Molecular interactions of polyvinylpyrrolidone and cellulose acetate butyrate solutions in dimethylformamide

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The ultrasonic velocity, density, and viscosities of polyvinylpyrrolidone (PVP) and cellulose acetate butyrate (CAB) solutions in dimethylformamide (DMF) have been measured in the temperature range, 303K-323 K. Using these data, free energy of mixing, solvation number and different polymer-solvent interaction parameters for the solution systems have been calculated to know the presence of molecular interactions in the system. The trends in the variation of the solution property parameters indicate the existence of positive molecular interactions between the polymer and the solvent in solutions. The results also show the presence of higher degree of interaction between PVP and DMF in solution compared to CAB and DMF.

The study of miscibility and molecular interactions present in polymer and solvent in a polymer solution system provide substantial information on the processes involving polymer production and their uses[1,2]. Further, polymer dissolution also plays a key role in many industrial applications and an understanding of the dissolution process allows the optimization of design and processing conditions as well as selection of a suitable solvent[3]. There are very few reports available on the quantitative study of the interactions in a polymer solution system[4,5]. Cellulose acetate butyrate (CAB) has several advantages in properties over other polymers[6,7]. These include lower moisture absorption, greater solubility and compatibility with plasticizers, higher impact strength, and excellent dimensional stability. It is also an excellent injection molding and melt extrusion material. CAB is used in a variety of solvent coating applications for automobiles, wood and leather. It is also used as the major film former or as an additive in coatings[6-8]. Polyvinylpyrrolidone (PVP) is used mainly as a binder in many pharmaceutical tablets; being completely inert to humans, it simply passes through the body when taken orally. PVP binds to polar molecules exceptionally well, owing to its polarity. This has led to its application in coatings for photo-quality ink-jet papers and transparencies, as well as in inks for inkjet printers and a host of other technical applications. Both CAB and PVP find enormous use in pharmaceutical, biomedical and industrial applications[9,10].

DMF is primarily used as a solvent in the production of many polymer products and acrylic fibers. It is also used in the pharmaceutical and petrochemical industries, in the formulation of pesticides and in the manufacture of synthetic leathers, fibers, films, and surface coating[11-13]. There have been few reports on the solution chemistry of cellulose esters and PVP in pure or in the form of a blend with other polymers in organic solvents such as DMF[14], acetone[15] and acetic acid[16,17]. To the best of our knowledge, no studies are reported on the miscibility of PVP and CAB in DMF. Hence, as a part of our research program on polymer blends and solutions[18], we present here the molecular interactions and miscibility behavior of PVP and CAB in DMF.

Experimental

PVP (molecular weight, M_w, 45000; Alfa Aesar) and CAB (molecular weight, M_w, 70000; Alfa Aesar) were used as received. DMF (Merck) was distilled before use.

Dilute solutions of 2% (*w/v*) PVP and CAB in DMF were prepared separately in different standard flasks. Solutions of lower concentrations were then prepared by appropriately diluting these stock solutions with DMF.

The densities of the polymer solutions in DMF were measured with a Mettler Toledo Digital density meter model Densito 30 PX. The temperature of measurement was within an uncertainty of ±0.1°C. The instrument was calibrated with standard density water supplied with the instrument. The estimated error in the density measurement was within ±0.05%.

Dilute solution viscosities of PVP, CAB solutions in DMF were measured at different temperatures using Ubbelhode viscometer with an accuracy of

±0.1%. Solution viscosities at different temperatures were determined by equilibrating the viscometer tube in a thermostat maintained at a desired temperature for about 10 min before the flow time measurement. The temperature of the bath was kept constant within an accuracy of ±0.1°C.

Ultrasonic velocity measurements were carried out on a fixed frequency continuous wave ultrasonic interferometer (Model F81, Mittal Enterprises, and New Delhi) operating at 2 MHz using the standard procedure. The error in the measurement of ultrasonic velocity was within ±0.1%. Measurements at different temperatures were carried out by circulating water at required temperatures from a thermostatic bath, inside the double walled jacket covering the interferometer cell. The accuracy of temperature maintenance was within ±0.1°C.

