

ULTRASONIC PROPAGATION IN AQUEOUS SOLUTION OF POLYVINYL ACETATE IN VARIOUS CONCENTRATIONS AT DIFFERENT TEMPERATURES

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For a polymer solution in the liquid phase, when the high intensity ultrasonic waves are passed over a certain range of temperatures and at atmospheric pressure, the thermodynamic parameters of such polymer can be evaluated by measuring ultrasonic velocity, compressibility and the density (Nozdrev 1974). In binary liquid mixture, the nonlinear variation in ultrasonic velocity with concentration have been frequently observed in many mixtures (Khan 1991; Pandey and Dubey 1994).

Polyvinyl acetate is a water soluble, nonionic polymer with a variety of industrial applications, mostly used as adhesive (Khan1991). Many investigators have studied solute solvent interactions in such non-electrolytic solution from the point of view of ultrasonic and volumetric behavior (Chenoweth and Schneider 1951; Litovitz 1959). In binary liquid mixtures, the nonlinear variations in ultrasonic velocity with concentration have been observed in Glycol + water mixtures (Ahmed *et al* 2000) but the samples were showing concentration dependent behavior in velocity and compressibility (Padmini 1963).

In doing so we assume that the size of the suspended particles is small as compared to the wavelength of sound. Here in PVAc samples, when the sound waves of high frequencies are passed, multiple scattering of the waves occurs, the ultrasonic velocity in such emulsion is affected due to its particle size and volume fraction. The sample was homogeneously polymerised to a degree of 300-400, had a high molecular weight after hydrolysis. This is an emulsion-based solution. By the scattering of the ultrasonic waves the heat energy is produced. Some of the parameters can be calculated by formulae of Wood (1941).

Calculations

The ultrasonic velocity u , velocity dependent adiabatic compressibility β_s and the apparent molar compressibility ϕ_k ,

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acoustic impedance Z and the relative association R_A these parameters can be calculated by;

$$\text{The ultrasonic velocity } u = v \cdot \lambda \dots\dots\dots(1)$$

Where, v and λ are the frequency and the wavelength of the waves. Adiabatic compressibility in a solution,

$$\beta_s = 1/u\rho^2 \dots\dots\dots(2)$$

where, ρ is the density of the solution, u is the ultrasonic velocity in the solution, equations (1) and (2) are the basic formulae derived by Wood (1941).

Specific acoustic impedance Z can be calculated by (3)

$$Z = u \cdot \rho \dots\dots\dots(3)$$

The relative association between solute and solvent molecules.

$$R_A = \rho/\rho_o(u/u_o) \dots\dots\dots(4)$$

where, u_o is the ultrasonic velocity in solvent, u is the ultrasonic velocity in the solution. The Apparent molar compressibility ϕ_k :

$$\phi_k = \frac{(\rho_o\beta - \rho\beta_{ad}^o)1000/\rho}{C\rho_o} + \beta_{ad} M_2/\rho_o \dots\dots\dots(5)$$

Where, C is the concentration, ρ is the density of the solution, ρ_o is the density of the solvent, β_{ad}^o is the adiabatic compressibility of the solution, PVAc. M_2 is the molecular weight of the solute and β_{ad} is the adiabatic compressibility of the solvent.

Interferometer technique. The wavelength of the sound waves was determined by observing the distance travel by the reflector between the number of successive minima of driving current of transducer upto 0.25mm, which repeats itself as the phase of the wave, by a multiple of $\lambda/2$. The wavelength of sound in liquid is determined by this technique. The interferometer was thermostated so that during the measurement, the temperature of the sample was kept at $\pm 0.5K$. The density of the polymer solution is determined as a function of concentration by Pycnometer at 303.15K and 313.15K. (The PVAc original sample has a molecular weight 68800).

Within certain limits the ultrasonic velocity, density and adiabatic compressibility, in aqueous PVAc have been measured at three temperatures, via 303.15K, 313.15K and 323.15K. The following results were obtained, which are in accordance with the previous workers. (McClements and Povey 1989; Maffezzoli *et al* 1998).

Some salient features of this experimental work. 1. The viscosity and the density of such high polymer solution was found to increase linearly with concentration which is in accordance with literature (Morse and Lingard 1982).

Table 1

Characteristic values of some measured acoustical parameters in aqueous solution of polyvinyl acetate (Emulsion based) of different concentrations (by weight at 303.15K)

S.no.	Conc. g/100ml	Density kg/m ³	U. velocity m/sec	Adiabatic compressi- bility $\beta_{ad} \times 10^{-10}$	Acoustic impedance Z=uxp Ω/m	Relative association R_A
1	22	1002.21	1508.25	4.5723	1511583.2	0.9199
2	33	1007.18	1499.5	4.7386	1510266.4	0.9228
3	44	1009.33	1488.66	4.7751	1515766.2	0.9432
4	55	1012.80	1467.11	4.8938	1465521.6	0.9314
5	66	1019.35	1464.77	4.9799	1498210.6	0.9654

Table 2

Characteristic values of some measured acoustical parameters in aqueous solution of polyvinyl acetate (Emulsion based) of different concentration (by weight at 313.15K) at atmospheric pressure

