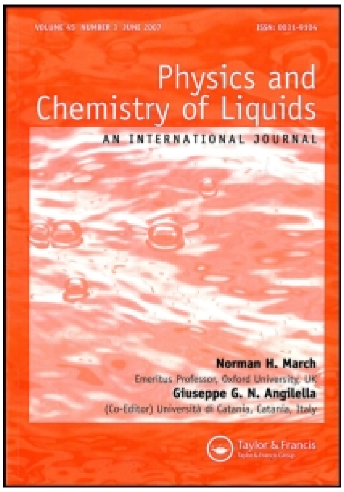

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ACOUSTIC BEHAVIOUR OF CETYLPYRIDINIUM BROMIDE (CPB) IN METHANOL

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Ultrasonic velocity measurement has been employed to obtain various acoustic parameters and the critical micelle concentration CMC (0.045 mol m^{-3}), which is found to be in good agreement with the one determined by conductance method (0.042 mol m^{-3}), for methanolic solutions of cetylpyridinium bromide CPB at 313.15 K. The results show that there is a significant interaction between solute and solvent molecules in dilute solutions. The values for intermolecular free length L'_f computed from thermodynamic method given by Eyring and Hirschfelder, are in good agreement with those of L_f evaluated from ultrasonic data using Jacobson's relation. Several other parameters, viz. molecular radius r_m, space filling factor r_j (B/V) and collision factor S, have also been evaluated from collision factor theory CFT of Schaaffs.

KEY WORDS: Ultrasonic velocity, critical concentration.

INTRODUCTION

Ultrasonic measurements may provide information concerning the structure of electrolytic solutions since they take into account the important consequences of ion solvation, such as reduced volume and compressibility of the solvent molecules. It is well established that when an electrolyte is added to polar liquids, the ions tend to establish a new structure wherein the solvent dipoles are oriented about each ion. Since the electric fields of the ions exert a considerable electrostrictive effect on the surrounding solvent molecules, the volume as well as the compressibility of the solvent molecules is reduced substantially.

NMR[1,2], IR[3,4] and Raman[5] have been used to study molecular interactions. The propagation of ultrasound waves and measurement of their speed[6-10] and absorption[11,12] have been shown to be useful in the study of molecular interactions in inorganic, organic and organo-metallic binary systems. Recently, research workers[13-18] have employed ultrasonic measurements as their study-matrix to look into the important consequences of ion-solvent interactions vis-a-vis the structure of electrolytic solutions.

The present work has been initiated with a view to secure information on ion-solvent interactions, to determine critical micelle concentration CMC and several acoustic parameters for cetylpyridinium bromide CPB in methanol.

EXPERIMENTAL

Cetylpyridinium bromide CPB, a sigma product, was crystallised twice from ethanol-acetone, washed with ethyl ether, and dried under vacuum for at least 48 h before use. All solutions were prepared by mass using reagent-grade methanol (E. Merck) of stated purity 99.5%, which was refluxed on sodium for 12 h and fractionally distilled before use. The solutions were kept at a constant temperature for about 2 h in a thermostat.

A multifrequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi), operating at a frequency of 4 MHz, was employed to measure the ultrasonic velocity of the methanolic solutions of CPB at a constant temperature 313.15 (± 0.01) K. The maximum uncertainty of velocity result was ± 0.2%. The densities of solutions were measured by a dilatometer, which was caliberated with distilled water and benzene, and buoyancy corrected. The volume of dilatometer was 15 ml and the accuracy of the density results was ± 0.0001.

