Viscosity of Some Aqueous Rare Earth Nitrate Solutions: Thermodynamic Aspect

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(Received 21st June, 2005, revised 30th August, 2005)

Summary: Viscosities of aqueous solutions of La $(NO_3)_3$, Ce $(NO_3)_3$ and Pr $(NO_3)_3$ in the concentration range of 0.2 to 1.0 M were measured in the temperature range of 293 to 333 K. Viscosity data obey the equation $\eta = A \exp (E_\eta/RT)$. Flow activation energies for all the three systems were calculated. Various thermodynamic parameters i.e. ΔH, ΔS and ΔG for these systems were also evaluated.

Introduction

Earlier investigations by Spedding *et al.* [1-2] have shown that the solution properties of rare earth salt are not the simple mono-atomic functions of ionic radius one might expect. In particular, the apparent molal volume and relative apparent molal enthalpy data of aqueous rare earth chloride salts indicate that a change in the water coordination number of the rare earth ions occurs within the series; and the change in water coordination number of rare earth were discussed in terms of ion-water interaction. Spedding and Pickal [3] have studied the viscosity behavior of some rare earth chloride solution to ascertain the ion-solvent interaction coefficients of some aqueous rare earth chloride solutions.

We have initiated a program to study the viscosity behavior of some aqueous rare earth nitrate solutions to obtain precise data for the better understanding of solutions of polyvalent electrolyte. The present communication report results of the viscosity behavior of $La(NO_3)_3$, $Ce(NO_3)_3$ and $Pr(NO_3)_3$ in aqueous solutions as a function of temperature in order to understand the temperature effect on the flow behavior of $La(NO_3)_3$, $Ce(NO_3)_3$ and $Pr(NO_3)_3$ in aqueous solutions.

Results and Discussion

The variation of determined viscosity values of aqueous solutions of $La(NO_3)_3$, $Pr(NO_3)_3$ and $Ce(NO_3)_3$ at different temperatures shown in Figures 1-3. These figures indicate that their values decrease with the rise of temperature at fixed concentration of solutions. The flow activation energies for the three systems were evaluated using the well known Andrade equation [4].

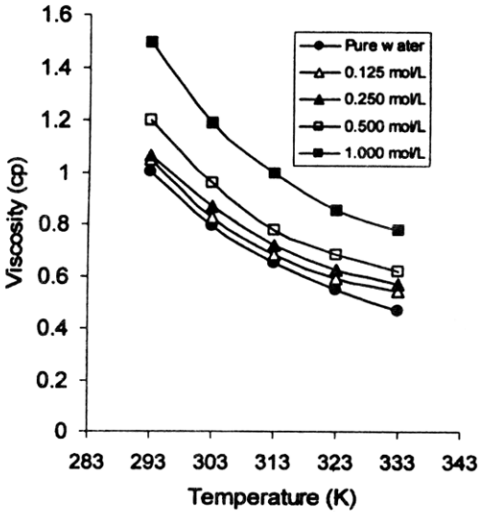

Fig. 1: Variation of viscosity with temperature of water and aqueous La $(NO_3)_3$ solutions.

$$\eta = A \exp (E_\eta/RT) \qquad 1$$

where η is the viscosity of solutions, E_η is flow activation energy, R is the gas constant and T is the temperature. Straight lines were obtained by plotting ln η versus 1/T for all the systems under study. Typical plots for aqueous $La(NO_3)_3$ solutions are given in Figure 4 as representative. Values of regression coefficient, r lies in the range of 0.992-0.999 for all systems. Values of flow activation

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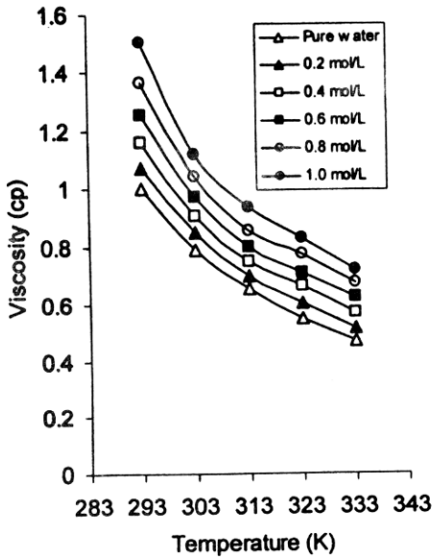

Fig. 2: Variation of viscosity with temperature of water and aqueous Ce $(NO_3)_3$ solutions.

