Measurement of infinite dilution activity coefficients of 1-alkanols (C1–C5) in water as a function of temperature (273–373 K)

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Abstract

Limiting activity coefficients (γ_1^∞) of lower (C1–C5) 1-alkanols in water were measured at several temperatures covering the range from the freezing to the normal boiling point of water. Five experimental techniques, namely headspace analysis, inert gas stripping, comparative tensimetry, Rayleigh distillation, and the method of circulation still, were employed for the purpose. To establish reliable temperature dependence of γ_1^∞ for each of the systems, careful goal-directed measurements were carried out applying the methods alternatively in accordance with the applicability conditions. The method-to-method accord of the results, their thermodynamic consistency with calorimetric data on related thermal properties and their accuracy were verified using two procedures.
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Keywords: Limiting activity coefficient; Infinite dilution; Temperature dependence; 1-Alkanol; Water

1. Introduction

Aqueous solutions of lower 1-alkanols (C1–C5) have been of great interest for experimental thermodynamicists over a number of decades and, as a result, relatively abundant data on vapor–liquid equilibrium and other properties of these solutions are now available. However, while the existing equilibrium data are in a reasonable agreement for concentrated solutions, in the region of high dilution they are considerably scattered. PLACID, Prague comprehensive database of limiting activity coefficients (γ_1^∞), indicates that even for such a common system as ethanol in water at ambient temperature the reported experimental values of γ_1^∞ vary within a factor of two, the excessive experimental scatter of these values obscuring their temperature dependence. A similar situation can be encountered also for other lower 1-alkanols in water as exemplified for 1-butanol in Fig. 1. This figure discloses additionally a lack of method-to-method reproducibility, a more general flaw, which often results from improper applications of experimental methods disregarding their applicability limitations.

The determination of $\gamma_1^\infty(T)$ of C1–C5 1-alkanols in water has not been systematically attempted in the literature except for several recent studies [1–5], which, however, have not resolved satisfactorily the problem. These $\gamma_1^\infty(T)$ measurements were carried over only limited ranges of temperature (typically 30–40 K, and never more than 50 K) and are in most cases either of insufficient precision or stained with significant systematic errors. As a result, severe inconsistencies typically emerge between these $\gamma_1^\infty(T)$ data and calorimetrically determined values of the infinite dilution partial molar excess enthalpies and/or heat capacities. In addition, γ_1^∞ values obtained in the mentioned studies are in a rather poor agreement mutually, the differences being in some cases as large as 30%.

With the aim to establish accurate temperature dependences of γ_1^∞ of C1–C5 1-alkanols in water in the range from the freezing to the normal boiling temperature of water we have undertaken a methodical experimental program to obtain new reliable underlying γ_1^∞ data which would spread over the entire temperature interval of interest and be sufficiently ample. To this end, we employed five different suitable experimental techniques, duly respecting their applicability conditions. In this paper, we report the obtained γ_1^∞ values and demonstrate the method-to-method accord of the results, their thermodynamic consistency with calorimetric data on related thermal properties and their accuracy by comparing with selected most accu-

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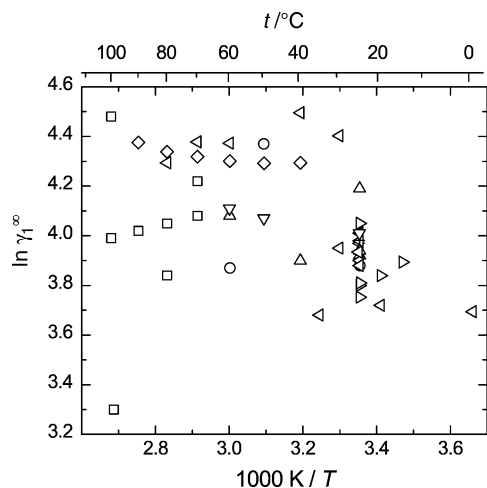*E-mail address:* dohnalv@vscht.cz (V. Dohnal).

