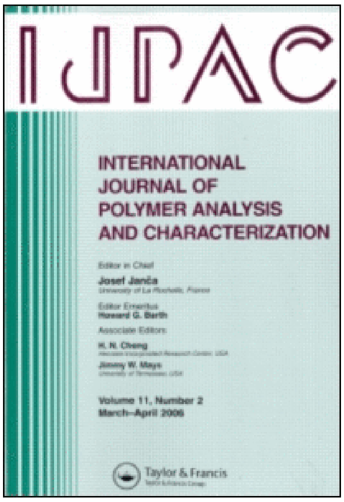

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Ultrasonic Studies of Poly(vinyl acetate) Solution in Dimethylformamide

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Acoustical parameters such as adiabatic compressibility, specific acoustic impedance, relaxation strength, space-filling factor, and molecular ratio are evaluated for the solutions of poly(vinyl acetate) in dimethylformamide by measuring viscosity, ultrasonic velocity, refractive index, and density at different temperatures, (30°, 35°, 40°, and 45°C) and for different concentrations of poly(vinyl acetate) in solution. The results are discussed based on the solute and solvent interactions.

Keywords: Acoustic parameters; Poly(vinyl acetate); Viscosity; Ultrasonic velocity; Refractive index; Density

INTRODUCTION

Many techniques such as X-ray diffraction, nuclear magnetic resonance (NMR), infrared (IR), and ultraviolet (UV) spectroscopy are used to investigate polymer structure. Acoustical parameters can also be used as a means to study the degree of solute–solvent interactions in polymer solutions and molecular structure. Acoustical properties are much

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simpler and more accurate to measure than absorption properties and can be performed at faster rates.

Ultrasonic absorption and dispersion in polymer solution[1–3] and in solid polymer[4] have been the subject of extensive research activity in recent years to study the intermolecular attraction in solute-solvent systems. Schaaffs[5] and Sette[6,7] summarized several empirical and semi-empirical relations between ultrasonic velocity and other acoustic parameters. Reddy and Singh[8] studied acoustical properties of poly (vinyl pyrrolidone) in aqueous solutions at different temperatures and concentrations. Rajulu et al.[9] and Naidu et al.[10] carried out studies on acoustic properties of poly(vinyl pyrrolidone) in water and dimethylformamide and studied the variation of adiabatic compressibility with temperature. Recently, John et al.[11] studied the ultrasonic measurements of solution blends of poly(vinyl acetate) with poly(methyl methacrylate) and poly(vinyl chloride). As poly(vinyl acetate) (PVAc) is a very important polymer due to its wide variety of applications, the authors measured the ultrasonic velocity, density, viscosity, and refractive index for this polymer in dimethylformamide (DMF) at various concentrations and temperatures to observe the variation of adiabatic compressibility (β_{ad}), specific acoustic impedance (Z), and relaxation strength (r) with concentration at different temperatures and the variation of molecular ratio (N_o/N_s) with space-filling factor (r') and β_{ad} at different temperatures.

EXPERIMENTAL

The ultrasonic velocities have been measured by employing an ultrasonic interferometer (Mittal Enterprises, New Delhi). The ultrasonic cell has a double-wall jacket, and thermostated water is circulated through it from a thermoset with thermal stability of ±0.05°C. The experimental frequency is 2 MHz and the velocity measurements have an accuracy better than ±0.5%. The density, viscosity, and refractive index measurements have been made using a pycnometer, an Ostwald viscometer, and an Abbe refractometer respectively, with accuracies of ±0.02%, ±0.2%, and ± 0.2%, respectively. The polymer sample used is poly (vinyl acetate) (SD, India) having an average molecular weight, M, of 150,000.

The adiabatic compressibility is based on the relationship:

$$\beta_{ad} = \frac{1}{v^2 \rho} \tag{1}$$

where v is the ultrasonic velocity and ρ is the density.

The space-filling factor, r', is given by the relationship:

