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Research Article

SOLVATION STUDY OF POLYVINYLIDENE FLUORIDE IN N-N DIMETHYLFORMAMIDE THROUGH PADOVA AND SHIIO MODEL

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ABSTRACT

Ultrasonic velocity and density measurements for the solutions of polyvinylidene fluoride in N-N dimethyl formamide have been made as a function of concentration and temperature. The data are used to compute the solvation number using the methodology based on Padova model and shiio model. Using solvation number, the parameters like apparent molar compressibility, apparent molal volume and molar solvated volume are estimated in both the models and compared with those values obtained by the traditional method.

INTRODUCTION

Ultrasonic technique proves to be a good tool for the study of kinetics of elementary chemical reactions occurring at the polymer- solvent interface. In the case of aqueous electrolytic solution the water molecules bound to an electrolyte ion are compressed by the strong electric field of the ion and form a very hard sphere.

On that basis Padova and other researchers[5] assumed that the compressibility of the bound water and that of the ion to be both negligibly small. So by neglecting the compressibility of the hydrated part that comprises both solute and bound water molecules they evaluated the degree of hydration of ions and this model is applied to the polymer solutions also.[4, 6] According to Shiio *et al*.,[8, 9] in the case of non-electrolytes or polymers, the bound solvent of the solute has appreciable compressibility and hence the compressibility of the bound solvent cannot be ignored.

They assumed the compressibility of bound solvent to be equal to that of ice and that of the solute to be zero. But according to Hemmes *et al*.,[2] the compressibility of the solute is not negligible. From the reports of Shiio *et al*., and Hemmes *et al*., one may consider that the compressibility of the solvated part has appreciable value. On the basis of Padova model and Shiio model, expressions for ultrasonic parameters such as solvation number, apparent molal compressibility, apparent molal volume, molar solvated volume have been derived by Kalyana sundaram *et al*. In the present paper, the methodology is verified for the solutions of Polyvinylidene fluoride in the solvent N-N Dimethyl formamide.

Experimental Techniques

The solutions of polyvinylidene fluoride of concentration range from 0% w to 2% w were prepared by dissolving known quantities of PVDF (Sigma Aldrich Chemical Pvt.Ltd., Bangalore) in polar solvent namely Dimethyl formamide. Ultrasonic velocities of the solutions were measured using a fixed frequency continuous wave ultrasonic interferometer (Model F80, Mittal Enterprises, New Delhi) to an accuracy of ± 0.1 at a frequency of 2 MHz at 308K, 313K, 318K and 323K.

The temperature of the samples was maintained constant to an accuracy of ± 0.1º using a thermostatically controlled water bath. Density was measured using 10 ml specific gravity bottle at all above temperatures.

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Table1 The values of U, ρ, and β for Polyvinylidene fluoride in DMF

TEMP K	n_2 M	ρ kg m^{-3}	U ms^{-1}	β × 10^{10} m^2N^{-1}
308	0.000	935.0	1433	5.21
	0.078	938.8	1452	5.05
	0.156	942.1	1463	4.96
	0.233	944.8	1470	4.90
	0.310	947.6	1480	4.82
	0.387	951.4	1486	4.76
313	0.000	931.1	1417	5.35
	0.078	935.3	1430	5.23
	0.156	938.3	1443	5.12
	0.233	941.1	1453	5.03
	0.310	944.2	1461	4.96
	0.387	947.6	1468	4.90
318	0.000	927.2	1399	5.51
	0.078	931.6	1411	5.39
	0.156	935.2	1423	5.28
	0.233	937.9	1432	5.20
	0.310	940.4	1442	5.11
	0.387	943.9	1448	5.05
323	0.000	922.8	1382	5.67
	0.078	927.3	1393	5.56
	0.156	931.2	1403	5.46
	0.233	934.9	1410	5.38
	0.310	938.1	1418	5.30
	0.388	941.4	1427	5.22