The adiabatic compressibility (β) has been calculated using the formula, $\beta=(C^2\rho)^{-1}$, where ρ is the density of the solution C the ultrasonic velocity of the solution. The intermolecular free length has been calculated using the formula, $L_f = k\beta^{1/2}$ where k is constant for different temperatures, known as the Jakobson constant[19]. The relaxation time (τ) and relaxation amplitude (α/f^2) have been calculated[20,21] using the formulae, $\tau = 4\eta_s/3\rho C^2$ and $\alpha/f^2 = 8\pi^2 \eta_s/3 \rho C^3$ respectively, where η_s is the reduced viscosity of the solution. The uncertainty of all the reported parameters has been found to be within ±0.1%.

Results and discussion

The solution property parameters namely, density, viscosity, ultrasonic velocity, adiabatic compressibility, relaxation time, relaxation amplitude, and intermolecular free lengths for PVP and CAB in DMF at 303 K, 313 K and 323 K are presented in Tables 1 and 2, respectively. All these parameters except adiabatic compressibility and intermolecular free length are found to increase with increase of concentration of polymer at all temperatures. The adiabatic compressibility of polymer solutions decreased with concentration. This observation is in accordance with those reported in the case of PVP in chlorobenzene and dioxane[22,23]. The ultrasonic velocity and viscosity varies gradually with the concentration in solutions. The motion of PVP and CAB macromolecule is affected by mutual interaction between the macromolecule and the solvent molecule and the interaction between one macromolecule with another macromolecule. The first type of mutual interaction is termed as hydrodynamic screening,

which is significant in determining the viscous flow properties of dilute polymer solutions. The interaction gives rise to the association between two types of molecules. At low concentrations, PVP/CAB and solvent interactions dominate whereas at high concentrations PVP-PVP/CAB-CAB interaction exists.

The attenuation of ultrasound energy depends on viscosity, thermal conductivity, scattering and intermolecular processes[23]. Since the thermal condition and scattering effects are known to be negligible as suggested by Pauling[20], the intermolecular processes and viscosity are mainly responsible for the observed changes in the solution properties. The relaxation time and the relaxation amplitude are found to increase with increase in concentration at all temperatures studied. At a fixed concentration, these values decreased with temperature. This trend is quite normal as the variation in these parameters is cumulative effect of the variations in ultrasonic velocity, density and viscosity of the solutions under the given condition.

The variation of ultrasonic velocity in solution also depends on intermolecular free length on mixing. As per the model of Eyring and Kincaid[24] for sound propagation, ultrasonic velocity increases on decrease of free length. Intermolecular free length is predominant factor in determining the variation of ultrasonic velocity in solutions. In the present investigation, the intermolecular free length was found to decrease linearly with concentration at all studied temperatures. This decrease is due to decrease in compressibility with increase in concentration. This shows significant interaction between the solute and solvent molecules in the system. However, at any solute concentration, the ultrasonic velocity decreased with increase of temperature and this may be due to the weakening of intermolecular forces.

The free energy of the polymer solution (G_{12}) can be expressed[4] in RT units as:

$$G_{12} = ln \left(\frac{\eta_{12}V_{12}}{hN} \right) \qquad \ldots (1)$$

where η_{12} and V_{12} are the viscosity and molar volume of the solution respectively and h and N are the Planck's constant and Avogadro's number, respectively.

Table 1 — Solution property parameters for PVP solutions in DMF at different temperatures. [K: temperature in Kelvin, Φ_2: volume fraction of PVP, C: ultrasonic velocity, ρ: density, η: viscosity, τ: relaxation time, L_f: intermolecular free length, α: relaxation amplitude, β: adiabatic compressibility, χ: interaction parameter, S_p: solvation number]

