Dielectric Behaviour of N-Methylacetamide & N, N-Dimethylacetamide in Benzene, Carbon Tetrachloride & Dioxane Solutions†

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Dielectric constants and dipole moments of N-methylacetamide (NMA) and N,N-dimethylacetamide (DMA) have been determined in benzene, carbon tetrachloride and dioxane solutions at 1 MHz by Guggenheim method. It has been inferred from the change in dielectric constant versus concentration curves that NMA exists in monomer (molecule) (8) while DMA exhibits dimer equilibrium at all concentrations as compared to monomer alone in dioxane solutions. These findings get further support from cryoscopic and infrared measurements.

Dielectric behaviour of amides has been investigated by a number of workers1-8 with a view to examining the mode of interaction and the role of intermolecular hydrogen bonding present in these amides. Although the subject has received considerable attention through Raman and infrared

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techniques, the findings are limited, scanty and inconclusive. Therefore, the present studies have been undertaken to examine the state of mono- and di-substituted amides inorder to elaborate their general feature in solutions from dielectric measurements.

N-methylacetamide (NMA) and N, N-dimethylacetamide (DMA) (E. Merck) and benzene, carbon tetrachloride and dioxane (all BDH grade) were purified by the usual methods. Refractive indices and boiling points of the purified samples were found to be in close proximity with the literatutue values. The dielectric constant measurements were carried out at 30° at a radio frequency of 1 MHz with the help of a Toshniwal dipole meter Type RL 09 and refractive indices of the solvent and solutions were determined with the help of “ASCO” abbe refractometer as described earlier.

The dipole moment has been calculated by Guggenheim method, i.e. by plotting a quantity \( L_{\alpha} \) against the concentration \( C \), in moles of polar solute per cm³. The quantity \( L_{\alpha} \) is given by the relation:

\[
L_{\alpha} = (E_{12} - n_{12}^2) - (E_1 - n_1^2) \quad \text{(1)}
\]

where \( E_1 \) and \( n_1 \) and \( E_{12} \) and \( n_{12} \) represent the dielectric constant and refractive index of pure solvent and solution respectively; the slope \( L_{\alpha}/C \) of the curve at \( C = 0 \) is then used to calculate \( \mu \) by Eq. (2),

\[
\mu^2 = \frac{kT}{4\pi N} \frac{3}{(E_1 + 2)(n_1^2 + 2)} \left( \frac{\Delta}{C} \right) \quad \text{(2)}
\]

The change in dielectric constant (\( \Delta\varepsilon \)) has been plotted against concentration \( C \) using the well known relation of Govinda Rau, i.e.

\[
\Delta\varepsilon = \varepsilon_1 (1 + aC) \quad \text{(3)}
\]

In order to arrive at the precision of dipole meter and refractometer, the dipole moments of methanol, pyridine, acetone and nitrobenzene were determined in benzene. The experimental and literature values agreed with in ±3%. The plots of \( \Delta\varepsilon \) against \( C \) for NMA and DMA in benzene carbon tetrachloride and dioxane solutions are shown in Fig. 1. Their slopes \( \Delta/C \) evaluated from \( \Delta \) vs \( C \) linear plots in tangent to curves and \( \mu \) values determined by Guggenheim method are summarised in Table 1.

The \( \Delta\varepsilon \) versus \( C \) plots are smooth curves for NMA in benzene and carbon tetrachloride solutions and linear in dioxane. However, for DMA the plots are generally linear (Fig. 1). This abnormality can be explained on account of the absence of -NH group in DMA restraining thereby to participate either in bonding or self-association.

The \( \mu \) values are in close agreement with those reported by other investigators 11. For DMA in dioxane and benzene and for NMA in dioxane solutions, but are found to be higher than those determined in vapour phase by Meighan and Cole6. This can be explained in terms of the solvent effect. The solvent effect of CCl₄, benzene, and dioxane for NMA and DMA has been determined from the Conner and Smyth relation using the literature values of \( \mu \) and has been classified in Table 2.

\[
\mu_s = \mu_0 [1 + C (\varepsilon_1 - 1)] \quad \text{(4)}
\]

where \( \mu_s \) and \( \mu_0 \) represent the dipole moment in solution and vapour phase respectively.

The data in Table 2 reveal that the dipole moment of DMA remains almost constant in benzene, CCl₄, and dioxane solutions; whereas it is found to increase with concentration for NMA in CCl₄ and benzene.

