IJARSCT
International Journal of Advanced Research in Science, Communication and Technology
International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal
ISSN: 2581-9429
Volume 5, Issue 11, March 2025
Impact Factor: 7.67

# Study of Thermodynamical Properties in Binary Mixtures of Chlorobenzene with Formamide

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**Abstract**: *A qualitative study of thermodynamical properties in binary mixtures of chlorobenzene with formamide has been carried out at various temperatures and 11 different concentrations using microwave dielectric technique. The thermodynamical properties of solute-solvent mixture in the microwave frequency range of 10 MHz to 20 GHz gives information about the formation of monomers and multimers as well as interaction between the molecules of the given binary mixtures. The thermodynamical parameters viz. enthalpy, entropy, Arrhenius plot, free energy of activation and its excess properties have been obtained by the least squares fit method using Debye equation characterized by a single relaxation time without relaxation time distribution.*

**Keywords**: Relaxation time; Free enrgy of activation; Excess free energy of activation; Microwave dielectric technique

## I. INTRODUCTION

In this work, we report the qualitative study of thermodynamic properties in a binary mixture of chorobenzene with formamide by using time domain reflectometry technique. The chlorobenzene (CBZ) is a non-associative liquid and formamide (FA) is an associative liquid, one with the chloro- group and other with C=O group.

The dielectric relaxation study provides useful information regarding solute-solvent interactions in liquid mixtures [1-17].

The objective of the present work is to report the thermodynamic properties in a binary mixture of (-Cl) functional group of CBZ with (-C=O) functional group of FA. These functional groups are industrially important solvents used in the chemistry, biochemistry, pharmaceutical and material science.

## II. EXPERIMENTAL

### 2.1 Materials

CBZ and FA (AR grade, Qualigens fine chemicals Pvt. Ltd., Bombay, India) were used without further purification. The solutions were prepared at 11 different volume percentages of CBZ from 0 % to 100 %. Using these volume percents the mole fraction is calculated as

$$x_1 = (v_1\rho_1/m_1) /[ (v_1\rho_1/m_1) + (v_2\rho_2/m_2) ] \quad (1)$$

where $m_1$, $v_1$, $\rho_1$ and $m_2$, $v_2$, $\rho_2$ represent the molecular weight, volume percent, density of the liquids 1 and 2, respectively.

### 2.2 Apparatus

The complex permittivity spectra were studied using Time Domain Reflectometry (TDR) method [19, 20] over the frequency range 10 MHz to 20 GHz [21, 22]. The basic TDR setup consists of a broadband sampling oscilloscope, TDR module and coaxial transmission line. Reflected pulse without sample $R_1(t)$ and with sample $R_X(t)$ were recorded in time window of 5 ns and digitized in 2000 points. The temperature of the sample was controlled electronically within ± 0.5°C.

The experimental values of $\varepsilon^*(\omega)$ are fitted with the Debye equation [23]


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## III. RESULTS AND DISCUSSION

### 3.1 Static dielectric constant and relaxation time

The static dielectric constant ($\varepsilon_0$) and relaxation time ($\tau$) obtained by fitting experimental data with the Debye equation are listed in Table 1.

