Physical Sciences

ULTRASONIC STUDIES OF GLYCOL SOLUTIONS AND THEIR MIXTURES WITH WATER

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Concentration dependence of the adiabatic compressibility and velocity in aqueous solutions of various concentrations of glycols atmospheric pressure have been studied using the ultrasonic interferometric technique, the measurements have been performed at 2 MHz, in the temperature range 25 to 40°C. The adiabatic compressibility has been evaluated from the collected data. The dependence of compressibility and sound velocity on the concentration at adiabatic conditions have been evaluated with average density at four different temperatures. The molecular interaction has also been evaluated from the data collected, using its excess value to determine their thermodynamic properties. It reveals that the change in velocity is maximum in one of the three glycol solutions and compressibility is minimum at a particular concentration.

Key words: Glycol solution, Ultrasonic velocity, Adiabatic compressibility.

Introduction

The ultrasonic measuring technique given by Klein and Hershberger 1931 provides a method for investigation of propagation of sound waves, frequency dependence of shear and compressional processes occurring in the liquids. This technique can be used over a wide range of temperature and pressures. On comparing the results of such aqueous solutions of different concentration, the deviation from rectilinear propagation of velocity and compressibility can be explained.

Darbari (1970) has calculated the effects of Van der Waal's forces in liquids and their effects on the speed of sound waves (Lagamnn *et al* 1947; Smith and Lawson 1954) noted a general decrease of ultrasonic velocity with the increase in molecular weight. Pandey and Dubey *et al* (1994a) have calculated these parameters and plotted them against concentration. Pandey *et al* (1994b) have also calculated isothermal compressibility of various binary mixtures and made a comparative study with significant structure theory and Flory's Patterson theory (1965). Despande and Bhatgadde (1968) have explained the deviation from a rectilinear propagation of waves due to the difference in the size of the molecules and the strength of interaction between them. Kulghadi *et al* (1996) have calculated the apparent molal compressibility of alcohal in aqueous solutions. Bowen (1969) reported the change in velocity with the passage of high frequency ultrasonic waves in concentrated solutions. His analysis has revealed an evidence for the structural change. Bowen *et al* (1962) have compared the increase in adiabatic compressibility with the difference in boiling points of solute and solvent. Wojciech (1996) calculated the speed of sound, density and adiabatic

compressibility in pyridin-heavy water solution. Moelwyn and low (1962) determined the heat capacities of mixtures in the liquid state.

In the reported work the sound velocity and density are measured for three glycol solutions at in the temperature range of 25-40°C. Here the values of ultrasonic velocity 'u' and diabatic compressibility βs have been obtained by using the following equations (Flory 1965; Gavish *et al* 1983).

$$\beta s = 1/V \, (\delta V/\delta p)s \dots\dots\dots\dots\dots\dots (1)$$
$$= 1/d \, (u)^2 \dots\dots\dots\dots\dots\dots\dots (2)$$

where V, p and s denote the volume, pressure and adiabatic conditions. In eq. 2, 'd' and 'u' denote the density and ultrasonic velocity.

Experimental

In this work with the ultrasonic (US) wave generator, the stationary waves have been generated by a source which also detects the nodal and antinodal planes of the system. For this purpose an oscillating magnetorestrictive-transducer was used. By moving the variable capacitor in the tank circuit of the generator the sound waves of variable frequency are generated from one face of the transducer and are sent into the liquid to a movable piston or reflector. It is plane parallel to the radiating face which detects the node of the sound waves, reflected from the piston. As the micrometer is moved through a series of nodal planes, the periodic maxima and minima are indicated on a current meter, suitably connected to the plate circuit. The distance travelled between the two current maxima, equal the US wavelength, is measured with the micrometer, (Klein and Hershberger 1931; Knight 1962).

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Here the US wave generator (Scholler, Germany) produces a range of frequencies between 0.3-5MHz. These frequencies were measured with a frequency counter (FC-754A, TRIO, Japan), used as frequency monitor. The generator shown in Fig 1 consists of magnetorestrictive transducer under a sample holder, excited by an oscillator.

In the proposed work, the US waves of 2MHz were used to determine the US velocity, in a solution. Four temperatures, i.e. 25, 30, 35, and 40°C, were obtained by exciting magnetorestrictive transducer. The measuring cell was a specially designed double walled brass cell for maintaining constant temperature. The least count of attached micrometer was 0.001mm. The temperature of the glycol solution was kept constant by circulating water within±0.5°C.

The cell was filled with aqueous glycol solution of known concentration. The solution was allowed to maintain a constant temperature within ±0.1°C for about 30 min before taking a reading. Each observation was repeated three times for each sample. About twenty wavelengths were generally passed through and a mean value of the wavelength was obtained. The obtained velocities were about 0.1% accurate.

