



THE STUDY OF ACOUSTIC AND THERMODYNAMIC PROPERTIES OF IRON ACETYLACETONATE IN AQUEOUS SODIUM HYDROXIDE

Neelam Shakya^{1,*}, Neha Shakya¹ and S.S. Yadav²

¹Department of Chemistry, Kr. R.C.M. (P.G.) College, Mainpuri (U.P.) India

²Department of Chemistry, Ganjundwara College, Ganjundwara (U.P.) India

*E-mail: nilam1.chem@gmail.com

ABSTRACT

Viscosity (η), density (ρ), and ultrasonic velocity (U) in binary mixtures of iron acetylacetonate with aqueous NaOH were measured at 30°C, 35°C, 40°C and atmospheric pressure by using a single-crystal interferometer at a frequency of 2 MHz. These parameters and concentrations were used to calculate adiabatic compressibility (β), intermolecular free length (L_f), specific acoustic impedance (Z), apparent molal compressibility (ϕ_k), solvation number (S_n) and relative association (Ra). The results indicate that there is a significant interaction between solute and solvent.

Keywords: Ultrasonic velocity, Iron acetylacetonate, Adiabatic compressibility.

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INTRODUCTION

Measurements of ultrasonic velocity in aqueous¹⁻², pure nonaqueous³⁻⁴, and mixed⁵⁻¹⁰ electrolytic solutions give information about physico-chemical behavior of liquid mixtures such as molecular association and dissociation. Mixed¹¹⁻¹³ 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 adjustment of the derived properties of the medium. The present paper is an investigation of the behavior of binary solutions of iron acetylacetonate in aqueous NaOH with regard to adiabatic compressibility, intermolecular free length, specific acoustic impedance and relative association from ultrasonic measurements at 30°C, 35°C and 40°C.

EXPERIMENTAL

All chemicals were used of analytical reagent (AR) grade. The purity of the used chemicals was checked by density determination at 35°C. The values of density obtained tally with the literature values. Binary liquids mixtures of different known compositions were prepared in airtight-stoppered measuring flask to minimize the leakage of volatile liquids. The weighing was done using electronic balance with precision ± 0.01 mg. The double walled bicapillary pycnometer was used for the measurement of densities of solvents and solutions¹⁴⁻¹⁵ with an accuracy of ± 0.0005 gm/cm³. An Ubbelohde viscometer, having frequency of 2 MHz (Mittal Enterprises, New Delhi, Model: F-81) with an accuracy of $\pm 0.05\%$ ¹⁶⁻¹⁷. Detailed of experimental techniques are given elsewhere¹⁸.

Theory and Calculation

Different thermodynamic parameters such as adiabatic compressibility (β), intermolecular free length (L_f), specific acoustic impedance (Z), apparent molal compressibility (ϕ_k), solvation number (S_n) and relative association (Ra), have been calculated at 30°C, 35°C, and 40°C using ultrasonic velocity (U), density (ρ) and viscosity (η) of these solutions with the help of the following equations.

$$\beta = U^{-2} \times \rho^{-1} \quad (1)$$

$$L_f = K \times \beta^{-1/2} \quad (2)$$

$$Z = U \times \rho \quad (3)$$

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

$$S_n = n_1/n_2 (1 - \beta / \beta^\circ) \quad (5)$$

$$Ra = (\rho / \rho^\circ) (U^\circ / U)^{1/3} \quad (6)$$

Where ρ , ρ° and U, U° are the densities and ultrasonic velocities of solution and solvent, respectively; K is Jacobson constant; M molecular weight of solute; β° and β the adiabatic compressibility of solvent and solution, C is concentration in mole/litre; n_1 and n_2 are the number of moles of solvent and solute, respectively.