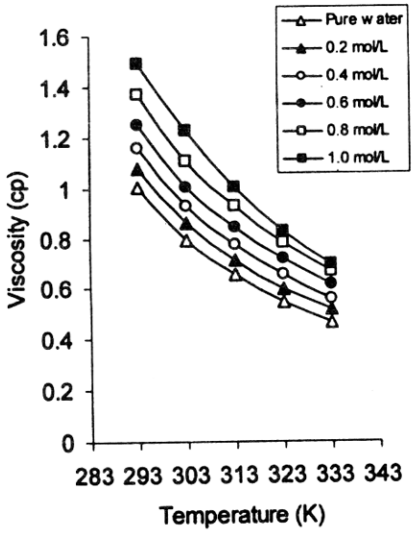

Fig. 3: Variation of viscosity with temperature of water and aqueous Pr $(NO_3)_3$ solutions.

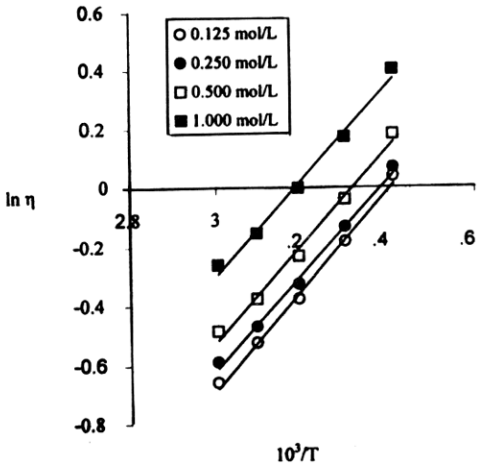

Fig. 4: Plots of ln η versus 1/T for aqueous La $(NO_3)_3$ solutions.

energies (E_η), determined from the slopes of the curves at different concentrations, are given in Table 1. Energy of activation can be related to the work needed to form holes in the liquid, which are necessary for the liquid to flow [5]. Results summarized in Table-1 indicate that generally the values of flow activation energy for $La(NO_3)_3$ remain almost constant with the increase in concentration. However, values of flow activation energy for $Ce(NO_3)_3$ and $Pr(NO_3)_3$ decrease and increase respectively with the rise of concentration of the salts with few exceptions. The decrease in the value indicates that the solvent structure is broken by the presence of solutes; where as the increase values attributed to the excess energy necessary to break the hydrogen bond. Constant value of flow activation energy indicates that the hydrogen bond breaking is not affected by increasing the concentration of solute [6].

Various thermodynamics parameters ΔH (enthalpy change) and ΔS (entropy change) for viscous flow were calculated using Eyring equation as used by Afzal *et al.*, [7].

$$\eta = \frac{hN}{v} \exp(\Delta H/RT - \Delta S/R) \qquad 2$$

Table-1: Determined values of flow activation energy of some aqueous rare earth nitrate solutions.

$La(NO_3)_3$		$Ce(NO_3)_3$		$Pr(NO_3)_3$	
Conc. ($mol.L^{-1}$)	E ($J.mol^{-1}$)	Conc. ($mol.L^{-1}$)	E ($Jmol^{-1}$)	Conc. ($mol.L^{-1}$)	E ($Jmol^{-1}$)
0.125	212.01 ± 6.66	0.200	243.52 ± 10.06	0.200	245.26 ± 11.06
0.250	211.18 ± 7.71	0.600	214.81 ± 6.75	0.600	229.55 ± 10.04
0.500	215.42 ± 7.12	0.800	206.10 ± 5.82	0.800	247.76 ± 15.36
1.000	213.67 ± 8.18	1.000	211.09 ± 5.94	1.000	261.39 ± 13.31

Table-2: Calculated values of the thermodynamic parameters for some aqueous rare earth nitrate solutions.