$$r' = \frac{B}{V} \tag{2}$$

TABLE I Acoustical parameters of poly(vinyl acetate) in dimethylformamide

T°C	C × 10^5 mol/L	$[\eta] \times 10^4$ P	v m/s	ρ g/cm^3	n_D	$\beta_{ad} \times 10^{11}$ cm^2/dyne	$(N_o/N_s) \times 10^3$	r'	r	Z g/cm^2/S^2
30	DMF	11.71	1465	0.9388	1.4165	4.9630	—	—	0.1616	137536.4
	1.366	13.29	1482	0.9389	1.4184	4.8491	1.8119	0.25221	0.1420	139151.5
	2.672	15.06	1491	0.9396	1.4186	4.7871	3.6288	0.25232	0.1316	140101.6
	5.344	18.42	1506	0.9404	1.4188	4.6884	7.2828	0.25242	0.1140	141627.5
	10.688	22.22	1518	0.9415	1.4190	4.6092	14.6743	0.25253	0.0998	142923.1
	13.360	29.57	1526	0.9423	1.4191	4.5570	18.4062	0.25258	0.0903	143800.2
35	DMF	10.72	1456	0.9366	1.4141	5.0363	—	—	0.1719	136371.3
	1.366	12.20	1478	0.9367	1.4163	4.8808	1.8161	0.25110	0.1466	138621.8
	2.672	13.92	1488	0.9374	1.4168	4.8178	3.6374	0.25137	0.1351	139490.6
	5.344	16.89	1498	0.9382	1.4172	4.7496	7.2998	0.25158	0.1234	140549.6
	10.688	20.03	1509	0.9392	1.4179	4.6754	14.7098	0.25195	0.1105	141738.6
	13.360	26.63	1517	0.9410	1.4184	4.6177	18.4324	0.25221	0.1010	142753.7
40	DMF	9.42	1448	0.9346	1.4112	5.1030	—	—	0.1809	135331.9
	1.366	11.24	1463	0.9347	1.4134	4.9980	1.8200	0.24956	0.1639	136758.8
	2.672	12.77	1474	0.9354	1.4138	4.9203	3.6453	0.24978	0.1512	137882.6
	5.344	15.61	1485	0.9363	1.4141	4.8430	7.3149	0.24993	0.1385	139045.7
	10.688	18.69	1497	0.9372	1.4146	4.7611	14.7426	0.25020	0.1246	140303.5
	13.360	24.84	1509	0.9381	1.4152	4.6811	18.4904	0.25052	0.1105	141565.1
45	DMF	8.88	1440	0.9328	1.4105	5.1697	—	—	0.1900	134327.7
	1.366	9.11	1452	0.9329	1.4126	5.0840	1.8236	0.24914	0.1764	135463.2
	2.672	11.36	1461	0.9340	1.4131	5.0158	3.6508	0.24940	0.1662	136459.1
	5.344	14.17	1471	0.9351	1.4135	4.9420	7.3244	0.24962	0.1547	137556.4
	10.688	17.00	1490	0.9360	1.4139	4.8121	14.7618	0.24983	0.1327	139469.2
	13.360	22.80	1508	0.9392	1.4146	4.6918	18.5082	0.25020	0.1116	141337.6

where B is the effective volume occupied by molecules per mole and V is the molecular volume. According to Gerecze[12], r' is related to n_D, the refractive index (sodium D line), by the equation:

$$r' = \frac{n_D^2 - 1}{n_D^2 + 2} \tag{3}$$

The relation between the ultrasonic velocity, v, and the space-filling factor, r', is given by the Schaaffs[5] formula:

$$v = U\, r'$$

where U represents the sound velocity when the entire volume of space is filled with molecules.

The specific acoustic impedance (Z) and the relaxation strength (r) are given by the following formulas:

$$Z = \rho v \tag{4}$$

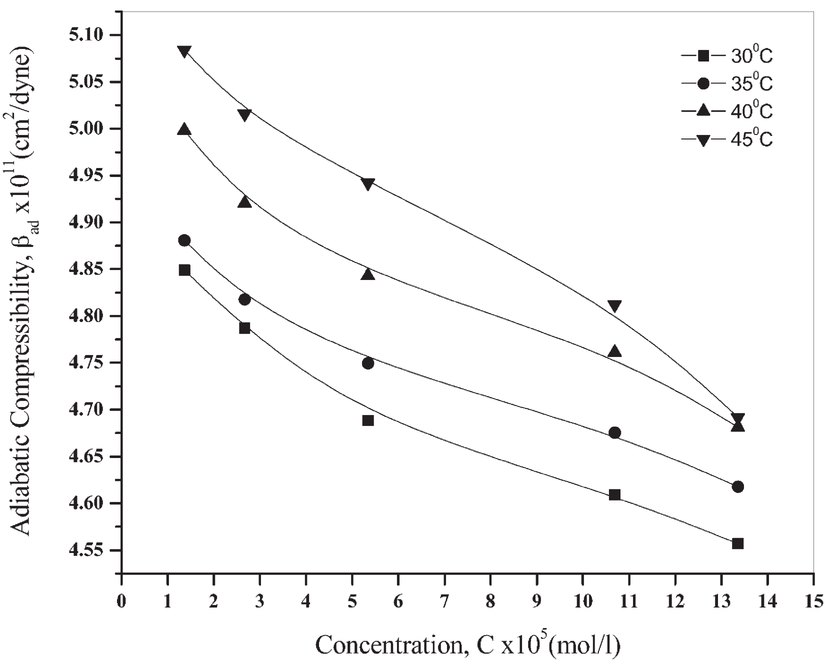

FIGURE 1 Variation of adiabatic compressibility with concentration of solutions of PVAc in DMF at different temperatures.

