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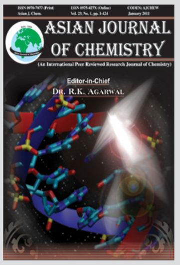

Molar Volume and Viscosities of Hydroxylamine Hydrochloride in Methanol-Water (50:50 v/v) at 303.15 K

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Densities and viscosities of hydroxylamine hydrochloride ($NH_3OH{\cdot}Cl$) were measured as a function of their concentration in methanol-water (50:50 v/v) at 303.15 K. This data is used to determine value of apparent molar volume (ϕ_v), limiting apparent molar volume (ϕ^*_v), experimental slope (S^*_v), molar volume (V) and excess molar volume (V^E). The viscosity of electrolyte systems in mixed solvent was also studied. Viscosity data was used to determine B-coefficient (B) and constant characteristic of ion-ion interactions (A), excess viscosity (η^E) and excess molar free energy of activation of flow (G^E). The interaction parameter Gurenberg and Nissan (d) was also calculated and reported. The parameter are analyzed to evaluated to understand solute-solvent interaction.

Key Words: Density, Viscosities, Molar volume, Excess viscosities.

INTRODUCTION

Densities and viscosities are important physico-chemical parameters widely studied in aqueous, aqueous organic and other systems[1-4]. The density and viscosity are important basic data used in chemical engineering designs, solution theory and molecular thermodynamics[3,5]. Hydroxylamine hydro chloride ($NH_3OH{\cdot}Cl$) has wide spectrum of industrial application like the preparation of antiskinning agents[6], corrosion inhibitors[7] and organic synthesis[8]. The data of hydroxylamine hydro chloride ($NH_3OH{\cdot}Cl$) in binary solvent system are scare in spite of its various use in industrial sectors[6]. In the present investigation hydroxylamine hydro chloride ($NH_3OH{\cdot}Cl$) is studies in methanol-water (50:50 v/v) system at 303.15 K as function of their concentration for the first time. The data of densities is used to analyze of apparent molar volume (ϕ_v), limiting apparent molar volume (ϕ^*_v), experimental slope (S^*_v), molar volume (V). Viscosity data is used to determine B-coefficient (B) and constant characteristic of ion-ion interactions (A). The interaction parameter Gurenberg and Nissan (d) was also calculated and reported. Excess molar volume (V^E), excess viscosity (η^E) and excess molar free energy of activation of flow (G^E) are also calculated.

EXPERIMENTAL

A stock solution of 0.10 M of each of hydroxylamine hydrochloride is prepared in 50:50 (v/v) methanol-water mixed solvent by direct weighing. Mass dilution technique used for preparation of other concentrations. The concentration of the solutions involved in the experiment was taken in range from 0.01 M to 0.10 M. Mass dilution technique was applied to prepare the solution of different concentration ranges from 0.01 M to 0.10 M. Densities of hydroxylamine hydrochloride solutions in mixed solvent were determined using 10 cm^3 double armed pycnometer at 303.15 K. The pycnometer was calibrated at these temperatures with distilled water and benzene. The estimated accuracy of density measurement of solution was 0.00003 g cm^{-3}.

Viscosities were measured by capillary viscometer of ostwald-Sprengle type (MaHaRaNa, Instruments MFG-Company, Ajmer India) with accuracy of ± 0.1 K. The viscometer was calibrated with triple distilled water. Viscosity values were determined using the relation[9],

$$\eta = \rho\left(\frac{Kt - L}{t}\right) \qquad (1)$$

where, η is a viscosity, ρ is the density of the liquid, t is the flow time and K and L are constants for given viscometer. The flow time was measured with digital stop watch with accuracy of ± 0.01 s. The K and L were obtained by measuring the flow time of triple distilled water at 298.15, 303.15 and 313.15 K. Linear regression analysis of a plot of $\eta t/d$ against t^2 for distilled water at three temperatures provide estimates of K = 2.56 × 10^{-5} cm^2 S^{-2} and L = -0.12986 cm^2. All measurements were carried out in triplicate. The uncertainty in density measurements of solutions was ± 0.0003 g cm^{-3}. Reported values of density and viscosity of solvent were 0.9957 and 0.7472 at 303.15 K, respectively.