Temp. (K)	Φ_2	C (m/s)	ρ (kg/m³)	η (10⁻³Nsm⁻²)	τ (10⁻¹²s)	L_f (Å)	α (10⁻¹⁵ s²m⁻¹)	β (10⁻¹¹ N⁻¹ m²)	X from η	X from τ	S_p
303	0	1436.0	939.0	0.781	0.538	0.4534	7.381	51.64	-	-	-
	0.001	1439.5	941.3	0.803	0.548	0.4518	7.523	51.26	0.18	0.15	47.9
	0.003	1441.2	941.9	0.830	0.565	0.4511	7.741	51.11	0.19	0.15	27.7
	0.004	1441.7	942.2	0.848	0.577	0.4509	7.901	51.01	0.20	0.16	24.0
	0.004	1442.5	942.6	0.863	0.586	0.4505	8.022	50.98	0.21	0.17	23.4
	0.006	1443.9	942.9	0.893	0.605	0.4500	8.271	50.86	0.22	0.18	19.3
	0.008	1444.6	943.0	0.922	0.624	0.4498	8.532	50.81	0.23	0.19	17.5
313	0	1392.0	926.5	0.556	0.442	0.4791	5.851	55.70	-	-	-
	0.001	1394.0	928.7	0.666	0.490	0.4778	6.960	55.41	0.15	0.12	45.4
	0.003	1396.0	929.1	0.685	0.503	0.4771	7.131	55.22	0.15	0.13	22.1
	0.004	1397.0	929.5	0.698	0.511	0.4766	7.240	55.12	0.16	0.13	20.1
	0.004	1398.0	929.8	0.711	0.520	0.4762	7.362	55.02	0.17	0.14	19.2
	0.006	1399.0	930.1	0.741	0.541	0.4758	7.650	54.93	0.18	0.15	15.7
	0.008	1401.0	930.3	0.772	0.562	0.4751	7.931	54.76	0.19	0.16	14.3
323	0	1360.0	916.1	0.491	0.386	0.5008	5.602	59.01	-	-	-
	0.001	1362.0	917.9	0.505	0.400	0.4996	5.731	58.72	0.11	0.09	27.8
	0.003	1363.0	919.4	0.523	0.423	0.4988	5.912	58.54	0.12	0.09	18.3
	0.004	1364.0	919.5	0.532	0.436	0.4984	5.993	58.45	0.13	0.10	18.1
	0.004	1365.0	919.9	0.541	0.449	0.4980	6.081	58.34	0.13	0.11	17.9
	0.006	1366.0	920.0	0.562	0.477	0.4976	6.303	58.25	0.14	0.12	15.5
	0.008	1367.0	920.7	0.584	0.507	0.4970	6.532	58.12	0.15	0.13	14.2

Table 2 — Solution property parameters for CAB solutions in DMF at different temperatures. [K: temperature in Kelvin, Φ_2: volume fraction of CAB, C: ultrasonic velocity, ρ: density, η: viscosity, τ: relaxation time, L_f: intermolecular free length, α: relaxation amplitude, β: adiabatic compressibility, χ: interaction parameter, S_p: solvation number]

Temp. (K)	Φ_2	C (m/s)	ρ (kg/m³)	η (10⁻³Nsm⁻²)	τ (10⁻¹²s)	L_f (Å)	α (10⁻¹⁵ s²m⁻¹)	β (10⁻¹¹ N⁻¹ m²)	X from η	X from τ	S_p
303	0	1436	939.0	0.781	0.538	0.4534	7.040	51.64	-	-	-
	0.0005	1448	942.5	1.172	0.790	0.4488	1.082	50.60	0.39	0.36	4.3
	0.0010	1450	943.0	1.231	0.829	0.4481	1.131	50.43	0.39	0.37	3.2
	0.0013	1452	943.3	1.761	1.180	0.4474	1.602	50.28	0.40	0.37	2.8
	0.0016	1454	943.9	2.192	1.460	0.4466	1.982	50.11	0.41	0.38	2.7
	0.0021	1456	944.2	2.392	1.595	0.4460	2.163	49.95	0.42	0.39	2.4
	0.0027	1458	945.9	3.051	2.020	0.4449	2.732	49.73	0.43	-0.40	2.0
313	0	1392	926.5	0.656	0.486	0.4786	6.250	55.70	-	-	-
	0.0005	1400	931.7	0.901	0.658	0.4750	9.271	54.76	0.31	0.28	3.5
	0.0010	1401	932.3	0.962	0.701	0.4745	9.873	54.64	0.31	0.29	2.9
	0.0013	1403	933.1	1.321	0.956	0.4737	13.51	54.44	0.32	0.29	2.8
	0.0016	1405	933.7	1.571	1.139	0.4728	16.03	54.25	0.33	0.30	2.7
	0.0021	1407	934.1	1.912	1.3740.	4721	19.31	54.07	0.34	0.31	2.3
	0.0027	1409	934.9	2.201	1.579	0.4712	22.12	53.87	0.35	0.32	2.2
323	0	1360	916.1	0.491	0.386	0.5008	5.603	59.01	-	-	-
	0.0005	1366	919.1	0.629	0.489	0.4992	7.131	58.30	0.27	0.25	3.3
	0.0010	1368	919.9	0.773	0.598	0.4981	8.702	58.10	0.28	0.26	2.7
	0.0013	1370	920.7	0.845	0.652	0.4977	9.461	57.91	0.28	0.26	2.5
	0.0016	1372	921.5	0.968	0.744	0.4972	10.80	57.61	0.29	0.27	2.5
	0.0021	1374	922.7	1.161	0.889	0.4968	12.91	57.40	0.30	0.28	2.2
	0.0027	1376	923.5	1.450	1.189	0.4963	15.93	57.20	0.31	0.29	2.0

