

Ultrasonic and Viscometric Investigations of a Poly(vinyl alcohol)–Dextran Mixture in Aqueous Solution

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Received 29 May 2002; accepted 17 September 2002

ABSTRACT: Ultrasonic spectroscopy provided a powerful, efficient, and reliable tool for a number of investigations, including those of polymer solution dynamics, molecular interaction, and the miscibility and compatibility of biopolymers in aqueous solutions. Ultrasonic velocity and related acoustic parameters were measured as a function of the concentration of poly(vinyl alcohol) (PVA), dextran, and a PVA–dextran mixture in water with the resonance method at a frequency of 3 MHz over a temperature range of 20–50°C. From the comparative results of sound velocity, density, adiabatic compressibility, acoustic impedance, and viscosity relaxation time as a function of temperature and concentration, the mode of interaction and the compatibility

and miscibility between the two biologically active macromolecules were probed and were considerable at all concentrations and temperatures because of crosslinking via hydrogen bonding involving the hydroxyl groups of both of the biomacromolecules. The interpretations of the acoustic results were confirmed by the intrinsic viscosities of the ternary systems. The significant interaction and compatibility of these biopolymers should lead to the development of pharmaceutically active molecules. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3196–3201, 2003

Key words: viscosity; compatibility; biopolymers

INTRODUCTION

In recent years, the application of ultrasonic methods for probing the structural dynamics¹ of biopolymers such as proteins and polysaccharides has been the subject of much research. Miyahara et al.² studied the ultrasonic absorption of some macromolecules, including dextran, likely to have a contribution from a coupling between the thermal motion of the polymer segments and water molecules, which changes the strength of their interaction with the polymer as a result of its motion. Only a few biologically important macromolecules have been subjected to thorough ultrasonic examination. For both hemoglobin,³ a globular protein, and dextran,^{2,4} a random coil molecule, the interaction between solvent and solute is probably the principal mechanism of acoustic absorption. Several workers have used ultrasonic velocity (U) together with density (ρ) and viscosity measurements to study polymer–solvent and polymer–polymer interactions.^{5–9} In addition, reports have recently been published on viscometric^{10,11} and differential scanning

calorimetry¹² studies on the interaction and compatibility of polymer–polymer mixtures in solution. However, published reports on compatibility and interaction studies of biomacromolecules probed by sound velocity and related acoustic parameters are rare.¹³

Water-soluble polymers such as dextran, a quasilinear uncharged, branched, bacterial mucopolysaccharide, and poly(vinyl alcohol) (PVA) have occupied a special area of investigations by researchers throughout the globe because of their versatile pharmaceutical and industrial applications. These include the preparation of many biomedical products, such as biocompatible hydrogels¹⁴ and anticoagulants¹⁵ through degradation and grafting onto these biopolymers. Because of this extensive applicability, we report in this article a comparative study of the U , related acoustic parameters, and viscosity of the pharmaceutically active biopolymers dextran and PVA and their mixture in aqueous solution; our aim in this study was to understand the polymer–polymer compatibility and their acoustic properties. Our particular interest in the acoustic properties of these substances was related both to the biomedical applications of ultrasound and to the relevance of the propagation parameters.

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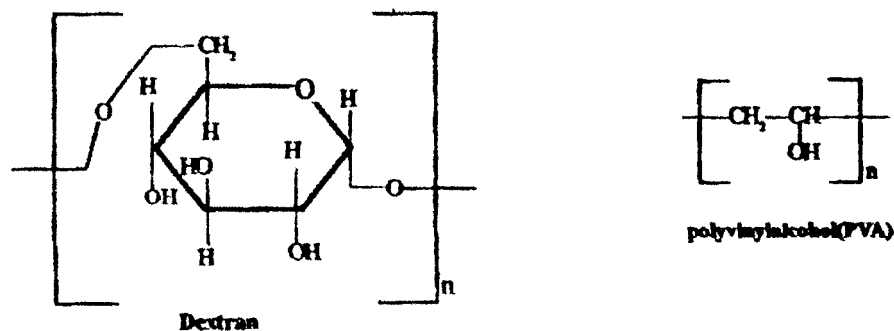
Contract grant sponsor: Royal Society of Chemistry, London.

Contract grant sponsor: Council of Scientific and Industrial Research, New Delhi, India.