The adiabatic compressibility was calculated by equation (2) and was accurate within ±0.2%. The liquid used were of Analar grade (Koch Tight light laboratories, France) which was further purified by Weissberger method. Densities were measured by relative density bottle with an accuracy of ± 1%. The tolerance agreed closely with the values of Knight (1962) and Weissbeger (1959), at different temperatures. The maximum uncertainity in the velocity measurement was ±0.5%. The observed US velocities were found close to the already reported values, in pure liquids; the measured values of densities were accurate to 100ppm. The maximum error in the adiabatic compressibility was ± 0.5%. The possible error in the concentration (mole fraction %) was ± 0.1%.

The apparatus was calibrated, in the beginning, by measuring the sound velocity in pure water at different temperatures; the values of sound velocities agreed to within ± 0.5 m sec^{-1} as referred by Knight (1962).

Results and Discussion

Ethylene glycol water mixture. (a) The results in Table 1 indicate that the ultrasonic velocity in ethylene glycol solution (i) increases with the rise in temperature and is in agreement with the results obtained by Knight (1962) (ii) β_s is minimum between conc. of 20-30% mole fraction at each temperature and (iii) velocity is high at high concentration of ethylene glycol in water. Between a concentration of 20-30%
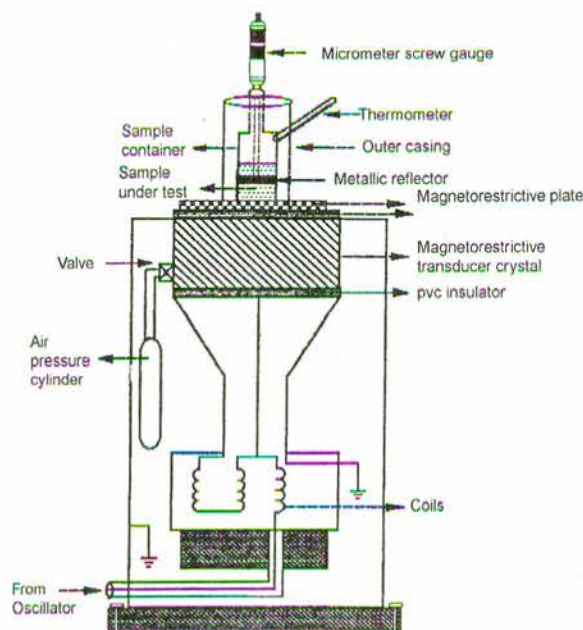

Fig 1. Ultrasonic interferometric system used for the velocity measurements.

Table 1
Measured values for the solutions of ethylene glycol in water at 25-40 °C of different concentrations in mole fraction %.

S. No	Concentration mole fraction %	Average density kg m^{-3} (d)	Velocity m sec^{-1} (μ)	Compressibility βs x 10^{-10} atom^{-1} (p)
At 25 °C				
1	0	1177.4	1260	5.31
2	10		1320	4.87
3	20		1400	4.33
4	30		1360	4.59
5	40		1325	4.48
6	50		1280	5.18
At 30 °C				
1	0	1114.8	1500	3.98
2	10		1520	3.88
3	20		1585	3.57
4	30		1490	4.05
5	40		1470	4.15
6	50		1415	4.48
At 35 °C				
1	0	1090.0	1580	3.67
2	10		1668	3.29
3	20 .		1650	3.37
4	30		1590	3.63
5	40		1555	4.02
6	50		1510	3.79
At 40°C				
1	0	1114.0	1680	3.18
2	10		1800	2.77
3	20		1805	2.75
4	30		1700	3.11
5	40		1665	3.24
6	50		1612	3.34

μ, velocity; d, density; p, compressibility.

mole fraction the velocity goes high. The average value of density has been calculated at a particular temperature for the range of concentration. (b) In the ethylene glycol water mixture, the adiabatic compressibility 'β_s' decreases with increasing temperature at all concentration in % mole fraction. (c) It is observed that the initial negative slope $d\beta_s\,dm^{-1}$ in all three solutions with the water represents on set of the solute molecules entering in the natural cavities and there by imparting some protection to the water structure H H. (d)

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The maximum values of compressibility β_s shifts towards the low temperature and high concentration, with the increase in chain length.

Diethylene glycol water mixture. (a) As the values of ultrasonic velocity u, the average values of density are tabu-

lated in Table 2 against the concentration 'm' with a difference of ten at four different temperatures. The Table shows that the velocity increases with the increase in concentration 'm' and rise in temperature this increase shifts towards higher temperatures. (b) The Table 2 also indicate that (i) at 25°C, the value of compressibility β_s against concentration 'm', first decreases gradually at all concentration this is the main difference with ethylene glycol. Here the maximum value of velocity is 1650m sec^{-1} at higher concentration and at upper value of temperature.

Propylene glycol water solution. Table 3 indicates that the trend of increasing velocity with increasing temperature and concentration is also maintained here. The maximum value of ultrasonic velocity is 1515 m sec^{-1} at 40°C with the highest mole fraction of 20%. As the concentration increases the

Table 2
Measured values of the solutions of ethylene glycol in water at 25-40 °C of different concentrations in mole fraction %.