RESULTS AND DISCUSSION

Densities of hydroxylamine hydrochloride solution and apparent molar volume, ϕ_v, determined as a function of their concentration and temperature are present in Table-1. Apparent molar volume (ϕ_v) is calculated by following the equation[10]:

$$\phi_v = \frac{(\rho_1 - \rho)}{c\rho\rho_1} + \frac{M}{\rho} \tag{2}$$

where, c is molarity of the solution, M is molar mass of the solute, ρ and ρ_1 are the densities of solution and solute, respectively.

TABLE-1
DENSITIES (ρ), APPARENT MOLAR VOLUME (ϕ_V) AND MOLAR VOLUME (M) OF HYDROXYLAMINE HYDROCHLORIDE 50 % v/v METHANOL + WATER AT 303.15 K

Conc. (mol L^{-1}) C	Density (Kg m^{-1}) ρ	Molar volume (m^3 mol^{-1}) V	Apparent molar volume (m^3 mol^{-1}) ϕ_v
0.0100	0.9997	24.0324	-907.6153
0.0200	0.9995	24.0242	-451.1322
0.0300	0.9992	24.0173	-293.2530
0.0400	0.9990	24.0107	-216.5332
0.0500	0.9987	24.0089	-167.0470
0.0600	0.9985	24.0105	-132.6190
0.0700	0.9983	24.0079	-109.2931
0.0800	0.9980	24.0075	-90.7156
0.0900	0.9978	24.0105	-76.2773
0.1000	0.9976	24.0124	-63.8546

The result of ϕ_v of hydroxylamine hydrochloride in mixed solvent are reported in Table-1. The apparent molar volume at infinite dilution ϕ_v were calculated by the method of least square and fit to plot of ϕ_v *versus* $c^{1/2}$ in accordance with the Masson's[10] empirical relation,

$$\phi_v = \phi_v^0 + S_v^* c^{1/2} \tag{3}$$

where, S^*_v is experimental slope. The slope is calculated by the extrapolation of the plots to zero concentration (using Microsoft excel.) The values of ϕ^o_v and S^*_v were 7022.4500 and -637.0560, respectively. The values of apparent molar volume are reported in Table-1. The molar volumes of solutions are derived from the following expression[11],

$$V = \frac{(X_1M_1 + X_2M_2)}{\rho} \tag{4}$$

where, X_1 and X_2 are mole fraction of mixed solvent and mole fraction of solute. M_1 and M_2 molecular weight of solvent and molecular weight of solute ρ is density of solution, respectively. The data of molar volume of solution is reported in Table-1. The molar volume of solute and solvent were 75.450 and 24.3210, respectively.

Viscosities of hydroxylamine hydrochloride solutions was calculated from eqn 1. Measured viscosities data of solutions in methanol-water 50:50 (v/v) at 303.15 K are reported in Table-2. The viscosities of the solute were obtained as the intercept of the plots of concentration *versus* viscosity of solutions. The viscosity of solute was 0.7569.

TABLE-2
VISCOSITIES AND RELATIVE VISCOSITIES OF HYDROXYLAMINE HYDROCHLORIDE 50 % v/v METHANOL + WATER AT 303.15 K

Conc. (mol L^{-1}) C	Viscosity (mPa s)η	Relative viscosity η_r
0.0100	0.7586	1.0152
0.0200	0.7644	1.0230
0.0300	0.7696	1.0299
0.0400	0.7717	1.0327
0.0500	0.7745	1.0365
0.0600	0.7748	1.0369
0.0700	0.7820	1.0465
0.0800	0.7866	1.0527
0.0900	0.7881	1.0547
0.1000	0.7913	1.0590

Jones-Dole equation was used to analyze the viscosities of given solutions[12]:

$$\eta_r = \frac{\eta}{\eta_1} + 1 + Ac^{1/2} + Bc \tag{5}$$

where, η_r is relative viscosities of the solution, η_1 is viscosities of the solvent. A and are coefficient of ion-ion interaction and function of solute-solvent interactions. The values of A and B are calculated by the method of least squares by fitting the experimental data in the Jones-Dole equation. The viscosities and relative viscosity are reported in Table-2. The value of coefficient A and B-coefficient were 0.0130 and 0.4675, respectively. These values show strong solute-solvent interaction.

