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## A shear viscosity study of cerium (III) nitrate in concentrated aqueous solutions at different temperatures

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**Abstract.** Kinematic viscosities and densities of  $\text{Ce}(\text{NO}_3)_3$  in aqueous solutions, from pure water to very concentrated solutions, were determined at different temperatures. Shear viscosity data for this asymmetrical 3:1 electrolyte were calculated. For the low concentrations ( $C < 0.1 \text{ mol dm}^{-3}$ ), the Jones–Dole coefficients  $A$  and  $B$  were determined for this rare-earth salt by fitting the quadratic behaviour of the square root of the molar concentration with the least-squares method. At concentrations above  $1 \text{ mol l}^{-1}$ , the logarithm of viscosity can be fitted by a third-order polynomial, where the coefficients exhibit a linear dependence on the reciprocal of the absolute temperature. This phenomenon is due to the strong ion–solvent correlation.

### 1. Introduction

Experience in our laboratory includes the study of the effects of the shear viscosity  $\eta$  on the self-diffusion coefficient  $D$  of ions in a critical binary mixture. This mixture is made up of isobutyric acid and water and is characterized by a critical point  $X_c = 38.9\%$  in acid, and  $T_c = 27^\circ\text{C}$ . The ion-transport properties in this system exhibit intriguing anomalies near a consolute critical point [1–3].

In refractive index measurements, the critical behaviour of these electrolytes is modified. The critical exponents are renormalized in the Fisher sense (see [4]). The experimental method necessitates adding a salt to the binary mixture, which can modify the mixture's properties [5]. However, various investigators have reported not only substantial shifts in the critical temperature [6], but also changes in the critical composition [7] and critical exponents [5, 8]. Investigators have also used salt as an impurity to move the critical point. Impurities have a significant impact on experiment and theoretical work in critical phenomena. In the present work we intend to study the shear viscosity of electrolyte concentrated aqueous solutions, using one salt with significant ion size and cation electrostatic charge, known for its important solvation and ion–ion interaction. The proposed rare-earth salt is cerium (III) nitrate  $\text{Ce}(\text{NO}_3)_3$ . The reasons for this choice are the following:

- (i) the asymmetrical electrolytes of high-valency cations are rarely studied;
- (ii) the shear viscosity of concentrated domains is not usually treated for different temperatures.

This paper shows the variation of the shear viscosity coefficient  $\eta$  as a function of the molarity  $M$  at different temperatures  $T$ . We have used the water as a solvent in which the electrolyte concentration reaches 11 M between  $18^\circ\text{C}$  and  $35^\circ\text{C}$ . We have compared

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our results to the literature values for diluted domains at 25 °C. In dilute solutions, the electrostatic theory of Falkenhagen (see [9]) may be used to evaluate and to interpret the ion–ion interaction and the ion–solvent interaction through the semi-empirical Jones–Dole  $B$ -coefficient.

## 2. Experimental details

The solutions were prepared from rare-earth salts (Merck product) by weighing, with a resolution of 0.1 mg, and using deionized and tridistilled water with a specific conductivity of about  $10^{-6} \Omega^{-1} \text{cm}^{-1}$ .

The densities were measured in a digital precision densitometer, DMA 46 (PAAR, Graz, Austria). The density of a solution was calculated from the electronically measured frequency of a mechanical oscillator filled with the solution. The oscillator was a U-shaped glass tube (volume  $0.7 \text{cm}^3$ ) placed in a metal block; its temperature was controlled to about  $\pm 10^{-3} \text{°C}$ . The temperature was measured with a quartz thermometer and the precision of the density measurements was better than  $\pm 0.1 \text{mg cm}^{-3}$ .

The shear viscosity coefficient  $\eta$  (cP) of the electrolytic solution, at different concentrations and temperatures, is calculated as the product (equation (1)) of the density  $\rho$  ( $\text{g cm}^{-3}$ ) and the kinematic viscosity  $\nu$  (cSt):

$$\eta = \rho\nu \quad (1)$$

which was calculated from the flow times using the following equation:

$$\nu = k(t - t') \quad (2)$$

where  $t$  is the flow time,  $k$  is a constant for a given viscometer (AVS/N-Chott-Gerate), and  $t'$  is the correction time. The viscometer was calibrated with fluids of known density and viscosity.