**Table 1.** Temperature dependent dielectric relaxation parameters for CBZ-FA mixtures*[18]

| $x_1$ | 15°C | 25°C | 35°C | 45°C |
|---|---|---|---|---|
| | $\varepsilon_0$ | | | |
| 1.0000 | 111.23 (17) | 108.18 (29) | 98.80 (19) | 90.57 (27) |
| 0.7783 | 93.81 (17) | 89.65 (24) | 85.56 (32) | 80.16 (23) |
| 0.6094 | 80.30 (21) | 76.57 (31) | 73.45 (29) | 69.73 (21) |
| 0.4765 | 68.34 (56) | 65.11 (62) | 62.30 (54) | 58.53 (48) |
| 0.3692 | 57.80 (18) | 53.97 (24) | 51.30 (21) | 47.74 (16) |
| 0.2806 | 46.76 (43) | 43.22 (59) | 40.12 (49) | 37.33 (23) |
| 0.2064 | 36.70 (70) | 33.73 (76) | 31.38 (57) | 28.18 (34) |
| 0.1375 | 27.23 (75) | 24.92 (83) | 22.80 (75) | 20.80 (67) |
| 0.0889 | 20.12 (11) | 18.70 (23) | 17.32 (18) | 16.25 (16) |
| 0.0415 | 13.16 (10) | 12.05 (14) | 11.28 (11) | 10.27 (10) |
| 0.0000 | 5.94 (5) | 5.54 (8) | 5.51 (9) | 5.33 (9) |
| | $\tau$ (ps) | | | |
| 1.0000 | 51.40( 15) | 38.10 (11) | 30.60 (9) | 24.60 (9) |
| 0.7783 | 45.80 (17) | 34.70 (10) | 27.15 (8) | 21.86 (9) |
| 0.6094 | 40.53 (19) | 31.71 (9) | 24.23 (9) | 19.83 (7) |
| 0.4765 | 35.50 (29) | 28.90 (23) | 21.55 (18) | 18.34 (16) |
| 0.3692 | 31.10 (31) | 26.05 (29) | 19.40 (23) | 17.30 (19) |
| 0.2806 | 27.23 (29) | 23.18 (22) | 17.91 (21) | 16.37 (17) |
| 0.2064 | 23.87 (28) | 20.50 (26) | 16.76 (17) | 15.37 (14) |
| 0.1375 | 20.50 (29) | 18.34 (19) | 15.65 (15) | 14.33 (13) |
| 0.0889 | 17.84 (21) | 16.25 (16) | 14.67 (13) | 13.41 (9) |
| 0.0415 | 15.13 (19) | 14.70 (14) | 13.83 (12) | 13.08 (7) |
| 0.0000 | 13.84 (17) | 13.78 (13) | 13.09 (11) | 13.02 (7) |

*$x_1$ is the mole fraction of FA in CBZ. Number in bracket represent error in the corresponding value, e.g. means 13.41(9) means 13.41 ± 0.9.

### 3.2 Thermodynamic parameters

The thermodynamic parameters like molar enthalpy of activation ΔH and molar entropy of activation ΔS are determined from the Eyring rate equation [19] utilizing least square fit method as

$$\tau = \frac{h}{KT}\exp\left(\frac{\Delta G}{RT}\right) \quad (2)$$

where, $\Delta G = \Delta H - T\Delta S$

The excess free energy of activation of CBZ-FA binary mixture is given by the equation.

$$\Delta G^E = \Delta G - \left[\Delta G_A X_A + \Delta G_B X_B\right] \quad (3)$$

where, $\Delta G_A$ and $\Delta G_B$ represents the activation energies for DCM and FA, respectively and $X_A$ is the mole fraction of CBZ. Here $X_B = 1 - X_A$ is the mole fraction of FA in the studied CBZ-FA mixture.

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**Table 2:** Values of thermodynamical parameters for the mixture of Chlorobenzene and Formamide.

| $x_2$ | ΔG (KJ/mol) | | | | ΔH (KJ/mol) | ΔS (KJ/mol) |
|---|---|---|---|---|---|---|
| | T=15°C | T=25°C | T=35°C | T=45°C | | |
| 0.0000 | 10.5945 | 10.9877 | 11.3809 | 11.7741 | 0.7301 | -0.0393 |
| 0.1522 | 10.8181 | 11.1500 | 11.4819 | 11.8138 | 1.2599 | -0.0332 |
| 0.2877 | 11.1968 | 11.4195 | 11.6422 | 11.8650 | 4.7818 | -0.0223 |
| 0.4091 | 11.5319 | 11.6935 | 11.8551 | 12.0167 | 6.8777 | -0.0162 |
| 0.5185 | 11.8797 | 11.9762 | 12.0727 | 12.1693 | 9.0996 | -0.0097 |
| 0.6177 | 12.2059 | 12.2443 | 12.2828 | 12.3212 | 11.0992 | -0.0038 |
| 0.7079 | 12.5350 | 12.5137 | 12.4925 | 12.4712 | 13.1471 | 0.0021 |
| 0.7903 | 12.8547 | 12.7866 | 12.7184 | 12.6503 | 14.8167 | 0.0068 |
| 0.8660 | 13.1574 | 13.0631 | 12.9688 | 12.8745 | 15.8736 | 0.0094 |
| 0.9356 | 13.4300 | 13.3315 | 13.2329 | 13.1344 | 16.2675 | 0.0099 |
| 1.0000 | 13.6852 | 13.6042 | 13.5233 | 13.4423 | 16.0167 | 0.0081 |

