Influence of Concentration and Temperature on Viscosity of Nitrate Solutions of Some Trivalent Lanthanides

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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) mol·L^{-1} were measured from (293 to 333) K. Relative viscosity data were interpreted in terms of the Jones−Dole equation, and values of ion−ion and ion−solvent interactions coefficients were evaluated. An empirical equation $\eta = a_0 \exp(b_0C + c_0C^2)$ was also applied to the viscosity data and values of coefficients a_0, b_0, and c_0 were calculated for all the three systems.

Introduction

Investigations carried out by Spedding et al.[1−3] shows that various thermodynamic properties such as apparent molal volumes, apparent molal heat capacities, and heats of dilution of aqueous rare-earth chloride salt solutions are not the simple function of rare-earth ionic radius, and some irregularities have been observed in the trend of thermodynamics properties of rare-earth chloride salt solution when studied as a function of their ionic radii at infinite dilution. These observed irregularities have been discussed in terms of ion−solvent interaction. The Jones−Dole equation[4] has been used to calculate the ion−solvent interaction coefficients of an aqueous rare-earth chloride salt solution from the viscosity data.[5]

Mohi-ud-din and Ismail[6] has developed an empirical isothermal equation to describe the concentration dependence of viscosity in term of the following equation

$$\eta = a_0 \exp(b_0C + c_0C^2) \qquad (1)$$

a_0, b_0, and c_0 are parameters for a particular system at a specific temperature, and C is the concentration.

Present investigations were carried out to study the viscosity behavior of $La(NO_3)_3$, $Ce(NO_3)_3$, and $Pr(NO_3)_3$ in aqueous solutions as a function of concentration and temperature as reference data. Viscosity data have been analyzed in term of Jones−Dole equation and values of interaction coefficients; *A* and *B* were determined in the concentration range studied. Equation 1 has also been fed to the viscosity data, and coefficients a_0, b_0, and c_0 were derived for all the three systems.

Experimental Section

Chemical Used. $La(NO_3)_3$, $Pr(NO_3)_3$, and $Ce(NO_3)_3$ having a purity of 99.999% supplied by M/S Rare Earth Products, were used in this study. Doubly distilled and deionized water was used to make the solutions.

Table 1. Variation of Density ρ of the Salt Solutions as a Function of Concentration and Temperature

	ρ/g·cm^{-3}				
c/mol·L^{-1}	T = 293 K	T = 303 K	T = 313 K	T = 323 K	T = 333 K
			$La(NO_3)_3$		
0.125	1.0265	1.0233	1.0201	1.0170	1.0142
0.250	1.0498	1.0465	1.0429	1.0398	1.0365
0.500	1.1025	1.0992	1.0952	1.0910	1.0800
1.000	1.2045	1.1995	1.1942	1.1899	1.1849
			$Ce(NO_3)_3$		
0.200	1.0434	1.0404	1.0372	1.0307	1.0275
0.400	1.0853	1.0815	1.0776	1.0710	1.0684
0.600	1.1265	1.1224	1.1184	1.1120	1.1082
0.800	1.1691	1.1639	1.1608	1.1530	1.1498
1.000	1.2050	1.2000	1.1950	1.1890	1.1845
			$Pr(NO_3)_3$		
0.200	1.0410	1.0386	1.0354	1.0292	1.0255
0.400	1.0835	1.0798	1.0768	1.0700	1.0655
0.600	1.1255	1.1223	1.1179	1.1112	1.1082
0.800	1.1682	1.1648	1.1609	1.1532	1.1496
1.000	1.2040	1.1990	1.1938	1.1762	1.1720

Density Measurements. Densities of solutions were determined in triplicate at different temperatures ranging from (293 to 333) K with an Anton Paar (Model DMA 45) digital densitometer thermostated to ±0.01 K. The accuracy and the precision of the density measurements are determined by measuring the density of water at different temperatures, and the measured density values of water in g/cm^3 are 0.9982 (0.99820) at 293 K; 0.9956 (0.99565) at 303 K; 0.9922 (0.99219) at 313 K; 0.9880 (0.98803) at 323 K; and 0.9832 (0.98319) at 333 K. The values given in parentheses are the density value of water from literature.[7] The uncertainty in the density measurement is ≤0.005%. Measured densities of $La(NO_3)_3$, $Ce(NO_3)_3$, and $Pr(NO_3)_3$ aqueous solutions are given in Table 1.