## 3. Results and discussion

### 3.1. Density

At 25 °C, density data were obtained from measurements over the range from 0 to 1 M for three rare-earth nitrates. The variation is practically linear versus molar concentration  $C$ . We can use the following equation:

$$\rho = \rho_0 + \delta C \quad (3)$$

where  $\rho_0$  is the pure water density ( $0.99705 \text{g cm}^{-3}$ ), and the slope  $\delta$  is in agreement with Spedding's data (see [10]) calibrated for concentrations from 0.001 to 0.1 M realized for some rare-earth nitrates (table 1).

**Table 1.** The coefficient  $\delta$  (equation (3)) for densities of some rare-earth nitrate aqueous solutions at 25 °C.

Salt	La(NO <sub>3</sub> ) <sub>3</sub>	Ce(NO <sub>3</sub> ) <sub>3</sub>	Nd(NO <sub>3</sub> ) <sub>3</sub>	Gd(NO <sub>3</sub> ) <sub>3</sub>	
$\delta$ ( $\text{g cm}^{-3}$ )	0.274	—	0.279	0.289	From [10]
Coefficient for equation (3)	0.275	0.278	—	0.291	This work

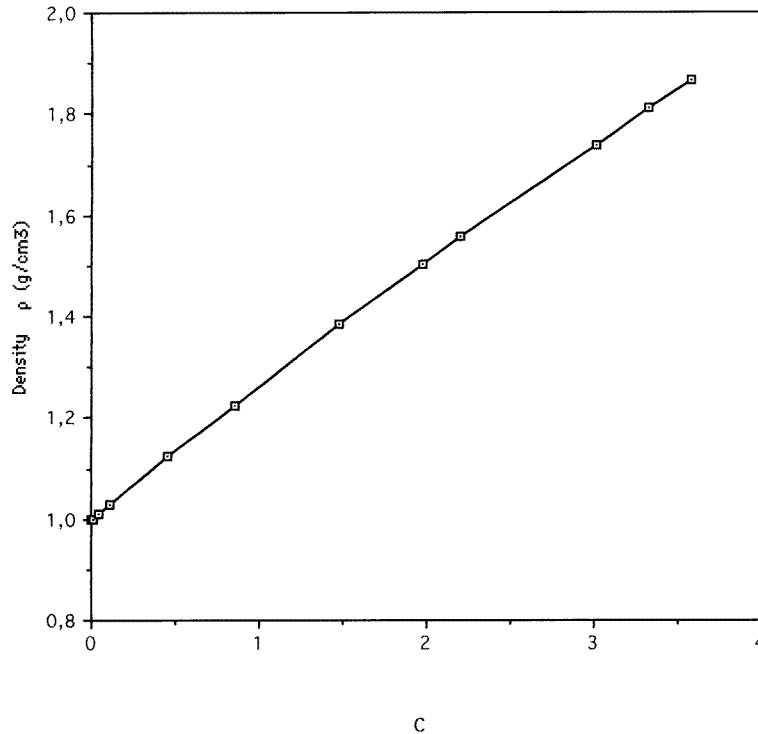


Figure 1. The density  $\rho$  of various solutions at 25 °C.

In the more concentrated range, the density behaviour becomes nonlinear (figure 1) and the fitting with the quadratic form (equation (4)) can be performed with a good precision:

$$\rho = 0.99712 + 0.27373C - 0.008643C^2. \quad (4)$$

### 3.2. Viscosity at 25 °C

Viscosity data for electrolyte in aqueous solutions at 25 °C for the whole concentration range can be represented by a function of the form

$$\ln(\eta/\eta_0) = \ln(\eta_{rel}) = a_j C^{j/2}. \quad (5)$$

For the dilute range where  $C < 0.11$  M, the Jones–Dole [11] equation can be used:

$$\eta_{rel} = \eta/\eta_0 = 1 + AC^{0.5} + BC. \quad (6)$$

Experimental data for  $\text{Ce}(\text{NO}_3)_3$  at 25 °C are listed in table 2. For the whole concentration range, the viscosity data can be represented by equation (5), and the fitting coefficients  $a_j$  are given in table 3, with  $C$  representing the molarity, which is calculated from the molality  $m$  via the following equation:

$$C = \rho m / (1 + mM_1/1000) \quad (7)$$

where  $\rho$  represents the density of the solution and  $M_1$  is the molar weight of the electrolyte.

