

Effects of hydration on the thermodynamic properties of aqueous ethylene glycol ether solutions

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Abstract

The densities and isobaric specific heat capacities of binary mixtures of water with various open-chain and cyclic ethylene glycol ethers have been measured at 298.15 K using vibrating tube densimetry, and flow or differential scanning calorimetry, respectively. Excess molar volumes were derived over the whole composition range. Molar isobaric heat capacities and the relative apparent thermodynamic quantities were determined in the water-rich region. The data reflect the changes in the structure and hydrogen-bond dynamics of water caused by these non-ionic solutes. The observed effects are discussed in terms of the influence of hydrophobic hydration on the thermodynamic properties of aqueous solutions. Correlations are given that enable the prediction of the thermodynamic properties of open-chain and cyclic oligo(ethylene oxide) ethers in their pure liquid state and at infinite dilution in water. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

Water shows distinctive properties relative to other solvents due to its strong intermolecular forces, which produce an extensive three-dimensional network of hydrogen (H) bonds. H-bonding in water is a highly cooperative phenomenon, mainly due to the small size of the water molecule and its considerable charge separation (high dipole moment) and its 1:1 ratio of donor to acceptor sites. The presence of non-ionic compounds in aqueous solutions typically results in significant changes to the local and long-range water structure. Particularly large thermodynamic effects occur in the presence of hydrophobic solutes. Such effects are of outstanding importance in understanding many biological processes and in polymer, surface and colloid science.

Straight chain oligo(ethylene glycol)s and their mono- and dimethyl ether analogues are miscible with water over the whole composition range, apparently without forming higher aggregates like micelles. As such, they provide a series of solutes with systematically varying characteristics, which can be used to probe the influences of hydrophobic hydration and the H-bond donor–acceptor ratio on the dynamics and structure of the H-bond network. Comparisons of the thermodynamic properties of aqueous solutions of open-chain oligo(ethylene glycol) ethers with those of related, but more rigid, cyclic ethers such as 1,4-dioxane and the crown ethers can in addition provide insights into the structural effects of organic solutes on water properties.

This investigation compares the molar excess volumes, V^E , and the relative apparent heat capacities, $\Delta C_{p,\phi,2}$, of mixtures of water with oligo(ethylene glycol) monomethyl ethers, C_1E_nOH , and dimethyl ethers, $C_1E_nC_1$, of oligomerisation degree $1 \leq n \leq 5$. For some of the compounds, the volume properties have been

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reported for the aqueous solutions by other investigators. However, because of serious inconsistencies among the reported values, it was considered appropriate to measure them again systematically with samples of well-established purity.

2. Experimental

2.1. Materials

1,4-Dioxane (Merck, pro analysi) was purified by refluxing over solid calcium hydride (CaH_2) for several hours [1] and subsequently distilled over a 40 cm column at atmospheric pressure, resulting in a final purity of 0.9997 mole fraction (g.c.); $\text{H}_2\text{O} \leq 30$ ppm (Karl Fischer coulometric titration). Ethylene glycol monomethyl ether ($\text{C}_1\text{E}_1\text{OH}$; Fluka; 0.999 mole fraction; $\text{H}_2\text{O} \leq 300$ ppm), ethylene glycol dimethyl ether ($\text{C}_1\text{E}_1\text{C}_1$; Sigma; 0.9994 mole fraction; $\text{H}_2\text{O} \leq 80$ ppm) and triethylene glycol monomethyl ether ($\text{C}_1\text{E}_3\text{OH}$; Fluka; 0.997 mole fraction; $\text{H}_2\text{O} \leq 300$ ppm) were used as received. Diethylene glycol dimethyl ether (Merck, for synthesis) was heated with solid CaH_2 , then fractionally distilled at atmospheric pressure using a 25 cm column, giving a product with a purity of 0.999 mole fraction; $\text{H}_2\text{O} \leq 60$ ppm. Triethylene glycol dimethyl ether ($\text{C}_1\text{E}_3\text{C}_1$; Merck, for synthesis) was distilled at ~ 1 mbar using a 65 cm column. The fraction used for measurements had a purity of 0.998 mole fraction; $\text{H}_2\text{O} \leq 500$ ppm.

