



Solute Solvent Interactions of Polyvinyl Pyrrolidone Wrapped Single Walled Carbon Nanotubes (PVP-SWNTs) in Water by Viscometric Studies

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ABSTRACT

Polymer wrapped single walled carbon nanotubes (SWNTs) have been synthesized to improve the solubility of SWNTs in water. The present study deals with experiments so as to highlight the solute solvent interactions during the solubilisation of polyvinyl pyrrolidone wrapped single walled carbon nanotubes (PVP-SWNTs) in water by viscometric methods. Viscosity values of both PVP and PVP-SWNTs have been determined in water with different concentrations (0.05-1.2 mg/ml) at temperatures 298.15, 303.15, 308.15 and 313.15K. The viscosity values have been evaluated in terms of A_F (Falken-Hagen coefficient), B_j (Jones-Dole coefficient), $dB/dt, \Delta\mu_2^\circ$ (contribution per mole of the solute to free), $\Delta\mu_1^\circ$ (corresponding value for pure solvent) and $\eta_0\Lambda_0$ (Walden product). The estimated parameters were discussed in terms of solute solvent interactions.

Keywords: Polymer wrapping, Viscosity, Polyvinyl pyrrolidone, Single walled carbon nanotubes.

INTRODUCTION

Since the discovery of carbon nanotubes in 1991 by Iijima¹, a lot of attentions have been imparted upon them²⁻³, owing to their unique characters. Carbon nanotubes possess outstanding mechanical, electrical and thermal properties. As a result of which they display excellent characteristics for wide range of applications, such as molecular wires, hydrogen storage materials, field emission displays, sensors and high strength fibers⁴⁻⁵.

The first work of utilization of carbon nanotubes as a novel gene delivery vector system was reported by Bianco *et al.*⁶. It has been reported that carbon nanotubes can be a very effective vector for the transport of genetic material into cells⁷. The studies have shown that physical methods can also be used to enhance gene transfer using carbon nanotubes. In this method, carbon nanotubes tips were entrapped with the nickel particle catalysts and a rotating magnetic field that mechanically spear the carbon nanotubes on to cells, with another static magnetic field pulling the carbon

nanotubes into the cells⁸. Another approach is a combination of both chemical and physical methods, where single-stranded DNA sequences were transported into HeLa cells on a carbon nanotube vector by endocytosis and then gets liberated because of the application of a short burst of near-infrared radiation⁹.

In drug delivery applications, carbon nanotubes have been evaluated for their suitability in case of both targeted and controlled release of drug from the delivery device⁷. In research conducted by Li *et al.*,¹⁰, single walled carbon nanotubes (SWNTs) have been shown to bind with the major groove of a human tetrameric DNA structure and the resultant electrostatic interactions between the positively charged cytosine (cytosine⁺) base pairs and the carboxyl groups on SWNTs leading to an increase in i-motif stability (10). Given that the i-motif is an attractive target for cancer chemotherapy and for modulation of gene transcription, making that an effective means of drug targeting.

Further the toxic effects of carbon nanotubes have not been fully explored and there is a need to carry out the toxicological assessments especially in light of the possible use of carbon nanotubes for the administration of the drugs in case of different human diseases. Recent studies¹¹⁻¹⁴ showed that the toxicity of inhaled carbon nanotubes depends on their physical properties, such as particle size, surface area and reactivity that also could affect, facilitate distribute and deposit the particles within the lung compartments. A few published reports have demonstrated the pulmonary toxicity of SWNTs¹⁵⁻¹⁹. An unusual inflammatory response to SWNTs delivered to the lung via pharyngeal aspiration was characterized by a brisk acute phase inflammatory response followed by an early onset of lung fibrosis¹⁶⁻¹⁷.

In light of the greater prospective of its utility in human health, one fundamental characteristic being noted as the major obstacle is a physical character that is its solubility that undermine the effective interaction with the biologic system and hence impeding the obtainment of the result that mimic the in vivo situation. Previous research reported the use of surfactant, DNA²⁰ and some kind

of peptide as the medium or vehicle for the SWNTs in order to interact with the experimental models. The major biological systems are aqueous in nature.

In this pre-text, we revalidated previously the enhancement of aqueous solubility of SWNTs as a result of polymer wrapping with polyvinyl pyrrolidone. Also the thermodynamic parameters involved during the solubilization and the related solute solvent interactions have been reported by acoustic analysis²¹⁻²². In our previous communication to this journal, we reported the thermodynamic parameters and the solute solvent interactions involved during the solubilization of PVP wrapped SWNTs in water.

In this research, we attempt to elucidate the solute (PVP-SWNTs) and solvent (water) interaction using viscometric analysis.

EXPERIMENTAL

Material

The SWNTs was purchased from Guangzhou Jiechuang Trading Co. Ltd., China. The polyvinyl pyrrolidone (PVP) was commercial product of Sigma-Aldrich Co. and had a reported K-value = 29-32. Sodium dodecyl sulfate (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 preparation of solutions.

