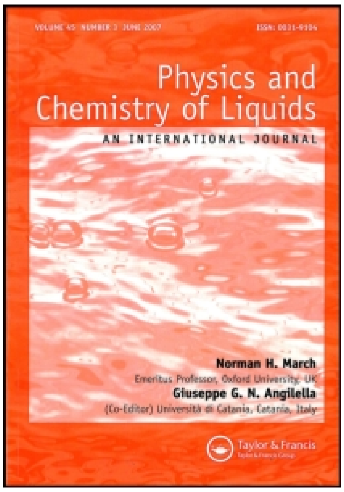

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Acoustical and Viscometric Studies of $CdCl_2$ and KCl in Aqueous-Acetone Co-Solvent Between 25 and 45°C

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ACOUSTICAL AND VISCOMETRIC STUDIES OF $CdCl_2$ AND KCl IN AQUEOUS-ACETONE CO-SOLVENT BETWEEN 25 AND 45°C

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Ultrasonic velocity of $CdCl_2$ and KCl in co-solvent of Acetone and Water is measured at different concentrations from 298.15 K to 318.15 K using single crystal interferometer; operating at frequency of 2 MHz. Various acoustical parameters such as adiabatic compressibility (β_s), specific impedance (Z), apparent molar compressibility ($\O_K$), relative association (R_A), Rao's molar sound function (R), molar compressibility (W), free volume (V_f) have been calculated. Results throw light on the solute–solvent and solute–solute interactions. Effect of temperature variation on these interactions has also been discussed.

Keywords: Adiabatic compressibilityspecific impedance; Rao's molar sound function

1. INTRODUCTION

Many thermodynamic properties of electrolytic solutions can be determined from sound velocity measurements. These properties allow some assessment of the role of ion–ion and ion–solvent interactions. Various aspects of physico–chemical behaviour of liquid mixtures such as molecular association, dissociation and complex formation can be characterized by isentropic compressibilities. Knowledge of acoustical properties of any solution provides information about interactions occurring in the solution. The present paper describes the evaluation of acoustical and viscometric parameters of $CdCl_2$ and KCl

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in binary mixture of solvents containing 1:1 Acetone and water from 25°C to 45°C [1–4].

2. EXPERIMENTAL

$CdCl_2$ and KCl were of AnalaR grade and used as such without purification. Ultrasonic interferometer and pyknometer were used for the measurements of ultrasonic velocity and density of solutions at 25°C, 30°C, 35°C, 40°C and 45°C. The densities of solutions were measured by a precalibrated bicapillary pyknometer. Ultrasonic velocity was measured at 2 MHz, using interferometer at above mentioned temperatures with refrigerated water bath using a circulating medium.

CH_3COCH_3 was used as such without purification. A detailed-procedure for the measurements of velocity and density of electrolytes in various solvent mixtures is described in the literature [4].

The accuracy of velocity measurements is ±0.02%.

3. RESULTS AND DISCUSSION

Different acoustical parameters such as adiabatic compressibility (β_s), specific impedance (Z), apparent molar compressibility ($\emptyset_K$), relative association (R_A), Rao's molar sound function (R), molar compressibility (W) have been calculated using ultrasound velocity (U), density (ρ) and viscosity (η) data (shown in Tabs. I–V) of $CdCl_2$ and KCl

TABLE I Sound velocity, density and viscosity of $CdCl_2-KCl-CH_3COCH_3-H_2O$ system at 298.15 K

Concentration of $CdCl_2$ $10^{-3}\times$ *mol/Lit.*	$\eta\times 10^{-3}$ *Poise*	ρ *gm/cm*^{3}	U *m/s*
0.024	2.9046	1.9712	1496.00
0.044	2.9051	1.9719	1499.00
0.086	2.9061	1.9733	1505.30
0.100	2.9064	1.9737	1526.30
0.200	2.9089	1.9772	1541.30
0.300	2.9114	1.9807	1556.30
0.400	2.9139	1.9842	1571.30
0.440	2.9149	1.9856	1577.30
0.500	2.9164	1.9877	1586.30

TABLE II Sound velocity, density and viscosity of $CdCl_2-KCl-CH_3COCH_3-H_2O$ system at 303.15 K