Table 2 the values of n_h, n_h', S and S′ for Polyvinylidene fluoride in DMF

TEMP K	n_2 M	n_h	$n_{h'}$	S	S'
308	0.078	4.69	4.90	5.08	5.31
	0.156	3.68	3.92	3.98	4.24
	0.233	2.97	3.25	3.21	3.52
	0.310	2.78	3.07	3.01	3.33
	0.387	2.55	2.82	2.76	3.06
313	0.078	3.53	3.67	4.61	4.79
	0.156	3.28	3.52	4.28	4.59
	0.233	2.94	3.21	3.84	4.19
	0.310	2.68	2.95	3.49	3.85
	0.387	2.49	2.76	3.25	3.60
318	0.078	3.40	3.51	3.69	3.81
	0.156	3.22	3.39	3.49	3.68
	0.233	2.82	3.05	3.06	3.32
	0.310	2.65	2.92	2.87	3.17
	0.387	2.44	2.70	2.64	2.93
323	0.078	3.23	3.31	3.33	3.42
	0.156	2.98	3.11	3.08	3.21
	0.233	2.64	2.79	2.72	2.88
	0.310	2.46	2.65	2.54	2.74
	0.388	2.41	2.61	2.49	2.69

THEORY

Padova Model

The solvent molecules bound to the polymer are compressed due to the strong electric field of the ion and form a very hard structure. Neglecting the compressibility of the solvated part that comprises both polymer and the bound solvent molecules, the degree of solvation has been estimated by Passynskii[7], R.P. Singh[6] and Kalyanasundaram *et al.*[3] In their treatment, the compressibility of the solution is mainly due to the free solvent molecules. Based on this (Padova model) expressions for the solvation number and its allied parameters have been obtained. The solvation number is the ratio of the incompressible solvent molecules in the solution (n_i) to the number of solute molecules (n_2). The solvation number obtained through Padova model is given by,

$$n_h = \left(n_1 - N\frac{\beta}{\beta_0} \right)\frac{1}{n_2} \qquad \text{---------- (1)}$$

where n_1 is the number of moles of the solvent. In molal scale,

$$n_h' = \frac{n_1}{n_2}\left[1 - \frac{\beta}{\beta_0} \right] \qquad \text{----- (2)}$$

The apparent molal compressibility of the solute is the compressibility of an amount of solution containing one mole of the solute minus the compressibility of the solvent.

$$\text{Thus,} \quad \Phi_k = \frac{(\beta V - n_1\beta_0 V_1)}{n_2} \qquad \text{---------- (3)}$$

Remembering that $V = NV_1$ where V_1 is the molar volume of the pure solvent and on rearranging the above equation, one gets,

$$\frac{\Phi_k}{\beta_0 V_1} = -\frac{1}{n_2}\left[n_1 - \frac{\beta N}{\beta_0} \right]$$

Thus from Eqn. (1), $\Phi_k = -V_1\beta_0 n_h$ ------- (4)

In molal scale, $\Phi_k = -n_h' V_1\beta_o + \Phi_v \beta$ -------- (5)

The apparent molal volume of the solute is the volume of the amount of solution containing one mole of the solute minus the volume of the solvent present in the solution. Thus,

$$\Phi_v = \frac{V - n_1 V_1}{n_2} = \left[\frac{N\Delta\beta}{\beta_0 n_2} - n_h \right] V_1 \qquad \text{---------(6)}$$

$$\text{In molal scale,} \quad \Phi_v = \frac{(n_h' - n_h)V_1\beta_0}{\beta} \qquad \text{---------- (7)}$$

The molar volume occupied by the solvated part of the solute is known as the molar solvated volume and it is denoted by Φ_s. Similar to compressibility, the volume of the solution can be written as the sum of the volume of the free solvent part and the volume of solvated part.

$$V = (n_1 - n_2 n_h)\, V_1 + n_2 \Phi_s \qquad \text{---------- (8)}$$

As for electrolyte solutions[1], Φ_s in molar concentration is written as,

$$\Phi_s = \frac{V - (n_1 - n_2 n_h)V_1}{n_2} \qquad \text{---------- (9)}$$

Φ_s can be computed by the equations,

$$\Phi_s = \frac{V}{n_2}\frac{\Delta\beta}{\beta_0} \qquad \& \ \Phi_s = \Phi_v + n_h V_1 \qquad \text{-------- (10\&11)}$$

$$\text{In molal scale} \quad \Phi_s = \frac{n_h' V}{n_1} \qquad \text{---------- (12)}$$

Shiio Model

According to Shiio *et al.*, [8, 9] in the case of non-electrolytes or polymers in aqueous solutions, the compressibility of the bound solvent cannot be neglected. The model treats the solute

as having a volume V_i with compressibility β_i surrounded by a region of solvent, which contains n_h molecules of solvent.