The molarities  $C$  and  $\sqrt{C}$  were fitted in polynomial form for later use:

$$C = \sum_{j=0}^5 e_j m^j \quad (8)$$

$$\sqrt{C} = \sum_{j=0}^5 f_j m^{j/2}. \quad (9)$$

The coefficients  $e_j$  and  $f_j$  are given in table 3.

**Table 2.** Experimental values of the density  $\rho$ , the kinematic viscosity  $\nu$  and the shear viscosity  $\eta$  for various electrolytes of  $\text{Ce}(\text{NO}_3)_3$  at different temperatures and concentrations.

$m$	$c$	$T = 25 \text{ }^\circ\text{C}$			$T = 18 \text{ }^\circ\text{C}$			
		$\rho \text{ (g cm}^{-3}\text{)}$	$\nu \text{ (cSt)}$	$\eta \text{ (cP)}$	$\rho \text{ (g cm}^{-3}\text{)}$	$\nu \text{ (cSt)}$	$\eta \text{ (cP)}$	
1	0	0	0.9970	0.8930	0.8904	0.9986	1.0547	1.0532
2	0.0001	0.0001	0.9971	0.8942	0.8917	0.9987	1.0575	1.0561
3	0.0005	0.0004	0.9973	0.8959	0.8931	0.9944	1.0595	1.0583
4	0.0010	0.0009	0.9974	0.8961	0.8938	0.9989	1.0598	1.0587
5	0.0020	0.0019	0.9977	0.8966	0.8946	0.9992	1.0602	1.0594
6	0.0049	0.0049	0.9984	0.8985	0.8971	1.0000	1.0623	1.0623
7	0.0099	0.0099	0.9998	0.9173	0.9172	1.0015	1.0858	1.0874
8	0.0438	0.0436	1.0091	0.9108	0.9191	1.0108	1.0751	1.0867
9	0.1126	0.1116	1.0279	0.9219	0.9476	1.0298	1.0852	1.1176
10	0.4743	0.4611	1.1224	1.027	1.1529	1.1251	1.2057	1.3565
11	0.9024	0.8520	1.2220	1.1650	1.4237	1.2254	1.3648	1.6724
12	1.6444	1.4817	1.3843	1.6606	2.2988	1.3889	1.9651	2.7295
13	2.2949	1.9741	1.5040	2.3323	3.5079	1.5094	2.8097	4.2410
14	2.6158	2.2019	1.5599	2.9521	4.6050	1.5656	3.6058	5.6452
15	3.9849	3.0159	1.7404	6.4012	11.1411	1.7470	8.1841	14.2929
16	4.5620	3.3238	1.2126	9.5494	17.3100	1.8124	12.6489	23.0134
17	5.1234	3.5822	1.8675	13.7274	25.3659	1.8743	18.7956	35.2295

$m$	$c$	$T = 35 \text{ }^\circ\text{C}$			
		$\rho \text{ (g cm}^{-3}\text{)}$	$\nu \text{ (cSt)}$	$\eta \text{ (cP)}$	
1	0	0	0.9940	0.7531	0.7193
2	0.0001	0.0001	0.9940	0.7538	0.7201
3	0.0005	0.0004	0.9942	0.7552	0.7215
4	0.0010	0.0009	0.9944	0.7554	0.7218
5	0.0020	0.0019	0.9947	0.7556	0.7222
6	0.0049	0.0049	0.9954	0.7582	0.7249
7	0.0099	0.0099	0.9969	0.7722	0.7391
8	0.0438	0.0436	1.0060	0.7683	0.7430
9	0.1126	0.1116	1.0247	0.7792	0.7677
10	0.4743	0.4611	1.1182	0.8707	0.9361
11	0.9024	0.8520	1.2166	0.9896	1.1582
12	1.6444	1.4817	1.3775	1.3912	1.8385
13	2.2949	1.9741	1.4963	1.9263	2.7574
14	2.6158	2.2019	1.5517	2.404	3.5539
15	3.9849	3.0159	1.7313	4.7124	8.1568
16	4.5620	3.3238	1.8031	7.1938	12.1433
17	5.1234	3.5822	1.8578	10.0564	17.3888