Concentration of $CdCl_2$ $10^{-3} \times$ *mol/Lit.*	$\eta \times 10^{-3}$ *Poise*	ρ *gm/cm^3*	U *m/s*
0.024	2.9048	1.9714	1497.00
0.044	2.9053	1.9721	1500.00
0.086	2.9063	1.9735	1506.30
0.100	2.9066	1.9739	1527.30
0.200	2.9091	1.9774	1542.30
0.300	2.9116	1.9809	1557.30
0.400	2.9141	1.9844	1572.30
0.440	2.9151	1.9858	1578.30
0.500	2.9166	1.9879	1587.30

TABLE III Sound velocity, density and viscosity data of $CdCl_2-KCl-CH_3COCH_3-H_2O$ system at 308.15 K

Concentration of $CdCl_2$ $10^{-3} \times$ *mol/Lit.*	$\eta \times 10^{-3}$ *Poise*	ρ *gm/cm^3*	U *m/s*
0.024	2.9048	1.9714	1497.00
0.044	2.9053	1.9721	1500.00
0.086	2.9063	1.9735	1506.30
0.100	2.9066	1.9739	1527.30
0.200	2.9091	1.9774	1542.30
0.300	2.9116	1.9809	1557.30
0.400	2.9141	1.9844	1572.30
0.440	2.9151	1.9858	1578.30
0.500	2.9166	1.9879	1587.30

TABLE IV Sound velocity, density and viscosity data of $CdCl_2-KCl-CH_3COCH_3-H_2O$ system at 313.15 K

Concentration of $CdCl_2$ $10^{-3} \times$ *mol/Lit.*	$\eta \times 10^{-3}$ *Poise*	ρ *gm/cm^3*	U *m/s*
0.024	2.9052	1.9718	1499.00
0.044	2.9057	1.9725	1502.00
0.086	2.9067	1.9739	1508.30
0.100	2.9070	1.9743	1529.30
0.200	2.9095	1.9778	1544.30
0.300	2.9120	1.9813	1559.30
0.400	2.9145	1.9848	1574.30
0.440	2.9155	1.9862	1589.30
0.500	2.9170	1.9883	1589.30

in Acetone and Water mix solvent from 25°C to 45°C by using the following equations:

$$\beta_s = 1/U^2\rho \tag{1}$$

TABLE V Sound velocity, density and viscosity data of $CdCl_2-KCl-CH_3COCH_3-H_2O$ system at 318.15 K

Concentration of $CdCl_2$ $10^{-3} \times$ *mol/Lit.*	$\eta \times 10^{-3}$ *Poise*	ρ *gm/cm*^{3}	*U* *m/s*
0.024	2.9054	1.9720	1500.00
0.044	2.9059	1.9727	1503.00
0.086	2.9069	1.9741	1509.30
0.100	2.9072	1.9745	1530.30
0.200	2.9097	1.9780	1545.30
0.300	2.9122	1.9815	1560.30
0.400	2.9147	1.9850	1575.30
0.440	2.9157	1.9864	1581.30
0.500	2.9172	1.9885	1590.30

$$Z = U\rho \tag{2}$$

$$\emptyset_K = (\rho_0\beta_s - \rho\beta_s^0)\frac{1000}{C\rho_0} + \frac{\beta_s^0 M_2}{\rho_0} \tag{3}$$

$$R_A = \frac{\rho}{\rho_0} \times \left(\frac{U_0}{U}\right)^{1/3} \tag{4}$$

$$R = \left(\frac{M}{\rho}\right)U^{1/3} \tag{5}$$

$$W = \left(\frac{M}{\rho}\right)\beta_s^{-1/7} \tag{6}$$

$$V_f = [MU/K_a\eta]^{3/2} \tag{7}$$

where U, U_0 and ρ, ρ_0 denote the ultrasonic velocities and densities of solution and solvent respectively; β_s^0, C, M_2 are the adiabatic compressibility of pure solvent, concentration (mol/litre) and molecular weight of solute respectively; M is the average molecular weight of solution. K_a is a constant having the value of 4.28×10^9 independent of temperature and nature of liquids. η is the solution viscosity [5, 6].

The density, ultrasound velocity and viscosity of the $CdCl_2-KCl-CH_3COCH_3-H_2O$ system have been measured at 298.15, 303.15, 308.15, 313.15 and 318.15 K and recorded in Tables I to V. It has been found graphically that the variation of U, η, ρ vary almost linearly with concentration (not shown here).