The Gibbs free energy G_1 of the solvent is:

$$G_1 = ln\left(\frac{\eta_1 V_1}{hN}\right) \qquad \qquad \dots (2)$$

where η_1 and V_1 are the viscosity and molar volume of the solvent alone.

Using viscosity (η), density (ρ) and ultrasonic velocity (C) data, the relaxation time (τ) is obtained through the relation[20]:

$$\tau = \frac{4\eta}{3\rho C^2} \qquad \qquad \dots (3)$$

Having known the value of τ, one can also estimate G_{12} through the expression[25]:

$$G_{12} = ln\left(\frac{\tau kT}{h}\right) \qquad \qquad \dots (4)$$

where k and T are the Boltzmanns constant and absolute temperature.

The relaxation time (τ) corresponding to that of the solvent is to be used in the above expression while G_1 is estimated.

The free energy per unit mole of the solution (ΔG_m) will be:

$$\Delta G_m = \frac{G_{12}}{n_1 + xn_2} \qquad \qquad \dots (5)$$

where n_1 and xn_2 represent the number of solvent molecules and polymer molecules with x segments, respectively.

Using the values ΔG_m, of a polymer –solvent interaction parameter 'χ' can be calculated using the expression[4]:

$$\chi = \frac{(\Delta G_m - G_1 \phi_1)}{n_1 \phi_2} \qquad \qquad \dots (6)$$

Both $\phi_1 and \phi_2$ are given by the relations:

where $\phi_1 = \dfrac{n_1}{n_1 + xn_2}$ and $\phi_2 = \dfrac{xn_2}{n_1 + xn_2}$

The obtained values of χ through the Eq. (6) have been included in both the Tables 1 and 2. It is evident from the results that there is a fair agreement between the values of χ obtained from the two routes. The χ values increased slightly with concentration at a given temperature. This may be taken as an indication of the extent of influence of concentration on the solution phase interactions.

A linear dependence of the interaction parameter on the volume fractions Φ_2 of the solute can be written as the first approximation[26].

$$\chi = \chi_o + \sigma \phi_2 \qquad \qquad \dots (7)$$

where χ_o is the interaction parameter at infinite dilution and σ denotes the change in the interaction parameter per unit volume fraction of the polymer. This represents the slope in the plot of χ versus $\emptyset_2$. Further, the equation is valid only at low concentrations of the polymer solution. For an accurate determination of χ_o and σ, least square fitting technique is adopted (r=0.99). The values of χ_o obtained from the plots are given in Table 3. There is an inner agreement between both the values of χ_o obtained through viscosity and relaxation time in the temperature range studied. From the value of χ_o, the type of interaction can be known[5,27]. In the present case, χ_o obtained by both routes for the polymers are found to be less than 0.5, indicating the strong interaction between the polymer and the solvent. The interaction is considered to be less[5,27] if the value is more than 0.5. The comparison of the values between PVP and CAB shows that the extent of interaction is more between PVP and DMF than that in CAB and DMF.

