

Apparent Molal Volumes & Apparent Molal Compressibilities of Some Carbohydrates in Dilute Aqueous Solutions at Different Temperatures

M V KAULGUD* & S S DHONDGE

Department of Chemistry, Nagpur University Campus, Nagpur 440 010

Received 9 December 1986; revised and accepted 23 April 1987

Apparent molal volumes (ϕ_v) and apparent molal compressibilities (ϕ_k) of some monosaccharides, disaccharides and methyl pyranosides in dilute aqueous solutions are reported at 5°, 15° and 25°C. The results are discussed in the light of solute-solvent interactions. The results suggest that the OH groups in D-glucose, D-fructose, sucrose, α -methyl and β -methyl glucosides interact with water in the manner similar to that of normal alcohols whereas galactose and lactose behave differently. Also the strength of stabilization of water structure in the case of galactose and lactose is more than that of other compounds. On the basis of results of ϕ_v^0 , $d\phi_k^0/dT$ and viscosity B -coefficients, a cooperative hydration model is proposed for the hydration of lactose and galactose.

Carbohydrates play an important role in animal and plant life. Understanding the behaviour of these in dilute aqueous solutions is of utmost importance in biology and medicine. This behaviour can be understood, among others, by measuring thermodynamic properties in dilute solutions, like limiting apparent molal volumes, adiabatic compressibilities, specific heats etc. It is known^{1,2} that the hydration of carbohydrates depends upon the percentage of axial and equatorial hydroxyl groups and it is more favourable when the hydroxyl group is at equatorial position. Lot of work has been done on such properties, albeit in the higher concentration range³⁻⁷. The extrapolated limiting parameters obtained from such measurements are not always reliable. Franks and coworkers⁸ were the first to study the thermodynamic properties of several carbohydrates like ribose, galactose, glucose, methyl pyranosides etc. and cyclic ethers at 5° and 25°C in low concentration region. Their density data (obtained by magnetic float method) were very accurate but sound velocity data measured by conventional interferometer (± 0.3 m/s) were not reliable so as to enable extrapolations to give true limiting apparent molal compressibilities. The aim of the present study is to measure the densities and sound velocities of glucose, fructose, galactose, sucrose, lactose, α -methyl glucoside and β methyl glucoside in dilute aqueous solutions to obtain limiting apparent molal volumes (ϕ_v^0) and limiting apparent molal compressibilities (ϕ_k^0).

Materials and Methods

The compounds used in this work were of A R grade. D-Glucose, sucrose (S M Chemicals); D-fructose, D-galactose, lactose (Loba Chemie Indoaustral Co); and α -methyl glucoside and β -methyl glu-

coside (Sigma Chemical Co). All compounds were dried *in vacuo* at 50°C and kept in vacuum desiccator for at least 24 hr before use. The measurements were made in doubly distilled water.

Density measurements

The single float method⁹ using a Sartorius model 2474 single pan semi-microbalance having facility to weigh below the pan was adopted.

A weighed quantity (~ 1850 g) of water was taken in the stainless steel cylinder. To this was added a weighed quantity of solid, which gave a difference of ~ 100 mg in the weight of plunger in water and solution at lowest concentration. The solution was stirred by a glass stirrer. In this way by adding solute successively to the water in stainless steel cylinder, 6-7 observations were taken in the concentration range 0-0.05 *m*. Density measurement of each compound in aqueous solution was made in 2-3 different runs. Considering the accuracy of temperature ($\pm 0.002^\circ\text{C}$), weight (± 0.01 mg) and the volume of the float (~ 166 cc) the accuracy in density determination was of the order of 3 ppm.

The volume of the plunger was determined accurately first by weighing it in air and then in distilled water held at 5°, 15°, and 25°C. It was calibrated by measuring the densities of dilute aqueous solutions of sodium chloride at 5°, 15° and 25°C. It was observed that our density values were in good agreement with literature.

