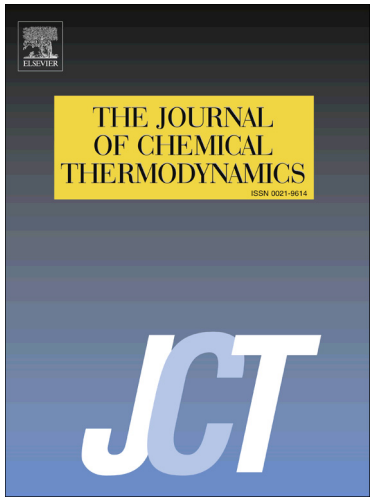

Temperature of maximum density for aqueous mixtures of three pentanol isomers

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Temperature of maximum density for aqueous mixtures of three pentanol isomers

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Abstract

Densities of several aqueous mixtures of 2-pentanol, 3-pentanol, and 2-methyl-2-butanol in the diluted alcohol region were determined in the temperature interval (273.65-282.15) K at atmospheric pressure using the Anton Paar DSA48 vibrating tube densimeter. The variation of the temperature of maximum density with respect to that in pure water ΔT, its structural contribution ΔT_{str}, as well as the partial molar volume of the alcohol v_2 and its excess magnitude v_2^{E} were calculated. It was found that ΔT decreases as the alcohol mole fraction x_2 increases whereas ΔT_{str} increases. In both magnitudes, the values for the mixtures of 2-methyl-2-butanol were higher than those of 2-pentanol and 3-pentanol which were found very similar. The secondary or tertiary character of the alcohol seems to be the origin of such differences in complete agreement with previous findings. The slope of the v_2-T curve was positive over the working mole fraction interval whereas that of the (v_2^{E}-T) curve was negative, in complete agreement with the tendencies observed for the ΔT-x_2 and ΔT_{str}-x_2 curves, respectively. The consistence check proposed by Armitage *et al*. was thus once fulfilled.

Keywords: aqueous solutions, pentanol isomers, temperature of maximum density

1. Introduction

Water is maybe the most studied liquid due to its role in everyday life, as a matrix of life, or as common solvent in chemical and biological process. Despite its apparent simplicity, water shows a eccentric thermodynamic behaviour very different to that of common organic liquids[1]. Among the whole set of anomalies identified for water, the variation of the density with temperature in the atmospheric pressure isobar with a maximum at 277.13 K[1] is the most known singularity. Addition of small quantities of solute to pure water modifies not only quantitatively the density values but also the temperature of maximum density (TMD). Thus, electrolytes provoke a decrease of the TMD being ΔT=TMD(x_2)-277.13 a monotonously decreasing function of the solute mole fraction x_2[2, 3, 4, 5]. Although this tendency was also found for most of the organic compounds[6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18], it does not hold for some alcohols such as methanol, ethanol, 1-propanol, 2-propanol, 2-butanol, and 2-methyl-2-propanol[19, 6, 20, 21, 22, 23]. The main feature for such aqueous mixtures is that for very low solute compositions the TMD increases as the solute mole fraction does. This increase stops at an specific mole fraction $x_{2,\mathrm{max}}$ and starts to decrease after this value. The resultant ΔT-x_2 function is thus a parabolic curve with a maximum at $x_{2,\mathrm{max}}$.

The shape of the ΔT-x_2 curves for aqueous mixtures of alkanols is only known up to isomers of butanol. The lack of measurements of the TMD for alkanols of higher molar mass has been probably due to their reduced miscibility in water. Nowadays, this shortcoming can not be considered as an impediment, at least for pentanol isomers, since the mole fraction interval in which they are miscible in water is not only known (approximately between x_2=0 and x_2= 0.01) but also coincides with the usual range where ΔT is defined. Thus, in this work, densities ρ for aqueous mixtures of 2-pentanol, 3-pentanol, and 2-methyl-2-butanol in the diluted region of alcohol were measured at atmospheric pressure in the temperature interval (273.65-282.15) K with a 0.5 K step. This information was used to study the variation of ΔT (and its structural contribution ΔT_{str}) with the alcohol mole fraction x_2 as well as the differences due to the secondary or tertiary character of the alcohol. In this context, a qualitative comparison with previous findings of Wada and Umeda [19] was accomplished. Moreover, the partial molar volume of the alcohol v_2 and its excess magnitude v_2^{E} was computed in order to carry out a thermodynamic consistence check between these magnitudes and ΔT and ΔT_{str}, respectively, following ideas of Armitage *et al*. [24].

2. Experimental

The origin, purity, and purification methods for the liquids of this work are given in Table 1. During the preparation of the mixtures, the Mettler balance AE-240, with a precision of $\pm 1.0 \cdot 10^{-8}$ kg, was used in order to calculate the mole fraction.

The Densimeter and Sound Analyser 48 of Anton Paar (DSA48) was used for the measurement of the density. It contains two cells connected serially, one for the density measurement (the vibrating tube clamped at both ends) and the other for the speed of sound. Both cells are surrounded by a thermostatic

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