Viscosity Measurements. 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 measurements of flow rates. The temperature of the bath was controlled to better than ±0.01 K. The precision in flow-rate measurements was determined by measuring the time of flow electronically with electronic timer of precision ±0.01 s with distilled water five times on three different days, with three independent fillings of the viscometer and give 93.147 s at 293 K with repeatability ∼0.2%. Flow-rate

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Table 2. Variation of Viscosities of the Salt Solutions at Different Temperatures

c/mol·L^{-1}	η/mP·s				
	$T = 293$ K	$T = 303$ K	$T = 313$ K	$T = 323$ K	$T = 333$ K
			$La(NO_3)_3$		
0.125	1.0485 ± 0.0008	0.8280 ± 0.0011	0.6851 ± 0.0002	0.5902 ± 0.0007	0.5433 ± 0.0007
0.250	1.0673 ± 0.0008	0.8701 ± 0.0010	0.7182 ± 0.0003	0.6242 ± 0.0010	0.5699 ± 0.0002
0.500	1.1976 ± 0.0006	0.9574 ± 0.0003	0.7795 ± 0.0001	0.6851 ± 0.0015	0.6193 ± 0.0004
1.000	1.4959 ± 0.0006	1.1911 ± 0.0003	0.9983 ± 0.0004	0.8555 ± 0.0010	0.7766 ± 0.0009
			$Ce(NO_3)_3$		
0.200	1.0712 ± 0.0021	0.8512 ± 0.0002	0.6983 ± 0.0007	0.6018 ± 0.0002	0.5149 ± 0.0006
0.400	1.1566 ± 0.0007	0.9080 ± 0.0004	0.7508 ± 0.0012	0.6661 ± 0.0016	0.5685 ± 0.0007
0.600	1.2529 ± 0.0007	0.9694 ± 0.0006	0.7986 ± 0.0006	0.7109 ± 0.0038	0.6218 ± 0.0006
0.800	1.3660 ± 0.0029	1.0395 ± 0.0001	0.8548 ± 0.0001	0.7752 ± 0.0017	0.6755 ± 0.0005
1.000	1.5019 ± 0.0011	1.1156 ± 0.0002	0.9337 ± 0.0015	0.8299 ± 0.0019	0.7186 ± 0.0008
			$Pr(NO_3)_3$		
0.200	1.0774 ± 0.0010	0.8628 ± 0.0017	0.7124 ± 0.0010	0.5961 ± 0.0006	0.5157 ± 0.0008
0.400	1.1559 ± 0.0052	0.9305 ± 0.0006	0.7756 ± 0.0010	0.6561 ± 0.0011	0.5550 ± 0.0008
0.600	1.252 ± 0.0021	1.0019 ± 0.0036	0.8414 ± 0.0005	0.7146 ± 0.0012	0.6140 ± 0.0005
0.800	1.3689 ± 0.0002	1.1041 ± 0.0004	0.9280 ± 0.0015	0.7783 ± 0.0001	0.6639 ± 0.0012
1.000	1.4932 ± 0.0009	1.2280 ± 0.0008	1.0024 ± 0.0029	0.8273 ± 0.0013	0.6964 ± 0.0002

Table 3. Calculated Values of Coefficients of Jones-Dole Equation Eq 3 of the Salt Solutions

	$La(NO_3)_3$		$Ce(NO_3)_3$,		$Pr(NO_3)_3$	
T/K	A/(mol/L)$^{-1/2}$	B/(mol/L)	A/(mol/L)$^{-1/2}$	B/(mol/L)	A/(mol/L)$^{-1/2}$	B/(mol/L)
293	0.125	0.5579	−0.0800	0.7257	0.1350	0.5340
303	0.123	0.4459	0.0600	0.4946	0.1680	0.4248
313	0.139	0.4180	0.0800	0.3781	0.1720	0.5842
323	0.210	0.5209	0.1600	0.3748	0.1750	0.6035
333	0.205	0.5696			0.2000	0.5024

measurements of $La(NO_3)_3$, $Pr(NO_3)_3$, and $Ce(NO_3)_3$ were carried out in triplicate. Viscosities of solutions were calculated by using the following relation[8]

$$\eta = t\rho\eta_0/t_0\rho_0 \tag{2}$$

where η, t, and ρ are the viscosity, flow time, and density of solute solution, and η_0, t_0, and ρ_0 are the viscosity, flow rate, and density of water. Measured values of viscosities of $La(NO_3)_3$, $Ce(NO_3)_3$, and $Pr(NO_3)_3$ solutions of different concentration at specific temperatures are reported in Table 2.