The density data were fitted into Eq (1)

$$d = d_0 + Am + Bm^2 + Cm^3 \quad \dots (1)$$

with the help of microprocessor HCL-1800 model S₂ of Hindustan Computers Ltd. at the National Environmental Engineering Research Institute, Nagpur.

Table 1—Coefficients of Density Interpolation Equation (see Eq. 1)

	$d_0 = 0.999965 \text{ g/cc}$			$d_0 = 0.999098 \text{ g/cc}$			$d_0 = 0.997048 \text{ g/cc}$		
	A	B	C	A	B	C	A	B	C
	Temp. = 5°C			Temp. = 15°C			Temp. = 25°C		
D-Glucose	0.070290	0.007873	-0.116074	0.070431	-0.007112	-0.299865	0.069069	-0.016452	0.042237
D-Fruc- tose	0.073260	-0.029318	0.149379	0.069545	0.048604	-0.630238	0.070687	-0.029093	0.146833
D-Galac- tose	0.070100	0.102667	-1.431279	0.070218	0.036196	-0.537876	0.069988	0.007659	-0.210868
Sucrose	0.133204	0.053994	-1.106920	0.131331	0.048304	-1.016690	0.128570	0.085986	-1.353346
Lactose	0.135540	0.037798	-0.752183	0.135120	-0.006860	-0.325900	0.134858	-0.071095	0.533130

Apparent molal volumes

The apparent molal volumes were calculated using Eq. (2)

$$\phi_v = \frac{1000}{md d_0} (d_0 - d) + \frac{M_2}{d} \quad \dots (2)$$

where d and d_0 are the densities of solution and solvent respectively; m is the molality; and M_2 is the molecular weight of the solute. The limiting apparent molal volumes (ϕ_v^0) were obtained by the method of least squares. For the extrapolation of ϕ_v versus m to zero concentration, the points at low concentration, which deviated considerably from linearity were not considered. The same procedure was adopted by Franks *et al.*⁸ because of the possibility of systematic error at low concentration due to dissolved air in solution.

Sound velocity measurements

The sound velocities were measured differentially in the carbohydrate concentration range of 0.0 to 0.05 m using a phase-comparison interferometer. The details of the apparatus and method of measurements adopted were the same as those described in the earlier works^{10,11}.

Solutions of carbohydrates of different concentrations were prepared *in situ* by successively adding known weight of sugar solution into the interferometer vessel containing a known amount of water.

Accuracies in sound velocity measurements were 1, 2 and 3 cm s^{-1} for a velocity change of 1, 3 and 8 m s^{-1} respectively.

The sound velocity data were fitted into Eq. (3)

$$U = U_0 + am + bm^2 \quad \dots (3)$$

From the sound velocity and density values the apparent molal compressibility (ϕ_k) was calculated using Eq. (4)

$$\phi_k = \frac{1000}{md d_0} (d_0 \beta - d \beta^0) + \beta \frac{M_2}{d} \quad \dots (4)$$

where d_0 , d and β^0 , β are the densities and compressibilities of solvent and solution, respectively; m is the molality; and M_2 is the molecular weight of the solute. The limiting apparent molal compressibility (ϕ_k^0) was obtained by extrapolating (using a least squares fit making use of a programmable calculator) ϕ_k versus m curves to zero concentrations, neglecting the points at low concentration, which deviated considerably from linearity as in the case of apparent molal volumes.