Relative association (R_A) is found to decrease with decrease in concentration of mixed solvent and temperature than that of calculated R_A of same solutes in water (reported earlier). This indicates significant interactions are present in the system between solute and solvent [7].

In the present investigation, the partial molar compressibilities ($\O_K$) of solutions are fitted to Gucker's relation.

$$\O_K = \O_K^0 + S_K\sqrt{C} \tag{8}$$

The values of $\O_K^0$ and S_K are reported in Table XI.

The plot of $\O_K$ *versus* $\sqrt{C}$ follows nonlinear relationship as shown in Figure 1. The negative value of $\O_K^0$ may be due to loss of compressibility of solvent due to strong electrostatic force in the vicinity of solute causing electrostatic solvation of ions. The positive of S_K signify a considerable solute–solvent interaction at lower concentration, but decrease in value of S_K with temperature suggests the high order of solute–solvent interactions at higher temperatures.

$\O_K^0$ values are comparatively higher for $CdCl_2$ in co-solvent than water (communicated earlier). Therefore it is concluded that solute–solvent interactions are comparatively higher that may be due to disruption of H_2O structure in acetone-water co-solvent [8].

The validity of Bachem's relation

$$\beta_s - \beta_s^0/C = A' + B'\sqrt{C} \tag{9}$$

can be tested by ploting $(\beta_s - \beta_s^0)/C$ *versus* $\sqrt{C}$ where C is the molar concentration of $CdCl_2$ and A', B' are constants. The values of A', B' are listed in Table XII which reveals the presence of solute–solvent interactions at all temperatures. As the temperature increases the negative value of A' decreases suggesting the presence of solute–solvent interactions [9].

From Tables VI–X, it is inferred that adiabatic compressibility (β_s) decrease with increase in concentration of $CdCl_2$ as well as with temperature. On the other hand, the ultrasound velocity is found to increase linearly with concentration, favouring ion–ion interactions whereas the decrease in β_s with addition of solvent leads to association between solute and solvent molecules. An increase in velocity is observed in all the mixtures as described by Eyring and Kincaid.

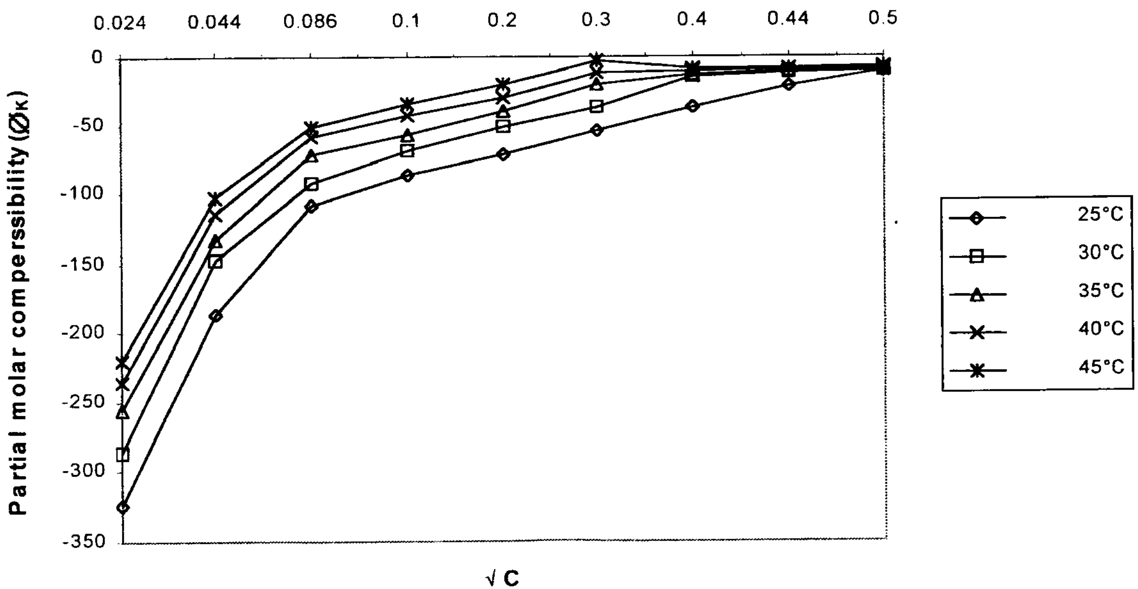

FIGURE 1 Variation of partial molar compressibility ($Ø_K$) at various temperatures of $CdCl_2-KCl-CH_3COCH_3-H_2O$ system.

