

Concentration and temperature dependence of viscosity of uranium solutions in H₂O and 3 mol/L HNO₃

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Abstract: Viscosities of uranium solutions in H₂O and 3 mol/L HNO₃ medium were measured by Ubbelohde flow viscometer in the concentration range of 0.5%–3.0% from 10 °C to 30 °C at 5 °C interval. Viscosity data were interpreted in terms of an empirical equation; $\eta = a_0 \exp(b_0 M + c_0 M^2)$. Values of coefficients a_0 , b_0 and c_0 were calculated for all the three systems studied. Flow activation energies and thermodynamic parameters were also evaluated.

Key words: Uranium, Viscosity, Solution, Interaction coefficients, Flow activation energy, Thermodynamic parameters

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INTRODUCTION

Jone-Dole equation (Jones and Dole, 1929) is being used extensively for studying ion-solvent interactions for dilute solutions (Fahim-ud-Din *et al.*, 1990). Values of ion-solvent interaction coefficient depend upon the particular electrolyte, concentration of electrolyte, temperature and solvent under consideration (Afzal *et al.*, 1989). Mohi-ud-Din and Ismail (1983) attempted to describe the concentration dependence of viscosity in terms of an empirical isothermal equation, Eq.(1), obtained from the Vogel-Tammann-Fulcher (VTF) equation (Vogel, 1921; Tamman and Hesse, 1926; Fulcher, 1925)

$$\eta = a_0 \exp(b_0 M + c_0 M^2) \quad (1)$$

a_0 , b_0 and c_0 are coefficients for a particular system and at a particular temperature and M is the molar concentration.

Present investigations were carried out to

study the viscosity behavior of uranium solutions in H₂O and 3 mol/L HNO₃ as a function of concentration and temperature. Viscosity data were analyzed in terms of an empirical equation, Eq.(1), and quantities a_0 , b_0 and c_0 were calculated. Ion-solvent interaction coefficients, flow activation energies and thermodynamic parameters were also determined.

EXPERIMENTAL DETAILS

Chemicals used: The chemicals uranyl nitrate hexahydrate (Merck; Product No. 108476), nitric acid (Selectipur; Merck Product No. 100442) were used in this study.

Double-distilled and de-ionized water was used to make solutions.

Density measurement: Densities of uranium solutions in H₂O and 3 mol/L HNO₃ were determined in triplicate at different temperatures ranging from 10 °C to 30 °C at interval of 5 °C with an Anton

Paar (Model DMA 45) digital densitometer thermostated to ± 0.01 °C. Measured densities of uranium solutions are given in Tables 1 and 2.

Viscosity measurement: The time of flow for double distilled water, 3 mol/L HNO₃ and the uranium solutions of different concentration were measured in triplicate with independent filling of suspended-level Ubbelohode viscometer at different temperatures ranging from 10 °C to 30 °C at interval of 5 °C. Gallenkamp's water bath (Model BKS-350) was used for temperature controlled measurement of flow rates. The temperature of the bath was controlled to better than ± 0.01 °C. The precision in flow rate measurement was determined by measuring the time of flow with distilled water

five times on three different days with three independent fillings of viscometer at 283 K. The relative standard deviation calculated in the flow rates measurement was $>2.0\%$. Viscosities of the uranium solution were calculated by using the following relation (Afzal *et al.*, 1989)

$$\eta = t\rho\eta_0 / t_0\rho_0 \quad (2)$$

where η , t , ρ is the viscosity, flow time and density of uranium solution, and η_0 , t_0 , ρ_0 is the viscosity, flow rate and density of water, respectively. Measured values of viscosities of uranium solutions of different concentration and at specific temperatures are given in Tables 3 and 4.