METHOD OF CALCULATIONS

The various acoustic parameters (Table 1), viz adiabatic compressibility β, specific acoustic impedance Z, intermolecular free length L_f, apparent molar compressibility ϕ_k, solvation number Sn, molar sound velocity R, molar sound compressibility w and average molar weight of the solution $\bar{M}$, have been evaluated using the following relationships:

$$\beta = \frac{1}{\rho v^2} \tag{1}$$

$$Z = \rho \mathrm{v} \tag{2}$$

$$L_f = \left[\frac{\beta}{K}\right]^{1/2} \tag{3}$$

$$\phi_k = \frac{1000}{C\rho_0}(\rho_0\beta - \beta_0\rho) + \frac{\beta_0 M}{\rho_0} \tag{4}$$

$$\mathrm{Sn} = \frac{n_1}{n_2}\left(1 - \frac{\beta}{\beta_0}\right) \tag{5}$$

$$R = \frac{M_1}{\rho} v^{1/3} \tag{6}$$

$$w = \frac{\bar{M}}{\rho}(\beta)^{-1/7} \tag{7}$$

$$\bar{M} = X_1 M_1 + X_2 M_2 \tag{8}$$

Table 1 Ultrasonic velocity and other acoustic parameters at 313.14 (± 0.01)K.

Concentration (C) mol m^{-3}	*Ultrasonic velocity (v) ms^{-1}*	*Density (ρ) kg m^{-3}*	*Adiabatic compressibility ($\beta \times 10^9$) m^2N^{-1}*	*Specific acoustic impedance ($Z \times 10^{-5}$) kg m^2 S^{-1}*	*Intermolecular free length ($L_f \times 10^{10}$) m*	*Apparent molar compressibility ($-\phi_k \times 10^9$) $m^5N^{-1}mol^{-1}$*	*Solvation number (Sn)*	*Molar sound velocity ($R \times 10^2$) $m^3mol^{-1}(N/m^2)^{1/3}$ $(m^3\ mol^{-1}(N/m^2)^{1/7}$*	*Molar sound compressibility ($w \times 10^3$)*	*Apparent molar volume ($\phi_v \times 10^6$) m^3mol^{-1}*	*Average molecular weight of solution ($\bar{M}$)*
0.01	1046	793.4	1.152	8.29	41.76	2256.65	44.94	514.9	790.88	331.40	33.16
0.02	1056	793.8	1.130	8.38	41.36	2257.28	44.94	516.3	796.39	394.53	33.32
0.03	1066	794.2	1.108	8.47	40.95	2260.85	44.94	517.7	801.82	415.58	33.47
0.04	1075	794.6	1.089	8.54	40.60	2184.14	43.40	518.9	807.00	426.10	33.62
0.05	1083	795.0	1.072	8.61	40.28	2097.76	41.67	519.9	812.00	432.41	33.78
0.06	1088	795.5	1.062	8.66	40.09	1926.68	38.13	520.4	816.44	434.52	33.93
0.07	1093	796.0	1.052	8.70	39.90	1806.28	35.60	520.8	820.88	436.02	34.09
0.08	1098	796.5	1.041	8.75	39.69	1727.02	33.96	521.3	825.22	437.15	34.24
0.09	1103	797.0	1.031	8.79	39.50	1654.16	32.45	521.8	829.45	438.02	34.39
0.10	1108	797.4	1.021	8.83	39.31	1593.35	31.25	522.3	833.81	439.99	34.54
0.11	1113	797.9	1.012	8.88	39.14	1537.86	30.08	522.7	838.21	440.44	34.70
0.12	1118	798.4	1.002	8.93	38.94	1498.98	29.28	523.2	842.50	440.83	34.85

where ρ_0, ρ; β_0, β; n_1, n_2; X_2, X_1 and M_2, M_1, are the density, adiabatic compressibility, number of moles, mole fractions and molar weights of solvent and solute, respectively; and K, C, v, $\bar{M}$ are the temperature dependent Jacobson's constant[19], concentration, ultrasonic velocity and average molar weight of the solution, respectively.

The acoustic parameters for collision factor theory CFT, viz. molecular radius r_m, space filling factor r_j and collision factor S, and those for computing intermolecular free length L_f from thermodynamic method, viz. molar volume V_T, available volume V_a and surface area per mole Y, have been evaluated as under:

$$V_a = V_T - V_0 \tag{9}$$

$$V_0 = V_T\left[1 - (T/T_C)^{0.3}\right] \tag{10}$$

$$L'_f = 2V_a/Y \tag{11}$$

$$Y = (36\pi N V_0^2)^{1/3} \tag{12}$$

where T, T_C, V_0, N are the experimental temperature, critical temperature, molar volume at 0°K and Avagadro's number, respectively.