Results and Discussion

The viscosities values of aqueous solutions of $La(NO_3)_3$, $Ce(NO_3)_3$, and $Pr(NO_3)_3$ at different temperatures are given in Table 2. The data indicate that there is a regular increment in the viscosities of solutions with the increase in concentration at fixed temperature, and their value decreases with the rise of temperature at fixed concentration of solutions. A similar trend was also observed in their measured densities values give in Table 1.

The viscosity data was analyzed by means of Jones−Dole equation

$$\eta/\eta_0 - 1 = AC^{1/2} + BC \tag{3}$$

where η/η_o is the viscosity of the solute relative to that of the solvent, water, C is the concentration, and A and B are the solute−solute and solute−solvent interaction coefficients, respectively, and their values depend on the particular electrolyte, concentration of electrolyte, temperature, and solvent under consideration.[9] The values of the A and B coefficients were calculated from the intercepts and slopes of linear plot of $(\eta/\eta_0 - 1)/C^{1/2}$ against $C^{1/2}$, using a least-squares fit program. Determined values of A and B coefficients of the Jones−Dole equation are summarized in Table 3. Negative values of the A coefficient do not have any significance.[10] Generally the values of As for all the three systems increases with the rise in temperature. This may be due to the cation−cation and cation−anion interpenetration effect which brings the ions together.[11]

The B coefficient of the Jones−Dole equation measures the 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.[9] The positive values of the B coefficient indicate the structure-making effect while negative values show structure-breaking effect.[12] Inspection of B coefficient values, given in Table 3, for aqueous solutions of $La(NO_3)_3$, $Pr(NO_3)_3$, and $Ce(NO_3)_3$, reveal that the B coefficient values are positive, indicating the structure-forming process with the solvated molecules. Some irregular variations of B values are observed. For the $La(NO_3)_3-H_2O$ system, its value decreases with the rise in temperature, whereas for the $Ce(NO_3)_3-H_2O$ system, the value first decreases up to 313 K and then starts increasing with the increase in temperature. Similarly for the $Pr(NO_3)_3-H_2O$ system, an irregular trend was observed in B values. This behavior can be explained in terms of various viscosity effects of Stokes equation[13]

$$\eta B = \eta E + \eta A + \eta D \tag{4}$$

where ηE and ηA are the viscosity increment due to the size and the shape of the ions and the orientation of the solvent molecules around the ions respectively, ηD is the viscosity decrement as a result of distortion of solvent structure by the ions. An increase in the B coefficient value with temperature indicates that ηD is small and that the B value is positive. Similarly, a decrease in the B coefficient value with rise in temperature indicates that the solvent-distortion term, ηD, is large and ηE and ηA are small. This is due to the competition between the ionic field and the bulk structure.[14] The magnitude of B coefficient values determined for aqueous solutions of $La(NO_3)_3$ and $Pr(NO_3)_3$, Table 3, matches fairly well with the values determined by Spedding and Pikal[5] for aqueous solutions of $LaCl_3$ and $PrCl_3$ at 25° as 0.554 and 0.562, respectively.

Table 4. Determined Values of Viscosity Coefficients of the Salt Solutions

salt	T/K	η/mP·s	a_0	b_0	c_0
$La(NO_3)_3$	293	1.0485 to 1.4959	1.0320	0.0327	0.2949
	303	0.8280 to 1.1911	0.8219	0.0315	0.1661
	313	0.6851 to 0.9983	0.6839	0.0179	0.2503
	323	0.5902 to 0.8555	0.5868	0.2324	0.1168
	333	0.5433 to 0.7766	0.5411	0.1643	0.1502
$Ce(NO_3)_3$	293	1.0712 to 1.5019	1.0380	0.0325	0.2104
	303	0.8512 to 1.1156	0.8260	0.2457	0.0845
	313	0.6983 to 0.9337	0.6821	0.0178	0.1093
	323	0.6018 to 0.8299	0.5786	0.2564	0.0363
	333	0.5149 to 0.7186	0.4851	0.2945	−0.0375
$Pr(NO_3)_3$	293	1.0774 to 1.4932	1.4200	0.3553	0.2411
	303	0.8628 to 1.2280	0.8429	0.2163	0.3090
	313	0.7124 to 1.0024	0.6820	0.3178	0.0935
	323	0.5961 to 0.8273	0.5632	0.3547	−0.0364
	333	0.5157 to 0.6964	0.4846	0.3031	−0.0490

The applicability of eq 1 to our data was checked by plotting ln η against $b_0C + c_0C^2$, which yields a straight line and indicates that the viscosity data for all three systems obey this equation in the concentration range studied. Values of a_0, b_0, and c_0 at different temperatures for all three systems have been calculated by a computer and are reproduced in Table 4.

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