Table 1 Measured densities of uranium solution in H₂O as a function of temperature and concentration

Conc. (%)	283 K	288 K	293 K	298 K	303 K
0.5	1.0064	1.0058	1.0043	1.0035	1.0023
1.0	1.0133	1.0126	1.0116	1.0102	1.0082
1.5	1.0202	1.0182	1.0174	1.0167	1.0156
2.0	1.0280	1.0269	1.0258	1.0245	1.0236
2.5	1.0341	1.0333	1.0317	1.0305	1.0295
3.0	1.0419	1.0405	1.0394	1.0386	1.0362

Table 2 Measured density of uranium solution in 3 mol/L HNO₃ as a function of temperature and concentration

Conc. (%)	283 K	288 K	293 K	298 K	303 K
0.5	1.1088	1.1072	1.1062	1.1056	1.1046
1.0	1.1109	1.1086	1.1071	1.1062	1.1056
1.5	1.1215	1.1176	1.1168	1.1156	1.1149
2.0	1.1252	1.1217	1.1210	1.1206	1.1191
2.5	1.1326	1.1292	1.1284	1.1273	1.1267
3.0	1.1393	1.1367	1.1360	1.1354	1.1349

Table 3 Variation of viscosities (CP) for uranium solution in H₂O as a function of temperature and concentration

Conc. (%)	283 K	288 K	293 K	298 K	303 K
0.5	1.3334	1.1637	1.0490	0.9152	0.8203
1.0	1.3600	1.1998	1.0733	0.9444	0.8449
1.5	1.3883	1.2228	1.1042	0.9636	0.8757
2.0	1.4181	1.2475	1.1336	0.9900	0.9086
2.5	1.4503	1.2719	1.1606	1.0217	0.9279
3.0	1.4753	1.2992	1.1937	1.0548	0.9522

Table 4 Variation of viscosities (CP) for uranium solution in 3 mol/L HNO₃ as a function of temperature and concentration

Conc. (%)	283 K	288 K	293 K	298 K	303 K
HNO ₃ (3 mol/L)	1.4639	1.2646	1.0809	0.9576	0.8685
0.5	1.4884	1.3640	1.2029	1.0521	0.9546
1.0	1.5503	1.4105	1.2424	1.0969	1.0129
1.5	1.6277	1.4708	1.2769	1.1249	1.0103
2.0	1.6622	1.5023	1.3324	1.1575	1.0429
2.5	1.7363	1.5652	1.3701	1.2079	1.0872
3.0	1.8457	1.6602	1.4264	1.2636	1.1543

RESULTS AND DISCUSSION

Viscosities values of uranium solutions, given in Tables 3 and 4, indicate that there was a regular increment in the viscosities of solutions with the increase in concentration at fixed temperature, and that their value decreased with the rise of temperature at fixed concentration of solutions. Similar trend was also observed in their measured densities values give in Tables 1 and 2.

The viscosity data was analyzed in terms of an empirical Eq.(1). Plotting of $\ln\eta$ against $(b_0M + c_0M^2)$ yielded straight lines, indicating that the viscosity data obey this equation in the concentration range studied. Values of coefficients a_0 , b_0 and c_0 were calculated and are given in Tables 5 and 6. The ion-solvent interaction coefficient, product of a_0 and b_0 terms (Mahi-ud-Din and Ismail, 1982), were evaluated and are given in Table 7. The ion-solvent interaction coefficient is a measure of the

Table 5 Determined values of interaction coefficients for uranium solution in H₂O

Temp. (K)	Viscosity range (cp)	a_0	b_0	c_0
283	1.3334–1.4753	1.3100	0.1903	0.00610
288	1.1637–1.2992	1.1420	0.2092	-0.03170
293	1.0490–1.1938	1.0280	0.1739	0.02390
298	0.9152–1.0548	0.9013	0.1300	0.05750
303	0.8203–0.9522	0.7924	0.2238	-0.04215

Table 6 Determined values of interaction coefficient for uranium solution in 3 mol/L HNO₃

Temp. (K)	Viscosity range (cp)	a_0	b_0	c_0
283	1.4884–1.8457	1.4590	0.2826	0.1850
288	1.3640–1.6602	1.3450	0.1813	0.2088
293	1.2029–1.4264	1.1750	0.2253	0.0795
298	1.0521–1.2636	1.0370	0.1606	0.1194
303	0.9546–1.1543	0.9584	0.05822	0.1910

