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Density and viscosity study of N-(4-bromophenyl) maleanilic acid and N-(4-bromophenyl) maleimide in aqueous DMSO at 298.15 and 303.15 K

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Abstract— Density and viscosity of N-(4-bromophenyl) maleanilic acid and N-(4-bromophenyl) maleimide have been measured in 80% aqueous dimethyl sulphoxide at 298.15 and 303.15 K. From the experimental data, parameters such as apparent molar volume, limiting apparent molar volume, semi-empirical parameter, Falkenhagen and Jones Dole viscosity coefficients were evaluated. Using theses parameters, molecular interactions such as solute-solute, solute-solvent and solvent-solvent were predicted.

Keywords — N-(4-bromophenyl) maleanilic acid, maleimide, apparent molar volume, solute-solute interactions.

INTRODUCTION

Maleimide is an important multifunctional heterocyclic moiety because of its applications in pharmacology [1-3] biology [4-5] synthetic chemistry [6]. The parameters such as density, viscosity, apparent molar volume, molar volume at infinite dilution, and Jones-Dole equation parameters 'A' and 'B' are useful to through light on the type of molecular interactions present and to understand different biochemical aspects at the body temperature. The results were interpreted in terms of solute-solute and solute-solvent interactions in these systems. Dimethyl sulphoxide (DMSO) is aprotic and strongly associated due to highly polar S=O group. The study of DMSO is important because of its application in medicine [7]. Density and viscosity of some 4-substituted N-phenyl maleimides in aqueous dimethyl sulphoxide have been studied at 308.15 K [8].

EXPERIMENTAL

N-(4-bromophenyl) maleanilic acid (1) and N-(4-bromophenyl) maleimide (2) were synthesized [9] and purified by recrystallization technique. Triple distilled water and analytical reagent grade DMSO of minimum assay of 99.9% obtained from SD Fine Chemicals were used for preparation of solution at room temperature in a molar range of 2×10^{-3} to 1×10^{-2} mol.L^{-1}.

The pycnometer and Ubbelohde viscometer was calibrated [10] using triple distilled water. The density and viscosity of distilled acetone and toluene were evaluated with respect to density of water.

Desired temperature was maintained with the help of thermostatic water bath. The flow time was recorded by using digital stop watch. The solution viscosities were measured by using Ubbelohde viscometer at 298.15 and 303.15 K. The apparent molar volumes, ϕ_v were calculated using the following equation [11-12].

$$\phi_v = \frac{1000\ (\rho_0 - \rho)}{C\ \rho_0} + \frac{M2}{\rho_0}$$

Where M2, C, ρ_0 and ρ are the molar mass, concentration (mol. L^{-1}) and densities of the solvent and the solution respectively. The apparent molar volumes ϕ_v were plotted against the square root of concentration according to the Masson's equation [13]

$$\phi_v = \phi o_v + S_v C^{1/2}$$

Where ϕo_v is the limiting apparent molar volume and S_v is semi empirical parameter or experimental slope, which depends on the nature of solvent, solute and temperature.

The viscosity results of the aqueous solutions of N-(4-bromophenyl) maleanilic acid and maleimides were analysed using Jone-Dole equation [14]

$$\frac{\eta_r - 1}{C^{1/2}} = A + B\ C^{1/2}$$

Where $\eta_r = \eta/\eta_o$, η and η_o are relative viscosity, viscosities of the solution, solvent respectively and C is the molar concentration. The linear plot for $(\eta_r-1)/C^{1/2}$ vs $C^{1/2}$ were obtained. The intercept (A) coefficient shows solute-solute interaction and the slope (B) reflect the solute-solvent interaction.