Results and Discussion

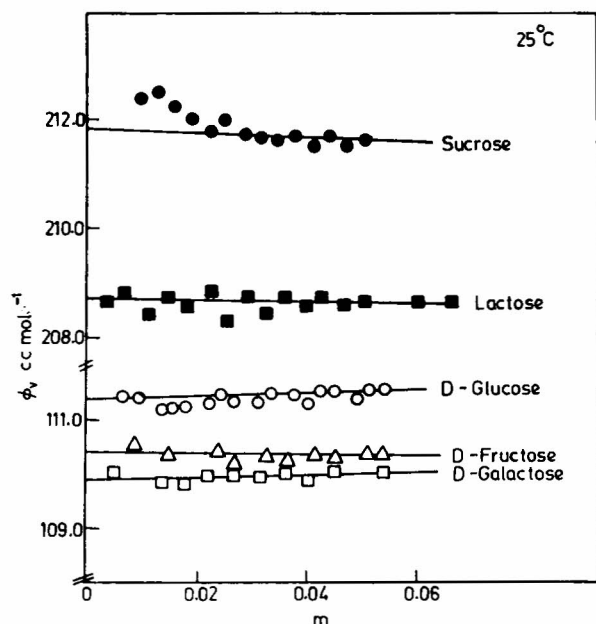
Values of the parameters A , B and C of Eq. (1) are listed in Table 1. The coefficients a and b of sound velocity interpolation equation (Eq. 3) are given in Table 2. Figure 1 shows the variation of apparent molal volume (ϕ_v) as a function of concentration at 25°C. Similar plots are obtained at 5° and 15°C. It is observed that the slopes are generally weakly positive and sometimes zero or even negative. The magnitudes of slopes are not significant from the point of view of solute-solvent interactions. Figure 2 shows the variation of ϕ_k as a function of concentration at 25°C. Similar curves are obtained at 5° and 15°C. It is observed that ϕ_k varies linearly with concentration. Our ϕ_k values obtained at 25°C at 0.025 m concentration are accurate to ± 0.7 units, whereas the ϕ_k values obtained by Franks *et al.*⁸ at same concentration are accurate to ± 4.5 units. Hence our extrapolations yield more reliable ϕ_k^0 values than those of Franks *et al.*

As observed in the case of ϕ_v , ϕ_k weakly depends upon concentration. The slopes of these curves are not very important for the interpretation of solute-solute interactions.

The limiting apparent molal volumes (ϕ_v^0) for carbohydrates at 5°, 15° and 25°C, listed in Table 3, show that ϕ_v^0 values of glucose at all temperatures are higher than those of galactose and fructose, though the difference is not very large. The higher ϕ_v^0 values in the case of glucose suggest that it is comparatively

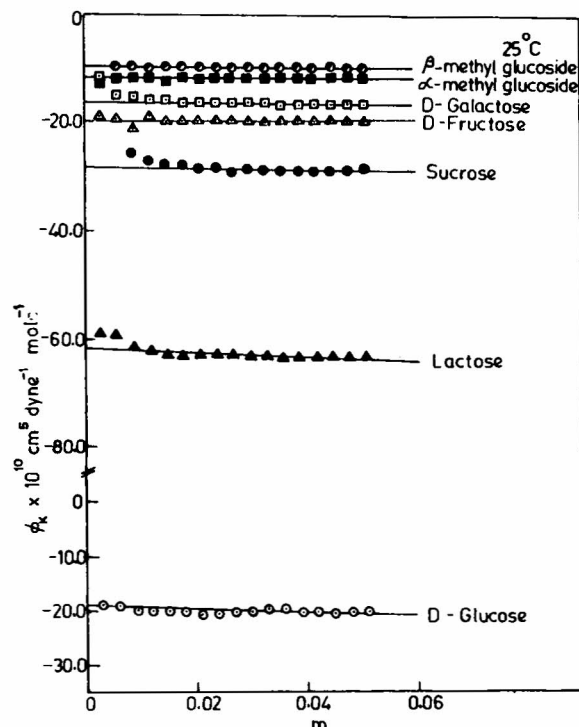
Table 2—Coefficients of Sound Velocity Interpolation Equation (see Eq. 3)

Compound	$U_0 = 1426.71 \text{ m/s}$		$U_0 = 1466.4 \text{ m/s}$		$U_0 = 1497 \text{ m/s}$	
	a	b	a	b	a	b
	Temp. = 5°C		Temp. = 15°C		Temp. = 25°C	
D-Glucose	95.72	-20.0	90.00	34.0	58.66	94.0
D-Fructose	87.49	-56.0	82.58	-90.0	59.38	86.0
D-Galactose	162.06	-6.0	115.55	78.0	46.75	263.0
Sucrose	118.30	85.0	119.37	23.0	110.19	-26.0
Lactose	252.03	-87.0	161.16	-21.0	168.92	-120.0
α -Methyl glucoside	119.40	-79.0	—	—	60.92	306.0
β -Methyl glucoside	108.49	27.0	—	—	78.48	-109.75


