indicate

that the appearance of a w shaped depend critically on temperature, the size of each components of mixture and the number of oxygen-alkyl interaction per ether molecule present in the solution.

These experimental results for c_p^E and S_{cc} agree with PATTERSON's hypothesis about no randomness in the mixture by concentration fluctuation [3].

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