EXPERIMENTAL

Materials

Dextran samples were given free of charge by the Research Center for Medical Polymers, Kyoto Univer-



Scheme 1

sity, Kyoto, Japan. PVA was a BDH (Poole, Dorset, UK) product and was used without further purification. The water used for the experiments was distilled three times over alkaline permanganate and deionized by passage through a Biodeminrolit (Permutit Co., London, UK) mixed-bed ion-exchange resin to remove any trace ions.

Instruments and theory

The molecular weight characteristics were as follows: for the dextran samples (1,6-linked polyanhydroglucose), weight-average molecular weight (M_w) = 1,61,000 and number-average molecular weight (M_n) = 74,000; for PVA, M_w = 86,000 and M_n = 65,000.

TABLE I
 ρ , $[\eta]$, U , β_s , Z , and τ Values for Dextran at Different Cs (w/v %) and Temperatures

C (w/v %)	Temperature (°C)	$\rho \times 10^{-3}$ (kg m ⁻³)	$[\eta]$ (dL/g)	U (m/s)	$\beta_s \times 10^7$ (m ⁻² s ² kg ² L)	Z (SI unit)	$\tau \times 10^7$ (min)
0.03	20	0.9976	1.1945	1475	4.60	1471.46	7.32
	25	0.9970	1.1973	1488	4.53	1483.53	7.20
	30	0.9966	1.1928	1492	4.50	1486.92	7.15
	35	0.9959	1.1919	1498	4.47	1491.85	7.10
	40	0.9953	1.1912	1506	4.43	1498.92	7.03
	45	0.9945	1.1906	1515	4.38	1506.66	6.95
0.02	50	0.9937	1.1900	1525	4.33	1515.39	6.87
	20	0.9968	1.1058	1432	4.89	1427.41	7.21
	25	0.9963	1.1052	1446	4.80	1440.65	7.07
	30	0.9958	1.1048	1452	4.76	1445.40	7.01
	35	0.9949	1.1038	1465	4.68	1457.52	6.89
	40	0.9942	1.1038	1482	4.57	1473.40	6.72
0.015	45	0.9939	1.1032	1490	4.53	1480.9	6.66
	50	0.9932	1.1028	1498	4.48	1487.81	6.58
	20	0.9978	1.0598	1445	4.79	1441.82	6.76
	25	0.9963	1.0593	1453	4.75	1447.62	6.70
	30	0.9957	1.0588	1461	4.70	1454.71	6.63
	35	0.9951	1.0578	1473	4.63	1465.78	6.53
0.01	40	0.9947	1.0578	1484	4.56	1476.13	6.42
	45	0.9939	1.0565	1495	4.50	1485.88	6.33
	50	0.9931	1.0561	1508	4.43	1497.59	6.24
	20	0.9972	1.0269	1446	4.8	1441.95	6.57
	25	0.9959	1.0264	1458	4.72	1452.02	6.46
	30	0.9956	1.0258	1470	4.65	1463.53	6.36
0.005	35	0.9951	1.0252	1477	4.60	1469.76	6.28
	40	0.9947	1.0246	1484	4.56	1476.13	6.23
	45	0.9941	1.0242	1499	4.47	1490.15	6.11
	50	0.9935	1.0235	1413	4.40	1503.16	6.00
	20	0.9951	1.00158	1501	4.46	1493.64	6.04
	25	0.9942	1.0150	1509	4.42	1500.24	5.98
0.005	30	0.9935	1.0145	1522	4.31	1512.10	5.82
	35	0.9930	1.0135	1534	4.28	1523.26	5.78
	40	0.9925	1.0128	1545	4.22	1533.41	5.70
	45	0.9921	1.0120	1554	4.17	1541.72	5.62
	50	0.9916	1.014	1562	4.13	1548.87	5.57

TABLE II
 ρ , $[\eta]$, U , β_s , Z , and τ Values for PVA at Different Cs (w/v %) and Temperatures

