Study of thermodynamical properties of polyvinylidene fluoride in aprotic solvent

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ABSTRACT

The state of any system can be defined completely by four observable properties, namely composition, pressure, volume and temperature. Study of thermodynamical properties of liquids and liquid mixtures play an important role in elucidation of the nature of molecular interactions. Internal pressure (π_i) and free volume (V_f) are the thermo dynamical parameters, which are useful in understanding the intra and inter molecular interactions in polymer solutions[1,2]. The internal pressure is known to be an inverse function of free volume. In the present work, the ultrasonic velocity, density and viscosity measurements have been made for the temperatures 303K, 313 K, 318 K and 323 K and at different concentrations of polyvinylidene fluoride in polar aprotic solvent i.e Dimethylacetamide. The variation of internal pressure and free volume with temperature and concentration has been carried out. The nature of polymer-solvent interaction and the effect of temperature and concentration on the molecular interaction are studied. The internal pressure is found to vary inversely with free volume and the values reveals that the relation $\pi_i V_f^{\,x}$ = constant, holds good for the above system.

Introduction

The liquid molecules may be held together because of the cohesive forces due to the presence of ions or electrons or due to the presence of hydrogen bonds as in water. The measurement of cohesive forces is provided by the internal pressure. The main advantage of considering internal pressure in calculating the transport property lies in the fact that, it is experimentally measurable and it depends on molar volume. Above all the internal pressure is closely related to the solubility parameter which determines the way in which interactions occur in the system. In the present work, the internal pressure (π_i) and the free volume (V_f) of the solution of Polyvinylidenefluoride in DMA at various concentrations have been studied at temperatures **303K, 313 K, 318 K and 323 K** . The empirical relation connecting π_i and V_f is also established.

Experimental

Computation of internal pressure and free volume requires measurements of ultrasonic velocity (U), density (ρ) and the viscosity (η). The solutions of Polyvinylidene fluoride of concentration range from 0% w to 3% w were prepared by dissolving known quantities of PVDF of molecular weight 5,30,000 (Sigma Aldrich Chemical Pvt.Ltd.,Bangalore) in polar aprotic solvent namely Dimethyl. Acetamide. 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 ± 0.2 m/s at a frequency of 2 MHz at 303 K, 313 K, 3183 K & 323 K. The temperature of the samples was maintained constant to an accuracy of ± 0.1° using a thermostatically controlled water bath. Density was measured using 10 ml specific gravity bottle at all above temperatures. The viscosity was measured using Ostwald's viscometer to an accuracy of ± 0.2%

Computation

Using the experimentally measured values of ultrasonic velocity (U), density (ρ) and viscosity (η), the internal pressure (π_i) is computed using the relation [4]

$\pi_i = bRT(k\eta/U)^{1/2}(\rho^{2/3}/M_{eff}^{7/6})$ ----(1)

Where $M_{eff} = M_1 X_1 + M_2 X_2$

X_1 = mole fraction of solvent and X_2 = mole fraction of solute.

Free volume V_f is computed using the formula[3]

$V_f = (M_{eff} U/k\eta)^{3/2}$ ----(2)

