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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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KEYWORDS

Polyvinyl pyrrolidone; Single walled carbon nanotubes; Polymer wrapping; Limiting molar conductance; Activation energy; Solute-solvent interaction **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 (\bigwedge_{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.

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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

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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_F^0) and limiting molar conductance (\wedge_a^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 PVPwater.

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 $\pm 0.5\%$ 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.

3. Results and discussion

3.1. Conductivity

The molar conductance data (Λ_m) with different concentrations of pure PVP and those of the polymer PVP-SWNTs are listed in Tables 1 and 2, respectively. The limiting molar conductivity (Λ_m^o) of the systems was obtained by least squares fitting of the experimental data to the expression (Harned and Owen, 1958) below:

$$\wedge = \wedge_m^0 - A\sqrt{c}/(1 + B\sqrt{c}) \tag{1}$$

where \wedge_m^0 , A and B are fitting parameters, c is the concentration. The obtained limiting molar conductivities of the PVP and PVP-SWNTs are summarised in Tables 1 and 2.

It can be seen from Table 1 that the values of Λ in PVP solutions decrease with increasing PVP content in solutions as well as with increase in temperature. This can be ascribed to the fact that (i) an increase in polymer concentration enhances the microscopic viscosity of the medium because of increased frictional coefficient of the medium thereby retarding the mobility of the polymeric units in the solution, (ii) an increase in polymer content, after being highly solvated causes an increase of the hydrodynamic radii of the polymeric unit hence decreasing their mobility and (iii) with increase in temperature the increased thermal energy results in a more ordered behaviour of the polymeric units in water, rather than getting momentum as in case of normal ionic molecules (Singh et al., 1968; Solanki et al., 2012; Yan et al., 2009).

In the PVP-SWNTs, the values of Λ decrease with increasing PVP-SWNTs' content in solutions and increase with in-

crease in temperature. The later observation highlights the contribution of the SWNTs being wrapped by the polymer in solvent water to the mobility of the PVP-SWNTs' units because of the increment in temperature, as increased thermal energy results in greater bond breaking and variation in vibrational, rotational and translational energy of the PVP-SWNTs' units that lead to higher frequency and higher mobility (Dash et al., 2006).

As observed in Table 1, the values of Λ_0 in PVP solutions at different temperatures are lower as compared with those in PVP-SWNTs' solutions. The \wedge_m^0 values are found to decrease with temperature in case of the PVP system, whereas reverse is the trend for the PVP-SWNTs' system. The higher values of Λ_0 in the PVP-SWNTs' system can be attributed to the contributions of SWNTs to the mobility of the PVP-SWNTs' units in water and to the positive response to temperature in attaining higher mobility.

Since the conductance measurements of an ion depend upon mobility (Coetzee and Ritchi, 1976), it is quite reasonable to treat the conductance data similar to the one employed for the rate process taking place with the change of temperature, i.e.:

$$\wedge^0_m = A e^{-E_s/RT} \tag{2}$$

where A is the frequency factor, R is the gas constant and E_s is the Arrhenius activation energy of the transport process.

From the plot of $\log \wedge_m^0$ vs. 1/T, the E_s values have been computed from the slope (= $-E_s/2.303$ R) and are recorded in Table 2 for the PVP-SWNTs' system. It can be seen that the values of E_s are positive pointing to the fact that the process of solubilisation is favourable.

Table 1 Values of molar conductance (Λ_m) and limiting molar conductance (\wedge_m^o) of pure PVP at different concentrations and temperatures.

c (g/L)	$(\Lambda_m, \operatorname{S} \operatorname{cm}^2 \operatorname{mol}^{-1})$					
	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15		
0.005	0.2060	0.2048	0.1964	0.1910		
0.01	0.1291	0.1287	0.1243	0.1203		
0.02	0.0798	0.0770	0.0741	0.0728		
0.04	0.0565	0.0555	0.0540	0.0523		
0.08	0.0391	0.0385	0.0374	0.0363		
0.1	0.0360	0.0355	0.0344	0.0333		
\wedge^o_m (S cm ² mol ⁻¹)	0.1990	0.1970	0.1890	0.1840		

Table 2 Values of molar conductance (Λ_m), limiting molar conductance (\wedge_m^0) and activation energy (E_s) of PVP-SWNTs at different concentrations and temperatures.

c (g/L)	$(\Lambda_m, \operatorname{S} \operatorname{cm}^2 \operatorname{mol}^{-1})$	$(\Lambda_m, \operatorname{S}\operatorname{cm}^2 \operatorname{mol}^{-1})$				
	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15		
0.005	1.206	1.212	1.224	1.244	1591.49	
0.01	1.179	1.197	1.199	1.202	1043.32	
0.02	1.110	1.125	1.140	1.140	1453.87	
0.04	1.010	1.023	1.025	1.040	1399.52	
0.08	0.8550	0.8738	0.8763	0.8910	1979.08	
0.1	0.8010	0.8080	0.8170	0.8500	2920.76	
\wedge_m^o (S cm ² mol ⁻¹)	1.342	1.355	1.364	1.366	1032.12	