RESULTS AND DISCUSSION

Density, apparent molar volume, viscosity and relative viscosity of N-(4-bromophenyl) maleanilic acid and maleimide in 80 % aqueous DMSO solution at 298.15 and 303.15 K temperature are shown in Table 1. For both maleanilic acid (1) and maleimide (2), the density and apparent molar volume ϕ_v increases with increase in concentration. The more negative ϕ_v values of 1 than 2 gives evidence of strong molecular association i.e. presence of electrostriction and hydrophilic interaction (solute solvent interactions). Figure 1 shows linear plots of ϕ_v vs $C^{1/2}$ of maleanilic acid and maleimide solution at 298.15 and 303.15 K respectively. Masson's parameter ϕo_v (limiting apparent molar volume) and S_v (experimental slope or semi empirical parameter or associated constant) were obtained from linear plots are listed in table 2. The negative values of ϕo_v shows weak or absence of solute-solvent interactions. The positive value of S_v indicates the presence of solute-solute interactions. Compound 1 has more solute-solute interactions than that of 2. The viscosity of solution increases with increase in concentration. Figure 2 shows variation of $(\eta_r-1)/C^{1/2}$ against $C^{1/}2$ at 298.15 and 303.15 K. Positive values of Falkenhagen coefficient 'A' shows strong solute-solute interactions. The negative values of Jones-Dole coefficient 'B' shows weak solute-solvent interactions. Jones-Dole coefficient representing measure of order and disorder introduced by solute in solvent (solute-solvent interactions). The Jones-Dole parameters are listed in Table 2. The value of 'A' for compound 1 is high indicates the presence of strong solute-solute interactions in an acid than in maleimide.

Table 1: Densities (ρ) (g.cm^{-3}), apparent molar volumes ϕ_v (cm^3.mol^{-1}), viscosities (η) and relative viscosities (η_r) of N-(4-bromophenyl) maleanilic acid (1) and maleimide (2) in aqueous DMSO solution at 298.15 and 303.15 K.

Comp.	Conc. (C) mol dm^{-3}	√C	Density (ρ) (g/cc)	ϕ_v (cm^3. mol^{-1})	Viscosity (η)	Relative viscosity (η_r)
298.15 K						
1	0.002	0.0447	1.09996	-1483.383	3.46082	1.04534
	0.004	0.0632	1.10014	-660.0618	3.46754	1.04737
	0.006	0.0775	1.10038	-394.7441	3.47446	1.04947
	0.008	0.0894	1.10074	-275.7692	3.48177	1.05167
	0.01	0.1	1.10124	-217.1561	3.48952	1.05401
2	0.002	0.0447	1.09935	-1221.571	3.41579	1.03174
	0.004	0.0632	1.09951	-532.8096	3.42860	1.03561
	0.006	0.0775	1.09973	-312.3451	3.43545	1.03768
	0.008	0.0894	1.10005	-213.5161	3.44877	1.04171
	0.01	0.1	1.10048	-164.2537	3.45629	1.04397
303.15 K						
1	0.002	0.0447	1.09771	-1422.262	3.12168	1.04341
	0.004	0.0632	1.09786	-622.4887	3.12826	1.04560
	0.006	0.0775	1.09808	-366.5612	3.14119	1.04993
	0.008	0.0894	1.09849	-260.3056	3.15467	1.05443
	0.01	0.1	1.09899	-204.7785	3.16226	1.05697
2	0.002	0.0447	1.09717	-1191.936	3.07712	1.02851
	0.004	0.0632	1.09734	-520.1268	3.08990	1.03278
	0.006	0.0775	1.09753	-299.2370	3.09658	1.03502
	0.008	0.0894	1.09776	-193.3623	3.10338	1.03729
	0.01	0.1	1.09812	-141.7198	3.11670	1.04170