**Table 3.** Least-squares constants for some polynomials.

$j$	$a_j$ (equation (5))	$e_j$ (equation (8))	$f_j$ (equation (9))	$g_j$ (equation (12))
0	0	0	0	0.0299
1	0.0298	0.998	1.010	0.532
2	0.833	-0.138	-0.093	-0.100
3	-2.195	-0.068	0.208	0.204
4	4.778	0.093	-0.352	—
5	-5.455	-0.022	0.161	—

We now consider the Taylor series expansion for the function:

$$\ln(1 + \varepsilon) = - \sum_{j=1}^{\infty} (-1)^j \varepsilon^{j/2} \approx \varepsilon - \varepsilon^{j/2} + \dots + (-1)^{j+1} \varepsilon^{j/2} \quad (10)$$

and the development of the relative viscosity (equation (11)) as a function of the square root of the concentration ( $x = \sqrt{C}$ ):

$$\eta_{rel} = \eta/\eta_0 = 1 + A'x + B'x^2 + C'x^3 + D'x^4 + \dots \quad (11)$$

We can combine (10) and (11) to determine the coefficients  $A'$ ,  $B'$ ,  $C'$ ,  $D'$ . We obtain:  $A' = 0.0298$ ;  $B' = 0.932$ ;  $C' = 2.168$ ; and  $D' = -5.179$ . For the dilute range ( $m < 0.114 \text{ mol kg}^{-1}$ ), the coefficients  $A'$  and  $B'$  may be equated to the Jones–Dole [11, 12] coefficients  $A$  and  $B$  (equation (6)). We have fitted the ratio of the specific viscosity  $\eta^*$  to a series in terms of the square root of the concentration  $C$  (equation (12)) in the dilute range (table 3):

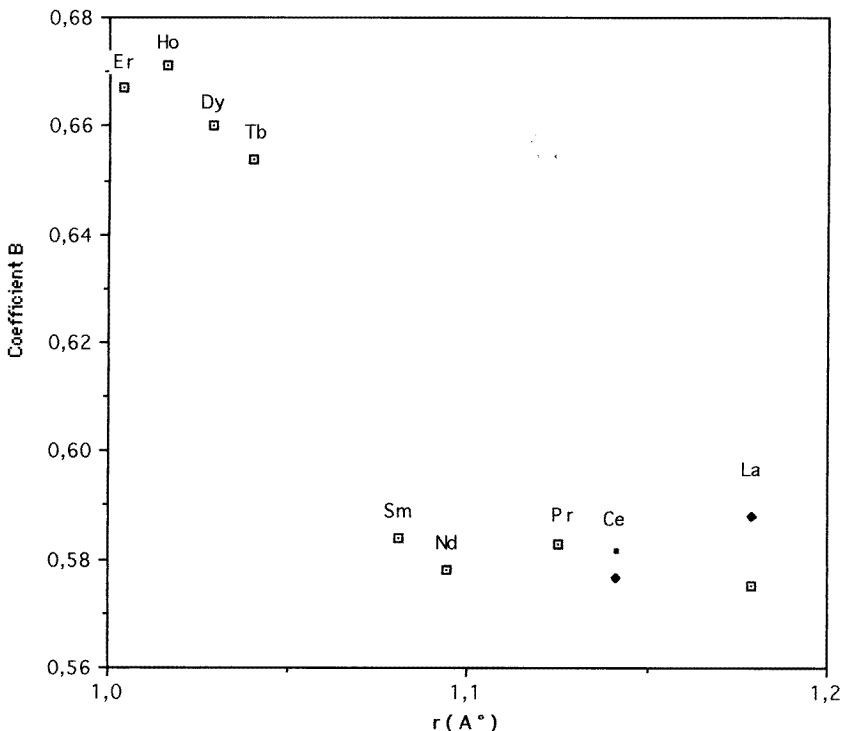
$$\eta^*/\sqrt{C} = (\eta/\eta_0 - 1)/\sqrt{C} = \sum_{j=0}^3 g_j C^{j/2} = A' + B'\sqrt{C} + \dots \quad (12)$$

and the resulting values of these coefficients are  $A \approx 0.0295 \pm 0.0015 \text{ dm}^{3/2} \text{ mol}^{-1/2}$  and  $B \approx 0.45 \pm 0.03 \text{ dm}^3 \text{ mol}^{-1}$ . We note that Jones–Dole coefficients can also be obtained by fitting the relative viscosities directly. It is characteristic of the values of the  $B$ -coefficient that they can be obtained additively from terms corresponding to anions and cations [13].