where ρ is the density and v is the ultrasonic velocity.

$$r = 1 - \frac{v^2}{v_o^2} \tag{5}$$

where v is the ultrasonic velocity and v_o is a constant having a value of 1600 m/s.

In the solutions used in the experiments, the number of moles of solvent and vinyl acetate is determined using the relation:

$$(N_o/N_s) = \frac{N(M/M_o)}{N_s} \tag{6}$$

where N_o is the number of vinyl acetate moles, N is the number of poly(vinyl acetate) moles, and N_s is the number of dimethylformamide moles per unit volume of solution given by:

$$N_s = C_s V_s \tag{7}$$

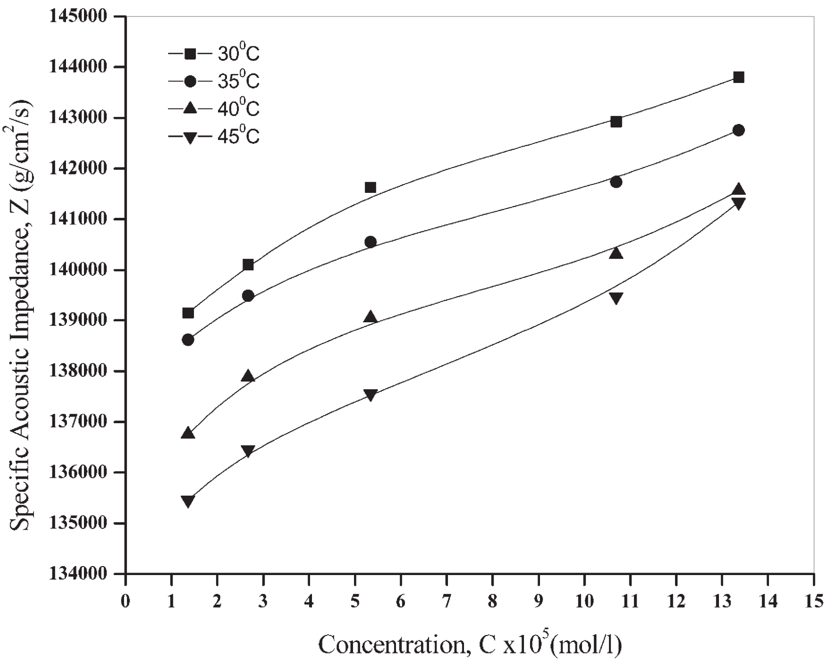

FIGURE 2 Variation of specific acoustic impedance with concentration of solutions of PVAc in DMF at different temperatures.

where C_s is the dimethylformamide molecular concentration in moles per unit volume of dimethylformamide and V_s is the volume of dimethylformamide in the solutions. Its value[13] is:

$$V_s = \frac{\rho - M\ C}{\rho_s} V \tag{8}$$

where ρ is the density of solution, ρ_s is the density of dimethylformamide, M is the molecular weight of the solute, and C is the molecular concentration in mol/L.

RESULTS AND DISCUSSION

The measured viscosity, density, velocity, and the index of refraction of poly(vinyl acetate) in dimethylformamide as functions of concentration and temperature are presented in Table I. Adiabatic compressibilities have been calculated using velocity and density data and are also presented in