S.no.	Conc. g/100ml	Density kg/m ³	U. velocity m/sec	Adiabatic compressi- bility $\beta_{ad} \times 10^{-10}$	Acoustic impedance Z=uxp Ω/m	Relative association R_A
1	22	1022.54	1538.55	4.77	1552167.75	0.9010
2	33	1033.62	1535.77	4.898	1556321.44	0.9107
3	44	1054.15	1514.35	4.900	1596352.53	0.9107
4	55	1067.00	1508.77	5.213	1609857.59	0.9233
5	66	1073.33	1497.15	5.493	1615918.91	0.9346

Table 3

Characteristic values of some measured acoustical parameters in aqueous solution of polyvinyl acetate (Emulsion based) of different concentration (by weight at 323.15K) at atmospheric pressure

S.no.	Conc. g/100ml	Density kg/m ³	U. velocity m/sec	Adiabatic compressi- bility $\beta_{ad} \times 10^{-10}$	Acoustic impedance Z=uxp Ω/m	Relative association R_A
1	22	1081.10	1512.33	4.455	1638004.75	0.8988
2	33	1093.62	1505.77	4.898	1556393.98	0.9069
3	44	1094.15	1494.25	4.900	1596352.53	0.9107
4	55	1097.00	1488.25	5.059	1587962.75	0.9129
5	66	1099.33	1469.77	5.293	1605012.50	0.9227

- The adiabatic compressibility of particle based solution depends upon density as well as the velocity of both suspension of particles and on suspended liquid.
- The variation of ultrasonic velocity in a solution depends upon intermolecular free length on mixing, which is on the basis of the model proposed by Eyring and Kincaid (1958), for sound waves propagation. It explains the reasons for decrease in velocity at a particular temperature.
- R_A increases with concentration suggesting that solution of acetate ions predominate over the breaking up of solvent aggregate for OH-OH- interaction.
- The adiabatic compressibility of the system in solution increases with concentration. β_s will contain a small dispersive contribution which is associated with the relaxation process of monomers.
- It is observed that when sound waves are passed through

an emulsion based solution, the particles of the medium oscillate and experience a complex drag force on them, which is the sum of the viscous part due to relaxation process and the inertial part, that contribute to a part of compressibility. The inertial part is proportional to acceleration of the large molecules (monomers) dv/dt , that is the velocity contribution hence the compressibility β , is a complex quantity.

7. The behavior observed in the present study is perhaps due to the strong interaction for making a long chain structure which consequently increases viscosity.
8. Generally it is observed that the acoustic impedance Z rises with the increase in compressibility (Nikam *et al* 1994).
9. The amount of heat is produced into the emulsion $\sim \rho V s dT/dt$, density, volume, specific heat and the temperature gradient.
Where, ρ is density of emulsion, s , specific heat, dT/dt temperature gradient in volume with time.
10. The ultrasonic velocity in solute is higher therefore, the compressibility is lower.

Key words: Emulsion, Ultrasonic Velocity, Compressibility, Viscosity.

References

- Ahmed S S, Naseer A, Naqvi S S H, Shaikh G H 2000 Ultrasonic studies of some glycol solutions and their mixtures with water. *Pak J Sci Ind Res* **43**(6) 329-333.
- Chenoweth A G, Schneider WG 1951 Ultrasonic propagation in binary liquid system near their critical solution temperature. *J Chem Phys* **12**(19) 1566-1569.
- Eyring H, Kincaid J F 1958 A model for the ultrasonic velocity in a solution. *J Chem Phys* **6** 620-627.
- Khan MB 1991 Polymer adhesives. *J European Coating* **12** 886-889.
- Litovitz T A 1959 Ultrasonic spectroscopy in liquids *J Acoustical Soc. Am.* **6** (31) 81-91.
- Maffezzoli A, Luprano A M, Montagna G, Nicolais L 1998 Ultrasonic characterization in 2-hydroxyethyl methacrylate hydro gel. *J App Polymer Science* **67**(5) 823-831.
- McClements D J, Povey M J 1989 Scattering of ultrasound by emulsion. *J Phy D App Phy* **22** 38-47.
- Melis S, Kemmere M, Meuldyik J, Storti G, Morbedelli M 2000 A model for coagulation of polyvinyl particles in emulsion. *Chemical Engineering Science* **55** 3101-3111.
- Morse P M, Lingard KU 1982 *Theoretical Acoustic*. McGraw Hill, New York, USA, Polymers, 3rd ed pp 163-169.
- Nikam P S, Nikam N, Hasan M, Suryawanshi R S 1994 Acoustical properties of monochloro acetic acid-acetone water system at different temperatures. *Asian J Chem* **6** 237-245.
- Nozdrev V F 1963 *Application of Ultrasound in Molecular Physic*. Gordon & Breach Publisher, New York, USA pp 37-41.
- Padmini P R K L 1963 Study of ultrasonic velocity in high polymer solutions. *Ind J Pure and Applied Physics* **1**(1) 66-69.
- Pandey J D, Dubey J P 1994 A comparative study of the isothermal compressibility from ultrasonic velocity and Flory's statistical theory for various binary mixtures. *Acoustica* **80** 92-96.
- Wood A B 1941 *A Textbook of Sound*. Bell Publisher, London, UK pp 361-364.