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# PHYSICOCHEMICAL STUDIES OF SOME AZOMETHINES OF P-AMINO PHENOL IN DMF AND DMSO SOLUTIONS AT 308.15 K

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**Abstract-** Some physicochemical properties such as the density, conductance and heat of solutions of some azomethines of p-amino phenol have been determined in dimethyl formamide (DMF) and dimethylsulfoxide (DMSO) solutions over a wide range of concentrations at 308.15 K.

**Keywords-** physicochemical properties, dimethyl formamide, dimethylsulfoxide

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## Introduction

Azomethines are known to have various applications in different fields[1-6] such as in perfumery, as corrosion inhibitor, as complexing agents and as intermediate in many reactions. Further, some of them are known to have a wide range of biological activities[7-9]. Thus, it will be useful to determine physicochemical properties of these compounds which will help to use these bases in other applications.

In the present work, the physicochemical properties such as density, conductance and heat of solution of some azomethines of p-amino phenol have been determined in dimethyl formamide (DMF) and dimethylsulfoxide (DMSO) at 308.15 K.

## Experimental

The solvents dimethyl formamide (DMF) and dimethylsulfoxide (DMSO) used for the study were purified by standard methods reported earlier [10].

All the synthesized azomethines were recrystallized from methanol. [Fig-1] shows the structure of all the azomethines along with their IUPAC names.

For the determination of density and conductance, a series of solutions of different concentrations were prepared for each azomethine in DMF and DMSO solvents. The density and conductance were measured by Pyknometer and Systronics Conductometer (Model No. 306) at 308.15 K.

The solubility of each azomethine was determined at 308.15 K by transferring 25 ml of saturated solution into a pre-weighed 50 ml beaker and solvent was evaporated to dryness until constant weight is obtained. Three replicate measurements were carried out at a particular temperature and average value of weight was determined. The weight of the solution was determined in a stoppered conical flask. The amount of solvent in 25 ml solution was then calculated by subtracting the weight of the solute from the weight of solution. Finally, the moles of solute and solvent were determined in one liter of saturated solution.

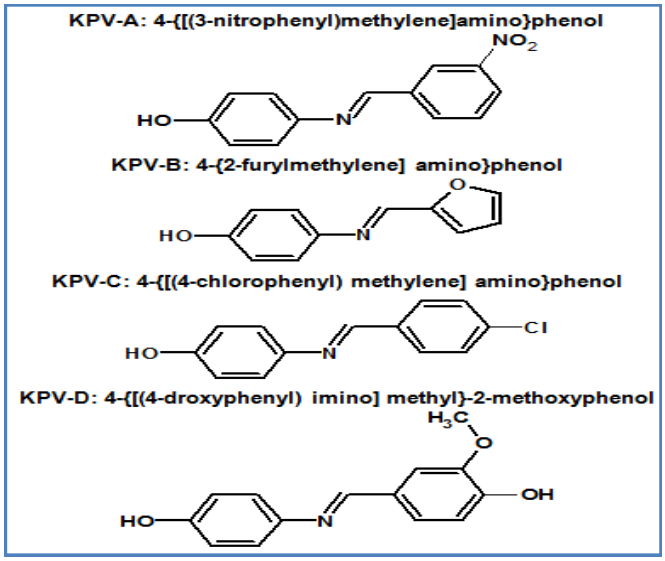


**Fig. 1-** Structure of the Schiff bases along with their IUPAC names.

## Results and Discussion

The density of solution ($r_{12}$) is related to densities of the solvent, solute and their weight fractions $g_1$ and $g_2$, according to the [Eq-1]

$$1/r_{12} = g_1/r_1 + g_2/r_2 \quad (1)$$

where $r_{12}$ is density of solution and $r_1$ and $r_2$ are the densities of the solvent and solute respectively. The density of each azomethine was determined form the slope of the plot of $1/r_{12}g_1$ verses $g_2/g_1$. The inverse of the slope gives $r_2$.

Further, from the knowledge of structural aspect, the densities of azomethines were also calculated by the following equation [11].

$$r = KM / N_A ASDV_i \qquad (2)$$

where r is the density of the compound, K is packing fraction (0.60), M is the molecular weight of the compound, $N_A$ is the Avogadro's number and $DV_i$ is the volume increment of the atoms and atomic groups present in the compound. The theoretical and calculated densities are given in [Table-1].