C (w/v %)	Temperature (°C)	$\rho \times 10^{-3}$ (kg m ⁻³)	$[\eta]$ (dL/g)	U (m/s)	$\beta_s \times 10^7$ (m ⁻² s ² kg ² L)	Z (SI unit)	$\tau \times 10^7$ (min)
0.03	20	0.9951	1.3498	1530	4.92	1522.50	7.72
	25	0.9944	1.3490	1540	4.24	1531.37	7.62
	30	0.9938	1.3482	1551	4.18	1541.38	7.51
	35	0.9932	1.3975	1562	4.12	1551.37	7.40
	40	0.9925	1.3468	1573	4.07	1561.20	7.30
	45	0.9920	1.3458	1582	4.02	1569.34	7.22
0.02	50	1.9914	1.3446	1589	3.99	1575.35	
	20	0.9972	1.2606	1518	4.35	1513.74	7.31
	25	0.9968	1.2506	1529	4.29	1524.10	7.20
	30	0.9962	1.2589	1542	4.22	1536.14	7.08
	35	0.9958	1.2580	1552	4.17	1545.48	6.99
	40	0.9951	1.2571	1563	4.11	1555.34	6.88
0.01	45	0.9937	1.2563	1588	4.06	1565.02	6.80
	50	0.9937	1.2550	1588	3.98	1577.99	6.67
	20	0.9989	1.1698	1478	4.58	1476.37	7.14
	25	0.9983	1.1690	1493	4.49	1490.46	6.998
	30	0.9979	1.1682	1504	4.43	1500.84	6.90
	35	0.9973	1.1675	1512	4.38	1507.9	6.82
0.005	40	0.9968	1.1668	1519	4.35	1514.13	6.77
	45	0.9964	1.1650	1529	4.29	1523.40	6.66
	50	0.9959	1.1646	1538	4.24	1531.69	6.58
	20	0.9998	1.0858	1448	4.77	1447.79	6.9
	25	0.9995	1.0850	1462	4.68	1461.26	6.77
	30	0.9993	1.0842	1468	4.64	1466.97	6.70
	35	0.9990	1.0836	1474	4.60	1472.52	6.64
	40	0.9988	1.0828	1482	4.56	1480.22	6.58
	45	0.9981	1.0820	1494	4.49	1491.16	6.47
	50	0.9974	1.0816	1510	4.40	1506.07	6.34

The structures of dextran and PVA are as shown in Scheme 1. U measurements were performed by an ultrasonic interferometer (Mittal Enterprises, New Delhi, India) at frequency of 3 MHz. We made the measurements by varying the concentration (C) of dextran, PVA, and their mixtures in aqueous solution at different temperatures from 20 to 50°C by circulating water from a thermostat (Mittal Enterprises) with a thermal stability of $\pm 0.05^\circ\text{C}$ through a double wall-jacket of the ultrasonic experimental cell. The intrinsic viscosity ($[\eta]$) of the component polymer solutions and their mixture was measured at 30°C with a Ubbelohde suspended level viscometer (Stuttgart, Germany). The ρ of these solutions was determined with a specific gravity bottle with a 5-mL capacity. The accuracy in the measurement of viscosity and ρ was on the order of 0.1% and $0.1 \times 10^3 \text{ g/cm}^3$, respectively. The ultrasonic acoustic parameters were calculated in these solutions in all the Cs and temperatures with the standard formulas as follows. Apparent molar volume (ϕ_v) was calculated from the ρ data by the standard procedure:¹⁶

$$\phi_v = M_2 \rho^{-1} [1 - 100(\rho - \rho_1)/C] \quad (1)$$

where M_2 is the molecular weight. The theoretical values of adiabatic compressibility (β_s) were calculated with Newton and Laplace equation:

$$\beta_s = 1/\rho U^2 \quad (2)$$

U also influenced the acoustic impedance (Z):¹⁷

$$Z = \rho \cdot U \quad (3)$$

Viscosity relaxation time (τ) was calculated by

$$\tau = 4\eta/3\rho U^2 \quad (4)$$

RESULTS AND DISCUSSION

Tables I–III show the variation of the U , ρ , viscosity, and other related parameters as a function of C at various temperatures for the solutions of dextran, PVA, and their 50:50 mixture, respectively. The U of propagation for dextran decreased and for PVA increased with increasing C ; for the 50:50 mixture of dextran and PVA, the U of propagation increased more rapidly with high solution viscosity, which may have been due to crosslinking, hydrogen bonding, and van der Waals forces¹⁸ between the molecules of PVA and dextran (Fig. 1). The abnormal behavior in the velocity of dextran at different Cs may be ascribed to 3 MHz, a frequency at which dynamic processes are known to occur for polymers.¹ The monomeric units may have hindered rotations or conformational inter-

TABLE III
 ρ , $[\eta]$, U , β_s , Z , and τ Values for Dextran-PVA at Different C_s (w/v %) and Temperatures