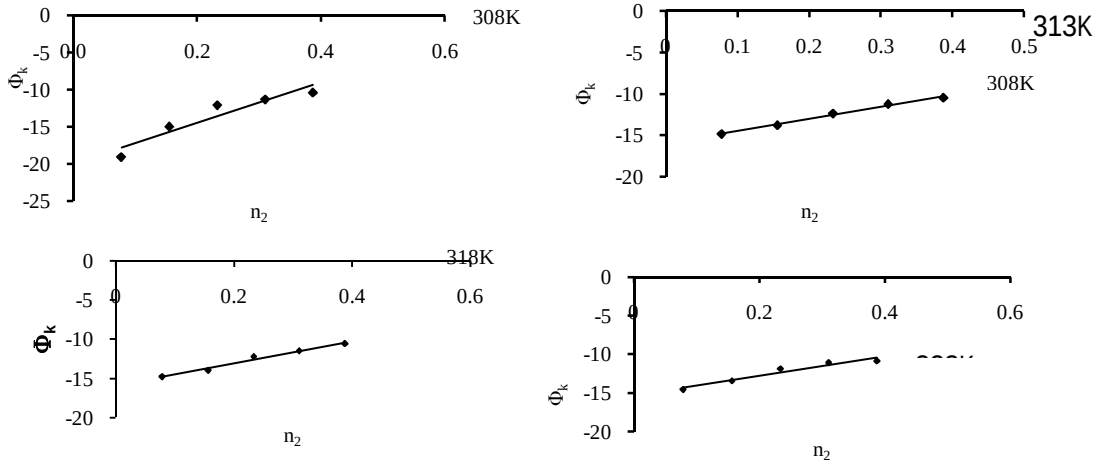

Figure 1 Variation of Φ_k with n_2 for Polyvinylidene fluoride in DMF

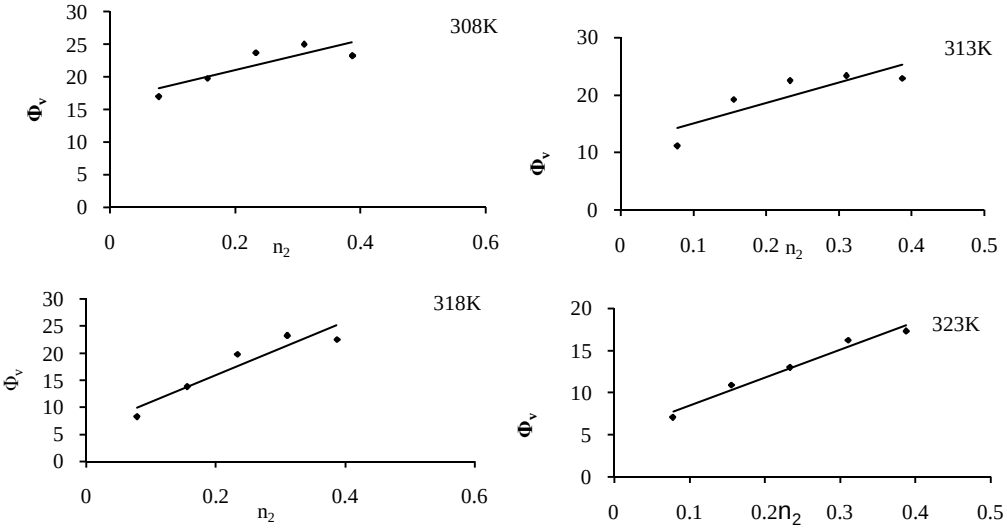

Figure 2 Variation of Φ_v with n_2 for Polyvinylidene fluoride in DMF

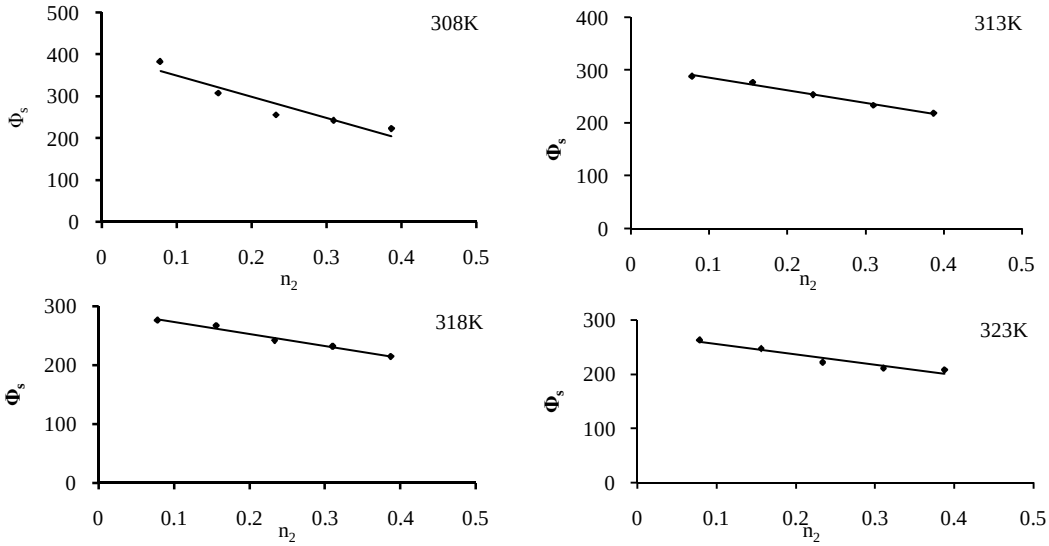

Figure 3 Variation of Φ_s with n_2 for Polyvinylidene fluoride in DMF

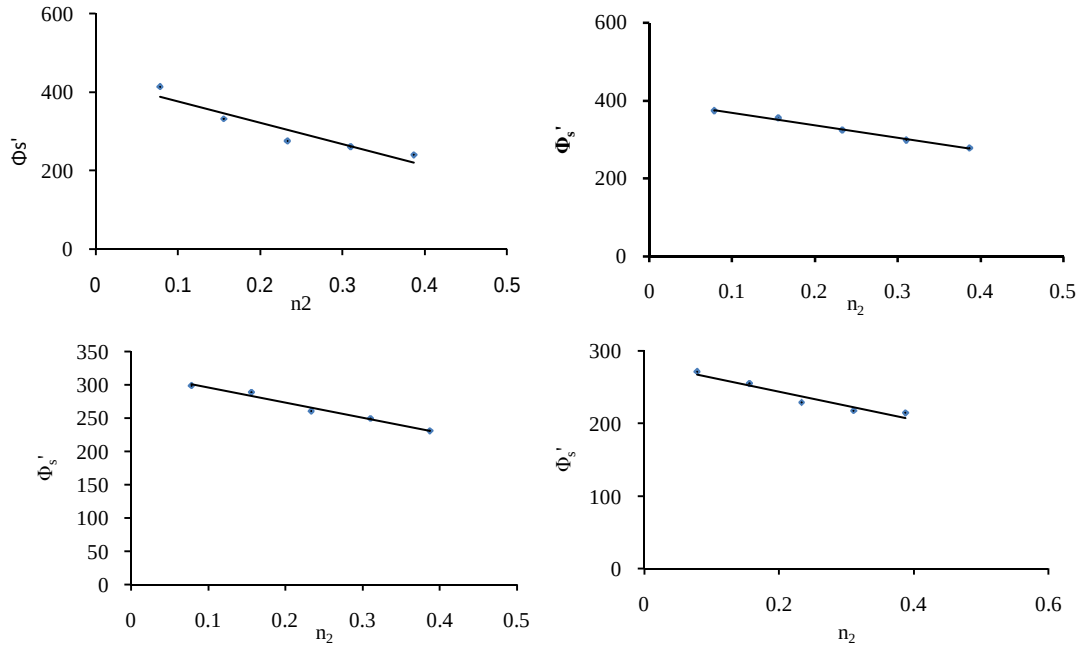

Figure 4 Variation of Φ_s' with n_2 for Polyvinylidene fluoride in DMF

This region has a volume v_h and compressibility β_h. Using β_h, expressions for molar solvation number and other allied parameters like Φ_k, Φ_v and Φ_s have been obtained based on Shiio model

The expression for the solvation number is given by

$$S = \left(\frac{\beta_0}{\beta_0 - \beta_h}\right)\frac{n_1}{n_2} - \left(\frac{N}{\beta_0 - \beta_h}\right)\frac{\beta}{n_2} \qquad \text{----------(13)}$$

$$S' = \frac{n_1}{n_2}\left[\frac{\Delta\beta}{\beta_0 - \beta_h}\right] \qquad \text{---------- (14)}$$