*Table 1- Experimental and calculated densities of azomethines in DMF and DMSO solutions at 308.15 K.*

| Compound Codes | Density gm/cm³ Solvents | | Density Calculated from |
|---|---|---|---|
| | DMF | DMSO | [Eq-2] gm/cm³ |
| KPV - A | 1.5263 | 1.18 | 1.1931 |
| KPV - B | 1.519 | 1.353 | 1.3899 |
| KPV – C | 1.2658 | 1.121 | 1.1722 |
| KPV - D | 1.2358 | 1.2 | 1.0771 |

It is observed from [Table-1] that in some cases, there is quite good agreement between theoretical and experimental density values where as in others, deviations between theoretical and experimental densities are larger. That indicates the molecular interactions exist in solutions.

Usually intermolecular interactions do not affect the density but due to different groups in different substituents, there may be change in volume as well as in the molecular weight of the compound. Thus, the deviations between experimental and calculated values again confirm the existence of intermolecular interactions between solute and solvent molecules.

The conductivity of azomethines in DMF and DMSO solution are given in the [Table-2].

*Table 2- The conductance (C) of azomethines in DMF and DMSO solutions at 308.15 K.*

| Conc. C (gm/lit) | C. $10^5$ (W)$^{-1}$ | C. $10^5$ (W)$^{-1}$ | C. $10^5$ (W)$^{-1}$ | C. $10^5$ (W)$^{-1}$ | C. $10^5$ (W)$^{-1}$ | C. $10^5$ (W)$^{-1}$ | C.$10^5$ (W)$^{-1}$ | C. $10^5$ (W)$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | DMF | | | | DMSO | | | |
| | KPV-A | KPV-B | KPV-C | KPV-D | KPV-A | KPV-B | KPV-C | KPV-D |
| 0.001 | 0.0504 | 0.0181 | 0.001 | 0.4284 | 0.024 | 0.026 | 0.0596 | 0.0395 |
| 0.002 | 0.0652 | 0.0247 | 0.002 | 0.2771 | 0.0271 | 0.0333 | 0.076 | 0.0424 |
| 0.004 | 0.0678 | 0.0381 | 0.004 | 0.1441 | 0.0332 | 0.0454 | 0.0842 | 0.0486 |
| 0.006 | 0.0694 | 0.0492 | 0.006 | 0.0983 | 0.0366 | 0.0569 | 0.0901 | 0.0539 |
| 0.008 | 0.0717 | 0.0594 | 0.008 | 0.0762 | 0.0423 | 0.0682 | 0.0995 | 0.059 |
| 0.01 | 0.0731 | 0.0673 | 0.01 | 0.0621 | 0.0438 | 0.0704 | 0.106 | 0.0617 |
| 0.02 | 0.0828 | 0.104 | 0.02 | 0.0352 | 0.0465 | 0.108 | 0.116 | 0.0876 |
| 0.04 | 0.1 | 0.1538 | 0.04 | 0.0213 | 0.058 | 0.193 | 0.162 | 0.126 |
| 0.06 | 0.119 | 0.1821 | 0.06 | 0.0169 | 0.0676 | 0.282 | 0.167 | 0.166 |
| 0.08 | 0.13 | 0.2124 | 0.08 | 0.0138 | 0.0728 | 0.349 | 0.174 | 0.192 |
| 0.1 | 0.141 | 0.25 | 0.1 | 0.012 | 0.081 | 0.425 | 0.192 | 0.231 |

The equivalent conductance ($l_C$) of each solution was calculated by the following equation:

$$l_C = 1000\,k / c \qquad (3)$$

where k is the specific conductance, c is the concentration (g.equi/lit) of the solutions respectively.

[Fig-2] and [Fig-3] shows the variation of equivalent conductance ($l_C$) verses Öc for DMF and DMSO systems. It is observed that the values of $l_C$ are higher for DMF than those in DMSO solutions. Further, it is obvious from these figures that almost all azomethines are weak electrolytes in nature.

