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Velocity and absorption of ultrasound in binary solutions of polyvinylpyrrolidone and water

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Ultrasonic velocity and absorption and shear viscosity measurements were made as a function of concentration and temperature for binary aqueous solutions of the polymer polyvinylpyrrolidone. The polymer has a molecular weight of 360 000 and was mixed with water in several concentrations ranging from 0% to 9% by weight. The frequency used was 21 MHz and the temperature range was 20 °C to 45 °C. The velocity shows a nonlinear increase with temperature and a nearly linear increase with concentration. The α/f^2 and viscosity values increase monotonically with concentration, and these values decrease with temperature. The temperature behavior, in a general sense, for the velocity and α/f^2 of the solution is similar to that of pure water. As the concentration increases from 0% to 9%, the viscosity increases by more than two orders of magnitude, while the α/f^2 value increases by less than one order of magnitude. No strong evidence of a critical concentration was observed.

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INTRODUCTION

The polymer polyvinylpyrrolidone has commercial use in clarifying liquids. It is, therefore, worthwhile to obtain information on how it behaves in water solutions.[1,2] This study provides values for the ultrasonic parameters, absorption and velocity, and also shear viscosity as a function of concentration and temperature. These measurements should complement measurements such as light scattering, aging, and perhaps others.

The polyvinylpyrrolidone used has an average molecular weight of 360 000 and is in the form of a fine white powder. The monomer (vinylpyrrolidone) has a chemical formula C_6H_9ON. The powder was carefully weighed, added to doubly distilled water, and then stirred for at least 20 h to insure that it was completely dissolved. After the solution was added to the ultrasonic test cell, it was allowed to reach thermal equilibrium before measurements were made. The temperature was controlled and measured to within a few hundredths of a degree centigrade. Measurements were made up to 9% concentration by weight. The solution becomes very viscous at concentrations greater than 9% and is difficult to prepare. Our measured water values for ultrasonic absorption and velocity agree well with previous literature values.[3,4] A check of the shear viscosity measurements was made by using viscosity-standard solutions provided by the manufacturer of the viscometer.

The absorption and velocity measurements were made with a Matec pulse-echo system that generates a train of ultrasonic pulses through the temperature-controlled cylindrical test cell. The test cell had a quartz crystal transmitter at one end. The other end of the cell had a reflector moved by a precision micrometer. As the reflector was moved, incident and reflected pulses interfered to show maxima. The distance between the maxima is the wavelength. Knowing the frequency driving the crystal and obtaining the sound wavelength allowed us to calculate the velocity. A pulse comparator signal was used to measure pulse amplitudes and, hence, the absorption. A frequency of 21 MHz was used for all of the ultrasonic measurements. Care was taken to align the metal reflector of the sound pulses in the liquid test cell, and the reflection loss was accounted for. Diffraction was not a problem at this frequency. The shear viscosity was measured with an error of less than 4% using a Brookfield model LVTD rotating-cylinder viscometer.

Light scattering (Tyndall effect) was observed for all concentrations. In addition, the Weissenberg effect, where the solution climbs up a rotating smooth rod, was observed. This effect is a characteristic of a polymeric fluid.[5] There appeared to the eye to be little or no settling of the solutions over a period of several weeks, indicating that the solutions were quite stable to settling out of the polymer. At higher concentrations—7% and 9%—some yellowing was seen in the solutions.

TABLE I. Ultrasonic velocity with temperature and concentration in polyvinylpyrrolidone–water solutions. The units are meter/second.

Temp (°C)	Concentration by weight 0%	1%	3%	5%	7%	9%
20°	1482	1489	1498	1508	1517	1529
25°	1495	1503	1511	1521	1530	1540
30°	1508	1515	1522	1531	1542	1551
35°	1518	1524	1533	1541	1550	1558
40°	1528	1535	1540	1548	1557	1566
45°	1535	1541	1548	1555	1564	1572

TABLE II. The α/f^2 for polyvinylpyrrolidone and water for different temperatures and concentrations. The units are 10^{-17} s^2/cm.

Temp (°C)	Concentration by weight 0%	1%	2%	3%	5%	7%	9%
20°	26	37	43	49	55	66	82
25°	24	32	37	43	51	59	74
30°	21	29	33	37	45	55	66
35°	19	27	30	32	42	50	62
40°	17	23	26	29	39	46	59
45°	14	20	23	26	35	43	55

TABLE III. Shear viscosity in centipoise for different temperatures and concentrations of polyvinylpyrrolidone and water.

Temp (°C)	Concentration by weight 1%	2%	3%	4%	5%	7%	9%
20°	5.3	13.2	24.0	47.0	86.3	223	504
25°	4.9	12.2	22.5	41.2	78.1	210	472
30°	4.4	10.8	20.6	36.8	72.0	187	415
35°	3.9	10.2	18.2	34.3	67.3	157	352
40°	3.5	8.8	17.2	31.2	61.6	136	307
45°	3.1	8.5	15.4	28.6	55.0	125	274

I. VELOCITY MEASUREMENTS

Table I presents the measured values of the ultrasonic velocity at 21 MHz as a function of temperature and concentration. The error in the velocity measurement is less than two-tenths of a percent. Each table value represents the average of at least four individual measurements. It is seen that there is a nonlinear increase in velocity with temperature similar to that of pure water. There is also a nearly linear increase in velocity with concentration. Measurements of the solution density with concentration at 23 °C show a monotonic increase of density with concentration. Since the velocity increases with concentration and the density does also, compressibility must decrease with concentration. This indicates, perhaps, that the molecules are forming a more tightly bound system.

II. ABSORPTION MEASUREMENTS

The results of the ultrasonic absorption measurements are presented in Table II. Each value is the average of at least four individual measurements. The error for repeatability for the values is 5% or less, except for one or two data points. It is seen, in general, that α/f^2 increases nonlinearly with concentration and decreases nonlinearly with temperature. The temperature behavior of α/f^2 of the solution is generally similar to that for water.

III. VISCOSITY MEASUREMENTS

In Table III are shown the measured values for the shear viscosity as a function of temperature and concentration. Each value represents the average of three measurements. The viscosity increases nonlinearly by more than two orders of magnitude at each temperature as the concentration goes from 0% to 9%. The viscosity also decreases at each concentration as the temperature increases.

While, as the concentration increases from 0% to 9%, the viscosity increases by more than two orders of magnitude, the α/f^2 value change is much smaller—less than a factor of 10. This may mean that, although the viscosity shows the presence of the large polymer molecules with a molecular weight of 360 000, the sound absorption does not, to the same degree, since the large molecules have too much inertia to follow the rapid sound oscillations at 21 MHz. This effect has been reported previously.[6,7] The increase in viscosity may be due, in part, to the attachment by hydrogen bonding of water molecules to the oxygen sites on the pyrrolidone rings. This mechanism can lead to solvation sheaths and increase the size of the molecule and also the viscosity. By this process of solvation the effective concentration of the polymer increases due to the removal from the solvent of free water molecules.

Neither the ultrasonic measurements nor shear viscosity seem to give significant evidence of a critical concentration.

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