Purification of SWNTs and Synthesis of polymer wrapped SWNTs

As received, SWNT material was washed with methanol followed by water. The SWNTs were then homogenized with a high shear mixer (Cat: X-120) and re-filtered repeatedly till the filtrate was clear and colourless. The material was further purified by gas phase oxidation, hydrochloric acid extraction and high temperature annealing²³. The purified SWNTs was used for the synthesis of polymer wrapped SWNTs. The synthesis was carried out by a method as described elsewhere²¹.

Physical measurements

The solutions of both PVP and PVP-

SWNTs were prepared freshly by mass (0.05-1.20 mg/ml) using a Metler balance with a precision of ± 0.01 mg in doubly distilled deionized and degassed water. The solutions were subjected to the viscosity.

Viscosities of the solutions including the viscosity values of water were measured with an Anton Paar precision viscometer at specific temperature with accuracy ± 0.02 K. The viscometer was calibrated by measuring the viscosity of water in 4 different temperatures $T(=25,30,35,40)^{\circ}\text{C}$.

RESULTS AND DISCUSSION

The viscosities values (η) with different concentration of PVP and PVP-SWNT solutions as well as pure water are listed in Table 1. Since viscosity is a property of liquid which depends on the intermolecular forces, therefore the values of viscosity were measured at four different temperatures (298.15, 303.15, 308.15 and 313.15K) to look at the structural aspects of liquids. The viscosity values were treated according to Jones and Doles, equation, which is in the form of:

$$\eta/\eta_0 = 1 + A_F c^{1/2} + B_J c \quad \dots(1)$$

Where η and η_0 are viscosities of solution and solvent respectively, c is the concentration, A_F is Falken-Hagen coefficient and B_J is Jones-Dole coefficient.

It can be seen from the Table 1, the values of viscosities in both PVP and PVP-SWNT solutions are decreased with increase in temperature. This finding can be ascribed to the fact that attractions between molecules become weak as the temperature is increased. This negative deviation suggests that in these mixtures, the forces between unlike molecules are lesser than the forces between like molecules. The study has shown the anomalous viscosity behavior of neutral polymer solutions at low concentrations. This can be ascribed to the anomalies associated with the measurement technique adopted during this experiment²⁴.

Table 2 shows the values of viscosity parameters A_F , B_J , dB/dT , $\Delta\mu_1^{\circ}$, $\Delta\mu_2^{\circ}$ and η_0 , Λ_0 . The values of A_F for both PVP and PVP-SWNT in water are very low indicating the presence of weak solute-solute interaction or absence of solute-solute interaction varying with the change of temperature. This observation is well supported by the fact that polymer wrapping around the SWNTs has reduced the solute-solute interaction and increased the solute-solvent interaction leading to a solubilization of the same in water. Further it was observed that at lower temperature (298.15K), the A_F value of PVP systems is higher than that of the PVP-SWNTs systems. The similar trend was also observed at 313.15K. But at the temperature of 303.15K, the value of A_F was found to be lesser in case of the PVP systems than that of the PVP-SWNTs. These

Table 1: The values of viscosity of PVP solution and PVP-SWNT solution

Samples	PVP η (Pa)				PVP-SWNT h (Pa)			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
DI	3.09	2.91	2.80	2.72	3.09	2.91	2.80	2.72
P1	5.56	5.50	5.28	5.17	5.56	5.43	5.24	5.16
P2	5.60	5.43	5.28	5.22	5.60	5.44	5.29	5.15
P3	5.65	5.44	5.30	5.20	5.61	5.41	5.26	5.15
P4	5.64	5.45	5.38	5.20	5.66	5.47	5.28	5.18
P5	5.70	5.48	5.39	5.21	5.75	5.44	5.30	5.19
P6	5.72	5.50	5.32	5.23	5.68	5.50	5.32	5.20
P7	5.72	5.51	5.39	5.26	5.69	5.55	5.37	5.26
P8	5.68	5.52	5.39	5.27	5.76	5.55	5.40	5.27

observation can be explained by the fact that PVP exhibited good interaction with water than that of PVP-SWNTs. As the temperature increased from 298.15 to 303.15K, the polymer showed a decreasing behavior in terms of interaction with water, reflecting more interactions within the intrapolymeric network that is quite usual with the materials like polymers, whereas PVP-SWNTs showed enhanced interaction with water because of the input from thermal energy. At higher temperature (313.15K) again PVP regained higher extent of interaction than that of PVP-SWNTs.

The coefficient B_j is a measure of effective sovodynamic volumes of solvated ions and is governed by solute-solvent interactions that have structural effect of the solvent in solutions. It is a fact that we must know when a solute dissolves in a solvent, some of the solvent molecules will be attached to the solute because of solute-solvent interactions. This phenomenon will cause the increase in viscosity of the solutions. However, as we can see from Table 2, values of B_j for both cases of PVP and PVP-SWNT are negative. A negative contribution of B_j values caused a decrease in viscosity of the solution because these solvent molecules have to be wrenched out of the bulk solvent and break the solvent structure.