C (w/v %)	Temperature (°C)	$\rho \times 10^{-3}$ (kg m ⁻³)	$[\eta]$ (dL/g)	U (m/s)	$\beta_s \times 10^7$ (m ⁻² s ² kg ² L)	Z (SI unit)	$\tau \times 10^7$ (min)
0.03	20	0.9971	1.2368	1508	4.41	1503.62	7.27
	25	0.9963	1.2358	1520	4.34	1514.37	7.15
	30	0.9956	1.2348	1538	4.24	1531.23	6.98
	35	0.9952	1.2340	1547	4.20	1539.57	6.91
	40	0.9947	1.2332	1555	4.16	1546.75	6.84
	45	0.9942	1.2324	1566	4.14	1556.91	6.74
0.02	50	0.9937	1.2314	1567	4.04	1568.05	6.63
	20	0.9974	1.1498	1522	4.32	1518.04	6.62
	25	0.9969	1.1490	1532	4.27	1527.25	6.54
	30	0.9964	1.1482	1547	4.19	1541.43	6.41
	35	0.9960	1.1470	1558	4.14	1551.76	6.32
	40	0.9953	1.1462	1564	4.10	1556.64	6.26
0.015	45	0.9947	1.1450	1578	4.04	1569.63	6.16
	50	0.9942	1.1442	1589	3.97	1579.78	6.05
	20	0.9982	1.1125	1538	4.23	1535.23	6.27
	25	0.9977	1.1114	1552	4.16	1548.43	6.16
	30	0.9973	1.1108	1561	4.11	1556.78	6.08
	35	0.9968	1.1101	1568	4.08	1562.98	6.04
0.01	40	0.9963	1.1092	1576	4.04	1570.16	5.97
	45	0.9958	1.1083	1584	4.00	1584.51	5.84
	50	0.9953	1.1072	1592	3.96	1584.51	5.84
	20	0.9983	1.0865	1520	4.33	1517.41	6.27
	25	0.9977	1.0856	1528	4.29	1524.48	6.21
	30	0.9974	1.0898	1540	4.22	1535.99	6.10
0.005	35	0.9971	1.0840	1548	4.18	1543.51	6.04
	40	0.9966	1.0830	1556	4.14	1550.70	5.98
	45	0.9962	1.0822	1566	4.09	1560.04	5.90
	50	0.9956	1.0812	1576	4.04	1569.06	5.82
	20	0.9958	1.0496	1488	4.53	1481.75	6.34
	25	0.9955	1.0490	1501	4.45	1494.24	6.22
0.005	30	0.9951	1.0482	1512	4.39	1504.59	6.13
	35	0.9949	1.0472	1516	4.37	1508.26	6.10
	40	0.9944	1.0463	1522	4.34	1513.47	6.05
	45	0.9940	1.0450	1526	4.32	1516.84	6.02
	50	0.9935	1.0444	1532	4.29	1522.04	5.97

conversion that occurred at or near this frequency. The sugar rings of dextran almost certainly underwent conformational changes in this frequency range. If there were a dynamic process at this frequency, the sound velocity would show a sharp change centered at that frequency. At different C_s , the U of the mixture varied almost linearly, which indicated the compatible/miscible nature of the polymers. The results of Neel and Sebille¹⁹ also support these findings. They reported that the nature of mixing in the poly(acrylic acid)-poly(vinyl pyrrolidone) system was uncertain. In confirmation, the intrinsic viscosities of the ternary systems comprising the two biopolymers and a solvent (Fig. 2 and Tables I-III) also reflected the dynamism and compatibility/miscibility. The interaction was possibly between the hydroxyl groups.

A polymer chain assumes a variety of conformational changes under different experimental conditions. Polymer chains are more compressible because of a chain-like structure²⁰ as can be shown by a decrease in β_s with C (Fig. 3). The molecular structures of dextran and PVA led to the assumption that thermal