When two liquids are mixed together, there is a change in the energy of the system. This change in energy can be interpreted in terms of its activation energies such as free energy of activation (ΔG), molar enthalpy of activation (ΔH) and molar entropy of activation (ΔS) are tabulated in Table 2.

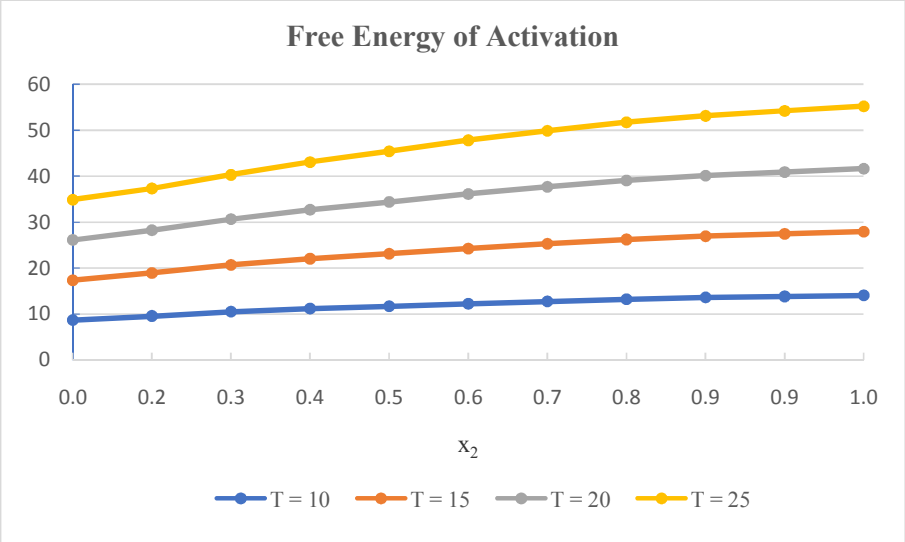


**Figure 1:** Free energy of activation (ΔG) versus mole fraction ($x_2$) of FA in CBZ at different temperatures.

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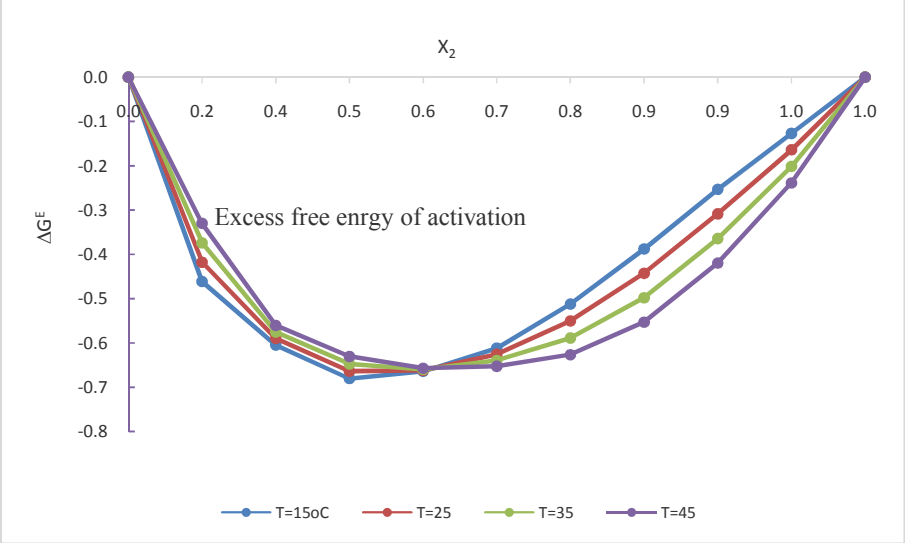