Table 3 — The values of χ_o, σ and S_{po} for PVP and CAB solutions in DMF at different temperatures

Polymer	Temp. (K)	χ_o		σ		S_{po}
		from η	from τ	from η	from τ	
PVP	303	0.17	0.13	7.49	6.36	44.9
	313	0.13	0.11	6.36	6.12	40.9
	323	0.10	0.07	5.79	5.90	26.6
CAB	303	0.37	0.35	20.2	18.5	4.24
	313	0.31	0.29	20.2	18.1	3.54
	323	0.25	0.24	18.5	17.7	3.31

To have further evidence on the polymer – solvent interactions, the polymer-solvent interaction parameter (χ_{ps}) was computed from Flory-Huggins theory[28] with:

$$\chi_{ps} = \left(\frac{V_i}{RT}\right)(\delta_2\text{-}\delta_1)^2 \qquad \ldots(8)$$

where δ_1 and δ_2 are the solubility parameters[1,2,7] of solvent and polymer, respectively, and V_i, R, and T are the molar volume of the solvent, universal gas constant, and temperature (K), respectively. The χ_{ps} values have been given in Table 4. It is evident from the results that the polymer solvent interaction parameter value for PVP in DMF is more compared to that of CAB in DMF. This may be indicative of higher order of interactions in PVP-DMF solution compared to that in CAB-DMF system. This result is also in conformity with the inference obtained from 'χ_o' studies. However, the χ_{ps} values did not vary significantly with temperature.

In the study of electric properties of macromolecules, OˈKonski has given the picture of the solvated water[29]. Solvation signifies a more or less firm attachment of the solvent molecules to polar or polarizable groups. Passynskii[30] has estimated the degree of salvation/hydration by the equation,

$$S_p = \left(\frac{m}{m_0}\right)\left(1-\left(\frac{\beta}{\beta_0}\right)\right)\left(\left(\frac{100-x}{x}\right)\right) \qquad \ldots(9)$$

where β and β_o are the adiabatic compressibility of the polymer solution and of the solvent respectively m and m_o are the molecular weights of polymer repeat unit and the solvent respectively. 'x' is the weight of polymer in 100 g of the solution and S_p is the number of solvent molecules taking part in the solvation of a repeat unit.

Solvation numbers computed for the PVP and CAB solutions have also been included in Tables 1 and 2. The solvation numbers decreased with increase in

polymer concentration indicating the increased solute-solute interaction with concentration. S_{po} values for both the systems have been determined from the y-intercepts of the S_p versus concentration plots and are included in Table 3. These values are found to decrease with increase of concentrations at all temperatures studied. Higher solvation numbers obtained in the case of PVP may be due to the presence of higher dipole-dipole type molecular interactions between PVP and DMF. The lower S_p values obtained in the case of CAB may be due to the lesser interaction with the solvent caused by the larger size of the repeat unit and also due to the higher molecular weight of the sample used. This observation is again in line with the previous results. When temperature is increased, S_{po} decreased showing that solute- solvent interactions also decrease with temperature. From the values of the solubility parameter for the solvent and the polymer, the heat of mixing of solution has been calculated by Scatchard[31]-Hildebrand[32] equation as,

$$\Delta H_m = V((\delta_2\text{-}\delta_1)^2\ \Phi_1\ \Phi_2 \qquad \ldots (10)$$

where V is the volume of mixture and Φ_1 and Φ_2 are volume fractions of the solvent and the solute. The plots of ΔH_m versus concentration of polymer solutions of PVP and CAB(not shown) shows that, the heat of mixing of the solutions varies linearly with concentration indicating complete miscibility without any phase separation. The slightly higher heat of mixing values in the case of PVP may be indicative of higher solute solvent interactions compared to CAB system. This also corroborates our previous results. However, the heat of mixing values did not vary appreciably with temperature indicating the insignificant effect of temperature on heat of mixing.

The molecular interactions present in PVP and CAB solutions with DMF as solvent have been investigated by viscosity, density and ultrasonic velocity studies. Polymer-solvent interaction parameters for the solution systems have been estimated based on Gibbs' free energy calculations using data on viscosity and ultrasonic velocity of solutions along with heat of mixing and solvation numbers for the solution systems between 293 K and 313 K. The results indicate the existence of positive interactions between the polymer and the solvent in their solutions. The results also show the presence of higher degree of interaction between PVP and DMF in solution compared to that in CAB and DMF.

Table 4 — Polymer-solvent interaction parameters for PVP and CAB in DMF

Temp. (K)	Polymer	χ_{ps} calculated from Eq.(8)
303	CAB	0.01
	PVP	1.16
313	CAB	0.01
	PVP	1.14
323	CAB	0.01
	PVP	1.11

Acknowledgement

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