Schaaffs[20] on the basis of collision factor theory CFT, developed the following relationship for the ultrasonic velocity in pure liquids:

$$v = V_a S r_j = V_a S(B/V) \tag{13}$$

where $v_a = 1600\ \mathrm{ms}^{-1}$, S is the collision factor, $r_j(= B/V)$ is the space filling factor, V is the volume of the pure liquid and B is the actual volume of the molecule, given by the relationship:

$$B = \frac{4\pi}{3}(r_m)^3 N \tag{14}$$

where r_m stands for molecular radius. The values of the molecular radius (r_m) have been computed using the relations given by Schaaffs[20] and Rao *et al*[21].

$$r_m\ \text{Schaaffs} = \alpha'\left[1 - \beta\left\{\left(1 + \frac{1}{3\beta}\right)^{1/2} - 1\right\}\right]^{1/3} \tag{15}$$

$$r_m\ \text{Rao} = \alpha^1\left[1 - \beta\left\{\left(1 + \frac{1}{\beta}\right)^{1/2} - 1\right\}\right]^{1/3} \tag{16}$$

where $\alpha' = (3V/16\pi N)^{1/3}$, $\beta = (\gamma RT/M_1 v^2)$: γ is the ratio of the principal specific heats, R is the gas constant, M is the molecular weight, and T is the absolute temperature.

RESULTS AND DISCUSSION

The various acoustic parameters computed from the ultrasonic velocity $v(\pm 0.2\%)$ for methanolic solutions cetylpyridinium bromide CPB are recorded in Table 1. The variation of velocity v with concentration C can be related to the variation of density ρ and adiabatic compressibility β with concentration:

$$v = \sqrt{\frac{1}{\rho\beta}} \tag{17}$$

Therefore,

$$\frac{dv}{dc} = -\frac{v}{2}\left(\frac{1}{\rho}\cdot\frac{\partial\rho}{\partial C} + \frac{1}{\beta}\cdot\frac{\partial\beta}{\partial C}\right) \tag{18}$$

The derivatives $\partial\rho/\partial c$ and $\partial\beta/\partial C$ are opposite in sign with the latter negative and numerically larger. Thus the velocity increases with increasing concentration (Table 1).

The variation of ultrasonic velocity v with concentration C follows the relationship:

$$v = V_0 + GC \tag{19}$$

where V_0 is the ultrasonic velocity in pure solvent and G is Garnsey's constant[22]. The computed value of G for methanolic solutions of CPB is 5.75×10^2. The ultrasonic velocity $v(\pm 0.2\%)$, adiabatic compressibility $\beta(\pm 0.5\%)$ and density (± 0.0001), when plotted as a function of CPB concentration C, show an intersection of two straight lines at definite concentration, CMC (0.045 mol m^{-3}) of CPB in methanol (Figure 1). However, the value of CMC for methanolic solutions of CPB at 313.15 K as determined by conductance method is 0.042 mol m^{-3}. These plots (Figure 1) when extrapolated to zero concentration give pure solvent values ($V_0 = 1.038 \times 10^3$ ms^{-1}, $\rho_0 = 0.7930 \times 10^3$ kg m^{-3}, $\beta_0 = 1.174 \times 10^{-9}$ m^2N^{-1}) in accordance with the experimental values ($V_0 = 1.035 \times 10^3$ ms^{-1}, $\rho_o = 0.7920 \times 10^3$kg m^{-3}, $\beta_0 = 1.170 \times 10^{-9}\text{m}^2\text{N}^{-1}$), indicating that CPB molecules do not aggregate to an appreciable extent below the CMC.

