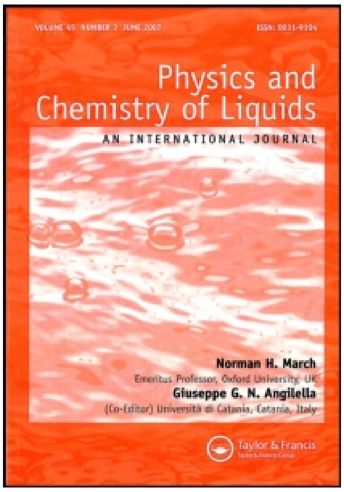

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ACOUSTICAL PARAMETERS OF CuCl-KCl SYSTEM IN ACETONITRILE-WATER SOLVENT MIXTURE

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Ultrasonic velocity (*U*) and density (*d*) have been measured for CuCl–KCl in acetonitrile water co-solvent at various temperatures from 298.15 to 318.15K. The adiabatic compressibility (β_{ad}), molar compressibility (β) specific acoustical impedance (*Z*), Rao Number (*R*) and Van der Waals Constant (*b*) have been computed. The variation of d, β_{ad}, β, Z, R and b with molarity of CuCl have been studied. The association between the components and the formation of complexes are treated.

Keywords: Acetonitrile; Acoustical parameters; Molecular association; Electrolytic mixtures

INTRODUCTION

The variation of ultrasound velocity and adiabatic compressibility of dilute aqueous solution of polyethylene glycol (PEG) with concentration was studied by Gereeze (see Ref. [1]) who concluded that there was no solute–solvent interactions. Recently Varada Rajulu and Mabu Sab [2] have studied interactions between PEG and water mixtures to improve its application as hydrogel, similarly in the present work, we have measured the ultrasound velocity, viscosity and density of $CuCl-KCl-CH_3CN-H_2O$ system at various temperatures from 25°C to 45°C to find out the nature of interactions. The

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acoustical parameters like molar compressibility (β), specific acoustic impedance (Z) and Rao number (R) have been computed. The Van der Waal's constant (b) has also been determined by an ultrasonic method. The variation of these parameters with molarity of CuCl has been studied. We have selected CuCl as the electrolyte to find out the nature of dipolar interactions between solvent component CH_3CN and CuCl as it has a wide range of applicability in chemical and in biological reactions.

EXPERIMENTAL

CH_3CN is stirred with CaH_2 which is added portionwise until H_2 evolution ceases. The solvent is purified by the recommended procedure and fractionally distilled at atmospheric pressure using a high efficiency column. The pure solvent is added with H_2O to make a mixed solvent in the ratio of 1:1. Viscosities and densities were measured with a precalibrated Ostwald viscometer and pyknometer using a thermostatic water bath. The experimental details have been given in our earlier papers.

RESULT AND DISCUSSION

The measured values of ultrasonic velocities (U) and density (d) are presented in Table I. The adiabatic compressibility (β_{ad}) was calculated using the relation (1)

$$\beta_{ad} = (dU^2)^{-1} \tag{1}$$

The Rao number (R) was calculated using the relation (2)

$$R = (M/d)U^{1/3} \tag{2}$$

where M is the molecular weight of the mixture given by

$$M = (n_1M_1 + n_2M_2)/(n_1 + n_2). \tag{3}$$

Here M_1 and M_2 are the molecular weights and n_1 and n_2 are number of moles of the components comprising the mixture. The

TABLE I Experimental ultrasonic velocity, density, acoustic impedance data, adiabatic compressibilities and molar sound velocity of $CuCl-CH_3CN-KCl-H_2O$ at different temperatures