By considering  $B$ -values of chloride and nitrate ions,  $B(\text{Cl}^-) = -0.007 \text{ dm}^3 \text{ mol}^{-1}$  and  $B(\text{NO}_3^-) = -0.046 \text{ dm}^3 \text{ mol}^{-1}$  [13, 14], we can calculate individual  $B_{\text{Ln(III)}}$ -coefficients of some rare-earth ions (table 4).

**Table 4.** Individual  $B$ -coefficients for some trivalent lanthanide ions Ln(III).

Ln(III)	$r$ (Å) [15]	$B$ [14]	$B$ [13]	$B$ (this work)
Er(III)	1.004	0.667	—	—
Ho(III)	1.016	0.671	—	—
Dy(III)	1.029	0.660	—	—
Tb(III)	1.040	0.654	—	—
Sm(III)	1.081	0.584	—	—
Nd(III)	1.190	0.578	—	—
Pr(III)	1.125	0.583	—	—
Ce(III)	1.143	—	0.5765	0.588
La(III)	1.179	0.575	0.588	—



**Figure 2.** The individual  $B$ -coefficient at 25 °C as a function of the ionic radius for some aqueous rare-earth solutions (squares with dots) from [14], (diamonds) from [13], and (full squares) from this work.

In figure 2, the  $B_{Ln(III)}$  are plotted as a function of ionic radius  $r$  of the rare-earth ion. We notice that the 'reverse-S'-shaped variation of  $B(r)$  is also observed for some thermodynamic properties [16]. The  $B_{Ln(III)}$  have high positive values which indicate that the ions of this salt exert a significant orientating effect on the water molecules [13].

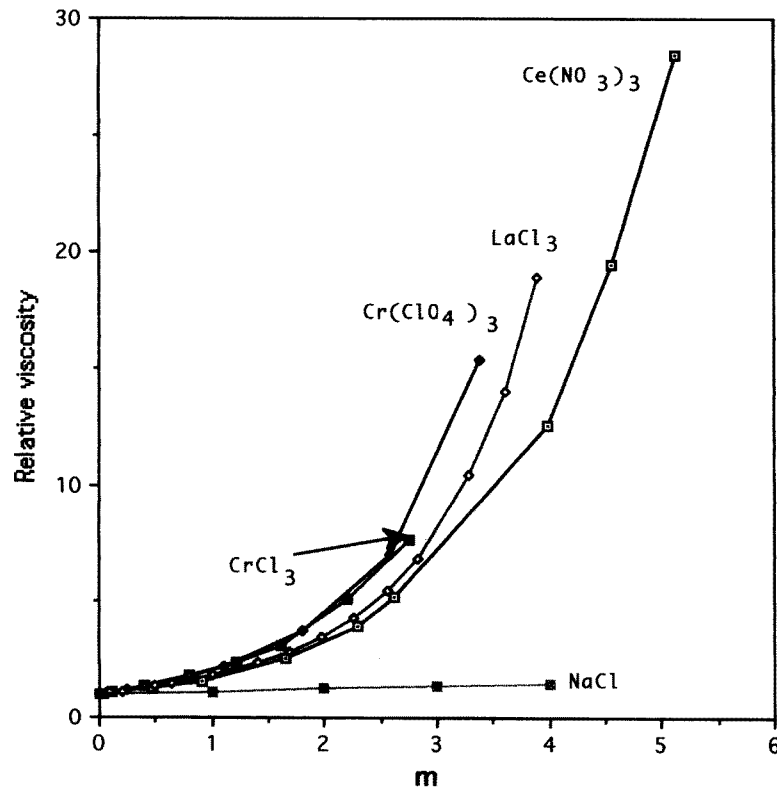
The  $A$ -coefficient is related to the electrostatic interaction of the solute ions with one another, while the  $B$ -constant corresponds to the interaction between the solvent and solute ions (solvation). The experimental value of the  $A$ -coefficient is in good agreement with the literature [9] ( $A \approx 0.029 \text{ dm}^{3/2} \text{ mol}^{-1}$ ) as calculated from the theory of Falkenhagen *et al* (equation (13)). This coefficient  $A$  was expressed using the dielectric constant  $\epsilon_0$  of water, the valences  $Z_1$  and  $Z_2$  of the ions, and their ionic conductivities ( $\lambda_1^0, \lambda_2^0$ ) for infinitely dilute solutions:

