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Acoustic and thermodynamic behavior of cobalt acetylacetonate in aqueous sodium hydroxide

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Abstract : Viscosity (η) density (ρ) and ultrasonicvelocity (U) in binary mixtures of cobalt acetylacetonate with aqueousSodium Hydroxide were measured at 35^0C, 40^0C, 45ºC and atmosphericpressure by using a single-crystal interferometer at a frequency of 2MHz,The Parameters and concentrations were used to calculating adiabatic compressibility (β), inter-molecularfree length (L_f), Specific acoustic impedance (Z). apparent molal compressility (ϕ_k) solvation number (S_n) and relative association (R_a). The resultsindicate that there is significant interaction between solute and solvent.

(**Keywords:** Ultrasonic velocity, cobalt acetylacetonate, Adiabatic compressibility, specific acoustic impedance, Intermolecular free length)

Introduction

Determination of ultrasonic velocity in aqueous[1-2], pure nonaqueous[3-4] and mixed[5-6] electrolytic solutions give information about physico-chemical of behavior of liquid mixtures such as molecular association and dissociation, Mixed[7] liquids rather than single pure liquids are of almost practical importance in most chemical and industrial processes as they provide a wide range of mixtures of two or more components in varying proportions so as to permit continuous adjustmentof thederived Properties of the medium. The present paper is an investigation of the behavior of binary solution of cobalt acetylacetonate in aqueous NaOH with regard to adiabatic compressibility, intermolecular free length, specific acoustic impedance, and relative association from ultrasonic measurements at 35ºC, 40ºC, 45ºC,.

Experimenal

All chemicals were used of analytical reagent (AR) grade. The purity of the used chemicals was checked by density determination at 40ºC, The values of density obtained tally with the literature values, Binary liquids mixtures of different known compositions were prepared inairtight-stopperedmeasuring flask to minimize the leakage of volatile liquids. The weighing was done using electronic balance with precision $\pm$ 0.01mg. The double walled bicapillaryPyknometer was used for the measurement of densities of solvents and solutions[8-9] with an accuracy of $\pm$ 0.0005gm/cm^3. An ubbelohde viscometer, having frequency of 2 MHz (Mittal Enterprises, New Delhi, Model: F-81) with an accuracy of $\pm$ 0.05%[10-11], Detailed of Experimental techniques are given elswhere[12]

Theory and calculation

Different thermodynamic parameters such as adiabatic compressibility (β), intermolecular free length (L_f), Specific acoustic impedance (Z), apparent molal compressibiliy (ϕ_k), solvation number (S_n) and relative association (R_a), have been calculated at 35ºC, 40ºC 45ºC using ultrasonic velocity (U), density (ρ) and viscosity (η) of these solutions with the help of following equations.

1. $\beta = U^2 \times \rho^{-1}$
2. $L_f = K \times \beta^{-1/2}$
3. $Z = U \times \rho$

4. $\phi_k = 1000(\rho^0\beta - \beta^0\rho)/C\rho^0 + (\beta^0 \times M)/\rho^0$

5. $S_n = n_1 / n_2 (1 - \beta / \beta^0)$

6. $R_a = (\rho / \rho^0)(U^0 / U)^{1/3}$

Where ρ, ρ^0 and U, U^0 are the densities and ultrasonic velocities of solution and solvent, respectively; K is Jacobson constant; M molecular weight of solute; β^0 and β the adiabatic compressibility of solvent, and solution, C is concentration in mole/Liter; and are the number of moles of solvent and solute, respectively.

Measured parameters of cobalt acetylacetonate with sodium Hydroxide

Table-1 : at 35^{oC}

C mol/lit	ρ g/cm^3	η c.p.	U m/sec	$\beta \times 10^{12}$ cm^2/dyne	$\phi_k \times 10^9$ cm^2/dyne	$Z \times 10^5$ g/s.cm	L_f A	R_a	S_n
0.0467	1.1070	0.6082	1418	44.92	-8.6682	0.1570	0.4229	0.2423	5.1169
0.0933	1.1117	0.6128	1421	44.45	-8.5481	0.1580	0.4211	0.0845	10.1118
0.1400	1.1164	0.6175	1424	44.17	-8.4704	0.1590	0.4194	0.1267	15.0492
0.1866	1.1210	0.6222	1427	43.80	-8.4037	0.1600	0.4176	0.1688	19.9300
0.2333	1.1257	0.6268	1430	43.44	-8.3418	0.1610	0.4159	0.2108	24.7551
0.2799	1.1303	0.6315	1433	42.08	-8.2825	0.1620	0.4142	0.2528	29.5252
0.3266	1.1350	0.6362	1436	42.72	-8.2249	0.1630	0.4124	0.2948	34.2411
03732	1.1397	0.6408	1439	43.37	-8.1686	0.1640	0.4107	0.3366	38.9037
0.4199	1.1443	0.6455	1442	42.02	-8.1133	0.1650	0.4091	0.3785	43.5137
0.4665	1.1490	0.6502	1445	41.68	-8.0588	0.1660	0.4074	0.4202	48.0718

