

A Thermodynamic Study of Supermolecular Order in Aqueous Solutions of Poly (Vinyl Alcohol)

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(Received 13th January, 1990, revised 27th March, 1990)

Summary: From the temperature viscosity data the various thermodynamic parameters were determined. It was observed that the free energy of viscous flow increase with the increase of concentration, but the effect with rise in temperature is uncertain. However, the value of ΔG_v of PVA in aqueous propyl alcohol were found to be high than water. It means that associations are high in water than aqueous Propyl alcohol solutions.

The values of heat and entropy of activation of viscous flow increases with concentration but no generalization can be made due to its irregular pattern at various temperature. The values of heat and entropy of activation show that solution of the polymer in aqueous propyl alcohol have a high order, whereas in water have low, but in no case there is complete order.

Introduction

In previous paper [1] it has been shown that polymer molecules are known to associate either inter or intramolecularly in aqueous solvents. Electrostatic, hydrophobic interactions as well as van der Waals forces and hydrogen bonding are the sources responsible for the formation of associations in polymer solutions.

Studies on the association and aggregation of polymers in their dilute solution date back to Staudinger's work. After a long time interval however, this subject has received renewed attention, perhaps in order to gain a better understanding of the behaviour of biopolymers in living systems. A series of papers published by Elies [2] cover the subject both on theoretical background and experimental details.

The hydrodynamic properties of polymer solutions are very sensitive to association. Thus informations on the presence and extent of association can be gathered from any experimental method involving polymer solutions. Among different experimental techniques namely, viscometric [3-6], Osmometric [7], Light scattering [8-9], IR [10], dielectric relaxation [11] etc, the viscometric technique has been very frequently used due to its simplicity and high sensitivity to aggregation.

In the present paper, the various thermodynamic parameters of aqueous PVA solutions, are presented. The parameters of activation of viscous

flow are very sensitive to the structure of a solution. The heat of activation of flow gives information on the strength of the structure, while the entropy of activation, on its order.

The determination of the values of ΔH_v for polymers and their comparison with those of ΔH_v for low molecular weight compounds of a similar structure was important in understanding the mechanism of polymer flow. It follows that the temperature dependence of polymer viscosity is determined by the dimensions of not entire macromolecules, but of their small parts-segments, which are kinetically independent structural elements of a polymer. It is the segments that shift from one position to another under the action of thermal motion.

The heats of activation of viscous flow and, accordingly the dependence of viscosity on temperature are determined, by the nature of macromolecules. Entropy is a function directly linked with the degree of order in a system and its diminution points to a loss of order. The large positive values of ΔS_v are evidence of the fact that the initial state is more ordered than the activated one.

The values of ΔG_v are not large for any polymer and have practically no dependence on temperature [12]. However, the values of activation energy changes with increase in concentration and molecular mass of the polymer.

Experimental

The polymer and the viscosity measurements procedure used here have been described previously [1]. Because of the dependence of viscosity on temperature, the activation parameters of viscous flow can be determined from the viscosity-temperature curve. To calculate them we used the Frenkel-Eyring Equation.

$$\eta = A_0 e^{\Delta G_v/RT} = A_0 e^{\Delta H_v - T\Delta S_v} / RT \quad (1)$$

Whereas ΔG_v is the free activation energy viscous flow; ΔH_v is the heat of activation of viscous flow; ΔS_v is the activation entropy of viscous flow.

Taking $A_0 = 10^{-3}$ [13] we have calculated the free energy, heat of activation, and activation entropy for various systems.