C mol/dm^3	T °C	U m/sec	d kg/m^3	Z $kg\text{-}sec^{-1}$ m^{-2}	β_{ad} $m\,sec^2$ kg^{-1}	$R \times 10^{-4}$ $m^{10/3}mol^{-1}$ $sec^{-1/3}$
	25	1632.0	1110.0	1811520.0	3.38	8.40
	30	1638.5	1111.5	1821202.5	3.35	8.40
0.00	35	1645.0	1113.0	1830885.0	3.32	8.40
	40	1652.0	1114.5	1841164.5	3.29	8.40
	45	1659.0	1116.0	1851444.0	3.25	8.40
	25	1635.0	1112.0	1818120.0	3.36	8.68
	30	1641.5	1113.5	1827820.0	3.33	8.68
0.024	35	1648.0	1115.0	1837520.0	3.30	8.68
	40	1655.0	1116.5	1847807.5	3.27	8.68
	45	1662.0	1118.0	1858116.0	3.24	8.68
	25	1638.0	1116.0	1828008.0	3.33	9.06
	30	1644.5	1118.5	1839389.5	3.30	9.05
0.032	35	1651.0	1121.0	1850771.0	3.27	9.04
	40	1658.5	1122.5	1847818.0	3.24	9.04
	45	1666.0	1124.0	1872584.0	3.21	9.05
	25	1642.0	1122.0	1842324.0	3.31	9.11
	30	1647.5	1126.0	1855107.0	3.27	9.09
0.044	35	1653.0	1130.0	1867890.0	3.24	9.07
	40	1661.0	1132.0	1861677.5	3.21	9.07
	45	1669.0	1134.0	1892646.0	3.17	9.07
	25	1645.0	1130.0	1858850.0	3.27	9.48
	30	1651.0	1132.5	1869772.5	3.24	9.47
0.054	35	1657.0	1135.0	1880695.0	3.20	9.47
	40	1665.5	1137.0	1880268.0	3.17	9.46
	45	1674.0	1139.0	1906686.0	3.13	9.46
	25	1647.0	1140.0	1877580.0	3.23	9.62
	30	1654.0	1141.5	1888051.5	3.20	9.62
0.086	35	1661.0	1143.0	1898523.0	3.17	9.62
	40	1668.5	1145.0	1893690.5	3.11	9.61
	45	1676.0	1147.0	1922372.0	3.10	9.60
	25	1653.0	1152.0	1904256.0	3.17	9.65
	30	1658.5	1157.0	1918912.0	3.14	9.62
.106	35	1664.0	1162.0	1933568.0	3.11	9.59
	40	1671.5	1163.0	1910447.5	3.06	9.60
	45	1679.0	1164.0	1954356.0	3.05	9.60
	25	1655.0	1164.0	1926420.0	3.14	9.59
	30	1663.5	1167.0	1941330.0	3.09	9.58
.156	35	1672.0	1170.0	1956240.0	3.06	9.58
	40	1679.5	1172.5	1943962.0	3.03	9.58
	45	1687.0	1175.0	1982225.0	2.99	9.57
	25	1661.0	1180.0	1959980.0	3.07	9.92
	30	1670.5	1184.5	1978750.0	3.03	9.90
.200	35	1680.0	1189.0	1997520.0	2.98	9.89
	40	1686.0	1192.0	1969232.5	2.95	9.88
	45	1692.0	1195.0	2021940.0	2.92	9.86

molar compressibility (β) was calculated using Wada's relation

$$\beta = (M/d)\beta_{ad}^{-1/7} \tag{4}$$

The specific acoustic impedance (Z) was obtained from the relation

$$Z = dU \tag{5}$$

The van der Waals constant was calculated using the measured values of U and b from the relation

$$b = (M/d)\left[1 - (RT/MU^2)\sqrt{1 + \left(\frac{MU^2}{3RT}\right) - 1}\right] \tag{6}$$

Though Eqs. (2) and (4) are empirical and additive in nature, Eqs. (1), (6) both have a semiempirical origin which soon found theoretical support (Blitz, 1967). Similarly Eq. (5) is analogous to mechanical and electrical impedance. The measured values of velocity (U) and density (d) and computed values of β_{ad} R and Z are presented in Table I. The variation of d, β_{ad}, R, η, β and b with molarity of CuCl is shown in Figures 1–6 respectively.

The variation of density is non-linear with molarity of CuCl suggesting the formation of a complex in the present system.

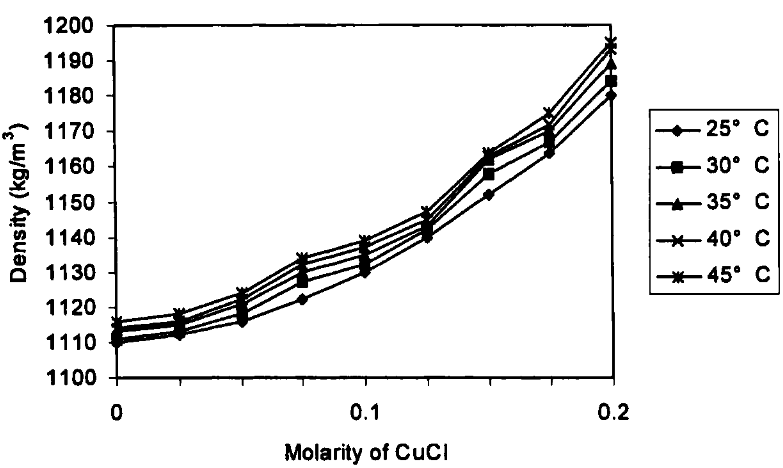

FIGURE 1 Variation of density (d) with molarity of CuCl in CuCl–KCl–CH_3CN–H_2O mix solvent at various temperatures.

