Fluid structure and molecular interaction of acetophenone derivatives

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Abstract. Dielectric constants of the binary mixtures of acetophenone, p-chloroacetophenone, p-methyacetophenone and α-hydroxyacetophenone in dilute solutions of benzene and 1,4-dioxane were measured at 303 K and at frequency 100 kHz. The low frequency molecular dynamics of acetophenone and its derivatives have been studied by evaluating the Kirkwood correlation factor $g$, molar polarization $P_2$, excess correlation factor $δg$ and excess free energy $ΔG$. The dipolar contribution to excess free energy of mixing arising from long-range electrostatic interaction and short-range interaction between identical molecules has been assessed separately. The presence of α- and β-multimers in the above systems was identified. The results have been used to interpret the fluid structure in such mixtures.

Keywords. Kirkwood correlation factor; molar polarization; short-range interaction; excess free energy; α- and β-multimers.

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1. Introduction

To understand the fluid structure of acetophenone and its derivatives it is necessary to determine the various dielectric parameters, which are related with inter and intramolecular association and internal rotation. Study of dielectric behaviour of polar molecules and their mixtures [1-4], under varying conditions of composition and temperatures has evoked considerable interest. Dielectric measurements of acetophenone and its derivatives have been made by various workers [1,5-8]. The Kirkwood correlation factor $g$ is a shape-dependent correlation factor and is a measure of short-range intermolecular force leading to dipole-dipole interaction. The value of $g$ is unity for a normal liquid while it departs from unity in an abnormal or associated liquid. On dilution with non-polar solvent, the value of $g$ undergoes a change, which signifies the change in the nature of multimerization.

Acetophenone is a rigid molecule, the acetyl group being in plane with the benzene ring. Recently, the authors [1] studied some rigid polar molecules and their mixtures and found formation of complexes. Singh and Sharma [7] have studied
the binary mixture of p-methyacetophenone with DMSO in dilute solutions. A strong hydrogen bond is expected for an acetyl group ortho to the hydroxy atom, because oxygen is a proton acceptor and because of intramolecular hydrogen bond it is sterically favoured in α-hydroxyacetophenone.

Earlier the authors [2] have reported the utility of dielectric measurements while studying the molecular interaction in a binary mixture of liquids by assessing some parameters like Kirkwood correlation factor \( g \), molar polarization \( P_2 \), excess correlation function \( \delta \epsilon \) and excess free energy of activation \( \Delta G \). Study of \( g \) can be used as a tool for the interpretation of liquid structure and intermolecular arrangement. With this in view, the present study is to design to extend our scope of investigation to another aspect of molecular dynamics at a microlevel by exploring the probability of multimers formation due to molecular association, long-range and short-range interaction in acetophenone (ACT), p-methyacetophenone (PMA), p-chloroacetophenone (PCLA) and α-hydroxyacetophenone (OHA) in the presence of benzene and 1,4-dioxane.

2. Experimental methods

The dielectric constant \( \varepsilon_0 \) was measured at 100 kHZ using a dipole meter by directly measuring the capacitance and calibrating it for standard liquids. The dielectric constant \( \varepsilon_\infty \) at optical frequency was obtained by squaring the refractive index for sodium D-lines, measured with the help of an Abbe’s refractometer. Using a water circulating thermostat, the temperature was maintained at 303 K. The accuracy of measurement of \( \varepsilon_0 \) and \( \varepsilon_\infty \) are nearly 0.1% and 0.03% respectively.

3. Theory

The Kirkwood correlation factor \( g \) has been calculated by the modified Kirkwood-Fröhlich [9] equation for dilute solutions in non-polar solvent.

\[
g\mu^2 = \frac{9K T (2\varepsilon_m + \varepsilon_\infty)^2}{4\pi N f_2 (2\varepsilon_m + 1)^2} \times \left[ \frac{V (\varepsilon_m - 1)}{\varepsilon_m} \varepsilon_1 - \frac{3V_1 f_1 (\varepsilon_1 - 1)}{2\varepsilon_m + \varepsilon_1} - \frac{3V_2 f_2 (\varepsilon_\infty - 1)}{2\varepsilon_m + \varepsilon_\infty} \right]. \quad (1)
\]

Here \( \varepsilon_m \) is the static dielectric constant of the solution, \( \varepsilon_\infty \) is the square of refractive index at the frequency of D-lines of sodium for pure solute, \( \varepsilon_1 \) is the static dielectric constant of pure solvent, \( f_1 \) is the mole fraction of the solute, \( f_2 \) is the mole fraction of the solute, \( V, V_1 \) and \( V_2 \) are the molar volume of solution, pure solvent and pure solute respectively. \( K, T \) and \( N \) are Boltzmann’s constant, absolute temperature and Avogadro’s number respectively. Molar polarization of solutions is

\[
P = f_1 P_1 + f_2 P_2 \quad (2)
\]

from which the molar polarization of the solute is