Results and Discussion

The various thermodynamic parameters of the polymer poly(vinyl alcohol) solutions investigated at various temperatures are listed in Tables 1-4. The values of ΔG_v show that the free energy of viscous flow increases regularly with increasing concentration, but the effect with rise in temperature is uncertain. It means that in dilute solutions the associations are weaker and they are easily overcome during flow; therefore the values of ΔG_v are small whereas in concentrated solutions, these associations are more stronger and are little effected during flow process, therefore the values of ΔG_v are high. Moreover, the values of ΔG_v were found to be high in aqueous propyl alcohol solutions as compared to water. The high values of ΔG_v in aqueous propyl alcohol solutions was explained by assuming that the interaction of polymer and alcohol molecules was determined not only by H-bonding between OH groups but also by hydrophobic interaction between the non-polar basic chain of the polymer and the alkyl chain of the alcohol molecules [14]. This indicates that aqueous propyl alcohol are better solvent than water which causes the strong supermolecular structure to collapse.

From the Tables it is also observed that the value of ΔG_v is approximately 17 KJ mol⁻¹ for 2 Kg/dm³ of PVA concentration in water and 5%

Table-1: Virous Thermodynamic Parameters of Aqueous PVA Solutions at Different Temperatures and Concentrations

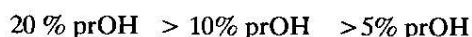
T ^o C	ΔG_v (kJ/mole)	ΔH_v (kJ/mol) (Conc. 2Kg/m ³)	$-\Delta S_v$ (J/mol)
10	17.2824	16.0538	4.3413
20	17.2433	15.9714	4.3410
30	17.2208	15.9056	4.3406
40	17.2518	15.8930	4.3412
50	17.2938	15.8918	4.3405
60	17.3825	15.9368	4.3414
70	17.4839	15.9951	4.3405
80	17.5982	16.0660	4.3405
		(Conc. 4Kg/m ³)	
10	17.7272	16.7615	3.4124
20	17.6541	16.6542	3.4126
30	17.6138	16.5798	3.4125
40	17.6304	16.5624	3.4121
50	17.6824	16.5801	3.4127
60	17.7647	16.6286	3.4117
70	17.8559	16.6853	3.4128
80	17.9686	16.7642	3.4119
		(Conc. 6Kg/m ³)	
10	18.1301	17.3608	2.7184
20	18.0605	17.2640	2.7184
30	18.0187	17.1947	2.7195
40	18.0414	17.1905	2.7186
50	18.0773	17.1992	2.7186
60	18.1514	17.2458	2.7195
70	18.2244	17.2921	2.71281
80	18.3192	17.3597	2.7181
		(Conc. 8 Kg/m ³)	
10	18.5353	17.8609	2.3830
20	18.4518	17.7538	2.3822
30	18.3919	17.6699	2.3828
40	18.4177	17.6723	2.3815
50	18.4481	17.6791	2.3808
60	18.5222	17.7291	2.3817
70	18.6062	17.7893	2.3816
80	18.6970	17.8564	2.3813
		(Conc. 10 Kg/m ³)	
10	18.9179	18.5231	1.3950
20	18.8407	18.4315	1.3966
30	18.7725	18.3492	1.3970
40	18.8082	18.3711	1.3965
50	18.8285	18.3779	1.3950
60	18.8769	18.4120	1.3961
70	18.9283	18.4493	1.3965
80	19.0141	18.5215	1.3955

propyl alcohol. The data suggests that the polymer molecules are spherical in water and at low propyl alcohol content in the temperature range 10-80°C forces between the solute and solvent molecules. Thus the solute-solvent interactions are greater for solutions of PVA in 20% proOH and small in other cases. Therefore, the structure of PVA is very strong in water while in aqueous proOH it is less

Table-2: Various Thermodynamic Parameters of Aqueous PVA Solutions in 5% PrOH at Different Temperatures and Concentrations