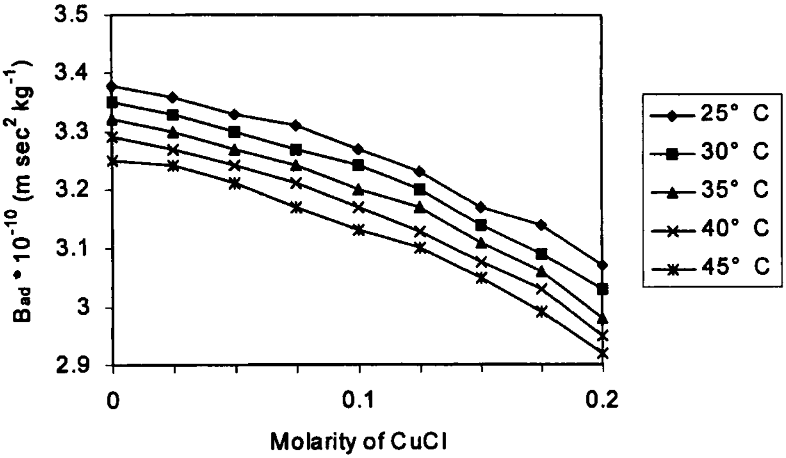

FIGURE 2 Variation of adiabatic compressibility of CuCl in CuCl–KCl–CH_3CN–H_2O mix solvent at various temperatures.

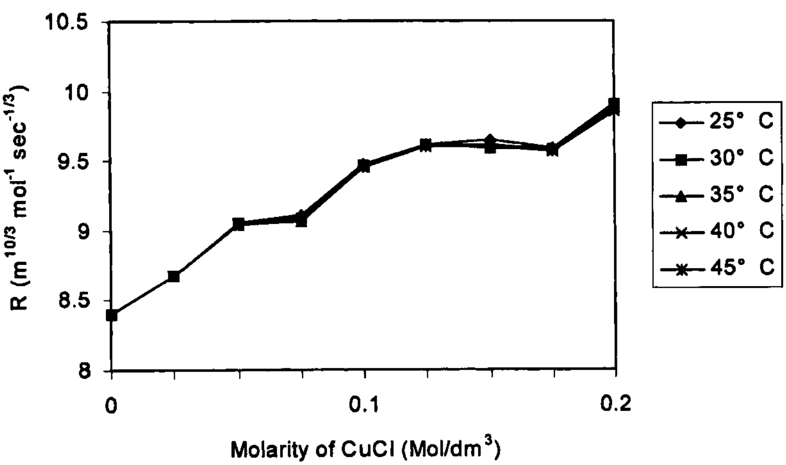

FIGURE 3 Variation of Rao constant (R) with molarity of CuCl in CuCl–KCl–CH_3CN–H_2O mix solvent at various temperatures.

Nomoto established the validity of Eqs. (2), (4), (6) in a large number of liquid mixtures and stated that for unassociated components in the liquid mixtures, the variation of R, β and b with mole fraction of solute will be linear. In the present study of electrolytic mixture, a non linear relation is observed indicating that association exists within

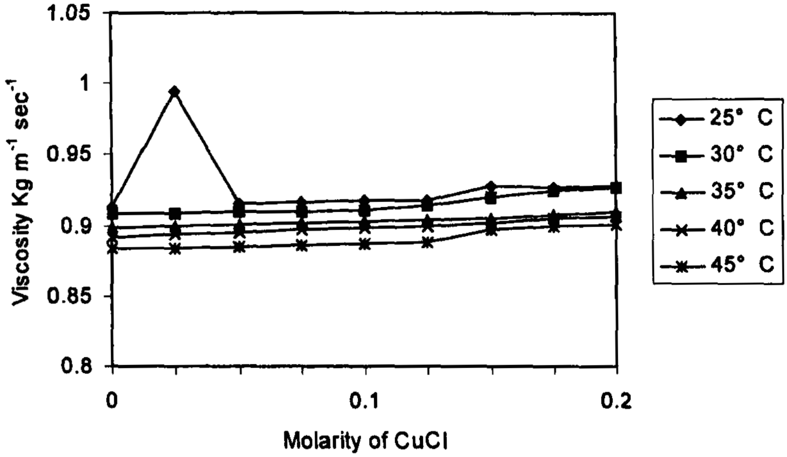

FIGURE 4 Variation of viscosity of CuCl in $CuCl-KCl-CH_3CN-H_2O$ mix solvent at various temperatures.