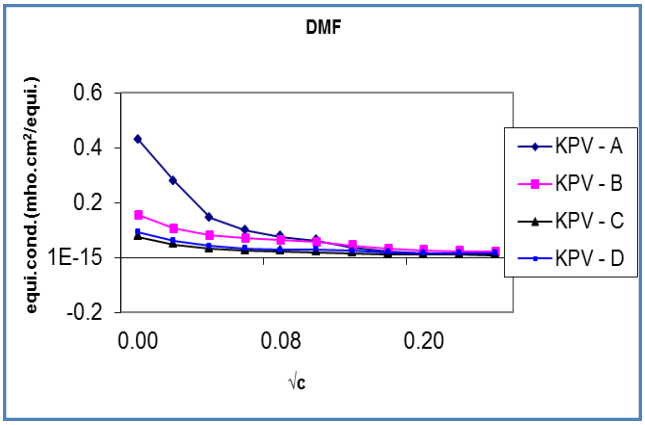


**Fig. 2-** The equivalent conductance (IC) verses √c of azomethines in DMF Solutions at 308.15 K.

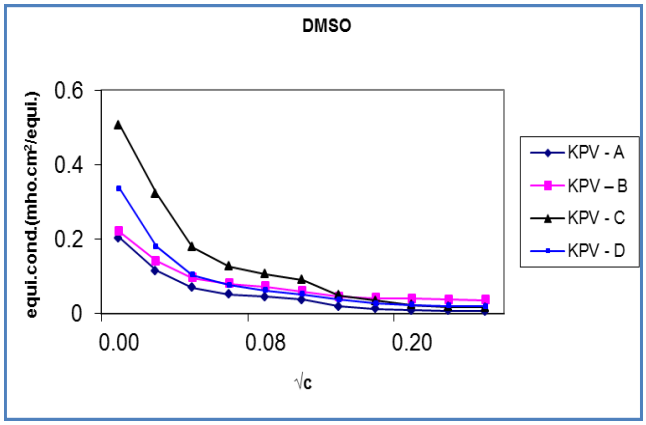


**Fig. 3-** The equivalent conductance (IC) verses √c of azomethines in DMSO Solutions at 308.15 K.

The equivalent conductance values decreases in the order :

In DMF: KPV-A > KPV-B > KPV- D > KPV-C.

In DMSO : KPV-C > KPV-D > KPV- B > KPV-A .

It is observed that in DMF, the equivalent conductance of KPV- A is maximum over the wide range of concentration whereas minimum $l_C$ is observed in KPV-C. However, in DMSO, highest $l_C$ value is observed in KPV- C and low $l_C$ is observed in KPV-A. This suggests that conducting behavior of azomethines depends on solvent and nature of solute under study rather than on its molecular weight [12].

In DMF, presence of nitro group increases the equivalent conductance whereas p-chloro- substitution decreases the conductivity. However, in DMSO, presence of -OH group at para-position increases while methoxy group at ortho-position decreases the equivalent conductance.

[Table-3] shows the solubility ($N_2$) of all the azomethines in DMF and DMSO. It is observed that the solubility of azomethines is greater in DMSO than in DMF as expected because dielectric constant (ε) of DMSO (ε = 46.6) is greater than that of DMF (ε = 36.71). However, dipole moment of both the solvents, DMSO and DMF are almost the same (μ (DMSO) = 3.90 and μ (DMF) = 3.86).

Further, using the [Eq-4], heat of solution was calculated.

| Compound code | DMF | | DMSO | |
|---|---|---|---|---|
| | $N_2$ (.$10^3$) | $DH_s$ (kcals/mole) | $N_2$ (.$10^3$) | $DH_s$ (kcals/mole) |
| KPV-A | 0.054 | 14.0998 | 0.0786 | 12.2898 |
| KPV-B | 0.0458 | 11.8315 | 0.095 | 9.0323 |
| KPV-C | 0.0431 | 12.2403 | 0.0841 | 9.6369 |
| KPV-D | 0.0521 | 12.8982 | 0.0926 | 10.3891 |

*Table 3- The solubility (N2) and heat of solution (ΔHs) of azomethines in DMF and DMSO solutions at 308.15 K.*

$$\ln N_2 = [DH(T - T_m)]/RT.T_m \quad (4)$$

where DH is the heat of solution, T and $T_m$ are the temperature of the experiment and melting temperature of the azomethines. $N_2$ is the solubility or mole fraction, T is temperature in Kelvin and R is gas constant. The evaluated values of heat of solution are also given in [Table-3] and are observed to be positive for all the azomethines in both the solvents, indicating thereby endothermic behavior of these azomethines in the studied solvents.

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