Table 7 Determined values of ion-solvent interaction coefficient for uranium solution in H₂O and 3 mol/L HNO₃

Temp. (K)	Ion-solvent interaction coefficient	
	Uranium solution in H ₂ O	Uranium solution in 3 mol/L HNO ₃
283	0.2493	0.4123
288	0.2389	0.2438
293	0.1788	0.2647
298	1.1171	0.1665
303	0.1774	0.0558

order or disorder introduced by the ions into the solvent structure and is a specific and approximately additive property of the ions at a given temperature (Cox and Wolfenden, 1934). Positive values of the B-coefficient indicate the structure making effect while negative value show structure breaking effect (Jabeen, 1993). Inspection of ion-solvent interaction coefficient values for uranium solutions, given in Table 7, reveal that the values are positive indicating the structure forming of the solvent. Generally, the ion-solvent interaction coefficient values were found decrease with the rise in temperature. Generally, ions strongly order the solvent in the cosphere about their ion. With increasing temperature, the solvent ordering is perturbed by the increase in thermal energy, and the ion-solvent interaction term value decreases in proportion to the increase in entropy of hydration (Nightingale Jr. and Benck, 1959).

The flow activation energies, for uranium solution in H₂O and 3 mol/L HNO₃ were evaluated using the well known Andrade equation (Da. Andrade, 1947)

$$\eta = A \exp(E_{\eta} / T) \quad (3)$$

where all symbols have their usual meanings. Straight lines were obtained by plotting $\ln \eta$ vs $1/T$ and the values of the regression coefficient; r lies in the range of 0.995–0.999. Values of flow activation energies (E_{η}), determined from the slopes of the curves at different concentrations of uranium in H₂O and 3 mol/L HNO₃, are given in Table 8. Energy of activation can be related to the work needed

to form holes in the liquid, which are necessary for the liquid to flow (Fahim-ud-Din and Farooqui, 1984).

Various thermodynamics parameters (ΔH and ΔS) for viscous flow were calculated using Eyring equation (Powell *et al.*, 1941);

$$\eta = \frac{hN}{V} \exp(\Delta H/RT - \Delta S/R) \quad (4)$$

h is Planck's constant, N is Avogadro's number, V is the volume of one mole of solution, and ΔG was calculated using equation

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

Straight lines were obtained by plotting $\ln \eta V / hN$ versus $1/T$ and the values of regression coefficient, r ranged from 0.9935 to 0.9999 in the whole concentration range studied for uranium solution. From the slopes and intercepts of straight lines, values of ΔH and ΔS were calculated and are given in Table 9. Calculated values of ΔG , using Eq.(5), at different temperatures are given in Table 8. Positive values of ΔH indicate that the flow process is endothermic in nature. The ΔS values are negative and no appreciable change in ΔS was observed with the rise in temperature. Values of ΔG increase with the rise in temperature and it control the rate of flow in fluid process (Varma and Jain, 1981). Flow process is governed by the ability of molecule to move into the prepared hole and the readiness with which the holes are prepared in the liquid.

Table 8 Determined values of flow activation energy for uranium solutions in H₂O and 3 mol/L HNO₃

Conc. (%)	Activation energy (J/mol)	
	Uranium in H ₂ O	Uranium in 3 mol/L HNO ₃
0.5	176.509	192.888
1.0	173.516	169.275
1.5	168.860	160.546
2.0	163.299	177.922
2.5	161.960	174.098
3.0	157.885	176.592

Table 9 Calculated thermodynamic parameters for uranium solution in H₂O and 3 mol/L HNO₃