T°C	ΔG_v (kJ/mol)	ΔH_v (kJ/mol) (Conc. 2Kg/m ³)	ΔS_v (J/mol)
10	17.7154	17.5316	-0.6495
20	17.6193	17.4291	-0.6491
30	17.5310	17.3344	-0.6488
40	17.5316	17.3285	-0.6489
50	17.5507	17.3413	-0.6483
60	17.6115	17.3956	-0.6483
70	17.6806	17.4583	-0.6481
80	17.7617	17.5333	-0.6470
		(Conc. 4Kg/m ³)	
10	18.1464	18.0555	-0.3212
20	18.0338	17.9401	-0.3198
30	17.9339	17.8369	-0.3201
40	17.9409	17.8408	+ 0.3198
50	17.9452	17.8421	-0.3192
60	18.0314	17.9252	-0.3189
70	18.0876	17.9781	-0.3192
80	18.1558	18.0433	-0.3187
		(Conc. 6Kg/m ³)	
10	18.5494	18.5065	-0.1516
20	18.4469	18.4026	-0.1512
30	18.3665	18.3208	-0.1508
40	18.3411	18.2941	+ 0.1502
50	18.3710	18.3224	-0.1505
60	18.4336	18.3836	-0.1502
70	18.4873	18.4360	-0.1496
80	18.5533	18.5004	-0.1499
		(Conc. 8Kg/m ³)	
10	18.9519	18.9557	0.0134
20	18.8633	18.8675	0.0143
30	18.7669	18.7715	0.0152
40	18.7560	18.7608	0.0153
50	18.7695	18.7745	0.0155
60	18.8224	18.8275	0.0153
70	18.8834	18.8890	0.0163
80	18.9576	18.9634	0.0164
		(Conc. 10 Kg/m ³)	
10	19.3441	19.4447	0.3555
20	19.2607	19.3649	0.3556
30	19.1518	19.2597	0.3561
40	19.1555	19.2672	0.3569
50	19.1673	19.2826	0.3570
60	19.2259	19.3449	0.3574
70	19.2499	19.3726	0.3577
80	19.3174	19.4438	0.3581

[15]. As more propyl alcohol is added ΔG_v increases sharply suggesting that a shape transition takes place. The data also shows that the shape transition occurs in the following order:



A glance at tables 1-4 tells that the values of heat of activation of viscous flow (ΔH_v) increases with concentration in a given solvent do not depend on temperature. These values like viscosity are larger in 20% prOH solutions and smaller in water systems. The high values of ΔG_v is due to strong

Table-3: Various Thermodynamic Parameters of Aqueous PVA Solutions in 10% PrOH at Different Temperatures and Concentrations.

T°C	ΔG_v (kJ/mol)	ΔH_v (kJ/mol)	ΔS_v (J/mol)
		(Conc. 2Kg/m ³)	
10	18.2103	18.8503	2.2615
20	18.0525	18.7152	2.2618
30	17.9337	18.6191	2.2620
40	17.8953	18.6036	2.2629
50	17.8914	18.6224	2.2632
60	17.9317	18.6854	2.2634
70	17.9869	18.7632	2.2633
80	18.0455	18.8447	2.2640
		(Conc. 4 Kg/m ³)	
10	18.6293	19.2566	2.2166
20	18.4792	19.1291	2.2181
30	18.3519	19.0239	2.2178
40	18.3259	19.0202	2.2182
50	18.3182	19.0349	2.2189
60	18.3713	19.1104	2.2195
70	18.3968	19.1579	2.2189
80	18.4713	19.2548	2.2195
		(Conc. 6 Kg/m ³)	
10	19.0615	19.7038	2.2696
20	18.9139	19.5791	2.2703
30	18.7996	19.4876	2.2706
40	18.7589	19.4697	2.2709
50	18.7546	19.4881	2.2709
60	18.7938	19.5502	2.2715
70	18.8359	19.6151	2.2717
80	18.9038	19.7057	2.2717
		(Conc. 8 Kg/m ³)	
10	19.4290	20.1530	2.5583
20	19.2989	20.0486	2.5587
30	19.2018	19.9771	2.5587
40	19.1296	19.9306	2.5591
50	19.1092	19.9358	2.5591
60	19.1668	20.0192	2.5598
70	19.2014	20.0794	2.5598
80	19.2628	20.1668	2.5609
		(Conc. 10 Kg/m ³)	
10	19.8452	20.4076	1.9873
20	19.7333	20.3158	1.9880
30	19.6241	20.2265	1.9881
40	19.5995	20.2221	1.9891
50	19.5787	20.2210	1.9885
60	19.6136	20.2762	1.9885
70	19.6599	20.3424	1.9898
80	19.7136	20.4160	1.9898