**Figure 2:** Excess free energy of activation ($\Delta G^E$) versus mole fraction ($x_2$) of FA in CBZ at different temperatures.

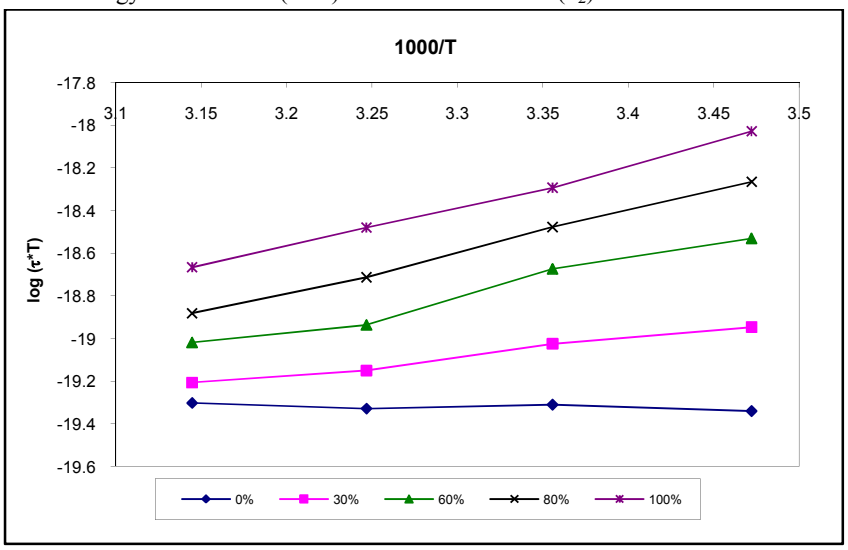


**Figure 3:** Arhenius behavior of DCM-FA mixture at various temperatures and concentrations.

The value of free energy of activation (ΔG) is least for CBZ and increases with increase in concentration of FA at all temperatures as shown in Figure 1. This indicated that the FA molecules in the mixture dominate over CBZ molecules. This dominance of FA over CBZ is primarily due to its large dipole moment values. From the Figure 2, the values of excess activation free energy ($\Delta G^E$) are negative for all concentrations and temperatures. These negative values confirms that there is an decrease in hindrance to the reorientation for the molecules of CBZ, FA and in their binary mixtures. Plot of ln (τT) versus 1000/T of CBZ-FA for various concentrations should be a straight line is as shown in Figure 3. The values of molar enthalpy of activation (ΔH) are positive for all concentrations of the system. The positive value shows endothermic interaction between CBZ-FA mixture of the system. The values of molar entropy of activation (ΔS) of the system are a measure of the orderly nature of the molecule. In this system, these values are negative in CBZ rich region and positive in FA rich region. These values are increases with increasing the mole fraction of FA in CBZ, it means the environment of the system is non-cooperative resulting in the activated state, which is more disordered than the normal state.


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## IV. CONCLUSION

Free energy of activation increases with increasing the mole fraction of FA in CBZ of the system. The free energy of activation (ΔG), molar enthalpy of activation (ΔH) and molar entropy of activation (ΔS) are studed from this work for the binary mixture of chlorobenzene and formamide by using microwave dielectric spectroscopy.

## ACKNOWLEDGEMENT

We are thankful to Prof. V.P. Pawar, Head, Department of Physics & Electronics, Maharashtra Udayagiri Mahavidylaya, Udgir, for their valuable guidance.

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