From the Debye-Hückel theory, it follows that the apparent molar compressibility $\phi_k(\pm 28\%)$ as well as apparent molar volume $\phi_v(\pm 30\%)$ are related to the molar concentration C by the relationship:

$$\phi_k = \phi_k^0 + S_K C^{1/2} \tag{20}$$

$$\phi_v = \phi_v^0 + S_v C^{1/2} \tag{21}$$

It is observed (Figure 2) that the plot of both ϕ_k versus $C^{1/2}$ and ϕ_v versus $C^{1/2}$ for solutions of CPB in methanol are not linear. The departure of linearity predicted by equations (20 and 21) may be due to the stepwise dissociation or association of CPB in the solvent. Khare[23] reported that the solutions of $NaHSO_4$ and $KHSO_4$ showed an abrupt change of slope when ϕ_k is plotted versus the square root of concentration. This change in slope (uncertainty in the low concentration slope being of the order of 5 to 10%) was ascribed[23] to the dissociation of HSO_4 into H^+ and SO_4^{2-} at low concentrations and not to a gradual shift to that predicted by Debye-Hückel theory.

The decrease in the values of β and increase in the values of both apparent molar compressibility ϕ_k and molar sound compressibility w, with the increase in CPB concentration (Table 1), may be attributed to the fact that CPB molecules in dilute

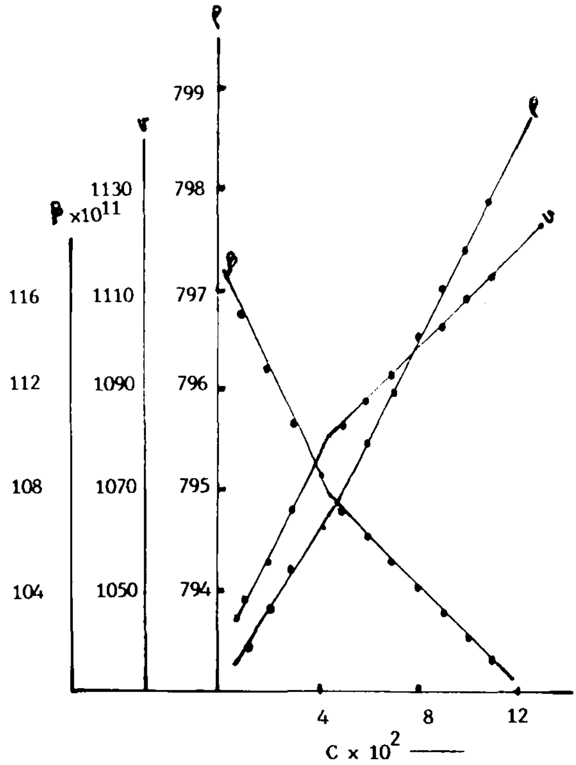

Figure 1 Plots of ultrasonic velocity (v), density (ρ) and adiabatic compressibility (β) as a function of concentration (C) of methanolic solutions of CPB at 313.15 K.

solutions are considerably ionised into $C_{16}H_{33}N(CH_3)_3^+$ and Br^-. These ions are surrounded by a thin film of solvent molecules firmly bound and oriented towards the ions. The orientation of solvent molecules around the ions is attributed to the influence of the electrostatic field of the ions and thus the internal pressure increases, which reduces the compressibility of the solutions, i.e. the solutions become harder to compress[24]. The decrease in β, increase in the values of both ϕ_k and w at higher concentrations may be explained on the basis of close-packing of ionic head-groups in the micelles, resulting in an increase in ionic repulsion and, finally, internal pressure.

The decrease in the values of intermolecular free length L_f ($\pm 0.2\%$) and increase in the values of specific acoustic impedance Z ($\pm$ 0.2%) with increase in CPB concentration can be explained on the basis of lyophobic interaction between CPB and solvent molecules, which increases the intermolecular distance, leaving relatively wider gaps between the molecules and thus becoming the main cause of obstruction to the propagation of ultrasound waves.