System/Conc.	ΔH (kJ/mol)	ΔS (kJ/mol·K)	ΔG (kJ/mol)				
			283 K	288 K	293 K	298 K	303 K
Uranium in H ₂ O Soln.							
0.5%	17.2798	-0.1596	62.4466	63.2446	64.0426	64.8406	65.6386
1.0%	16.9863	-0.1550	60.8513	61.6263	62.4013	63.1763	63.9513
1.5%	16.5455	-0.1533	59.9294	60.6959	61.4624	62.2289	63.5105
2.0%	15.7211	-0.1540	59.3031	60.0731	60.8431	61.6131	62.3831
2.5%	15.8220	-0.1520	59.4040	59.5980	60.3580	61.1180	61.8780
3.0%	13.1860	-0.1519	56.1737	56.9332	57.6927	58.4522	59.2117
Uranium in 3 mol/L HNO ₃ Soln.							
0.5%	16.3612	-0.1639	62.7449	63.5644	64.3839	65.2034	66.0229
1.0%	15.7297	-0.1606	61.1795	61.9825	62.7855	63.5885	64.3915
1.5%	17.4246	-0.1517	60.3557	61.1142	61.8727	62.6312	63.3897
2.0%	17.0046	-0.1510	59.7376	60.4926	61.2476	62.0026	62.7576
2.5%	17.0463	-0.1493	59.2982	60.0447	60.7912	61.5377	62.2842
3.0%	17.2909	-0.1470	58.8919	59.6269	60.3619	61.0969	61.8319

References

- Afzal, M., Saleem, M., Mahmood, M.T., 1989. Temperature and concentration dependence of viscosity of aqueous electrolytes from 20 to 50 °C. Chlorides of Na⁺, K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Sr²⁺, Co²⁺, Ni²⁺, Cu²⁺, and Cr³⁺. *J. Chem. Eng. Data*, **34**:339-346.
- Cox, W.M., Wolfenden, J.H., 1934. Viscosity of strong electrolytes measured by a differential method. *Proc. Royal Soc. London*, **A145**:475-488.
- Da. Andrade, E.N., 1947. Viscosity and Plasticity. W. Heffner and Sons Ltd., Cambridge.
- Fahim-ud-Din, F., Farooqui, A.N., 1984. The influence of salt concentration and temperature on the activation energy of aqueous salt solutions by viscosity method. *Pak. J. Sci. Ind. Res.*, **27**:271-274.
- Fahim-ud-Din, Zahid, M., Husaini, S.M., 1990. Viscosity of sodium tartarate solutions in methanol. *J. Sci. Res.*, **XIX**: 110.
- Fulcher, G.S., 1925. Analysis of recent measurements of the viscosity of glasses. *J. Am. Ceram Soc.*, **8**:339-355.
- Mahi-ud-Din, S., Ismail, K., 1982. Temperature and concentration dependence of viscosity of Mg(NO₃)₂-H₂O system. *Can. J. Chem.*, **60**:2883-2888.
- Mahi-ud-Din, S., Ismail, K., 1983. Concentration dependence of the viscosity of aqueous electrolytes. A probe into higher concentration. *J. Phys. Chem.*, **87**:5241-5244.
- Nightingale Jr., E.R., Benck, R.F., 1959. Viscosity of aqueous sodium fluoride and sodium periodate solutions. Ionic energies and entropies of activation for viscous flow. *J. Phys. Chem.*, **63**:1777-1781.
- Jabeen, S., 1993. The study on viscosity of cinnamic and mandelic acids in pure and mixed solvents. *Pak. J. Sci. Ind. Res.*, **36**:451-458.
- Jones, G., Dole, M., 1929. The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride. *J. Am. Chem. Soc.*, **51**:2950-2964.
- Powell, R.E., Roseveare, W.E., Eyring, H., 1941. Diffusion, thermal conductivity and viscous flow of liquids. *Ind. Eng. Chem.*, **33**:430-435.
- Tamman, G., Hesse, W., 1926. The dependence of viscosity upon the temperature of supercooled liquids. *Z. Anorg. Allgem. Chemie.*, **156**:645-657.
- Varma, R.P., Jain, P.K., 1981. Studies on the behavior of cobalt and calcium soap Part VII. Viscosity and surface tension studies in benzene and carbon tetrachloride. *J. Indian. Chem. Soc.*, **58**:959-962.
- Vogel, H., 1921. The law of relation between the viscosity of liquids and the temperature. *Phys. Z.*, **22**:645-646.