TABLE VI Various acoustical parametres of $CdCl_2-KCl-CH_3COCH_3-H_2O$ system at 298.15 K

Concentration of $CdCl_2$ $10^{-3}\times mol/Lit.$	$\beta_s\times10^{-10}$ m^2/N	R_A ----	$R\times10^{-4}$ $m(10/3)sec-(1/3)$	$V_f\times10^{-6}$ m^3mol^{-1}	W $m(19/7)N(1/7)$
0.024	2.266	1.952	6.047	0.04446	1261.38
0.044	2.256	1.9510	7.051	0.05606	1470.12
0.086	2.236	1.9500	8.460	0.07396	1763.08
0.100	2.174	1.9410	8.832	0.08000	1840.04
0.200	2.128	1.9380	10.343	0.10250	2153.97
0.300	2.084	1.9360	11.110	0.11550	2312.88
0.400	2.041	1.9330	11.580	0.12410	2409.46
0.440	2.024	1.9306	11.718	0.12700	2439.14
0.500	1.999	1.9304	13.395	0.15620	2782.94

TABLE VII Various acoustical parametres of $CdCl_2-KCl-CH_3COCH_3-H_2O$ system at 303.15 K

Concentration of $CdCl_2$ $10^{-3}\times mol/Lit.$	$\beta_s\times10^{-10}$ m^2/N	R_A ----	$R\times10^{-4}$ $m(10/3)sec-(1/3)$	$V_f\times10^{-6}$ m^3mol^{-1}	W $m(19/7)N(1/7)$
0.024	2.263	1.9547	6.0495	0.04450	1262.125
0.044	2.253	1.9539	7.0520	0.05611	1471.12
0.086	2.233	1.9528	8.4605	0.07403	1764.28
0.100	2.167	1.9440	8.8330	0.08010	1844.21
0.200	2.124	1.9410	10.3430	0.10263	2155.62
0.300	2.077	1.9385	11.1115	0.11560	2315.08
0.400	2.038	1.9356	11.5760	0.12420	2411.10
0.440	2.021	1.9340	11.7165	0.12710	2440.84
0.500	1.994	1.9331	13.3945	0.15640	2787.64

TABLE VIII Various acoustical parametres of $CdCl_2-KCl-CH_3COCH_3-H_2O$ system at 308.15 K

Concentration of $CdCl_2$ $10^{-3}\times mol/Lit.$	$\beta_s\times10^{-10}$ m^2/N	R_A ----	$R\times10^{-4}$ $m(10/3)sec-(1/3)$	$V_f\times10^{-6}$ m_3mol^{-1}	W $m(19/7)N(1/7)$
0.024	2.260	1.9575	6.052	0.04455	1262.87
0.044	2.250	1.9569	7.053	0.05616	1472.12
0.086	2.230	1.9556	8.461	0.07410	1765.47
0.100	2.160	1.9470	8.834	0.08020	1848.40
0.200	2.120	1.9441	10.343	0.10275	2157.26
0.300	2.070	1.9412	11.112	0.11570	2317.30
0.400	2.035	1.9385	11.572	0.12430	2412.74
0.440	2.018	1.9374	11.715	0.12720	2442.52
0.500	1.990	1.9358	13.394	0.15650	2792.34

Thus the considerable decrease in β_s with increase in concentration of $CdCl_2$ indicate the existence of specific interactions between the components of the system.

TABLE IX Various acoustical parametres of $CdCl_2-KCl-CH_3COCH_3-H_2O$ system at 313.15 K

Concentration of $CdCl_2$ $10^{-3} \times$ mol/Lit.	$\beta_s \times 10^{-10}$ m^2/N	R_A ----	$R \times 10^{-4}$ m(10/3)sec−(1/3)	$V_f \times 10^{-6}$ $m^3 mol^{-1}$	W m(19/7)N(1/7)
0.024	2.255	1.9612	6.053	0.04459	1263.17
0.044	2.245	1.9602	7.055	0.05621	1472.42
0.086	2.225	1.9589	8.463	0.07417	1765.89
0.100	2.160	1.9502	8.837	0.08028	1845.74
0.200	2.115	1.9474	10.345	0.10280	2157.74
0.300	2.070	1.9445	11.114	0.11558	2317.05
0.400	2.033	1.9418	11.577	0.12440	2412.93
0.440	2.014	1.9407	11.721	0.12730	2442.85
0.500	1.985	1.9391	13.399	0.15665	2793.07