Passynskii[25] has developed a slightly different equation for the calculation of solvation numbers Sn. If the ions and the primary solvation sheaths are assured to be incompressible, then

$$V\beta = n_1 \bar{V}_1^0 \beta_0 (1 - X) \tag{22}$$

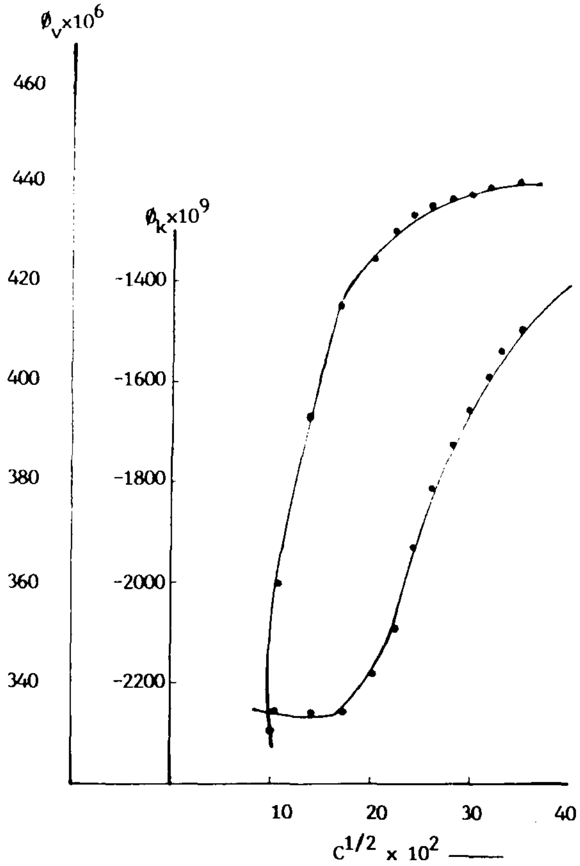

Figure 2 Plots of apparent molar compressibility (ϕ_k) and apparent molar volume (ϕ_v) as a function of square root of concentration ($C^{1/2}$) of methanolic solutions of CPB at 313.15 K.

where V, $\bar{V}_1^0$ and X signify volume of the solution containing n_2 moles of solute, partial molar volume of pure solvent and the fraction of the solvent in solution which is incompressible. The solvation number for the electrolyte can then be calculated from the equation:

$$\mathrm{Sn} = \frac{n_1}{n_2} X = \frac{n_1}{n_2}\left(1 - \frac{V\beta}{n_1 \bar{V}_1^0 \beta_o}\right) \tag{23}$$

Passynskii[25] assumed that $V = n_1 \bar{V}_1^0$ for dilute solutions, therefore, Equ. (23) can be written:

$$\mathrm{Sn} = \frac{n_1}{n_2}\left(1 - \frac{\beta}{\beta_o}\right)$$

The above expression, which has been used for evaluating solvation number Sn (Table 1), is the same as Eq. (5).

Table 2 The values of solvation number Sn for CPB and other electrolytes.

Electrolyte	*Sn*	*Temp (K)*	*Reference*
Cetylpyridinium bromide	29.28-44.94	313.15	Table 1
Barium butyrate	8.5-16.1	313.15	18
Strontium butyrate	8.2-23.7	313.15	18
Lanthanum laurate	59.5-63.8	313.15	15
Lanthanum caprate	40.5-48.9	313.15	15
Cobalt acetate	28.5	298.15	26
Beryllium chloride	8.5	-	25
Lithium sulphate	17.3	-	27
Barium bromide	15.4	-	26

The values of Sn($\pm$ 30%) correspond to the number of solvent molecules in the primary solvation sheaths of the ions. On account of electrostriction, molecules in the solvation sheath will be highly compressed so that these molecules will be less compressible than those in the bulk of the solution when an external pressure is applied. The compressibility of solvent molecules near but not in the primary solvation sheaths is the same as that of pure solvent. The values of Sn (Table 1) are indicative more of electrostriction effects of the ions on surrounding solvent molecules than of the actual primary solvation numbers. The values of Sn (Table 2) are in good agreement with other solvation numbers in the literature[15,18,25–27].