The apparent molal compressibility of the solute is given by,

$$\Phi_k = -V_1(\beta_0 - \beta_h)\, S \qquad \text{------ (15)}$$

In molal scale, $\Phi_k = -V_1 S'(\beta_0 - \beta_h) + \Phi_v \beta$ ---------- (16)

The apparent molal volume is given by

$$\Phi_v = \left[\frac{N\Delta\beta}{\beta_0 n_2} - \frac{S(\beta_0 - \beta_h)}{\beta_0}\right]V_1 \qquad \text{---------- (17)}$$

$$\text{In molal scale, } \Phi_v = \frac{V}{\beta_0}(\beta_0 - \beta_h)\left[\frac{S'}{n_1} - \frac{S}{N}\right] \qquad \text{---------- (18)}$$

In Shiio model, let the molar solvated volume be denoted as Φ_s'. Similar to Φ_s it is expressed as

$$\Phi_s' = \frac{V - (n_1 - n_2 S)V_1}{n_2} \qquad \text{---------- (19)}$$

This can also computed by the equation,

$$\Phi_s' = V_1\left(\frac{N\Delta\beta}{\beta_0 n_2} + \frac{S\beta_h}{\beta_0}\right) \qquad \text{---------- (20)}$$

$$\text{In molal scale, } \Phi_s' = V_1\left[\frac{\beta_0 - \beta_h}{\beta_0}\right]\frac{NS'}{n_1} + SV_1\left(\frac{\beta_h}{\beta_0}\right) \text{--- (21)}$$

RESULTS AND DISCUSSION

The values of apparent molal compressibility at various concentrations in molar and molal scale are estimated through Padova Model. The values are given in Table- 3. Φ_k values are same in both molar and molal scales as well as in both models as seen from the Table. It is obvious that whatever be the models considered, the Φ_k value is the same as it is measured from the basic parameters like sound velocity and density. The Φ_k values are obtained using traditional Eqn. (22) also and are included in the table.

$$\Phi_k = (\beta\rho_0 - \beta_0\rho)\left(\frac{1000}{n_2\beta_0}\right) + \left(\frac{M_2\beta_0}{\rho_0}\right) \qquad \text{--------- (22)}$$

The agreement of these values at all temperatures indicating that the methodology described is on the correct lines. Similarly, the computed values of Φ_v are given in the Table-3. These values are compared with those computed through the usual expression involving density

$$\Phi_v = (\rho_0 - \rho)\left(\frac{1000}{\rho_0 n_2}\right) + \left(\frac{M_2}{\rho_0}\right) \qquad \text{------ (23)}$$

There is good agreement between these values.

The values of Φ_s for PVDF solutions are given in Table -4 It is found that Φ_s values obtained through all the equations are equal at all concentrations and temperatures.