 Fig. 1—Plots of ϕ_v (cc/mol) versus m for different carbohydrates at 25°C

more hydrated than fructose and galactose. Glucose and galactose are present in the form of pyranose forms, with the difference that in galactose the OH group at C-4 is configurationally different from that in glucose. Galactose has higher percentage of axial OH groups than that in glucose and hence will exhibit lower values of ϕ_v^0 as compared to glucose⁸. Slightly higher hydration in glucose over fructose can be ascribed to six-membered pyranose ring being more favourable for interaction with water than the five-membered furanose ring in fructose.

The stereospecific hydration observed in aqueous monosaccharide solutions is also observed in solutions of disaccharides. The ϕ_v^0 values of sucrose and lactose bear this out (Table 3). On the basis of the discussion made earlier, one should have expected higher ϕ_v^0 values for lactose than those for sucrose, since sucrose is made up to glucose and fructose and lactose that of glucose and galactose. But a reverse


 Fig. 2—Plots of $\phi_k \times 10^{10}$ ($\text{cm}^5 \text{ dyne}^{-1} \text{ mol}^{-1}$) versus m for different carbohydrates at 25°C

trend is observed i.e. ϕ_v^0 (sucrose) $>$ ϕ_v^0 (lactose). We believe that this is due to specific configuration of furanose and pyranose ring playing an important role in hydration.

It is seen from the data in Table 3 that limiting apparent molal expansibility (ϕ_E^0) increases sharply with increase in temperature for glucose, only slightly in the case of sucrose and lactose and decreases slightly for galactose and sharply for fructose. These results suggest that water around glucose is loosely bound and in other compounds it is relatively firmly bound, as has been concluded by Neal and Goring from expansibility studies²⁵.

In Table 4 are collected the limiting apparent molal compressibilities (ϕ_k^0) of carbohydrates at 5°, 15° and 25° and of NaCl and MeOH, EtOH etc at 25°C

Table 3—Limiting Apparent Molal Volumes (ϕ_V^0) and Mean Limiting Expansibilities ($\phi_E^0 = d\phi_V^0/dT$) of Carbohydrates

Compound	ϕ_V^0 (cc/mol)			ϕ_E^0 (cm ³ mol ⁻¹ deg ⁻¹)	
	5°C	15°C	25°C	10°C	20°C
D-Glucose	109.5(109.5 ⁸)	110.0	111.4 (111.9 ⁸ , 112.04 ⁴ , 111.7 ³ , 112.2 ⁵)	0.05	0.14
D-Fructose	107.2	109.2	110.4 (110.4 ⁵)	0.20	0.12
D-Galactose	107.8 (107.7 ⁸)	109.0	109.9 (110.7 ⁸ , 110.2 ³ , 111.9 ⁵)	0.12	0.09
Sucrose	207.8 (207.62 ¹⁵)	209.6 (209.97 ¹⁵)	211.8 (211.32 ⁴ , 211.6 ³ , 211.82 ¹⁴ , 210.2 ⁵)	0.18 (0.23 ¹⁵)	0.22 (0.16 ¹⁵)
Lactose	205.4	206.8	208.7 (209.1 ³ , 207.6 ⁵)	0.14	0.19
α -Methyl-glucoside	(130.9 ⁸)	—	(133.2 ⁸)	—	—
β -Methyl-glucoside	(134.6 ⁸)	—	(135.5 ⁸)	—	—

Literature values are given in parentheses.