Table-1: Measured parameters of iron acetylacetonate with aqueous NaOH

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_r A	R_a	S_n
30°C									
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	44.55	-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
0.3732	1.1397	0.6408	1439	42.37	-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
35°C									
0.0467	1.0831	0.5676	1412	46.31	-8.2679	0.1529	0.4331	0.0432	5.1363
0.0933	1.0877	0.5722	1415	45.92	-8.1940	0.1539	0.4313	0.0864	10.1964
0.1400	1.0924	0.5769	1418	45.53	-8.1311	0.1549	0.4295	0.1295	15.1975
0.1866	1.0971	0.5816	1421	45.14	-8.0715	0.1559	0.4277	0.1725	20.1404
0.2333	1.1017	0.5862	1424	44.76	-8.0135	0.1569	0.4258	0.2155	25.0260
0.2799	1.1064	0.5909	1427	44.39	-7.9565	0.1579	0.4241	0.2585	29.8552
0.3266	1.1111	0.5956	1430	44.01	-7.9004	0.1589	0.4223	0.3013	34.6287
0.3732	1.1157	0.6002	1433	43.65	-7.8451	0.1599	0.4205	0.3441	39.3475
0.4199	1.1204	0.6049	1436	43.28	-7.7904	0.1609	0.4188	0.3869	44.0123
0.4665	1.1251	0.6096	1439	42.92	-7.7363	0.1619	0.4170	0.4296	48.6239
40°C									
0.0467	1.0586	0.5393	1405	47.86	-7.8371	0.1487	0.4441	0.0442	5.1551
0.0933	1.0632	0.5439	1408	47.44	-7.8140	0.1497	0.4422	0.0882	10.2860
0.1400	1.0679	0.5486	1411	47.03	-7.7675	0.1507	0.4403	0.1325	15.3562
0.1866	1.0726	0.5533	1414	46.63	-7.7156	0.1517	0.4384	0.1766	20.3664
0.2333	1.0772	0.5579	1417	46.23	-7.6618	0.1526	0.4365	0.2205	25.3177
0.2799	1.0818	0.5626	1420	45.84	-7.6074	0.1536	0.4347	0.2645	30.2109
0.3266	1.0866	0.5673	1423	45.45	-7.5529	0.1546	0.4328	0.3083	35.0468
0.3732	1.0912	0.5719	1426	45.07	-7.4985	0.1556	0.4310	0.3521	39.8265
0.4199	1.0959	0.5766	1429	44.69	-7.4444	0.1566	0.4292	0.3959	44.5506
0.4665	1.1006	0.5813	1432	44.31	-7.3907	0.1576	0.4274	0.4395	49.2200

RESULT AND DISCUSSION

The measured parameters viz. ultrasonic velocity (U), density (ρ), viscosity (η) are given in the table (1). The table shows these three parameters increase with concentration of iron acetylacetonate. This indicates that strong interaction observed at higher concentrations of iron 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 (ρ) and adiabatic compressibility (β) by the relationship.

$$dU/dC = U/2 [1/\rho(d\rho/dC) + 1/\beta (d\beta/dC)]$$

The result indicate that the density increases while the adiabatic compressibility decreases with increasing solute concentration and so the quantity $[d\rho/dC]$ is positive while $[d\beta/dC]$ is negative. Since the quantity $1/\beta[d\beta/dC]$ predominates over $1/\rho[d\rho/dC]$ for the solution, the concentration derivative of velocity $[dU/dC]$, will be positive and so the velocity increases with increasing concentration of iron acetylacetonate. This is an agreement with the result of several workers reported for electrolytic solutions¹⁹⁻²¹. The adiabatic compressibility, β for the solution of iron acetylacetonate decrease with increase in solute concentration (table-1). The decrease in adiabatic compressibility is attributed to the fact that the solute molecules, in dilute solution ionize in simple metal cations and anions. These solutions are surrounded by a layer of solvent molecules, firmly bound, and oriented towards the ions. The orientation of solvent molecules around the ions is attributed to the influence of electrostatic field of ions and thus the internal pressure increases, which lowers the compressibility of solution i.e. the solutions become harder to compress²². 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 30°C to 40°C shows the same trend.

The intermolecular free length (L_f) decrease while specific acoustic impedance (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 waves²³ and affects the structural arrangement. The specific acoustic impedance, a product of the density of the solution and the velocity, has shown the reverse trends to that of inter molecular free length. Thus the fact that increase of velocity, decrease of adiabatic compressibility, decrease of intermolecular free length and increase of specific acoustic impedance with increase in molar concentration at all temperatures is an indicative of the increase 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 factors²⁴ (i) the breaking up of 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 literature²⁵. Solvation number (S_n) are calculated using Passynsky⁷ equation and are listed in table (1). The S_n values are found to increase with the increase in solute, which also suggested close association between solute and solvent.

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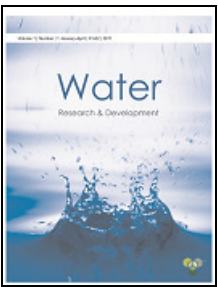
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