System/ Conc (mol/L)	ΔH (kJ/mol)	ΔS (kJ/mol.K)	ΔG (kJ/mol) 293K	303K	313K	323K	333K
$La(NO_3)_3$							
0.125	12.9700 ± 1.2300	-0.1879 ± 0.0038	68.0247	69.9037	71.7827	73.6617	75.5407
0.250	12.7100 ± 0.8300	-0.1845 ±0.0029	66.7685	68.6135	70.4585	72.3035	74.1485
0.500	13.1035 ± 1.1570	-0.1837 ± 0.0039	66.9276	68.7646	70.6016	72.4386	74.2756
1.000	12.7709 ± 0.8980	-0.1859 ± 0.0029	67.2396	69.0986	70.9576	72.8166	74.6756
$Pr(NO_3)_3$							
0.200	14.6666 ± 0.3218	-0.1782 ± 0.0011	66.8792	68.6612	70.4426	72.2253	74.0072
0.400	14.4005 ± 0.2088	-0.1974 ± 0.0007	72.2387	74.2127	76.1867	78.1607	80.1347
0.600	13.9848 ± 0.3361	-0.1811 ± 0.0008	67.0471	68.8581	70.6691	72.4801	74.2911
0.800	14.2343 ± 0.1536	-0.1807 ± 0.0005	67.1794	68.9864	70.7934	72.6004	74.4074
1.000	15.4730 ± 0.1929	-0.1788 ± 0.0001	67.8614	69.6494	71.4374	73.2254	75.0134
$Ce(NO_3)_3$							
0.200	12.0559 ± 1.4000	-0.1859 ± 0.0128	66.5246	68.3836	70.2426	72.1016	73.9606
0.400	13.7437 ± 0.7597	-0.1814 ± 0.0024	66.8939	68.7079	70.5219	72.3359	74.1499
0.600	14.6666 ± 0.1.0060	-0.1786 ± 0.0033	66.9964	68.7824	70.5684	72.6877	74.1404
0.800	13.5358 ± 1.3220	-0.1827 ± 0.0041	67.0669	68.8939	70.7209	72.5479	74.3749
1.000	14.1095 ± 1.2638	-0.1813 ± 0.0041	67.2304	69.0434	70.8564	72.6694	74.4824

h is the Planck's constant, N is the Avogadro's number, V is the volume of one mole of solution and R is gas constant. ΔG (free energy change) was calculated using equation

$$\Delta G = \Delta H - T\Delta S \qquad 3$$

Straight lines were obtained by plotting ln ηV/hN versus 1/T and the values of regression coefficient, r lie in the range of 0.9900-0.9998 in the whole concentration range studied for all the three systems. Representative plots for aqueous $La(NO_3)_3$ solutions are given in Figure 5. From the slopes and intercepts of straight lines, values of ΔH and ΔS were calculated and are given in Table-2. Calculated values of ΔG, using equation 3, at different temperatures are also reported in Table-2. Positive values of ΔH indicate that the flow process is endothermic in nature and association and dipole-dipole interactions increase [7]. Values of ΔS are negative for all the three systems for spontaneous flow process [8-9]. The flow process is governed by the ability of molecule to move into the prepared holes and the readiness with which the holes are prepared in the liquid.