Measured parameters of Cobalt acetylacetonate with sodium Hydroxide

Table-2 : at 40^{o}C

0.0467	1.0830	0.5674	1410	46.31	-8.2675	0.1530	0.4330	0.430	5.1360
0.0933	1.0876	0.5720	1414	45.90	-8.1938	0.1540	0.4310	0.860	10.1960
0.1400	1.0923	0.5767	1416	45.50	-8.1310	0.1550	0.4290	0.1290	15.1970
0.1866	1.0970	0.5814	1418	45.12	-8.0710	0.1560	0.4270	0.1720	20.1400
0.2333	1.1016	0.5860	1422	44.74	-8.0130	0.1570	0.4250	0.2150	25.0256
0.2799	1.1063	0.5907	1424	44.37	-7.9560	0.1580	0.4240	0.2580	29.8550
0.3266	1.1110	0.5954	1428	44.00	-7.9000	0.1590	0.4220	0.3010	34.6280
03732	1.1156	0.6000	1430	43.63	-7.8450	0.1600	0.4200	0.3440	39.3470
0.4199	1.1203	0.6047	1432	43.24	-7.7900	0.1610	0.4180	0.3870	44.0120
0.4665	1.1250	0.6094	1434	42.90	-7.7360	0.1620	0.4165	0.4290	48.6230

Measured parameters ofCobalt acetylacetonate with sodium Hydroxide
Table-3 : at 45ºC

0.0467	1.0584	0.5390	1402	47.84	-7.8370	0.1485	0.4440	0.0440	5.1550
0.0933	1.0630	0.5436	1406	47.40	-7.8140	0.1495	0.4420	0.0880	10.2855
0.1400	1.0677	0.5484	1410	47.00	-7.8672	0.9505	0.4401	0.1320	15.3560
0.1866	1.0724	0.5531	1412	46.60	-7.7154	0.1515	0.4380	0.1760	20.3660
0.2333	1.0770	0.5577	1416	46.20	-7.6616	0.1520	0.4360	0.2201	25.3170
0.2799	1.0816	0.5624	1418	45.80	-7.6072	0.1530	0.4340	0.2640	30.2105
0.3266	1.0864	0.5670	1420	45.40	-7.5527	0.1540	0.4325	0.3080	35.0460
03732	1.0910	0.5717	1422	45.02	-7.4981	0.1550	0.4305	0.3520	39.8260
0.4199	1.0957	0.5763	1426	44.64	-7.4440	0.1561	0.4290	0.3950	44.5502
0.4665	1.1004	0.5811	1430	44.30	-7.3905	0.1572	0.4270	0.4390	49.2200

Results and Discussion

The measured parameters viz ultrasonic velocity (U), density (ρ), viscoisty (η) are given in the table (I) The table shows three parameters increase with concentration of cobalt acetylacetonate. This shows that strong interaction observed at higher concentrations of cobalt acetylacetonate and suggests more association between solute and solvent molecules in the system. The variation of ultrasonic velocity (U) With solute concentration (C) can be expressed in terms of the concentration derivatives of density () and adiabatic compressibility () by the relationship.

dU/dC = U/2 [1/ (d/dC)+1/ (d/DC)]

The result indicate that the density increases while the adiabatic compressibility decreases with increasing solute concentration and so the quantity [d/dC] is positive while [d/dC] is negative, Since the quantity predominates over for the solution, the concentration derivative of velocity , will be positive and so the velocity increases with increasing concentration of cobalt acetylacetonate. This is an agreement with the result of several works reported for electrolytic solutions[13-14]. The adiabatic compressibility, for the solution of cobalt acetylacetonate decrease with increase in solute concentration (table-1) The decrease in simple metal cations and anions. These solutions are surrounded by a layer of solvent molecules, firmly bound, and oriented towards the ions. The and thus the internal pressure increases, which lowers the compressibility of solution i.e. the solutions become harder to compress[15]. The intermolecular free length (L_f), which is expected to decrease as a result of mixing of the two components, decreases with the increase in solute concentration. Rise in temperature generally increases the internal energy of the system by distorting the local structure, resulting in an increase in intermolecular free length and subsequently decreasing the ultrasonic velocity. in the present study, the elevation of temperature from 35ºC to 45ºC show the same trends.

The intermolecular free length (L_f) decrease while specific acoustic impendance (Z) increase with increase in solute concentration (table-1) which can be explained on the basis of lyophobic interaction between the solute and solvent molecule which increases the inter molecular distance leaving relatively wider gaps between the molecules and thus becoming the main cause impediment to the propagation of ultrasound waves[16]and affects the structural arrangement. The specific acoustic impedance, a product of the density of the solution and the velocity, his shown the reverse trends to that of inter molecular free length. Thus the fact that increase of velocity, decrease in intermolecular forces with the addition of solute forming aggregates of solvent molecules around solute ions and supports the strong solute-solvent interactions, due to which structural arrangement is affected.

Relative association is influence by two factors[17] (i) the breaking up the solvent molecules on addition of electrolyte to it and (ii) the solvation of ion that are simultaneously present; the former resulting in a decrease and later increase of relative association. In the present investigation, it has been observed that relative association value increases with increase in concentration. Similar results have been reported in literature[18-19]. Solvation number (S_n) are calculated using Passnsky equation and are listed in table (1). The $S_n$valuesare found to increase with the increase in solute, which also suggested close association between solute and solvent.

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