Table 4—Limiting Apparent Molal Compressibilities (ϕ_k^0) and $(d\phi_k^0/dT)_s$ of Carbohydrates (This Work) and Some Other Solutes

Compound	$\phi_k^0 \times 10^{10}$ (cm ⁵ dyne ⁻¹ mol ⁻¹)			$(d\phi_k^0/dT)_s$ (cm ⁵ dyne ⁻¹ mol ⁻¹ deg ⁻¹)
	5°C	15°C	25°C	
D-Glucose	-45.19 (-38.8 ⁸)	-40.17	-20.13 (-16.0 ⁸ , -16.0 ⁶)	0.502
D-Fructose	-42.02	-32.22	-19.79	0.98
D-Galactose	-91.25	-59.68	-16.06	3.157
Sucrose	-46.39	-39.81	-28.53 (-16.0 ⁶)	0.65
Lactose	-133.55	-68.18	-62.88	6.06
α -Methyl-glucoside	-48.32 (-35.3 ⁸)	—	-11.95 (-13.0 ⁸ , -11.0 ⁶)	—
β -Methyl-glucoside	-39.51 (-29.2 ⁸)	—	-9.81 (-5.9 ⁸)	—
NaCl	—	—	-50.5 ¹⁶	—
MeOH	—	—	12.6 ¹¹	0.50 ¹³ , 0.29 ¹²
EtOH	—	—	9.9 ¹¹	—
THFA	—	—	4.4 ¹⁶	—
EtNH ₂	—	—	13.32 ¹⁸	—
N-Bu ₄ Br	—	—	-15.2 ¹⁸	—

for comparison. It is observed that ϕ_k^0 values for all the carbohydrates at all temperatures are negative. The values at 25°C are less negative than those of NaCl, more negative than those of alcohols, ethylamine and THFA and are of comparable magnitude with those of tetraalkylammonium bromide.

The negative ϕ_k^0 values obtained in the case of carbohydrates can be explained by postulating that polar OH groups interact with the surrounding solvent water through dipole-dipole interaction in such a way that the surrounding water loses its own compressibility to a certain extent but not as completely as in the case of electrolytes. Water in the hydration shell of these molecules must be less compressible than that of bulk water but certainly not having zero compressibility as in the case of highly electrostricted water.

As a first approximation, one can expect a one to one relationship between the number of dipoles interacting with solvent water and the magnitude of ϕ_k^0 . To examine this point further we have plotted ϕ_k^0 against the number of OH groups in a carbohydrate (Fig. 3) at 25°C. It is observed that as the number of OH groups increases, the ϕ_k^0 becomes more and more negative. The relationship is almost linear. This indicates that OH groups of carbohydrates interact with water in a manner similar to the OH groups in alcohols. This fact is also supported by the viscosity B -coefficients of alcohols and carbohydrates. It is observed that the B -coefficient increases linearly with number of OH groups (Fig. 3). B -coefficient gives direct idea about the amount of water attached firmly to the solute molecule when the molecule is in motion.