$$A = \left\{ \left[ 1.461 / \left( \eta_0 \sqrt{\epsilon_0 T_0} \right) \right] \sqrt{\nu_1 |z_1| / (|z_1| + |z_2|)} / (\lambda_1^0 \lambda_2^0) \psi \right\} \quad (13)$$

at absolute temperature  $T_0$ , where  $\nu_1$  is the number of ions formed from dissociation of the solute molecule and

$$\psi = (\lambda_1^0 z_2^2 + \lambda_2^0 z_1^2) / 4 - (|z_1| \lambda_1^0 |z_2| \lambda_2^0)^2 + \left\{ \sqrt{\lambda_1^0 + \lambda_2^0} + \sqrt{|z_2| \lambda_1^0 + |z_1| \lambda_2^0} \sqrt{(|z_1| + |z_2|) / |z_1| |z_2|} \right\}^2 \quad (14)$$

with  $\lambda_1^0(\text{Ce}^{3+}) = 69.7 \text{ } \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ ; and  $\lambda_2^0(\text{NO}_3^-) = 71.46 \text{ } \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$  [17];  $z_1 = 3$ ;



**Figure 3.** The relative viscosity of aqueous  $\text{Ce}(\text{NO}_3)_3$  (this work),  $\text{LaCl}_3$  and  $\text{NaCl}$  [14],  $\text{CrCl}_3$  and  $\text{Cr}(\text{ClO}_4)_3$  [22] solutions at  $T = 25^\circ\text{C}$  as a function of molality.

$z_2 = -1$ ;  $T_0 = 298.15\text{ K}$  and  $\nu_1 = 4$ . The coefficient  $B$  depends on the size of the solvent ions, the orientation of the water molecule, and the change in solvent structure. We may assume additivity for coefficient  $B$  of terms corresponding to anions and cations [13]. With the value  $B(\text{NO}_3^-) = -0.0460\text{ dm}^3\text{ mol}^{-1}$  [18], the mean coefficient  $B$  for the hydrated rare earth in  $\text{Ce}(\text{III})$  used in our solutions is  $0.587\text{ dm}^3\text{ mol}^{-1}$ . Substitution of the Einstein equation

$$\eta_{rel} = \eta/\eta_0 \approx 1 + 2.5\phi \quad (15)$$

(where  $\phi$  is the solute volume fraction) into equation (6) gives  $2.5\phi \approx BC$  (ignoring the term  $A\sqrt{C}$  in equation (6)). The volume fraction can be replaced by  $\phi = CV_h$ , where  $V_h$  is the molar hydrated volume of the solute, so  $V_h(\text{Ce}(\text{III})) = \phi/C \approx B/2.5$ . Using  $B(\text{Ce}(\text{III})) \approx 0.587\text{ dm}^3\text{ mol}^{-1}$  gives  $V_h(\text{Ce}(\text{III})) \approx 235\text{ cm}^3\text{ mol}^{-1}$ , assuming that the molar volume of water in the hydration sphere of the  $\text{Ce}(\text{III})$  ion is the same as in pure water ( $18.07\text{ cm}^3\text{ mol}^{-1}$ ). Including a term containing the square of the concentration (equation (16)), the Jones–Dole-type equation (equation (6)) can be extended to higher concentration [19, 20] as well:

$$\eta_{rel} = \eta/\eta_0 = 1 + A\sqrt{C} + BC + D''C^2. \quad (16)$$

The constant  $D''$  can be determined by plotting the left-hand-side term of equation (17) as