Fig. 1. Limiting activity coefficient of 1-butanol in water as a function of temperature. Values from the literature measured by (□) ebuliometry; (○) tensimetry; (△) GLC; (▽) relative GLC; (◇) phase ratio variation method; (◁) HSA; (▷) IGS.

rate measurements from the literature. In a follow-up paper we then present a comprehensive compilation and critical evaluation of all experimental literature data on γ_1^∞, limiting partial molar excess enthalpy $\bar{H}_1^{E,\infty}$ and heat capacity $\bar{C}_{P,1}^{E,\infty}$ and their simultaneous processing together with data measured in our laboratory, which results in recommended values of these infinite dilution excess properties of a significantly improved accuracy. For 1-butanol, for which we have established such a recommendation previously within a framework of a broader pilot study on $\gamma_1^\infty(T)$ for a group of moderately hydrophobic organic solutes in water [6], we present its update involving besides new data from the literature also newly measured data from this laboratory.

2. Experimental

2.1. Materials

Methanol (p.a.) supplied by Merck was fractionally distilled on a 1 m long packed column; the purity of the final product was better than 99.9% as determined by GC with DB-WAX capillary or Carbowax 20 M packed columns. Ethanol (absolute, 99.8%) from Riedel-de-Haen and 1-pentanol (99%) from Fluka, whose stated purities were checked in the same manner, were used without further purification. Analar 1-propanol and analar 1-butanol, which were both obtained from Lachema (Czech Rep.), were pre-dried by calcium oxide and then fractionally distilled on a 1 m long packed column. Their purities, determined as indicated above, were better than 99.95 and 99.8%, respectively. Before measurements, all alkanols were finally dried and stored over 0.4 nm Merck molecular sieves, ethanol being the exception as it had been subjected to the same treatment by the supplier. Water was distilled and subsequently treated by Milli-Q Water Purification System (Millipore, Milford, USA).

2.2. Apparatus and procedure

Five experimental techniques, which were employed to obtain our γ_1^∞ values in this work, are headspace analysis, inert gas stripping, comparative tensimetry, Rayleigh distillation, and the method of circulation still. Since we have used these methods previously and described the respective instrumentation and experimental procedures in detail, given here is only a brief overview of their principles supplemented with particularities, if any, that are specific to the present application. For a full account of our experimental techniques we refer the reader to our previous papers [6–10].

Except for the comparative tensimetry, all the methods involve the use of gas chromatography: here, we employed computer driven gas chromatographs, a Hewlett-Packard HP 5890 II or an Agilent 6890 Plus, allowing us to automate our experiments to a great extent.

2.2.1. Headspace analysis (HSA)

The HSA method consists in gas chromatographic determination of the equilibrium solute partial pressure above a dilute solution of known composition. In our apparatus [6] the vapor phase is circulated by an inert pump through the liquid phase in the equilibrium cell and the gas sampling loop of GC, which avoids perturbation of the equilibrium during sampling and suppresses sorption effects. For the present systems, the HSA measurements were carried out typically in the range of alkanol mole fractions from 0.0004 to 0.002 and at lower temperatures (273–293 K). A wide-bore, 15 m long capillary column DB-WAX was used for the GC analysis at oven temperatures from 45 to 90 °C depending upon the solute.

2.2.2. Inert gas stripping (IGS)

In the IGS method, an entraining inert gas is passed through a highly dilute solution and the rate of the solute elution is measured analyzing periodically the outlet gas by gas chromatography [7,11]. The technique is inherently suited for enhanced solute volatilities and hence it was applied here just to 1-pentanol. In the present measurements we used a small stripping cell of 13/17 ml (liquid loading/total volume) and the DB-WAX capillary column specified above.

2.2.3. Comparative tensimetry (TENS)

This method consists in measuring, under isothermal conditions, the difference between the equilibrium pressures above a dilute solution and the pure solvent as a function of composition of the synthetically prepared dilute solution. The differential static cell apparatus and the procedure used in this work were the same as described recently [8]. The TENS technique was applied in the range of temperatures from 303 to 333 K.

2.2.4. Rayleigh distillation method (RDIST)

The RDIST technique is based on measuring the changes of the solution mass and the solute concentration resulting from a partial one-stage equilibrium distillation of a dilute solution. In the RDIST technique developed in our laboratory [9], the distillation is promoted by bubbling an inert gas through the