TABLE X Various acoustical parametres of $CdCl_2-KCl-CH_3COCH_3-H_2O$ system at 318.15 K

Concentration of $CdCl_2$ $10^{-3} \times$ mol/Lit.	$\beta_s \times 10^{-10}$ m^2/N	R_A ----	$R \times 10^{-4}$ m(10/3)sec−(1/3)	$V_f \times 10^{-6}$ $m^3 mol^{-1}$	W m(19/7)N(1/7)
0.024	2.250	1.9649	6.055	0.04462	1263.46
0.044	2.240	1.9635	7.057	0.05626	1472.71
0.086	2.220	1.9622	8.465	0.07423	1766.31
0.100	2.160	1.9536	8.839	0.08035	1843.08
0.200	2.110	1.9507	10.350	0.10290	2158.21
0.300	2.070	1.9479	11.116	0.11590	2316.81
0.400	2.030	1.9451	11.582	0.12450	2413.12
0.440	2.010	1.9440	11.726	0.12740	2443.19
0.500	1.980	1.9424	13.404	0.15680	2793.79

It is interesting to note that the free volume (V_f) increases with increase in concentration of $CdCl_2$ as well as with temperature. This is due to the breakening of bonded structure of solvent which favours both ion–ion as well as ion–solvent interactions [10]. The unusual increase in V_f is shown in Figure 2.

The data of viscosity were analyzed with the help of the well known Jones-Dole equation. The values of A and B of this equation have been determined from the intercept and the slope of a linear plot of $\eta/\eta_0 - 1/\sqrt{C}$ *versus* $\sqrt{C}$ (shown in Fig. 3) and also by least square methods. The values are listed in Table XII.

The viscosity of system depends of course upon the composition of the electrolytic mixtures. The value of coefficient A is positive which indicates the role of ion–ion interactions in the system. The value of A increases with increase in temperature suggesting strong ion–ion

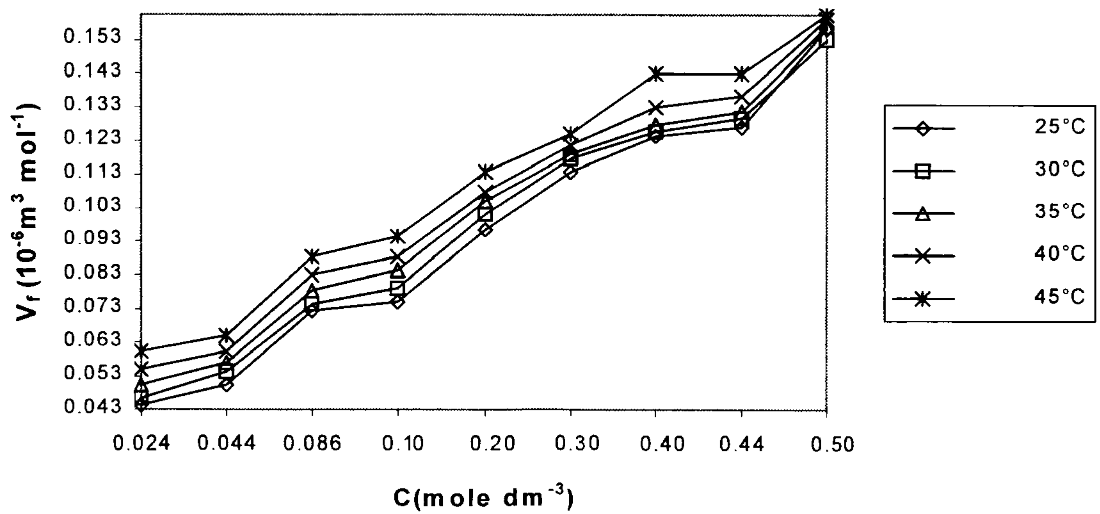

FIGURE 2 Plot of free volume *versus* concentration of $CdCl_2-KCl-H_2O-CH_3COCH_3$ system.