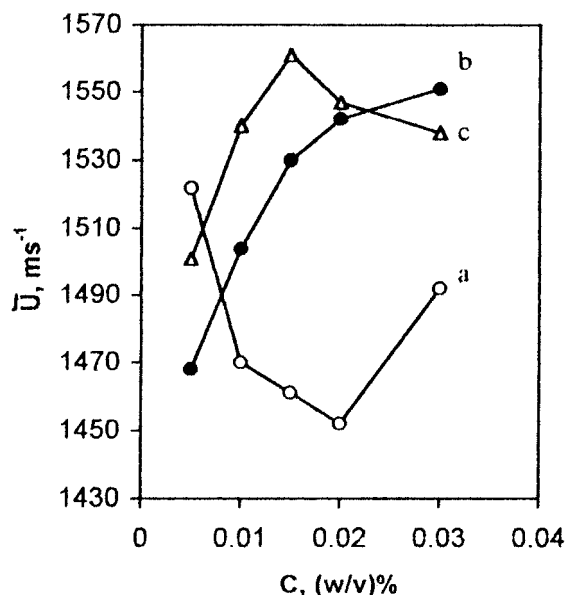


Figure 1 Variations of U with C (w/v %) in aqueous solution at 30°C for (a) dextran, (b) PVA, and (c) PVA-dextran.

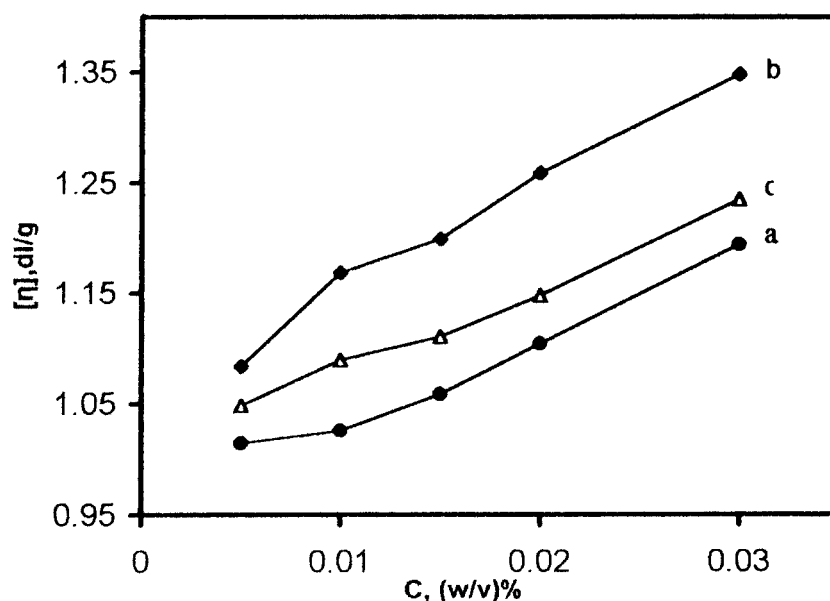


Figure 2 Variation of $[\eta]$ with C (w/v %) in aqueous solution at 30°C for (a) dextran, (b) PVA, and (c) PVA-dextran.

relaxation due to the rotation of small segments hardly occurred; it was probable that the volume relaxation process was predominant in aqueous solutions of dextran and PVA.

To understand the structural effect and molecular interactions occurring in the solutions, we derived several acoustic and thermodynamical parameters from the experimental data on ρ , $[\eta]$, and U , according to the standard equations and correlated with C . We found an excellent correlation with U , β_s , τ , and Z (Figs. 1 and 3–5). Comparing these results, we assumed that the acoustic wave perturbed the segmental motion of both the polymer chains, dextran and PVA, in such a way as to cause rearrangement of the water molecules weakly interacting with the polymer chains.

This interaction due to rearrangement gave rise to volume relaxation. This was in good agreement with the results obtained due to the ultrasonic relaxation in aqueous solutions of dextran.² The results were also explained and were in excellent agreement with the results obtained from a viscometric investigation of polymer-polymer miscibility¹⁰ and compatibility.¹¹

β_s increased with dextran C and decreased with PVA C in an almost linear manner (Fig. 3), but for the PVA-dextran mixture, it decreased linearly. In turn, the Z of dextran decreased, where the impedance of PVA increased, but the impedance increased for the PVA-dextran mixture (Fig. 4). The increasing trend of Z with C of the mixture could be interpreted on the

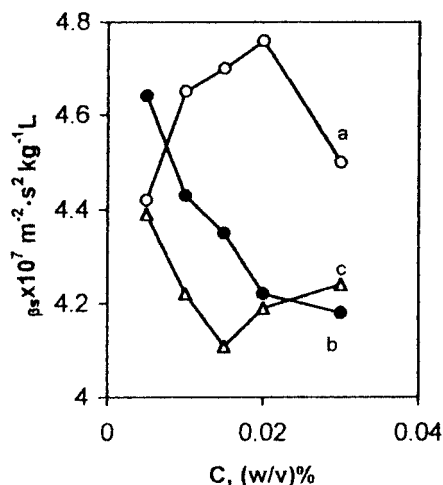


Figure 3 Variation of β with C (w/v %) in aqueous solution at 30°C for (a) dextran, (b) PVA, and (c) PVA-dextran.