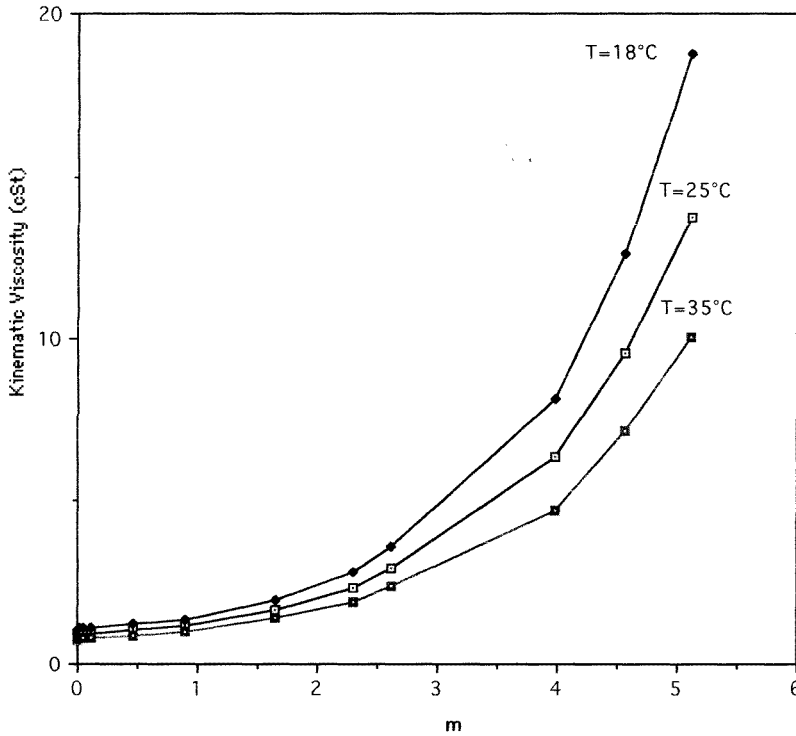


Figure 4. The kinematic viscosity dependence of the molality and the temperature.

a function of  $\sqrt{C}$ :

$$\left[ \eta/\eta_0 - (1 + A\sqrt{C} + BC) \right] / C^2 = D'' + E''\sqrt{C}. \quad (17)$$

Using the experimental values of  $A$  (0.0295) and  $B$  (0.45) leads to a straight line with a neglected slope  $E''$  and an intercept  $D''$  on the ordinate. Fitting the parameters of this equation to the data yields a value of  $D''$  about  $0.1 \text{ dm}^6 \text{ mol}^{-2}$  with a range of validity up to 0.5 M. Moreover, using an adjusted value of  $D'' \approx 0.205 \text{ dm}^6 \text{ mol}^{-2}$  represents the composition range studied (up to 1.5 M). The variation of the relative viscosity  $\eta$  at 25 °C, plotted in figure 3, shows a rapid increase of  $\eta_0$  for rare-earth salt aqueous solutions. This variation is affected by the high positive value of  $B$  for cations. We can conclude that the divergence of  $\eta$  at high concentration is mainly due to the correlation between water and solute molecules.

### 3.3. The effect of temperature on viscosity

Densities, and kinematic and dynamic viscosities are listed in table 2 versus molality  $m$  for different temperatures  $T$ . Figure 4 shows that the kinematic viscosity varies exponentially versus molality, inducing a divergence for the shear viscosity  $\eta$  (figure 5) for concentration more than  $2.5 \text{ mol kg}^{-1}$ . However, it is interesting to plot the logarithm of the viscosity versus molality (figure 6). We note that the expression