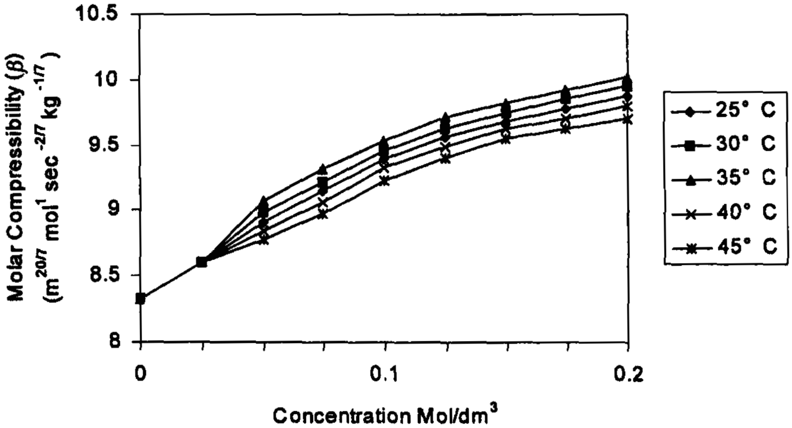

FIGURE 5 Variation of molar compressibility of CuCl in $CuCl-KCl-CH_3CN-H_2O$ mix solvent at various temperatures.

CuCl, CH_3CN, KCl and H_2O. The non-linear behaviour is due to the fact that there will be a change of molecular weight due to the association and the weight of the associated groups is different from that of pure components. Further the smooth non-linear behaviour is observed only in the case of the variation of parameters β, R and b which involves molecular term. Similar observations, were also made

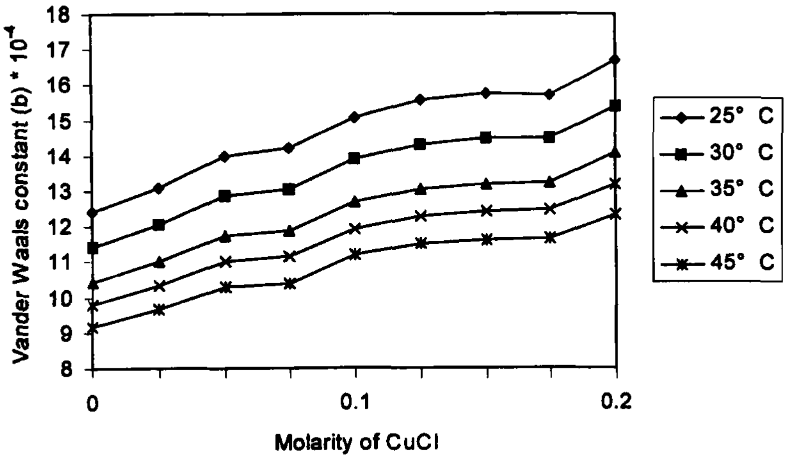

FIGURE 6 Variation of Vander Waals constant (*b*) with molarity of CuCl in CuCl–KCl–CH_3CN–H_2O mix solvent at various temperatures.

by Varada Rajulu and Mabu Sab [2] in liquid mixtures in the case of polyethylene glycol/water mixtures. These observations helped us to confirm the association. Thus the association between CuCl, CH_3CN, KCl and H_2O can be confirmed using ultrasonic velocity data in the present case and the effect of temperature on such association has also been observed. The decrease of β_{ad} and increase of U and Z with concentration and temperature indicates the presence of strong interaction through complexation. This is further supported by the small increase of viscosity (η) with concentration.

In the present study, molar sound velocity R and compressibility β are found to vary with concentration of solute. This, we suggest, may imply the presence of complex formation in the present system. However the small variation in R and b with concentration of solute supports the existence of a dipole–dipole type of interaction between components. It is clear from Figures 1–6 that temperature does not affect much the complexation tendency of the components Refs. [3–9].

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