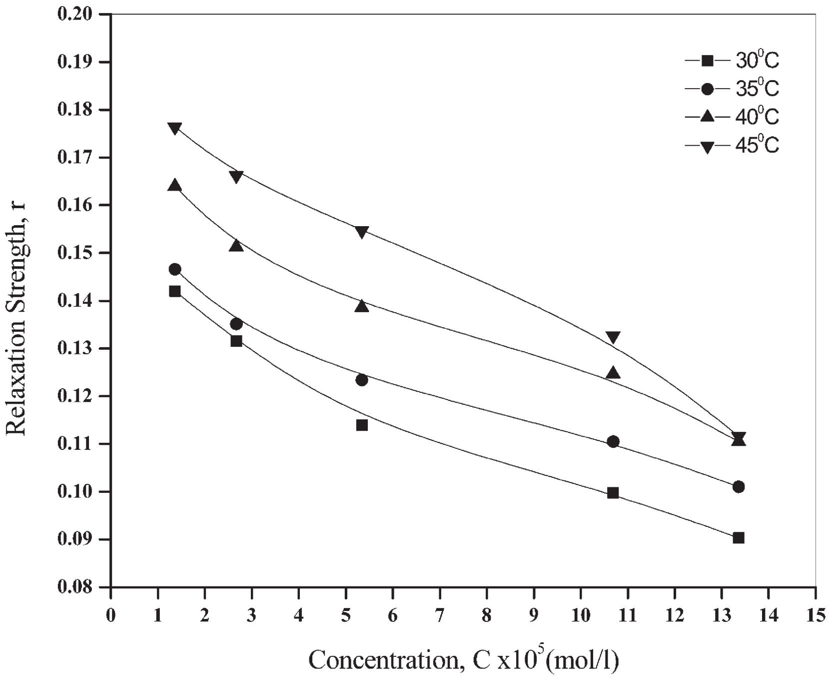

FIGURE 3 Variation of relaxation strength with concentration of solutions of PVAc in DMF at different temperatures.

the same table. Table I also contains the values of space filling factor r' calculated using Equation (3). The variation of β_{ad}, Z, and r with concentration at different temperatures is shown in Figure 1, Figure 2, and Figure 3 respectively. The variation of molecular ratio with r' and β_{ad} at different temperatures is shown in Figure 4 and Figure 5 respectively.

From the values recorded in Table I, it is clear that the ultrasonic velocity (v) in solutions of poly(vinyl acetate) in dimethylformamide gradually increases with increase in concentration and decreases with increase in temperature. This behavior is due to strengthening of intermolecular forces with increase in concentration and weakening of molecular forces with increase of temperature. The formation of molecular aggregates reduces the compressibility of the medium. This can be observed from Figure 1 where adiabatic compressibility (β_{ad}) for poly(vinyl acetate) solution in dimethyl formamide is plotted against concentration of the solution. It is also observed from the plot that there is a gradual increase of β_{ad} with increase in temperature, which is due to weakening of intermolecular forces with the supply of heat energy.

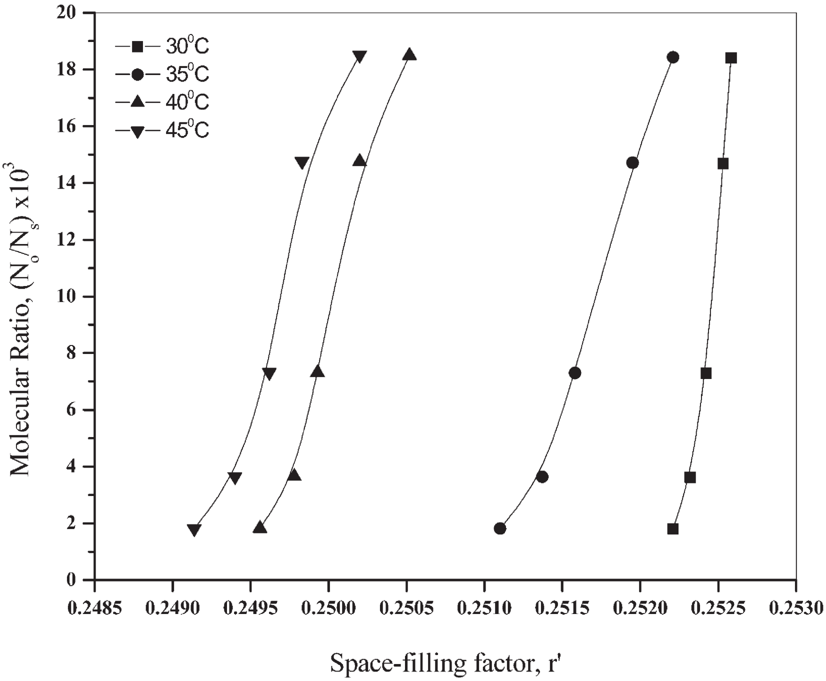

FIGURE 4 Variation of molecular ratio with space-filling factor at different temperatures for solutions of PVAc in DMF.

