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On the ideality of liquid mixtures of long-chain *n*-alkanes

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Abstract

Calorimetric measurements show that the heats of mixing two *n*-alkanes (of similar chainlength) in the liquid phase, are very small, and may often be neglected. Also, calculation of the entropy of *n*-alkane binary mixtures in the liquid and in the high temperature solid α-RII Rotator phase, by integration of experimentally obtained enthalpies, show that the excess entropies are negligible for all practical purposes. *n*-Alkane liquid mixtures between neighbouring homologs may therefore be considered as ideal solutions. © 1997 Elsevier Science B.V.

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1. Introduction

Liquid hydrocarbon mixtures have been, and are still being, widely-used to check liquid-state theories. In particular, solutions of *n*-alkanes in organic solvents have been very often used to model solution behaviour in an attempt to predict the wax precipitation temperatures in hydrocarbon fuels. Such *n*-alkane solutions show short-range order phenomena, leading to quite important positive contributions to excess enthalpies [1].

In multicomponent systems, in which at least two *n*-alkanes are present, many solid–liquid equilibrium data have been published [2–19]. Over the years, a number of surprising and curious phenomena have been elucidated and explained. For example, the increased solubility of a heavy *n*-alkane in the presence of another heavy *n*-alkane reported by Belaadi [14] and Ghogomu [2,3,15] is now believed to be the result of the strong non-ideality of the solutions formed by them, the phenomenon depicts the difficulty of crystal formation in the presence of impurities [8]. However, if the binary phase diagrams of *n*-alkanes in the solid state are at least better understood today than yesteryears, the same is not true of the liquid phase.

Some authors have proposed that the liquid binary system of two long chain alkanes be considered as athermal, as very small or, no energetic interactions arise between the molecules [8]. The non-ideality will be attributed solely to entropic effects (size difference

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or free-volume effects). In this work, we report results of calorimetric measurements of the heats of mixing n-alkane liquids at 330 K. Also, we give a thermodynamic treatment developed to calculate the entropic effects in the liquid and α-RII Rotator phase of some three binary mixtures.

2. Experimental

2.1. Materials

The n-alkanes (docosane, tricosane, tetracosane) were purchased from Aldrich Chemie, and checked by gas chromatography and mass spectroscopy to be over 99% pure. They were used without further purification.

2.2. Apparatus and procedure

The measurement of the mixing enthalpy of n-alkane liquids was carried out in an isothermal Calvet-type microcalorimeter as previously described [14,15]. The apparatus and procedure were modified: the measuring cell, a long pyrex-glass tube, was fitted with a tap mounted at its exit. A long compact glass cylinder was attached to the tap such that when the tap is closed the cylinder descends by about 1 cm, getting to some 50 mm from the bottom of the measuring cell. One of the alkanes was directly introduced into the tube, while the second was blocked in a small glass bulb, which was then lowered into the measuring cell also.

When thermal equilibrium was reached, the tap was closed, and the sealed bulb was crushed by the descending glass cylinder. The two n-alkane liquids were mixed, and the heat change was measured as described elsewhere [16]. It should be noted that the contribution of the 'breaking of glass' in a liquid n-alkane was measured, and found to be insignificant – the baseline of the recorder did not move at all.

3. Results and discussion

3.1. Excess enthalpy

All our experimental measurements show that when two n-alkanes ($C_{22}+C_{24}$ or $C_{23}+C_{24}$) mix in the liquid phase, there is no appreciable heat change. With a very high specific sensitivity of the calorimeter (minimum detectable range of 50 mJ), and the small quantities of n-alkanes used in each experiment (less than 1 g), it is found that $h^E \leq 15\ \mathrm{J\,mol^{-1}}$ for the following systems studied at 330.00 K (mole fractions of n-C_{24}):

$$\begin{aligned} C_{22}{-}C_{24} &: 0.0328, 0.0667, 0.0861, 0.0982,\\ &\times 0.4215, 0.6549, 0.7943, 0.9146, 0.9396,\\ &\times 0.9542, 0.9901. \end{aligned} \tag{1}$$

$$\begin{aligned} C_{23}{-}C_{24} &: 0.0243, 0.0410, 0.0742, 0.1536,\\ &\times 0.4685, 0.6366, 0.8543, 0.9004, 0.9367,\\ &\times 0.9787, 0.9912, 0.9986. \end{aligned} \tag{2}$$

In the limit of experimental errors, these systems are athermal.

Brady et al. [17] report measurements of h^E that vary between -10 and $+16\ \mathrm{J\,mol^{-1}}$ for C_6+C_{16} systems at 333.15 K, while Peters et al. [19] report values varying between -15 and $70\ \mathrm{J\,mol^{-1}}$ for mixtures of alkanes of very different chainlength. These results, with those reported herein, show that the energetic interactions in liquid mixtures of similar chainlength normal paraffins, are very small, and may be neglected in modelisations. This condition ($h^E=0$) is necessary, but however not sufficient, for the mixtures to be assimilated to ideal solutions.

3.2. Excess entropy

Since the molar mixing enthalpy is zero, the molar excess entropy in the liquid phase is independent of temperature, and can be expressed by a Margules equation with one constant, i.e. at any concentration x, we have:

$$s^E(x, L) = x(1-x)S_L$$

where S_L is the Margules parameter.

In high-temperature stable solid phase (Rotator α-RII), the enthalpy of mixing is nil [13]; and the excess entropy is independent of temperature and may also be expressed by a Margules development with one parameter:

$$s^E(x, \mathrm{RII}) = x(1-x)S_{\mathrm{RII}}$$

These assertions lead to the calculation of the entropy variations by integration of enthalpy measurements between a chosen temperature in the liquid (T_L) and high-temperature solid (T_{RII}):

$$S(x, T_{RII}) - S(x, T_L) = \int_{T_L}^{T_{RII}} \frac{dH(x, T)}{T} = A(x)$$

The difference between $A(x = 0)$ and $A(x = 1)$ is of the order 30 J mol^{-1} for all binaries studied [20,21]. For each composition x, it is possible to express the total molar entropy of any mixture in the liquid phase at T_L, and in the solid phase at T_{RII}, in function of $A(x)$. The dispersion of the values of the difference $S_D = S_L - S_{RII}$ for measured values of x, is such that the term S_D may conveniently be taken as zero, i.e. the excess entropy in the liquid phase is equal to the excess entropy in the α-RII solid, with an error limit of $\pm R/30$ (R = gas constant).

From the phase diagrams of the C_{22}–C_{24} [9,22], C_{23}–C_{24} [11,23] and C_{24}–C_{26} [24–26] systems studied, the entropy constant $S_L = S_{RII}$ is determined by writing the uniformity of the chemical potentials of each of the two constituents in the liquid and the α-RII phase at equilibrium. By optimization of experimental liquidus and solidus measurements, it is shown that the r.m.s. deviations are minimum for S_L of the order of $+1$ J mol^{-1} K^{-1} for all the systems studied. This shows that the absolute $|s^E(x, L)| = |s^E(x, RII)| \leq 0.25$ J mol^{-1} K^{-1}, irrespective of the system studied. We can therefore conclude that in the limit of experimental errors, the excess entropy in these phases is zero.

In conclusion, the liquid solution formed between two n-alkanes of similar chainlength, can be considered as an ideal solution. The influence exerted on the 'structure' of pure liquid alkane when a second component is added, is very small and may be neglected in this case, with respect to ideal mixing entropy effects.

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