Marks[27,28] attempted to obtain further information concerning ionic solvation in solutions through the consideration of so called molar sound velocity R, $[R = (M/\rho)v^{1/3}]$. This constant was found by Rao[29] to be independent of temperature for various unassociated liquids. Marks[27,28] examined that the value for the ratio: $\rho(v_0)^{1/3}/\rho_0(v)^{1/3}$, evaluated at 293.15 K with 273.15 K as reference, increased linearly with concentration for several sulphates[27] and hydroxide[28]. Similar results were observed by Subrahamanyam and Bhimasenachar[30] for various univalent chlorides and uni-and divalent nitrates. The increase in the ratio: $\rho(v_o)^{1/3}/\rho_o(v)^{1/3}$, produced by the ionic solutes was ascribed to the strong interaction of the ions with the solvent molecules. It is observed that molar sound velocity R($\pm$ 0.05%) increases with increase in CPB concentration (Table 1), and the value for the ratio: $\rho(v_o)^{1/3}/\rho_o(v)^{1/3}$, evaluated for pre-micellar region of methanolic solutions of CPB at 313.15 K, varied between 0.995 and 0.997.

The values for intermolecular free length L'_f, available volume V_a and surface area per mole Y, as recorded in Table 3, have also been evaluated from thermodynamic method given by Eyring and Hirschfelder[31], employing Eqs (9)–(12). The values for intermolecular free length L'_f computed from thermodynamic method (Table 3) are in good agreement with those of L_f (Table 1) calculated from ultrasonic data using Jacobson's relation[19]. It is observed that over the entire concentration range, the values of L'_f are more consistent than those of L_f. However, available volume V_a and surface area per mole Y decrease with increase in concentration.

Several other parameters, viz molecular radius r_m, space filling factor r_j (B/V) and collision factor S, have been evaluated (Table 3) from collision factor theory CFT of

Table 3 Parameters for collision factor theory CFT, and those for computing intermolecular free length from thermodynamic method at 313.15 (± 0.01)K.

Molar volume $(V_T \times 10^6)$ $m^3 mol^{-1}$	*Available volume* $(V_a \times 10^3)$ m^3	*Surface Area per mole* $(Y \times 10^{-4})$ m^2	*Intermolecular free length* $(L_f \times 10^{10})$ m	*Molecular radius* $(r_m \times 10^{10})$		*Space filling factor,* $r_j(B/V) \times 10^2$		*Collision factor* $(S \times 10^{-3})$	
				r_m *Rao*	r_m *Schaaffs*	r_j *Rao*	r_j *Schaaffs*	*S Rao*	*S Schaaffs*
507.3	0.5285	31.320	33.76	11.197	9.317	0.850	0.490	7.69	13.35
507.0	0.5282	31.305	33.74	11.233	9.347	0.858	0.494	7.69	13.35
506.8	0.5280	31.297	33.74	11.268	9.376	0.866	0.499	7.69	13.35
506.5	0.5277	31.284	33.74	11.300	9.403	0.873	0.503	7.69	13.35
506.2	0.5274	31.273	33.73	11.328	9.426	0.880	0.507	7.69	13.35
505.9	0.5271	31.260	33.72	11.345	9.441	0.884	0.510	7.69	13.35
505.6	0.5268	31.248	33.72	11.363	9.455	0.888	0.512	7.69	13.35
505.3	0.5264	31.235	33.70	11.380	9.469	0.893	0.514	7.69	13.35
505.0	0.5261	31.223	33.70	11.397	9.484	0.896	0.517	7.69	13.35
504.7	0.5258	31.211	33.69	11.415	9.498	0.901	0.519	7.69	13.35
504.4	0.5255	31.199	33.69	11.432	9.513	0.905	0.521	7.69	13.35
504.1	0.5252	31.186	33.68	11.449	9.527	0.909	0.524	7.69	13.35

Schaaffs[20] using Eqs (13)-(16). In the collision factor theory, the molecular radius r_m is evaluated using Eq. (15) and (16). These values are employed in the calculation of the actual volume per mole, *B*, using Eq. (14). From the experimental values for the ultrasound velocities and space filling factor (B/V), the collision factor *S* has been computed from Eq. (13). The values of r_m, r_j and *S* evaluated for both Rao and Schaaffs are recorded in Table 3. It is observed (Table 3) that the values of r_m and r_j for Rao are higher than their respective values for Schaaffs whereas S Schaaffs is greater than *S* Rao (Table 3). The evaluated values of collision factor *S* for both Rao and Schaaffs are consistent over the entire range of concentration.