S. No	Concentration mole fraction %	Average density kg m^{-3} (d)	Velocity m sec^{-1} (μ)	Compressibility β_s x 10^{-10} atom^{-1} (p)
At 25 °C				
1	0	1105.2	1275	5.56
2	10		1325	5.15
3	20		1375	5.78
4	30		1390	4.68
5	40		1408	4.56
6	50		1440	4.36
At 30 °C				
1	0	1071.5	1370	4.79
2	10		1395	4.79
3	20		1445	4.46
4	30		1490	4.20
5	40		1480	4.26
6	50		1505	4.12
At 35 °C				
1	0	1052.7	1450	4.52
2	10		1500	4.22
3	20		1525	4.08
4	30		1565	3.88
5	40		1571	3.85
6	50		1580	3.80
At 40°C				
1	0	996.5	1520	4.34
2	10		1580	4.02
3	20		1625	3.80
4	30		1622	3.81
5	40		1650	3.68

μ, sound velocity; d, density; p, compressibility.

Table 3
Measured values of the solutions of ethylene glycol in water at 25-40 °C of different concentrations in mole fraction %.

S. No	Concentration mole fraction %	Average density kg m^{-3} (d)	Velocity m sec^{-1} (μ)	Compressibility β_s x 10^{-10} atom^{-1} (p)
At 25 °C				
1	0	1031.7	1395.0	4.98
2	10		1420.0	4.80
3	20		1435.0	4.71
4	30		1362.0	5.22
5	40		1340.0	5.39
6	50		1122.0	5.54
At 30 °C				
1	0	1053.4	1415	4.74
2	10		1410	4.77
3	20		1428	4.65
4	30		1440	4.58
5	40		1355	5.17
6	50		1330	5.36
At 35 °C				
1	0	1026.7	1430	4.76
2	10		1435	4.73
3	20		1460	4.57
4	30		1435	4.75
5	40		1425	4.79
6	50		1395	5.00
At 40°C				
1	0	987.8	1440	4.88
2	10		1450	4.81
3	20		1515	4.41
4	30		1410	4.05
5	40		1440	4.88
6	50		1435	4.91

μ, sound velocity; d, density; p, compressibility.

velocity decreases upto 30% mole fraction whereas it increases for higher values of mole fraction. The velocity increases with the increase in temperature.

The above results also show that (i) there is a consistent trend of decrease in velocity with increase in molecular weight and (ii) there is minimum compressibility at low concentration in water in one of the three mixtures. Since the density of the liquid mixture decreases with the increase in temperature, in propylene glycol mixture, the ultrasonic velocity will also decrease with the increase in temperature. The temperature co-efficient of velocity $\Delta\mu/\Delta t$ is always negative, except for such mixture where the situation is complicated.

Conclusion

In all the three glycol mixtures, the behaviour of ultrasonic velocity with concentration have been studied. It is found to be different in ethylene glycol water mixture. It is minimum at a concentration of 20-30% mole fraction then increases with the increase of concentration. This is in agreement with the results obtained by Kulgadi *et al* (1996) and Knight (1962). The average value of density has been taken at these temperatures to calculate the adiabatic compressibility in diethylene glycol which decreases with the increase in concentration and temperature.

In propylene glycol the ultrasonic velocity is maximum between 20-30% concentration of P.G. βs increases with the increase in concentration at one temperature, it is significant in the solution of higher molecular weight, i.e. propylene glycol solution. The ultrasonic velocity 'u' for each glycol solution goes through maximum when it is observed with the maximum change in each concentration 'm' and shifts towards higher values with the rise in temperatures, especially in diethylene glycol. The value of β is maximum in the beginning them it drops. The minimum shifts towards concentration 20-30% mole fraction due to increase in chain length.

From the above measurements it is noted that the density of the three glycol-water solutions decreases with the increase in temperature. The velocity increases linearly if the solution becomes more concentrated. This is observed in diethylene glycol solution in water. The greatest fractional change observed with the magnetorestrictive transducer is about 15%.

The data have also been evaluated for the assessment of molecular interaction through its excess value and to determine their thermodynamic properties. Minimum value of compressibility is $3.11 \times 10^{-10} a^{-1}$ for ethylene glycol water mixture, and maximum value of velocities 1805 m sec^{-1} with a maximum

value of density of 1177.47 kg m^{-3} for ethylene glycol at 25°C. This is related with the structural changes caused by increasing bond length with the addition of water molecules.

With the increase in chain length like in propylene glycol the velocity becomes high and the compressibility becomes less as compared to ethylene glycol. This is expected because as the chain length increases the contribution to the interaction of polar OH group with the water molecules remains the same but the size of hydrophobic moiety becomes large and the interaction between the groups themselves leads to the hydrophobic hydration. This results in the loss of compressibility β_s of propylene glyco-water mixture.

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