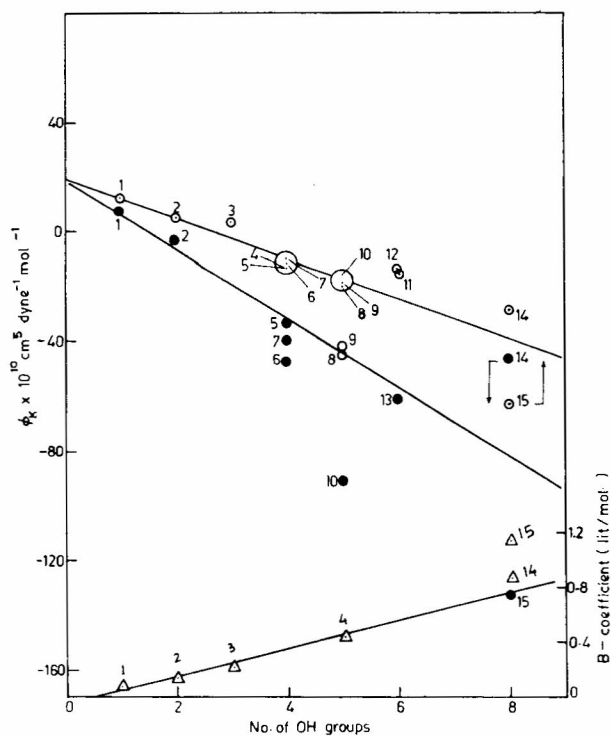


Fig. 3—Plots of ϕ_k^0 versus number of OH groups (\circ — \circ) at 25°C and (\bullet — \bullet) 5°C (left hand scale [1, Methanol (ref. 11); 2, ethylene glycol (ref. 19); 3, glycerol (ref. 20); 4, xylose (ref. 3); 5, ribose (ref. 8); 6, α -methyl glucoside (this work); 7, β -methyl glucoside (this work); 8, D-glucose (this work); 9, D-fructose (this work); 10, D-galactose (this work); 11, manitol (ref. 3); 12, glucitol (ref. 3); 13, myoinositol (ref. 8); 14, sucrose (this work); 15, lactose (this work)]; and plot of B-coefficient versus number of OH groups (Δ — Δ) (right hand scale) [1, methanol (ref. 21); 2, ethylene glycol (ref. 21); 3, glycerol (ref. 21); 8-D-glucose (ref. 22); 14, sucrose (ref. 23); 15, lactose (ref. 24)]

The only notable exception, lactose, shows more negative value of ϕ_k^0 and higher value of B-coefficient as compared to those of sucrose. This suggests that lactose is more extensively hydrated than sucrose. Since the number of interacting OH groups in sucrose and lactose is same, the authors strongly feel that hydration of lactose must be of different type than that of sucrose and other sugar molecules. In the case of other carbohydrates the OH groups can be visualized to interact with water as if they are separate alcohols. But in the case of lactose the water molecule which is attached to one OH group must be involved in H-bond formation with another water molecules attached to adjacent OH group. This type of hydration may be called as cooperative hydration which yields more negative value of ϕ_k^0 and also higher B-coefficient.

It is observed from the data in Table 4 that at 25°C, negative ϕ_k^0 values increase in the order galactose < fructose < glucose. The ϕ_k^0 values are in the order: galactose < fructose < glucose. It is shown by

Franks *et al.*¹ that the hydration is more favoured when the OH group are in equatorial position and compound fits well with tetrahedral arrangement of water molecules. However, they could not distinguish the hydration of glucose and galactose. Our ϕ_k^0 values of glucose and galactose clearly indicate that glucose is more hydrated than galactose for the same reason that glucose has more number of equatorial OH groups than galactose. This differentiation in the hydration of glucose and galactose on the basis of ϕ_k^0 values has been possible on account of more reliable estimate of ϕ_k^0 .

The ϕ_k^0 values of α -methyl and β -methyl glucosides at 25°C are approximately equal. This indicates that the hydration of the remaining three OH groups, which are all equatorial is similar.

Further Fig. 3 shows that ϕ_k^0 varies linearly as a function of OH groups at 5°C also. It means that even at 5°C, like at 25°C, carbohydrates behave like alcohols in water. The slope of the plot of ϕ_k^0 versus number of OH groups (Fig. 3) is higher than that at 25°C. However, galactose and lactose show deviations from linearity. These carbohydrates show high negative values. Also sucrose, α -methyl glucoside and β -methyl glucoside show deviation from linearity. This might be due to the fact that at 5°C, the ordered structure of solvent water must be forcing these carbohydrates into such stereochemical configuration which is more favourable for interaction with water dipoles. At 5° and 15°C galactose shows much larger negative values for ϕ_k^0 than those of glucose and fructose. Here the changed order of negative value of ϕ_k^0 is fructose < glucose < galactose. This indicates that at low temperature galactose seems to acquiring such a stereochemical reorientation/transformation that still more extensive hydration is made possible. The results of ϕ_k^0 for sucrose and lactose also strongly support the above contention, as lactose molecules are built-up of glucose and galactose of necessity show very large negative value (−133.5) than sucrose which is made up of fructose and glucose.

