



Viscosity Measurement of Substituted Schiff's Bases in 70% DMF-Water Mixture at Different Temperature And Determination of Thermodynamic Parameters

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Abstract

By measuring viscosity of substituted Schiff's bases in 70% DMF-water mixture at different temperature, thermodynamic parameters like ΔG , ΔH and ΔS have been determined. The results have been interpreted in the light of solute-solvent and solute-solute interactions taking place in solutions of pure electrolytes.

Key Words: Dimethyl Formamide, α -para nitro phenyl imino, ethyl benzene, Gibb's free energy, Change in enthalpy, Change in entropy

Introduction:

The Jones-Dole¹ equation accounts for the observed viscosity concentration dependence of dilute electrolyte solutions, while Nreslau-Miller², Vand³, Moulik⁴, Thomson⁵ and Einstein⁶ equations account for the concentration dependence of viscosity in concentrated electrolyte solutions. Agrawal et al⁷ have studied thermodynamic parameters of substituted 2,3-propane dione. Many attempts have been made to study viscosities of binary liquid mixtures. But no satisfactory result seems to have been obtained, especially for ligand systems showing appreciable departure from ideal behaviour⁸.

The structure of making and breaking properties of liquids, have been considered as a measure of solute-solute and solute-solvent interactions^{9, 10}. Bary and Irving¹¹ determined the viscosities of concentrated aqueous electrolyte solution at various concentrations. The relative viscosities of ternary, aqueous, mixed electrolytic solutions for the system KRr-NaBr, KBr-Bu₄NBr, NaCl-NaBr and NaCl- Bu₄NBr at various constant ionic strengths with varying electrolyte mole fractions (at 25 °C) have been determined by Patil¹². Pandey Yasmin¹³ have measured viscosities and densities of aqueous binary electrolyte solutions of different molalities. Mahajan¹⁴ have studied viscosity B-coefficient of sulphonic acid ligands in different percentages of dioxane-water mixtures. Sondawale¹⁵ have also studied the viscosity at different temperature using 20% dioxane-water and methanol-water mixtures. Recently, Agrawal¹⁶ have determined the viscosity and some thermodynamic parameters in 70% acetone-water mixture.



Experimental:

The solvents N-N dimethyl formamide AR grade (purity 99.9%) and doubly distilled water was used. Weighing was made on Mechaniki Zaktady Precyzyjnej Gdansk Balance, made in Poland (± 0.001 gm). Densities of solutions were determined by a bicapillary Pyknometer (± 0.001 gm) having a bulb volume of about 10 cm^3 and capillary having an internal diameter of 1 mm and calibrated with deionised doubly distilled water. The accuracy of density measurement was within $\pm 0.1\text{ Kgm}^{-3}$. The viscosities were measured by means of Ostwald's Viscometer thoroughly cleaned and dried. The viscometer was kept in Elite thermostatic water bath and temperature variation was maintained within $\pm 0.1\text{ }^\circ\text{C}$. Each measurement, sufficient time was allowed to attain thermal equilibrium between viscometer and water bath. The accuracy of measurement was within $0.11\%\text{Kgm}^{-1}\text{s}^{-1}$. Different constant temperatures were maintained with the help of elite thermostatic water bath ($\pm 0.1\text{ }^\circ\text{C}$). For each measurement, sufficient time was allowed to attain thermal equilibrium.

Following ligands are used in the present study.

1. Ligand (L_5)
2. Ligand (L_6)

Results and Discussion:

The viscosity of a liquid generally decreases with rise in temperature. The decrease is appreciable being about two% per degree rise of temperature in many cases. This has been explained in terms of 'hole theory' of liquids. According to this theory, there are vacancies or holes in a liquid. The liquid molecules keep on moving continuously into these vacancies also keep on moving around as otherwise the liquid will not be able to flow. This process however, requires energy. A liquid molecule, therefore, needs some energy to move into hole. As the energy becomes increasingly available at increasing temperature, a liquid can flow more easily at higher temperature. The coefficient of viscosity, thus, falls appreciably with rise in temperature as presented in Table 1 & 2.

The relationship between coefficient of viscosity of a liquid and temperature is expressed mathematically as –

$$\eta_r = Ae^{\Delta G/RT}$$

The graphs are plotted between $\log \eta$ and $1/T$.

The thermodynamic parameters were calculated by using following expressions –

$$\Delta G = -2.303 R \times \text{slope}$$

$$\log \eta_{r1} - \log \eta_{r2} = [\Delta H/2.303] [1/T_1 - 1/T_2]$$

$$\text{and } \Delta S = (\Delta G - \Delta H) / T$$

These thermodynamic parameters for different systems are listed in Table 4



The positive and negative values of entropy indicate that reaction may be exothermic and endothermic respectively. Burghate et al¹⁷ have also done thermodynamic studies in 70% dioxane-water. Arbad et al¹⁸ and many workers¹⁹⁻²³ have also studied viscosity at different temperature.

Table – 1 Determination of Relative Viscosities at different Temperatures

Temp. °K	$\frac{1}{T} \times 10^{-3}$	Density $d \times 10^3$ (Kg.m ⁻³)	$\eta_r = \frac{\eta}{\eta_0}$	log η_r
301.5	3.3167	0.9691	2.4318	0.3859
304.5	3.2841	0.9682	2.2653	0.3551
307.5	3.2520	0.9673	2.0992	0.3221
311.0	3.2154	0.9662	1.9373	0.2872
315.0	3.1746	0.9652	1.7604	0.2456

Table – 2 Determination of Relative Viscosities at different Temperatures

Temp. °K	$\frac{1}{T} \times 10^{-3}$	Density $d \times 10^3$ (Kg.m ⁻³)	$\eta_r = \frac{\eta}{\eta_0}$	log η_r
301.5	3.3167	0.9697	2.4526	0.3896
305.5	3.2733	0.9682	2.2563	0.3534
309.5	3.2310	0.9670	2.1165	0.3256
313.5	3.1898	0.9654	1.9339	0.2864
317.5	3.1496	0.9638	1.8053	0.2566

**Table –3 Values of Thermodynamic Parameters
 Medium – 70% DMF - Water**

Systems	ΔG (J mole ⁻³ k ⁻¹)	ΔH (J mole ⁻³ k ⁻¹)	ΔS (J mole ⁻³ k ⁻¹)
Ligand (L ₅)	-19147.142	18806.25702	123.2201
Ligand (L ₆)	-14770.6798	15082.1551	96.5469

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