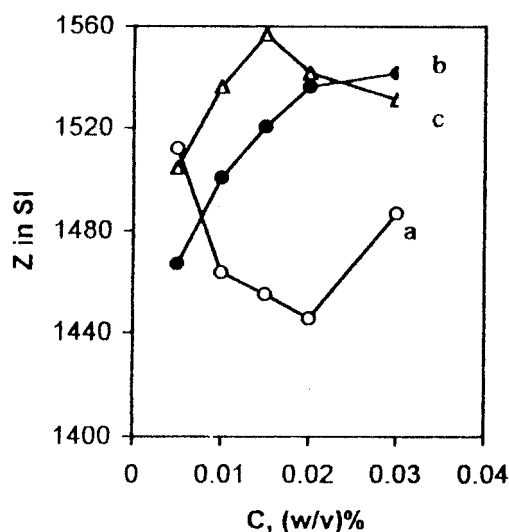


Figure 4 Variation of Z with C (w/v %) in aqueous solution at 30°C for (a) dextran, (b) PVA, and (c) PVA-dextran.

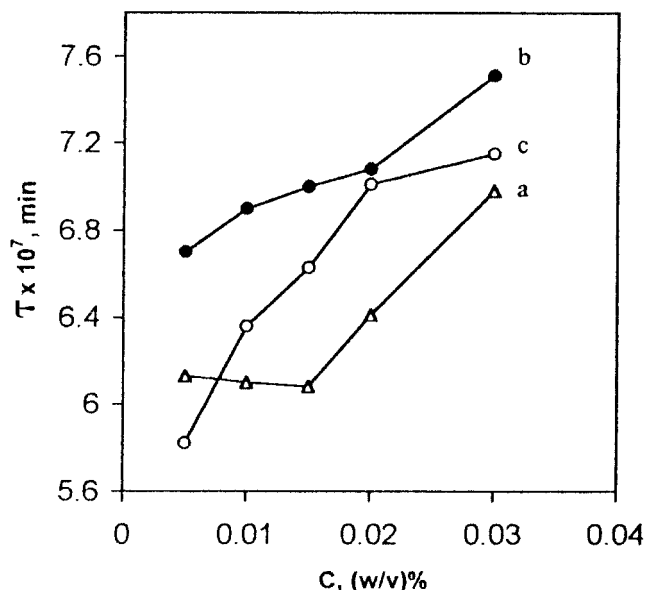


Figure 5 Variation of τ with C (w/v %) in aqueous solution at 30°C for (a) dextran, (b) PVA, and (c) PVA-dextran.

basis that most of the solvent molecules were engaged in interaction with them by crosslinking via hydrogen bonds and were compatible in almost all C ranges and temperatures.

The variation of τ with C is shown in Figure 5. It is further evident from Figure 5 that the interaction and compatibility of the polymer mixture in aqueous solution were prominent via structural changes due to entropy fluctuation.^{21,22}

The previous interpretations of the acoustic results on the interaction of the two samples were confirmed by independent $[\eta]$ measurements of the ternary systems composed of two biopolymers and water as a solvent at different C s, as shown in Tables I–III and Figure 2. The plots in Figure 2 are linear, and no crossover was found, which showed that the two biopolymers were compatible. A sharp crossover in the plots of reduced viscosity versus C is characteristics of incompatible blends.²³

CONCLUSIONS

Correlation of the ultrasonic results presented here with thermodynamic magnitudes such as the interaction parameters between the unlike polymer chains

PVA and dextran, a 1,6-linked polyanhydroglucose, showed remarkable interaction and compatibility in aqueous solution in all C s and temperature ranges in the light of polymer–solvent and polymer–polymer interactions. These most interesting and significant outcomes of this study will enable the development of pharmaceutically active molecules²⁴ from the interaction of two biopolymers and will find ample biomedical applications.

One of the authors (P.K.S.) expresses his sincere thanks to P. Balam, Molecular Biophysics Unit, Indian Institute of Science, Bangalore, India, for his fruitful suggestions and inspirations.

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