As we know, the values of dB/dT are better criteria for determining solute-solvent interactions. It is found that almost all values of dB/dT in both cases of PVP and PVP-SWNT are negative. Only one case in PVP solution has a positive value of dB/dT , 0.0012 which is at temperature 303.15K. The positive value of dB/dT can be ascribed to the structure making character where as reverse is the case, when the values are negative.

The viscosity data are also analysed on the basis of transition state theory for relative viscosity of the solution as suggested by Feakins *et al.*, by using equation:

$$\Delta\mu_2^\circ = \Delta\mu_1^\circ + (RT/v_1^\circ)1000B_j - (v_1^\circ - v_2^\circ) \quad \dots(2)$$

Where $\Delta\mu_2^\circ$ is the contribution per mole of the solute to free energy of activation for viscous flow of solution, $\Delta\mu_1^\circ$ is the corresponding value for

Table 2: The values of viscosity parameters of PVP and PVP-SWNTs solutions

	PVP				PVP-SWNT			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
$A_F (10^{-6} \text{ dm}^{3/2} \text{ mol}^{1/2})$	0.92	0.89	0.91	0.91	0.91	0.90	0.91	0.90
$B_j (\text{dm}^3 \text{ mol}^{-1})$	-0.21	-0.18	-0.19	-0.18	-0.21	-0.19	-0.19	-0.18
dB/dT	-0.00550	0.00120	-0.00108	-	-0.00312	-0.00004	-0.00124	-
$\Delta\mu_1^\circ [10^3] (\text{kJ mol}^{-1})$	63.60	64.52	65.48	66.47	63.60	64.52	65.48	66.47
$\Delta\mu_2^\circ [10^3] (\text{kJ mol}^{-1})$	74.70	79.01	78.77	80.13	75.35	78.00	78.62	80.14
$\eta_0/\Lambda_0 (\text{Pa S cm}^2 \text{ mol}^{-1})$	0.61	0.57	0.53	0.50	4.15	3.94	3.82	3.72

pure solvent, v_1° is the partial molar volume of the solvent, v_2° is the partial molar volume of the solute.

$\Delta\mu_1^\circ$ is calculated from the following equation :

$$\Delta\mu_1^\circ = RT \ln (\eta_0 v_1^\circ/hN) \quad \dots(3)$$

Where h is the plank's constant, N is Avogadro's number and η_0 is the viscosity of pure solvent.

A perusal of Table 2 shows that the values of $\Delta\mu_1^\circ$ and $\Delta\mu_2^\circ$ are positive and increased with increase in temperature in case of both PVP and PVP-SWNT solutions. The positive and larger values of $\Delta\mu_2^\circ$, as compared to that of $\Delta\mu_1^\circ$ indicated that, the behavior of $\Delta\mu_2^\circ$ is quite similar to that of B_j in solvent which is having stronger solute-solvent interactions. Besides, the formation of transition state is accompanied by the rupture and distortion of the intermolecular forces in solvent structure. The $\Delta\mu_2^\circ$ in case of PVP systems was found to be smaller than that of PVP-SWNTs at temperature of 298.15 and 313.15K. This observation is well correlated with the fact that higher values of $\Delta\mu_2^\circ$ indicate the increasing hydrophobic component of the solute in water (PVP-SWNTs contains the super hydrophobic SWNTs).

Deviations were observed at temperature of 303.15K where the $\Delta\mu_2^\circ$ value of PVP become higher than that of the PVP-SWNTs which can be attributed to ore intrapolymeric interactions at that temperature. It can be noted that the observations in regard to A_f and $\Delta\mu_2^\circ$ compliment each other.

Walden noted that the product of equivalent conductance at infinite dilution and the viscosity of the solvent is approximately constant and is independent of the nature of solvent ($\eta_0 \Lambda_0 = \text{constant}$). While Stoke's law stated that $\eta_0 \Lambda_0$ would

be constant only if the effective radius of the ions were the same in different media. As observed, the values of $\eta_0 \Lambda_0$ for PVP are decreasing as the temperature increased. Same goes with the values of $\eta_0 \Lambda_0$ for PVP-SWNT which decreases with increase in temperature. This phenomenon can be attributed to the structure breaking of solutes in water and the dimensional structure of water getting affected under such conditions with a decrease in mobility of ions. Smaller $\eta_0 \Lambda_0$ value may be due to larger effective radius where smaller effective radius contributes to larger values of $\eta_0 \Lambda_0$ as the size of the solvation sphere that is dragged along by the ion in an electric field varies with the ions.

CONCLUSION

Determination of viscosities of PVP and PVP-SWNTs in water at different concentration has been done at temperature between 298.15 and 313.15 K.

The study has shown that the viscosity for both PVP and PVP-SWNTs solution were reduced with increasing of temperature due to weakening interaction. Through the parameters of A_f , B_j , dB/dT , $\Delta\mu_1^\circ$, $\Delta\mu_2^\circ$ and $\eta_0 \Lambda_0$, it was observed that solute-solute interaction influence the viscosity values at certain temperature. Besides, hydrophobic character of ions in water resulted in the increasing of $\Delta\mu_2^\circ$ values.

Overall, the effects of temperature and solvent compositions on the intrinsic viscosity of polyvinyl pyrrolidone were also investigated.

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