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References

1. W. Lin and S. J. Tsay, *J. Phys. Chem.*, **74**, 1037 (1970).
2. W. G. Schneider, in D. Hadri (Ed.), *Hydrogen Bonding* (Pergamon Press, London, 1959), p. 55.
3. E. Grunwald and W. C. Coburn, *J. Am. Chem. Soc.*, **80**, 1322 (1958).
4. N. D. Coggeshall and E. L. Saier, *J. Am. Chem. Soc.*, **73**, 5414 (1951).
5. G. C. Pimentel and A. L. Meclellan, *The Hydrogen Bond* (W. H. Freeman and Co., San Francisco, (1960), p. 67.
6. N. Prasad and S. Prakash, *Acustica*, **36**, 313 (1976).
7. K. Gopal and N. P. Rao, *Acoustics Letters*, **4**, 164 (1981).
8. F. Franks, M. A. J. Quickenden, D. S. Reid and B. Watson, *Trans. Faraday Soc.*, **66**, 583 (1970).
9. M. V. Kaulgud and K. S. M. Rao, *J. Chem. Soc. Faraday Trans. I.*, **75**, 2237 (1979).
10. T. N. Srivastava, R. P. Singh and B. Swaroop, *Ind. J. Pure Appl. Phys.*, **21**, 67 (1983).
11. D. Sette, *Ricerca Sci.*, **25**, 576 (1955).
12. A. Djavanbakht, J. Long and R. Zana, *J. Phys. Chem.*, **81**, 2620 (1977).
13. C. Sharma, S. P. Gupta and Pankaj, *Acoustics Letters*, **10**, 63 (1986).
14. K. N. Mehrotra and S. K. Upadhyaya, *Acoustics Letters*, **11**, 66 (1987).
15. K. N. Mehrotra, A. S. Gahlaut and M. Sharma, *J. Colloid Interface Sci.*, **120**, 110 (1987).
16. V. N. P. Srivastava, *Acoustics Letters*, **12**, 72 (1988).
17. K. N. Mehrotra, R. K. Shukla and M. Chauhan, *Acoustics Letters*, **12**, 66 (1988).
18. A. Kumar, *Colloids and Surfaces*, **34**, 313 (1989).
19. B. Jacobson, *Acta Chem. Scand.*, **5**, 1214 (1951); **6**, 1485 (1952).
20. W. Schaaffs, *Z. Phys.*, **114**, 110 (1939); **115**, 69 (1940).
21. R. V. Gopala Rao and V. Venkatoseshaiah, *Z. Phys. Chem.*, **242**, 193 (1969).
22. R. Garnsey, R. J. Boe, R. Mahoney and T. A. Litovitz, *J. Chem. Phys.* **50**, 5222 (1969).
23. P. Khare, *Trans. Faraday Soc.*, **58**, 359 (1962).
24. S. Prasash, F. M. Ichihaporia and J. D. Pandey, *J. Phys. Chem.*, **58**, 3078 (1964).
25. A. Passynskii, *Acta Physicochim* (*URSS*), **8**, 385 (1938).
26. P. Padmini and B. Rao, *Indian J. Phys.*, **34**, 565 (1960).
27. G. Marks, *J. Acoust. Soc. Am.*, **31**, 936 (1959).
28. G. Marks, *J. Acoust. Soc. Am.*, **32**, 327 (1960).
29. M. Rao, *J. Chem. Phys.*, **9**, 682 (1941).
30. S. Subrahamanyam and J. Bhimasenachar, *J. Acoust. Soc. Am.*, **32**, 835 (1960).
31. H. Eyring and H. O. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937).