The ϕ_k^0 values of α -methyl and β -methyl glucosides at 5°C and like the one at 25°C were expected to be identical. However, the values are more negative for α -methyl glucoside than those for β -methyl glucoside. This points to some stereochemical orientation/transformation in the case of α -methyl glucoside favouring extensive hydration. However, further experimentation on methyl derivatives of other pyranosides is necessary before drawing final conclusion.

Temperature coefficient of ϕ_k^0 at 4°C has been shown to give an idea of relative structure strengthening abilities of solutes on structure of water¹³. As

an approximation $(d\phi_k^0/dT)_4$ values have been computed from values of ϕ_k^0 at 15° and 5°C (Table 4). The values of temperature coefficient of ϕ_k^0 for glucose, fructose and sucrose are of the order of methyl alcohol, whereas the values are very high for galactose and lactose. This suggests that glucose, fructose and sucrose behave like alcohols and strength of stabilization of water structure is of the same order even though there are more number of hydroxyl groups. In the case of galactose and lactose the strength appears to be more than that of other carbohydrates. This might be due to the cooperative hydration in the case of galactose and lactose.

Acknowledgement

S S D thanks the UGC, New Delhi for the award of a junior research fellowship.

References

- 1 Franks F, Tait M J, Suggett A, Ablett S & Quickenden P A, *J soln Chem*, **1** (1972) 131.
- 2 Franks F, Reid D S & Suggett A, *J soln Chem*, **2** (1973) 99.
- 3 Høiland H & Holvik H, *J soln Chem*, **7** (1978) 587.
- 4 Millero F J, Surdo A Lo & Shin C, *J chem & Engng Data*, **23** (1978) 197.
- 5 Edward J T, Shahidi F & Farrell P G, *J soln Chem*, **5** (1976) 807.
- 6 Shio H, *J Am chem Soc*, **80** (1958) 70.
- 7 Gereze N G, *Acoustica*, **32** (1975) 201.
- 8 Franks F, Ravenhill J R & Reid D S, *J soln Chem*, **1** (1972) 3.
- 9 Kaulgud M V, Bhagde V S & Shrivastava A, *J chem Soc Faraday Trans-I*, (1982) 313.
- 10 Kaulgud M V, Pandya G H & Rao K S M, *Indian J pure & appl Phys*, **16** (1978) 459.
- 11 Kaulgud M V & Rao K S M, *J chem soc Faraday Trans-I*, (1979) 2237.
- 12 Moharil A G, Ph D Thesis, Nagpur University (1985).
- 13 Kaulgud M V, *J chem Soc Faraday Trans-I*, (1979) 2246.
- 14 Dipaola G & Belleau B, *Can J Chem*, **55** (1977) 3825.
- 15 Garrod J E & Herrington T M, *J phys Chem*, **74** (1970) 363.
- 16 Owen B B & Kronik K L, *J phys Chem*, **65** (1961) 84.
- 17 Kaulgud M V, Shrivastava A & Awode M R, *Indian J pure & appl Phys*, **18** (1980) 864.
- 18 Desnoyers J E & Philip P R, *Can J Chem*, **50** (1972) 1094.
- 19 Nakajima T, Komatsu T & Nakagawa T, *Bull chem Soc Japan*, **48** (1975) 788.
- 20 Kuhnies & Schaaffs W, *Akust Beih*, **12** (1962) 254; *Chem Abstr*, **58** (1963) 3918a.
- 21 Heroskovitz T T & Kelly T M, *J phys Chem*, **77** (1973) 381.
- 22 Ihnat M, Szabo A & Goring D A I, *J chem Soc (A)*, (1968) 1500.
- 23 Jones G & Talley S K, *J Am chem Soc*, **55** (1933) 624.
- 24 Palvermacher, *Z anorg allgm chem*, **113** (1920) 141.
- 25 Neal J L & Goring D A I, *J phys Chem*, **74** (1970) 658.