Table 3 The values of Φ_k and Φ_v for Polyvinylidene fluoride in DMF

TEMP K	n_2 M	$\Phi_v \times 10^6 m^3 M^{-1}$					$\Phi_k \times 10^{14} m^5 N^{-1} M^{-1}$				
		Padova		Shiio		Trad. Eqn	Padova		Shiio		Trad. Eqn
		Eqn 6	Eqn 7	Eqn 17	Eqn 18	Eqn 23	Eqn 4	Eqn 5	Eqn 15	Eqn 16	Eqn 22
	0.078	16.98	16.98	16.98	16.98	16.98	-19.08	-19.08	-19.08	-19.08	-19.08
	0.156	19.77	19.77	19.77	19.77	19.77	-14.97	-14.97	-14.97	-14.97	-14.97
308	0.233	23.67	23.67	23.67	23.67	23.67	-12.08	-12.08	-12.08	-12.08	-12.08
	0.310	24.98	24.98	24.98	24.98	24.98	-11.30	-11.30	-11.30	-11.30	-11.30
	0.387	23.23	23.23	23.23	23.23	23.23	-10.38	-10.38	-10.38	-10.38	-10.38
	0.078	11.09	11.09	11.09	11.09	11.09	-14.83	-14.83	-14.83	-14.83	-14.83
	0.156	19.17	19.17	19.17	19.17	19.17	-13.78	-13.78	-13.78	-13.78	-13.78
313	0.233	22.45	22.45	22.45	22.45	22.45	-12.36	-12.36	-12.36	-12.36	-12.36
	0.310	23.32	23.32	23.32	23.32	23.32	-11.24	-11.24	-11.24	-11.24	-11.24
	0.463	22.85	22.85	22.85	22.85	22.85	-10.46	-10.46	-10.46	-10.46	-10.46
	0.078	8.29	8.29	8.29	8.29	8.29	-14.78	-14.78	-14.78	-14.78	-14.78
	0.156	13.87	13.87	13.87	13.87	13.87	-13.98	-13.98	-13.98	-13.98	-13.98
318	0.233	19.85	19.85	19.85	19.85	19.85	-12.23	-12.23	-12.23	-12.23	-12.23
	0.310	23.32	23.32	23.32	23.32	23.32	-11.49	-11.49	-11.49	-11.49	-11.49
	0.462	22.56	22.56	22.56	22.56	22.56	-10.58	-10.58	-10.58	-10.58	-10.58
	0.078	7.05	7.05	7.05	7.05	7.05	-14.50	-14.50	-14.50	-14.50	-14.50
	0.156	10.90	10.90	10.90	10.90	10.90	-13.39	-13.39	-13.39	-13.39	-13.39
323	0.233	12.98	12.98	12.98	12.98	12.98	-11.85	-11.85	-11.85	-11.85	-11.85
	0.310	16.20	16.20	16.20	16.20	16.20	-11.05	-11.05	-11.05	-11.05	-11.05
	0.462	17.29	17.29	17.29	17.29	17.29	-10.82	-10.82	-10.82	-10.82	-10.82

Table 4 The values of Φ_s (Padova model) and Φ_s' (Shiio model) for Polyvinylidene fluoride in DMF

TEMP K	n_2M	$\Phi_s \times 10^6 m^3 M^{-1}$			$\Phi_s' \times 10^6 m^3 M^{-1}$			
		Eqn 10	Eqn 11	Eqn 12	Eqn 9	Eqn 19	Eqn 20	Eqn 21
	0.078	383.39	383.39	383.39	383.39	413.92	413.92	413.92
	0.156	307.11	307.11	307.11	307.11	331.06	331.06	331.06
308	0.233	255.52	255.52	255.52	255.52	274.84	274.84	274.84
	0.310	241.93	241.93	241.93	241.93	260.01	260.01	260.01
	0.387	222.44	222.44	222.44	222.44	239.04	239.04	239.04
	0.078	288.40	288.40	288.40	288.40	372.88	372.88	372.88
	0.156	276.84	276.84	276.84	276.84	355.34	355.34	355.34
313	0.233	253.61	253.61	253.61	253.61	324.03	324.03	324.03
	0.310	233.50	233.50	233.50	233.50	297.53	297.53	297.53
	0.387	218.48	218.48	218.48	218.48	278.08	278.08	278.08
	0.078	276.51	276.51	276.51	276.51	299.51	299.51	299.51
	0.156	267.53	267.53	267.53	267.53	289.28	289.28	289.28
318	0.233	241.83	241.83	241.83	241.83	260.86	260.86	260.86
	0.310	231.92	231.92	231.92	231.92	249.81	249.81	249.81
	0.387	214.56	214.56	214.56	214.56	231.02	231.02	231.02
	0.078	262.65	262.65	262.65	262.65	270.93	270.93	270.93
	0.156	246.83	246.83	246.83	246.83	254.48	254.48	254.48
323	0.233	221.87	221.87	221.87	221.87	228.64	228.64	228.64
	0.310	211.02	211.02	211.02	211.02	217.34	217.34	217.34
	0.387	207.97	207.97	207.97	207.97	214.16	214.16	214.16

The agreement between these values and those obtained from the traditional equation proves the correctness of the theory. In Shiio model, the values of molar and molal solvated volume are calculated and presented in Table -4 and are observed to be equal in both molar and molal scales.

The values of Φ_s' obtained through Shiio model are found to be different from those obtained through Padova model (Φ_s). This is expected since the solvation number values are different in both models. The value of Φ_s' for the PVDF solutions in the system studied is greater than the Φ_s values at all temperatures and concentrations since S is positive.

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