**Table 1** — Slopes of \( \Delta\varepsilon \) versus \( C \) and the Dipole Moments of the Amides in Different Solvents at 30°

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conc. ( C \times 10^{-4} ) (mol/ml)</th>
<th>( \mu ) (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-methylacetamide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>0.044</td>
<td>2.434</td>
</tr>
<tr>
<td></td>
<td>0.105</td>
<td>3.348</td>
</tr>
<tr>
<td></td>
<td>0.173</td>
<td>3.998</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td></td>
<td>4.82</td>
</tr>
<tr>
<td></td>
<td>0.050</td>
<td>4.633</td>
</tr>
<tr>
<td></td>
<td>0.150</td>
<td>5.906</td>
</tr>
<tr>
<td>Dioxane</td>
<td></td>
<td>2.061</td>
</tr>
<tr>
<td>N, N-dimethylacetamide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>1.671</td>
<td>3.71</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td></td>
<td>3.88</td>
</tr>
<tr>
<td>Dioxane</td>
<td>1.523</td>
<td>3.67</td>
</tr>
</tbody>
</table>

**Table 2** — \( \mu_s/\mu_0 \) Values of NMA and DMA in Carbon Tetrachloride, Benzene and Dioxane Solutions

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \mu_s/\mu_0 ) for NMA</th>
<th>( \mu_s/\mu_0 ) for DMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon tetrachloride</td>
<td>1.30</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>1.74</td>
<td>1.92</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.20</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>1.42</td>
<td>1.52</td>
</tr>
<tr>
<td>Dioxane</td>
<td>1.15</td>
<td>0.96</td>
</tr>
</tbody>
</table>
solutions. The unusual large magnitudes of $\mu_a$ and $\mu_a/\mu_s$ for NMA in CCl$_4$ can be traced to the absence of electrostatic interaction, causing the maximum polarization and orienting the NMA dipoles in such a fashion as to yield largest $\mu$ in this solvent.

On the other hand, the presence of $\text{-NH}$ group in NMA appears to be responsible for (i) $\text{-CONH ... dioxane}$, CCl$_4$ and benzene interactions and (ii) $\text{-CONH ... OCNH ... intermolecular hydrogen bonding}$, depending upon the availability of electrons in these solvents. The linear plots in dioxane points to strong $\text{-CONH ... dioxane}$ interaction than $\text{-CONH ... OCNH ... hydrogen bonding}$. The smooth curves of NMA in benzene and carbon tetrachloride points to dimerization of NMA as the concentration increases. The observed behaviour can be interpreted on the basis of $\text{(-CONH ... free and bonded equilibrium)}$, i.e., $\text{(-CONH ... bonded)}$ from lower to higher concentration of NMA. This is supported by cryoscopic and infrared spectra. However, this peculiarity is found to be absent in a non-hydrogen bonded amide like DMA because of the absence of amino hydrogen for bonding to oxygen of neighboring molecules or to interact with solvent molecules. The overall behaviour can be represented as shown in Chart 1.

The infrared spectra show free v NH at 3470 cm$^{-1}$ in solution of concentration $< 0.01M$. The intensity of vNH decreases with increasing concentration and finally vanishes in 0.1M solution resulting in a simultaneous shift vCO from 1690 to 1680 cm$^{-1}$, which is found to be absent in DMA on account of the absence of $\text{-NH}$ group.

Further, the degree of association and observed molecular weight have been found to increase with increase in concentration of NMA as compared to almost constant molecular weight for DMA.

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References

**Polarographic Reduction of Nitrobenzene at Different Temperatures**

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The polarographic behaviour of nitrobenzene (in 25% of ethanolic solution) has been studied in McIlvaine (McI) buffers of pH 3.2 and 8 and Britton-Robinson (BR) buffers of pH 2.21 and 11 at different temperatures (25-55°). The reduction of nitrobenzene at d.m.e is found to be irreversible and diffusion-controlled at different temperatures. The variation of kinetic parameters with temperatures suggests that the irreversible electrode reaction of nitrobenzene becomes more so at elevated temperatures.

Unlike inorganic depolarizers, the effect of temperature on the electrode kinetics of the irreversible reduction of organic depolarizers has not attracted much attention. Kuznetsova\textsuperscript{1} investigated the effect of temperature on the reduction of organic depolarizers at d.m.e and found the temperature coefficient of $\log k$ lying between 1.15 and 1.5° per degree. Gupta and Kishore\textsuperscript{2} reported that with increasing temperature $\alpha_{\text{irr}}$ for nitrobenzene decreased while $k'_{\text{irr}}$ value indicated that the system was less irreversible at increasing temperature. However this observation is self-contradictory since a decrease in $\alpha_{\text{irr}}$ values signifies\textsuperscript{3-4} that the system is tending to become more irreversible. It was therefore thought worthwhile to study the polarographic reduction of nitrobenzene at different temperatures in the range 25° to 55° in McIlvaine (McI) and Britton-Robinson (BR) buffers.