where k is a constant given as

$k = 4.28 \times 10^9$ independent of temperature and nature of the system, R is the gas constant, T is the temperature in Kelvin, b is the packing factor and M_{eff} is the effective mass. The computed values of ultrasonic velocity, Internal Pressure and Free Volume and are presented in Tables 1, 2 and 3.
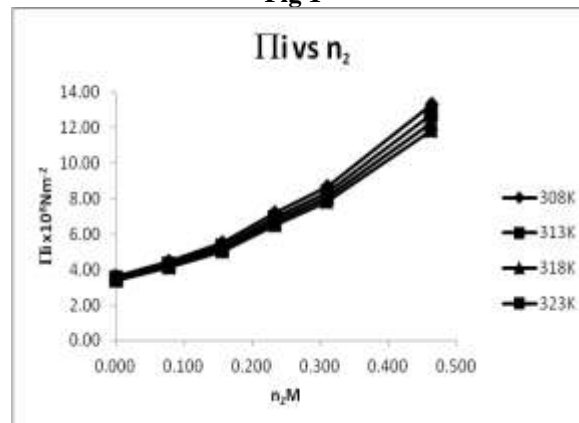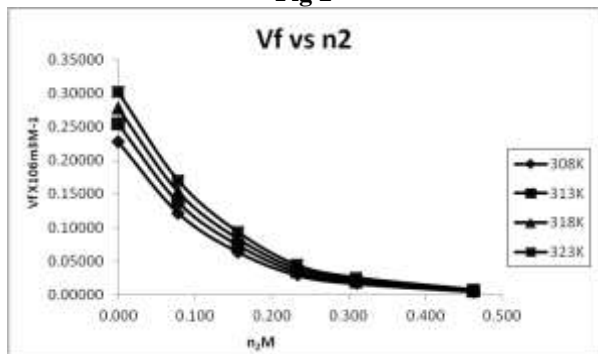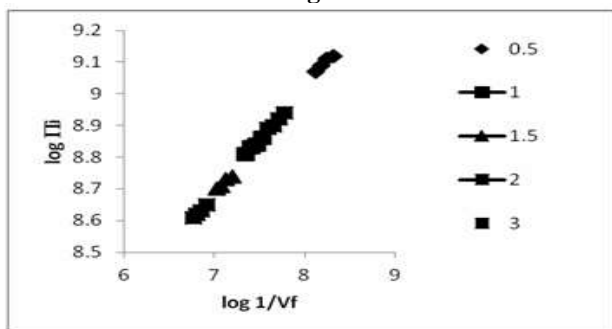
Fig 1

Fig 2

Fig 3

RESULTS AND DISCUSSION

Internal pressure is a measure of the totality of forces of attraction, repulsion and overall cohesion between the component molecules in solution. The variation of internal pressure with concentration is shown in fig (1).The internal pressure shows a general increase with increase in concentration. This may be attributed to the strong interaction between the solute and the solvent molecules. The internal pressure is found to decrease with increase in temperature at a given concentration[3]. This indicates reduction of cohesive forces as the molecules move away from each other with increase in temperature.

The variation of free volume with concentration and temperature is shown in fig (2).The continuous decrease in free volume indicates close packing of molecules with increase in solute concentration[4]. For the polymer solution of PVDF in DMA, the free volume is found to increase with temperature. When the temperature is increased there is a tendency for the molecules to move away from each other which results in the reduction of cohesive forces and thus leading to an increase in free volume.

In the case of liquid system, it is found that [5,] at a given concentration, for the change of temperature, the internal pressure is inversely proportional to V_f^x, that is, $\pi_i V_f^x$ is a constant. A plot between the values of log (π_i) and log $(1/V_f)$ [fig (3)] resulted in a family of parallel straight lines with a constant slope. Thus it is found that internal pressure, free volume and temperature are the variables which fix up the thermodynamic behaviour of liquid system.

References
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TABLE 1 Ultrasonic Velocity (U) of PVDF+ DMA system

n_2 M	ULTRASONIC VELOCITY(U) m/s			
	303 K	313 K	318 K	323 K
0.000	1428	1413	1395	1377
0.078	1439	1424	1403	1384
0.156	1448	1432	1408	1389
0.233	1450	1434	1412	1392
0.311	1453	1437	1415	1396
0.464	1456	1439	1420	1401

TABLE 2 Internal Pressure (π_i) of PVDF + DMA system

n_2 M	INTERNAL PRESSURE (π_i) X 10^{-8} Nm^{-2}			
	313 K	318 K	323 K	328 K
0.000	3.58	3.49	3.44	3.38
0.078	4.42	4.30	4.20	4.11
0.156	5.51	5.30	5.17	5.04
0.233	7.17	6.91	6.69	6.49
0.310	8.67	8.34	8.08	7.81
0.462	13.28	12.72	12.23	11.82

TABLE 3 Free Volume (V_f) of PVDF + DMA system

n_2 M	FREE VOLUME (V_f) X 10^6 m^3 M^{-1}			
	313 K	318 K	323 K	323 K
0.000	0.22746	0.25525	0.27813	0.30244
0.078	0.12167	0.13819	0.15354	0.17049
0.156	0.06381	0.07438	0.08356	0.09355
0.233	0.02923	0.03392	0.03895	0.04423
0.310	0.01671	0.01953	0.02232	0.02556
0.462	0.00474	0.00561	0.00655	0.00753