Table-4: Various Thermodynamic Parameters of Aqueous PVA Solutions in 20% PrOH at Different Temperatures and Concentrations

T°C	ΔG_v (kJ/mol)	ΔH_v (kJ/mol) (Conc. 2 Kg/m ³)	ΔS_v (J/mol)
10	19.1351	21.5137	8.4049
20	18.8543	21.3173	8.4061
30	18.6490	21.1962	8.4066
40	18.5610	21.1923	8.4067
50	18.4985	21.2142	8.4077
60	18.4379	21.2378	8.4081
70	18.5203	21.4044	8.4084
80	18.5453	21.5134	8.4082
(Conc. 4 Kg/m ³)			
10	19.5839	21.9627	8.4056
20	19.3026	21.6397	7.9764
30	19.1016	21.5185	7.9765
40	19.0062	21.5031	7.9773
50	19.9598	21.5368	7.9783
60	19.9661	21.6227	7.9777
70	19.9629	21.6994	7.9781
80	19.0128	21.8293	7.9787
(Conc. 6 Kg/m ³)			
10	20.001	22.0871	7.3745
20	19.7479	21.9090	7.3759
30	19.5528	21.7876	7.3755
40	19.4641	21.7729	7.3763
50	19.4114	21.7942	7.3770
60	19.4205	21.8770	7.3768
70	19.4362	21.9668	7.3778
80	19.4770	22.0813	7.3776
(Conc. 8 Kg/m ³)			
10	20.3799	22.3438	6.9395
20	20.1331	22.1665	6.9399
30	19.9454	22.0487	6.9415
40	19.86662	22.0398	6.9415
50	19.8212	22.0633	6.9414
60	19.8402	22.1520	6.9423
70	19.8437	22.2249	6.9422
80	19.8798	22.3308	6.9433
(Conc. 10 Kg/m ³)			
10	20.7753	22.7093	6.8339
20	20.5280	22.5303	6.8337
30	20.3460	22.4492	6.9412
40	20.2919	22.4313	6.8351
50	20.2397	22.4474	6.8349
60	20.2365	22.5127	6.8354
70	20.2404	22.5851	6.8358
80	20.2821	22.6953	6.8362

structured. The process of degradation of structure and orientation of macro-molecules occur during flow, so that ΔH_v is always positive.

The values of entropy of activation of viscous flow (ΔS_v) in water are negative, while in 10% and 20% of prOH it is positive. In 5% prOH some values are positive and some values are negative. The values of ΔS_v in all these solvents increase with increase in concentration. It means that in 10% and

20% prOH the process of fracture of solution structure prevails, the system becomes less ordered, when there is a flow. But the fracture of solution structures are greater in 20 % prOH than 10% prOH. On the other hand in water the uncoiling and orientation of macromolecules prevails, the system becomes more ordered in the course of flow and the entropy of activation is negative.

In case of 5% prOH, the values of ΔS_v are negative from 2-6 Kg/m³ at all temperatures except 40°C. At that temperature the ΔS_v values are negative for the concentration 2 Kg/m³, while in all other concentrations the values of ΔS_v are positive. It means that for concentration 2-6 Kg/m³ the system becomes more ordered during flow at all temperatures except 40°C while for the solutions of 8-10 Kg/m³ becomes less ordered, shows, that the process of solution fracture is more dominant in the course of viscous flow.

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