Pentaethylene glycol monomethyl ether ($\text{C}_1\text{E}_5\text{OH}$) was prepared from diethylene glycol and 1-(2-chloroethoxy)-2-(2-methoxyethoxy)-ethane as follows. Using stirring throughout, a stoichiometric amount of sodium metal (12.7 g) and 0.1 g of powdered, anhydrous sodium iodide (NaI) were added to 233.5 g diethylene glycol (dried by distillation). The mixture was heated to 120 °C until all the sodium dissolved. Then 100.5 g of 1-(2-chloroethoxy)-2-(2-methoxyethoxy)-ethane (prepared from triethylene glycol monomethyl ether and thionyl chloride [2], fractionated at ~ 0.1 mbar) was added dropwise and the resulting mixture heated (120 °C) for several hours. After standing overnight, sodium chloride was removed by filtration and washed with methanol. The filtrate was evaporated and the excess diethylene glycol removed by distillation at ~ 0.03 mbar using a 25 cm column. Phosphoric acid ($\sim 20\%$ w/w, 25 mL) was added to the residue and the aqueous phase extracted with dichloromethane ($4 \cdot 100$ mL). The combined extracts were evaporated and the residue was fractionated at 0.02 mbar. The middle fraction was further purified using a short-path molecular distillation apparatus at $\sim 3 \cdot 10^{-5}$ mbar. Pentaethylene glycol monomethyl ether (58 g) with a final purity of 0.994

mole fraction ($\text{H}_2\text{O} \leq 500$ ppm, $n_D^{25} = 1.4481$) was collected.

Pentaethylene glycol dimethyl ether ($\text{C}_1\text{E}_5\text{C}_1$) was prepared in a similar way from ethylene glycol monomethyl ether and 1,2-bis-(2-chloroethoxy)-ethane: 69 g sodium was cut into small pieces and added under stirring to 500 g ethylene glycol monomethyl ether ($\text{C}_1\text{E}_1\text{OH}$; distilled from CaH_2). This mixture was heated to 100 °C until the sodium dissolved. Anhydrous NaI (1 g, finely powdered) and 281 g 1,2-bis-(2-chloroethoxy)-ethane (dropwise) were added, and heating (100 °C) continued for 3 days. After evaporation of excess $\text{C}_1\text{E}_1\text{OH}$ the remainder was dissolved in water and extracted with dichloromethane ($4 \cdot 100$ mL). The organic layers were combined, dried over anhydrous sodium sulfate and evaporated. The residue was then distilled at 0.04 mbar. The fraction boiling between (95 and 119) °C was heated with 100 mL of $\sim 5\%$ hydrochloric acid for a few hours to decompose byproducts (acetals), washed with *n*-pentane (3.50 mL) and the water evaporated at atmospheric pressure. 300 mL dichloromethane was added to the residue. After stirring over anhydrous potassium carbonate for several hours the dichloromethane was removed under vacuum. The raw product was fractionated over a 40 cm column at 0.03 mbar and the center fraction (b.p. ~ 105 °C) was further distilled at ~ 0.008 mbar using a Fischer Spaltrohr apparatus (60 theoretical plates at 1013 mbar). The pentaethylene glycol dimethyl ether (73 g) so obtained had a purity of 0.997 mole fraction ($\text{H}_2\text{O} \leq 500$ ppm; $n_D^{25} = 1.4376$).

The structures of the pentaethylene glycol ethers were confirmed by n.m.r. spectroscopy (^1H , ^{13}C and ^{13}C DEPT 135°).

Note that all reactions were carried out with anhydrous reagents under a dry nitrogen atmosphere. All distillation employed vacuum-jacketed Vigreux columns.

Aqueous mixtures were prepared gravimetrically on an analytical balance without buoyancy corrections. Concentrations are thus accurate to four significant figures. Water, deionized and purified with a Millipore Milli-Q system (with a final pass through a 0.22 μm filter) was used throughout. All pure liquids were carefully degassed at low pressure prior to mixture preparation.

2.2. Apparatus and procedure

Solution densities, ρ , were determined by vibrating tube densimetry (Anton Paar DMA602/mPDS4000 system) and are accurate to $\sim 5 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$. The temperature was kept constant to ± 4 mK with a circulating thermostat (Julabo F33 SD). The densimeter was calibrated using water and air as references. The density of water at 298.15 K was taken as $997.047 \text{ kg} \cdot \text{m}^{-3}$ consistent with the IAPWS-IF97 value [3], and that of air was calculated from generally accepted equations [4].

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