The excess molar volume (V^E) for these solutions are obtained by the given expression[13]:

$$V^E = V - (X_1V_1 + X_2V_2) \tag{6}$$

where, V, V_1 and V_2 are the molar volume of solution, mixed solvent and solute, respectively. It is well known that negative excess molar volume arises due to increased interaction between the unlike molecules.

The excess viscosity (η^E) have been evaluated from the observed viscosity of the solution and that of its pure components using the relation[14],

$$\eta^E = \eta - (X_1\eta_1 + X_2\eta_2) \tag{7}$$

where η, η_1 and η_2 are the viscosities of solution, mixed solvent and solute, respectively. The data are listed in Table-3.

TABLE-3
EXCESS VISCOSITY (η^E), EXCESS MOLAR VOLUME (V^E) HYDROXYLAMINE HYDROCHLORIDE IN 50 % v/v METHANOL + WATER AT 303.15 K

Conc. (mol L^{-1}) C	Excess molar volume V^E	Excess viscosity η^E
0.0100	-0.4653	-0.4653
0.0200	-0.3216	-0.3216
0.0300	-0.3409	-0.3409
0.0400	-0.3601	-0.3601
0.0500	-0.3717	-0.3717
0.0600	-0.3849	-0.3849
0.0700	-0.3995	-0.3995
0.0800	-0.4119	-0.4119
0.0900	-0.4209	-0.4209
0.1000	-0.4233	-0.4233

The impact of solute on viscosity is understood in terms of the parameter d, regarded as a measure of the strength of interaction between component of solution. It has been estimated using relationship proposed by Gruenberg and Nissan[15],

$$\ln\eta = X_1 \ln\eta_1 + X_2 \ln\eta_2 + X_1X_2 d \qquad (8)$$

where d is the parameter proportional to W/RT, W is the interchange energy or a measure of interactions. It is observed that value of d and η^E are positive suggesting complex formation involving mixed solvent.

The extra thermodynamic property, excess Gibb's free energy of activation of flow (G^E) for the solution have been computed from the Erying equation[16],

$$G^E = RT[\ln\eta V - (X_1 \ln\eta_1 V_1 + X_2 \ln\eta_2 V_2)] \qquad (9)$$

The positive value of G^E indicates the presence of strong interactions between the solute and mixed solvent accompanied by the complex formation. The value of d and G^E are reported in the Table-4. The value of G^E increases with increase in concentration of solute and also increases with increase in temperature suggesting the interaction becomes more and more strong.

TABLE-4
GRUENBERG-NISSAN CONSTANT (d) AND FREE ENERGY FLOW (G^E), HYDROXYLAMINE HYDROCHLORIDE IN 50 % v/v METHANOL + WATER AT 303.15 K

Conc. (mol L^{-1}) C	Gurenberg-Nissan (m^3 mol^{-1}) d	Free energy flow G^E
0.0100	52.27361	6.4243
0.0200	261.2421	10.8727
0.0300	174.3222	17.6713
0.0400	130.7746	20.0162
0.0500	104.6817	23.9152
0.0600	87.0419	23.8078
0.0700	74.9624	33.5125
0.0800	65.5781	39.6451
0.0900	58.3573	41.5825
0.1000	52.5008	45.7693

Conclusion

The densities and viscosities increases as function of concentration. The positive value of ϕ_v indicate greater solute-solvent interactions. The values of ϕ^0_v are large and positive in the system, suggesting the presence of solute-solvent interaction. The positive values of B-coefficient indicate strong solute-solvent interactions in the present systems. The positive values of G^E indicate the presence of strong interactions between the solute and mixed solvent.

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