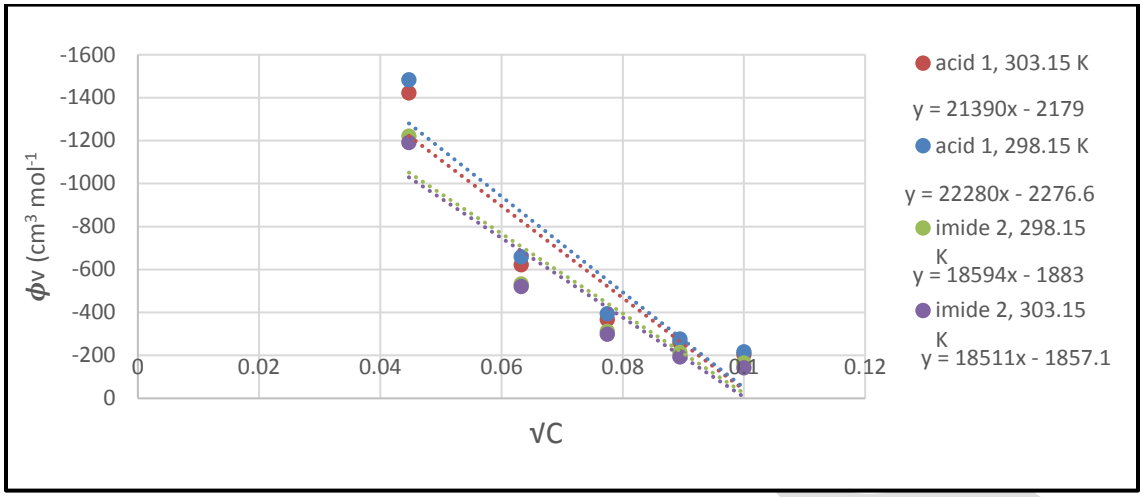

Figure 1: Plot of ϕ_v vs c½ of N-(4-bromophenyl) maleanilic acid and maleimide in 80 % aqueous DMSO solution at 298.15 and 303.15 K.

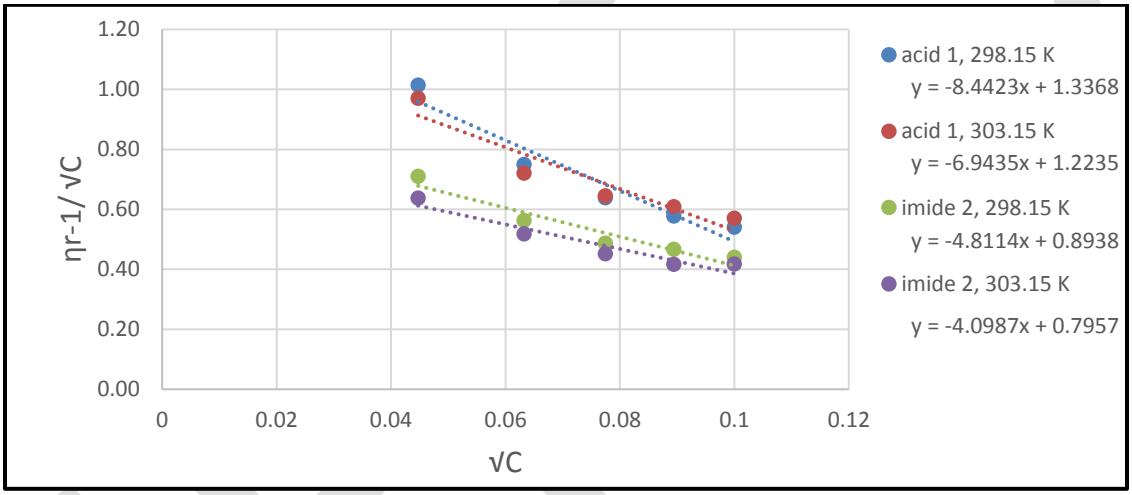

Figure 2: Plot of $(\eta_r\text{-}1)/c^{½}$ vs $c^{½}$ of N-(4-bromophenyl) maleanilic acid and maleimide in aqueous DMSO solution at 298.15 and 303.15 K.

Table 2: Masson and Jones-Dole Parameters of N-(4-bromophenyl) maleanilic acid (1) and maleimide (2) in aqueous DMSO Solution at 298.15 and 303.15 K.

Comp.	ϕo_v	S_v	A ($dm^{3/2}mole^{-1/2}$)	B (dm^3mole^{-1})
298.15 K				
1	-2276.6	22280	1.3368	-8.442
2	-1883.0	18594	0.894	-4.811
303.15 K				
1	-2179.0	21390	1.2235	-6.944
2	-1857.1	18511	0.796	-4.099

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CONCLUSION

In the present work we have systematically reported densitometry and viscometric study of N-(4-bromophenyl) maleanilic acid and maleimide in 80 % aqueous DMSO solution at 298.15 and 303.15 K. It has been observed that negative values of apparent molar volume indicates strong molecular association in both 1 and 2. Positive values of Sv and viscosity constant 'A' indicate the presence of strong solute-solute interaction which decreases with rise in temperature. These interactions are found to be more in N-(4-bromophenyl) maleanilic acid than the N-(4-bromophenyl) maleimide. The value of Jones-Dole coefficient 'B' indicates strong interactions between solute and solvent at higher temperature, whereas Falkenhagen coefficient 'A' indicates strong solute-solute interaction at lower temperature. The Jones Dole and Masson's equations are found to be obeyed for study of maleimides and its derivatives in 80 % aqueous DMSO solution system at 298.15 and 303.15 K.

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