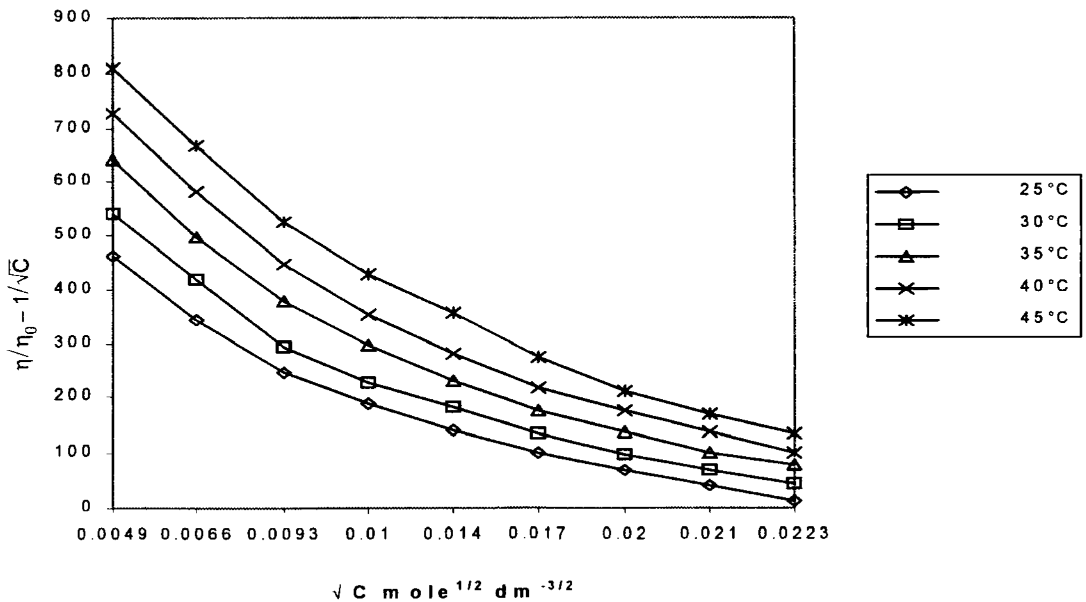

FIGURE 3 Variation of $\eta/\eta_0 - 1/\sqrt{C}$ with concentration at various temperatures of $CdCl_2-H_2O-KCl-CH_3COCH_3$.

TABLE XI $\O_K^0$ and S_K Values of $CdCl_2-KCl-CH_3COCH_3-H_2O$ system at various temperatures

Temperature (K)	$\O_K^0 \times 10^{-7}$	$S_K \times 10^{-7}$
298.15	− 180.490	+ 26.7670
303.15	− 177.806	+ 26.3690
308.15	− 175.122	+ 25.9725
313.15	− 173.481	+ 25.7250
318.15	− 171.839	+ 25.4790

TABLE XII Values of Jone-Dole coefficient (*A*, *B*) and Bachem's constants (*A*′, *B*′) at various temperatures

Temperature (K)	*A*	*B*	$A' \times 10^{-7}$	$B' \times 10^{-7}$
298.15	+ 376.676	− 41.643	− 61.101	+ 8.954
303.15	+ 440.817	− 48.730	− 59.550	+ 8.720
308.15	+ 504.959	− 55.832	− 58.016	+ 8.495
313.15	+ 581.770	− 64.300	− 57.000	+ 8.340
318.15	+ 658.591	− 72.780	− 55.987	+ 8.197

interaction, which may possibly be due to unusual cation–cation and cation–anion interactions. Recently it has been emphasized that the sign of the temperature coefficient of viscosity is a better criterion than the magnitude of *B* itself for determining the ion–solvent interactions. Accordingly, electrolytes which are structure promotors will have negative value of dB/dT. In the present study, dB/dT is negative, showing that electrolytes posses structure promoting tendency [11]. *B*-coefficient for the respective system is negative at every temperature suggesting weaker ion–solvent interactions.

Molar sound velocity (*R*) and molar adiabatic compressibility represented as Wada's constant (*W*) are temperature independent for unassociated weak molecules. *R* and *W* are found to be vary non linearly with change in solvent composition and this suggests the presence of complex formation in the system. However variation in *R* and *W* values with solvent composition supports the existence of dipole–dipole type of interactions between aqueous acetone and $CdCl_2$, KCl molecules [7, 12].

Hence some assessment has woved possible of the role of solute–solute and solute–solvent interactions in the $CdCl_2-KCl-CH_3COCH_3-H_2O$ System.

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