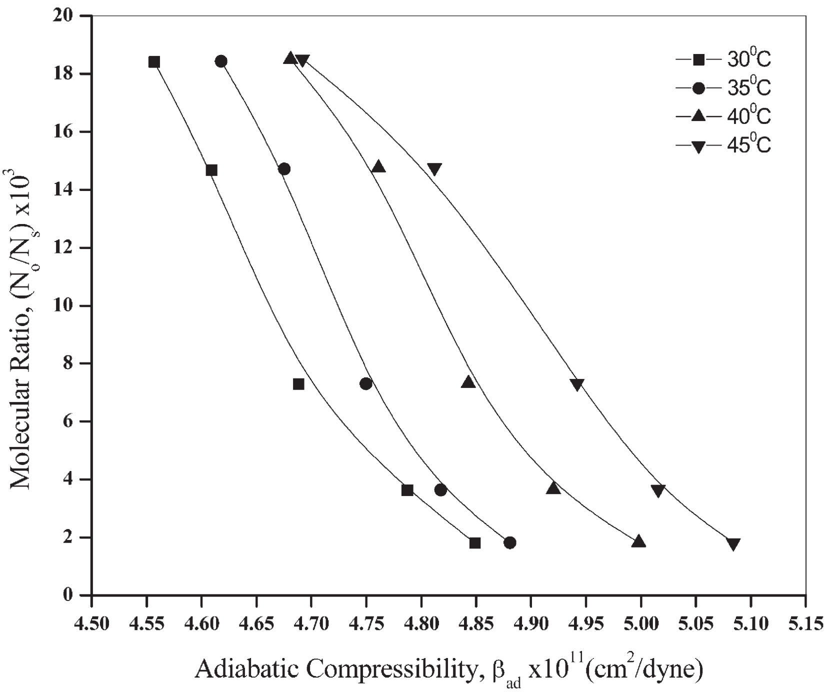

FIGURE 5 Variation of molecular ratio with adiabatic compressibility at different temperatures for solutions of PVAc in DMF.

The increase of specific acoustic impedance (Z) with concentration (Figure 2) is attributed to increase of ultrasonic velocity with concentration. Z shows a decrease with increase in temperature due to decrease in ultrasonic velocity with increase in temperature. This kind of behavior is due to association of molecules and formation of molecular aggregates[14,15]. Figure 3 shows how the relaxation strength (*r*) varies with concentration of the polymer in the solution. The relaxation strength decreases with increase in concentration at a given temperature. This may be interpreted in terms of increase in intermolecular forces due to increase in concentration and subsequent decrease in relaxation of the molecules. The increase in relaxation strength with temperature is due to the supply of thermal energy.

From Figure 4, it is evident that space-filling factor (r') at a given temperature increases with increase in the molecular ratio (N_o/N_s). Adiabatic compressibility (β_{ad}) shows a decreasing trend with increase of molecular ratio (N_o/N_s) at a given temperature (Figure 5). This is because a higher number of solute molecules in solution decreases compressibility in the medium.

In all the figures, the curves at four temperatures are nonlinear, which confirms the hypothesis of association of molecules and strong solute-solvent interactions.

REFERENCES

[1] Dunn, F., P. D. Edmundus, and W. J. Fry. (1969). *Biological Engineering*. New York: McGraw Hill.

[2] Matheson, A. J. (1971). *Molecular Acoustics*. London: Wiley Interscience.

[3] Pethric, R. A. (1973). *Macromol. Chem.* **C9**, 91.

[4] Philips, D. W. and R. A. Pethric, (1977/78). *Macromol. Sci.* **C16**, 1.

[5] Schaaffs, W. (1968). *Molecularkustik*. Berlin: Springer-Verlag.

[6] Sette, D. (1968). In *Study of Simple Liquids by Ultrasonic Methods*, ed. H. N. V. Temperley. Amsterdam: North Holland.

[7] Sette, D. (1961). In *Handbuch der Physik*, ed. S. Flugge, Vol.XI/1. Berlin: Springer-Verlag.

[8] Reddy, G. V. and R. P. Singh. (1980). *Acoustica* **46**, 342.

[9] Rajulu, A. V., S. V. Naidu, and K. C. Rao. (1984). *Acoustica* **55**, 60.

[10] Naidu, S. V., A. V. Rajulu, and K. C. Rao. (1989). *J. Polym. Mater.* **6**, 293.

[11] John, K., G. J. Reddy, and S. V. Naidu. (2003). *Int. J. Polym. Anal. Charact.* **8**, 295.

[12] Gerecze, N. G. (1977). *Acoustica* **38**, 51.

[13] Vigoureux, P. (1951). *Ultrasonics*. New York: John Wiley.

[14] Johri, G. K. and R. C. Misra. (1985). *Acoustica* **57**, 292.

[15] Rao, K. C., S. V. Naidu, and A. V. Rajulu. (1990). *Eur. Polym. J.* **26**, 657.