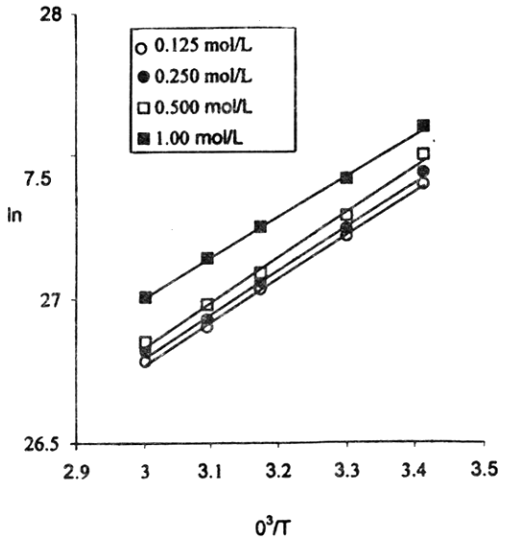

Fig. 5: Plots of ln (ηV/hN) versus 1/T for aqueous $La(NO_3)_3$ solutions.

Experimental

Chemical used

Chemicals; $La(NO_3)_3$, $Pr(NO_3)_3$ and $Ce(NO_3)_3$ having purity 99.999% supplied by M/S Rare Earth Products, were used in this study. Doubly-distilled and de-ionized water was used to make salt solutions.

Density measurement

Density of solutions was measure in triplicate at different temperatures ranging from 293 to 333 K with an Anton Paar (Model DMA 45) digital densitometer thermo-stated to ± 0.01 K. The uncertainty in the density measurement is ≤ 0.005%.

Viscosity measurement

The time of flow for double distilled water and the aqueous solutions of variable concentration of $La(NO_3)_3$, $Pr(NO_3)_3$ and $Ce(NO_3)_3$ were measured

in triplicate with independent filling of suspended–level Ubbelohode viscometer at different temperatures ranging from (293 to 333) K. 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 K. The precision in flow rate measurement was determined by measuring the time of flow electronically with electronic timer of precision ± 0.01s with distilled water five times on three different days, with three independent fillings of the viscometer and give 93.147 ± 0.157 s at 293 K. Flow rates measurement of $La(NO_3)_3$, $Pr(NO_3)_3$ and $Ce(NO_3)_3$ were carried out in triplicate, and relative standard deviation calculated has value less than 3.0%. Viscosities of solutions were calculated by using the following relation [10]:

$$\eta = t.\ \rho.\eta_o / t_o.\ \rho_o \qquad 4$$

where η, t, ρ is the viscosity, flow time and density of solute solution, and η_o, t_o. ρ_o is the viscosity, flow rate and density of water. Variation of measured values of viscosities of $La(NO_3)_3$, $Ce(NO_3)_3$ and $Pr(NO_3)_3$ solutions at different temperatures are given in Figures 1-5.

References

1. F.H. Spedding, D.A. Csejka and C.W. DeKock, *J. Phys. Chem.*, **70**, 2423 (1966).
2. F.H. Spedding, M.J. Pikal and B.O. Ayers, *J. Phys. Chem.*, **70**, 2440 (1966).
3. F.H. Spedding and M.J. Pickal, *J. Phys. Chem.*, **72**, 2430 (1968).
4. E.N. Da Andrade, Viscosity and Plasticity, W. Heffner and Sons Ltd., Cambridge, (1947).
5. F. Fahimuddin and A.N. Farooqui, *Pak. J. Sci. Ind. Res.*, **27**, 271 (1984).
6. M. Afzal, H. Ahmed and Z. Ali, *Pak. J. Sci. Ind. Res.*, **33**, 321 (1990).
7. M. Afzal, H. Ahmad and Z. Ali, *J. Chem. Soc. Pak.*, **13**, 4 (1991).
8. R.P. Varma and P.K. Jain, *J. Ind. Chem. Soc.*, **58**, 959 (1981).
9. R. Qadeer, *J. Zhejiang Univ. Sci.*, **5**, 457 (2004).
10. M. Afzal, M. Saleem and M.T. Mahmood, *J. Chem. Eng. Data.*, **34**, 339 (1989).