System	T/K	$\Phi^0_{\nu} (\mathrm{cm}^3 \mathrm{mol}^{-1})$	$Sv \ (\mathrm{cm}^{9/2} \ \mathrm{mol}^{-3/2})$	$\Phi_E^0 \; (\mathrm{cm}^3 \mathrm{mol}^{-1} \mathrm{K})$	$S_E ({ m cm}^{9/2}{ m mol}^{-3}/^2{ m K}^{-1})$
PVP	298.15	40,111	-1.395	40,051	-3.575
PVP-SWNTs	298.15	40,104	6.250	40,064	-3.032
PVP	303.15	40,138	-16.72	40,033	-4.243
PVP-SWNTs	303.15	40,131	-8.983	40,043	-3.509
PVP	308.15	40,206	-11.70	40,035	-3.848
PVP-SWNTs	308.15	40,198	-2.937	40,054	-3.439
PVP	313.15	40,231	26.85	40,021	-5.192 -4.083
PVP-SWNTs	313.15	40,276	-21.50	40,028	

Table 3 Values of limiting apparent molar volume (Φ_v^0) , limiting apparent molar expansibility (Φ_E^0) , Sv and S_E of pure PVP and PVP-SWNTs.

3.2. Density

The results of the density measurements are given in Table 3 along with the values of limiting apparent molar volume (Φ_E^0) and limiting apparent molar expansibility (Φ_E^0) of the PVP and PVP-SWNTs in water at T = (298.15, 303.15, 308.15, 313.15) K. The values of Φ_v^0 and Φ_E^0 have been determined from the intercepts of the plot of Φ_v vs. $c^{1/2}$ and of Φ_E vs. $c^{1/2}$, respectively, which are in turn determined from the experimentally measured densities as follows:

$$\Phi_{\nu} = 1000(cd_0)^{-1}(d_0 - d) + M_2/d_0 \tag{3}$$

and

$$\Phi_E = \alpha \Phi_v^0 + (\alpha - \alpha_0) 1000 c^{-1}$$
(4)

where c is the molar concentration of the solution, d_0 is the density of pure water, d is the density of the solution, M_2 is the molecular mass of the solute and α_0 and α are the coefficients of expansion of the solvent and solution (with or without drug), respectively, and determined by means of the relation available in the literature (Millero, 1971).

The Φ_{ν} and Φ_{E} showed linear dependence with square root of concentration and were found to obey the Masson equation,

$$\Phi_{\nu} = \Phi_{\nu}^{0} + S_{\nu}c^{1/2} \tag{5}$$

and

$$\Phi_E = \Phi_E^0 + S_E c^{-1} \tag{6}$$

The values of S_V and S_E obtained from the slopes of the corresponding plots are also given in Table 3.

A perusal of Table 3 shows that the values of Φ_{ν}^{0} are positive for the polymer, PVP as well as for the PVP-SWNTs at the experimental temperatures. Since the Φ_{ν}^{0} is a measure of ion– solvent interaction, the positive values of Φ_{ν}^{0} indicate strong solute–solvent interactions. However if compared between the two, PVP showed stronger interactions than that of the PVP-SWNTs as supported by higher values of Φ_{ν}^{0} , but at the higher temperature of 313.15 K the reverse is the case. The results indicate that the solute–solvent interactions in both the cases increase with increase in temperature. The presence of solute–solvent interaction amongst the molecules, promotes the structure making effects of the solute in water.

As observed, the S_V values are negative and low at the experimental temperatures for the PVP systems except that at 313.15 K, where the value is positive. This suggests the presence of PVP-solvent interactions in the system at the temper-

atures of 298.25, 303.15, and 308.15 K, whereas at the higher temperature of 313.15 K, the PVP–PVP interactions prevailed. Further, it is seen that the values of S_V for the PVP-SWNTs' system are positive at 298.15 and negative at all higher temperatures. These observations indicate that solute–solute (PVP-SWNTs) interaction prevails at lower temperatures, whereas at higher temperatures solute–solvent interaction predominates. The S_V values are higher in case of the PVP-SWNTs' system as compared to that of the PVP systems at the temperatures of 298.25, 303.15 and 308.15 K, while lesser at the temperature of 313.15. These point to the fact that the solvent structure is too much enhanced at lower temperatures as compared to that at higher temperatures (Solanki et al., 2010).

The values of Φ_E^0 for all the systems at all temperatures (except at 313.15 K for all the systems with the drug) are small but positive and vary irregularly with increase of temperature. However, the values of Φ_E^0 in in case of the PVP-SWNTs' system as compared with those of PVP systems indicated the presence of caging or packing effect (Millero, 1971) supporting to the earlier contention that the solvent structure is too much enhanced except at higher temperatures, i.e., 313.15 K.

4. Conclusion

In this study, conductivities and densities of the PVP and PVP-SWNTs in water at different concentrations were determined at the temperature range between 298.15 and 313.15 K. The limiting molar conductivity of PVP was lower than that of the PVP-SWNTs' systems. These suggest that the solute–solvent interaction in the PVP system is less as compared to that of the PVP-SWNTs' system. The positive values of activation energy in the PVP-SWNTs' system suggested a favourable solubilisation process in water. The positive values of Φ_v^0 indicated a strong solute–solvent interaction in both the cases. The values of S_v suggested solute–solvent interactions that prevail at lower temperatures for PVP-SWNTs, while the reverse is the case for the PVP system.

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