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ORIGINAL ARTICLE

Studies on the thermodynamics and solute–solvent interaction of Polyvinyl pyrrolidone wrapped single walled carbon nanotubes (PVP-SWNTs) in water over temperature range 298.15–313.15 K

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Abstract The water solubilisation of single walled carbon nanotubes (SWNTs) has been achieved by polymer wrapping. The present study aims at highlighting the solute–solvent interaction and thermodynamic parameters in the solubilisation of polyvinyl pyrrolidone wrapped single walled carbon nanotubes (PVP-SWNTs) in water. Conductivity and density values of both PVP and PVP-SWNTs have been determined in water maintaining different concentrations (0.005–0.1 g/L) at temperatures 298.15, 303.15, 308.15 and 313.15 K. The conductance values have been used to evaluate the limiting molar conductance ($\wedge_o^m$) and the activation energy (E_s). From the density values, the limiting partial molar volumes and expansibilities have been calculated. The estimated parameters were discussed in terms of solute–solvent interactions.

1. Introduction

In recent years, carbon nanotubes (CNTs) have gained the attention of researchers in the field of biomedical sciences and biological applications. It has been considered as potential reinforcement materials in bio-composites due to their remarkable electrical (Colbert and Smalley, 1999), mechanical (Salvetat et al., 1999) and thermal properties. They possess a surface area as well as have the potential for surface functionalisation (Al-Saleh and Sundarajaj, 2009; Huang et al., 2005; Ma et al., 2010; Wakamatsu et al., 2009).

It is extremely difficult to disperse carbon nanotubes to single tube level. Even though SWNTs are a versatile vector because of their unique architecture and wonderful chemistry, the poor solubility characteristic has limited their chemical modifiability as well as applicability. For that, non-covalent and covalent modifications of the SWNTs with polymers are commonly used to improve their dispersion and orientation in aqueous solutions (Hong et al., 2008; Lou et al., 2004; Petrov et al., 2003; Sinani et al., 2005; Zhao et al., 2006). How-

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ever, for SWNTs as solubilisation involves the covalent modification of the tubes the desirable properties are altered significantly. Alternatively, the medium used for the solubilisation of SWNTs has relied upon the surfactants which are toxic enough to denature the biological molecules (O'Connel et al., 2001).

Among non-covalent methods, polymer wrapping is the simplest route (O'Connel et al., 2001; Star and Stoddart, 2002). For instance, polyvinyl pyrrolidone (PVP), PSS (polystyrene sulphonate), and BSA (bovine serum albumin) can wrap around carbon nanotubes, leading to their solubilisation in water (O'Connel et al., 2001). The method as reported is robust and can manipulate the solubility aspect reliably thus simplifying their use as a chemical agent. Although the phenomenon is reported, no explanation relating to the mechanism in terms of solute–solvent interactions and the structural effects is available in the literature.

Polyvinyl pyrrolidone (PVP), $(C_6H_9NO)n$, a water-soluble synthetic polymer, has a number of interesting properties and frequently has been the subject of different investigations to understand the interactions such as hydrogen bonding, dipole–dipole, ion–dipole between small organic molecules, ionic species and that of a polymer (Kirci and Guner, 2001). Polyvinyl pyrrolidone is used by a wide variety of industries, such as pharmaceutical, cosmetic, coating and adhesive. This is due to the unique physical and chemical properties of PVP, particularly its good solubility in water, its strong complexing ability with both hydrophilic and hydrophobic substances and its nontoxic character. Therefore, a significant amount of research has been conducted with regard to studying polyvinyl pyrrolidone solutions, and the majority of these studies are in water, non-ionic aqueous solutions, and aqueous salt solutions (Kirci and Guner, 2001; Guner and Kara, 1998; Guner, 1996; Yang et al., 2005; Sadeghi and Zafarani-Moattar, 2004; Rathbone et al., 1990).

The aim of this research is to synthesise the PVP-SWNTs in order to reaffirm their solubilisation in water and to further study the solution chemistry of PVP-SWNTs in water. It is well known that conductometric and volumetric studies of the solute at definite and infinite dilution in a solvent system provide valuable information regarding the solute–solvent interactions. By examining the limiting apparent molar volume (Φ_v^0), limiting molar expansibilities (Φ_E^0) and limiting molar conductance ($\wedge_o^m$) of solution's nature, temperature and composition of the solvent, it is possible to examine the parameters on solute–solvent interaction, to obtain better understanding of the interactions in solutions. The present study deals with experiments so as to highlight the solute (PVP-SWNTs) and solvent (water) interactions at different temperatures ranging from 298.15 to 313.15 K and to compare with that of PVP-water.

2. Experimental

2.1. Material

The SWNTs used in this study were purchased from Ghuangzhou Jiechuang Trading Co. Ltd., China. The polyvinyl pyrrolidone was purchased from Sigma–Aldrich Co. and had a reported *K*-value = 29–32. Sodium dodecyl sulphate (SDS) was purchased from Sigma–Aldrich Co. and had a micellar average molecular weight of 18,000. Polyvinyl pyrrolidone and SDS were used without further purification. Distilled water was used for the preparation of solutions.

2.2. Purification of SWNTs

SWNTs' material was washed with methanol followed by water. The SWNTs were then homogenised with a high shear mixer (Cat: X120) and refiltered repeatedly till the filtrate was clear and colourless. Further the material was purified by gas phase oxidation, hydrochloric acid extraction and high temperature annealing (Salvetat et al., 1999).

2.3. Synthesis of polymer wrapped SWNTs

The purified SWNTs' materials were further used for the synthesis of polymer wrapped SWNTs. The synthesis was carried out following a previous literature (O'Connel et al., 2001) with modification. Briefly 50 mg of the SWNTs was dispersed in 1000 ml of water containing 1% sodium dodecyl sulphate (SDS) by sufficient sonication to ensure the individual presence of the particles. Then enough polyvinyl pyrrolidone was added to the dispersions to get a 1% solution by weight and the system was further sonicated followed by 12 h incubation at 50 °C. The mixture was then filtered. In order to remove the residual SDS, the polymer filtrate underwent three cycles of high speed centrifugation (Jouan, BR4i) and the supernatant was decanted followed by re-dispersing in pure water with mild sonication. The final dispersion produced a stable solution of PVP wrapped SWNTs (PVP-SWNTs) in water which was freeze-dried to obtain the PVP-SWNTs. The yield was up to 1.8 g/L.

2.4. Physical measurements

The solutions of both PVP and PVP-SWNTs were prepared freshly by mass (0.005–0.1 g/L) using a Metler balance with a precision of ±0.01 mg in doubly distilled deionised and degassed water. The solutions were used for the density and conductivity measurements.

2.4.1. Density

The densities were measured using an Anton Paar DMA 35 N U-tube measuring cell. Dried air was used for the calibration of the densimeter at each temperature. The temperature maintenance and control of the systems were performed in a jacketed container with circulated water being thermostated by a thermostat (WiseCircu), with a temperature uncertainty of ±0.01 K. The uncertainties in densities are ±0.0001 g cm^{-3}.

2.4.2. Conductivity

A conductivity metre with accuracy of ±0.5% with a conductivity cell (Eutech-Con 700) was used for the measurement of conductivity of each sample. The conductance cell was equipped with a water circulating jacket, and the temperature was controlled within ±0.02 K in a water thermostat. The cell constant is 1.01 cm^{-1} which was calculated by repeated measurements of KCl solutions. All data were corrected with specific conductivity of pure water at the experimental temperatures.

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