$$\ln(\eta_{rel}) = A_3C/(1 - Q'C) \quad (18)$$

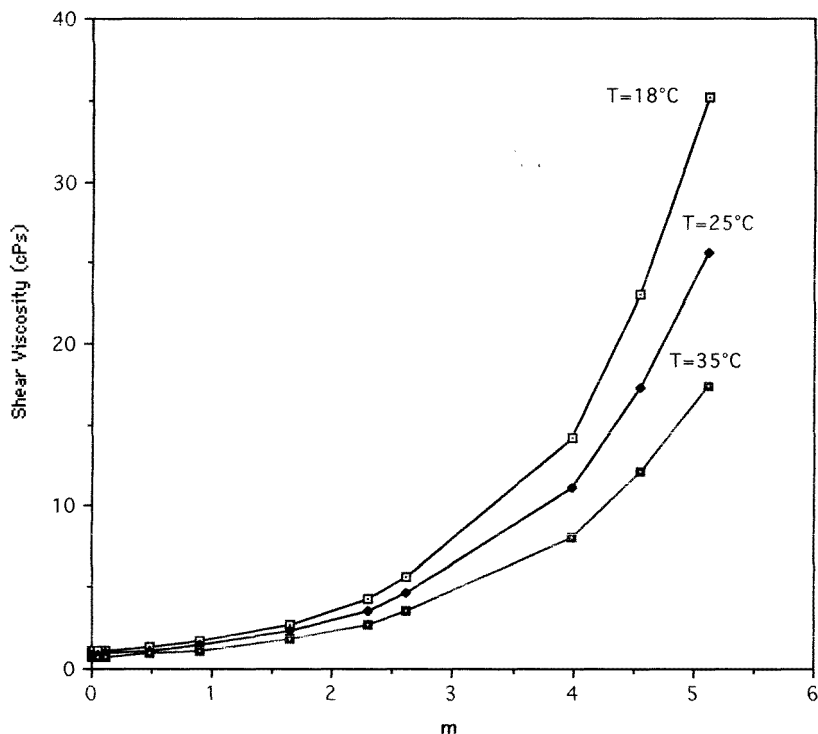


Figure 5. The shear viscosity dependence of the molality and the temperature.

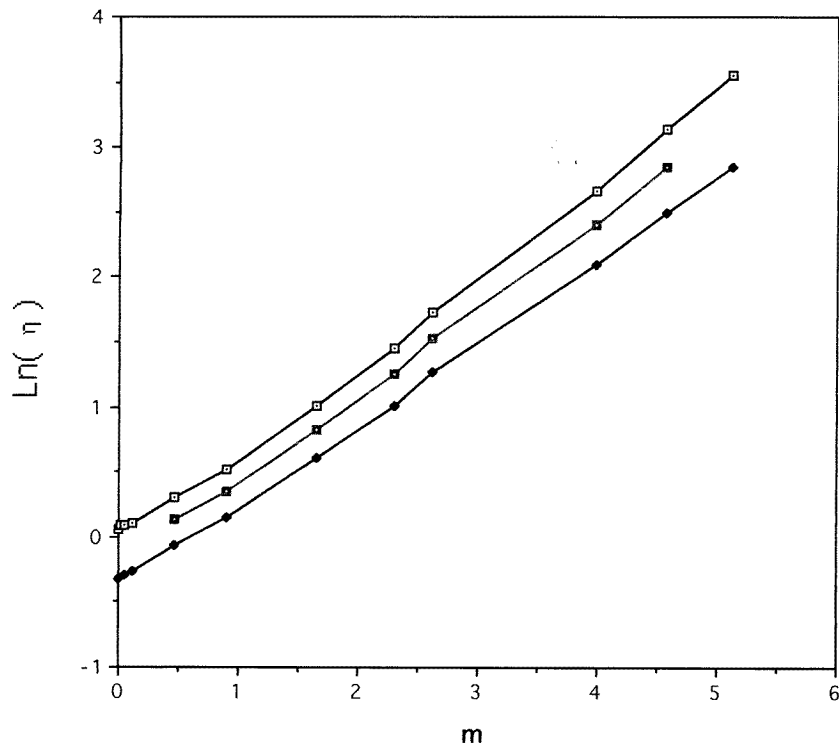
(where  $A_3$  and  $Q'$  are adjustable parameters) gives an excellent representation of  $\eta$  for some strongly hydrated electrolyte solutions in regions of from moderate to high concentration [14, 21], but it deviates where the viscosity is approximately more than twelve times that of water at the same temperature. The very sharp rise of shear viscosity  $\eta$  could be assigned to strong ion–solvent–ion interactions inducing a long-range structuring of liquid. We propose a semi-empirical cubic form in terms of the molality  $m$  to represent the whole range of concentrations:

$$\ln(\eta) = a_0 + a_1m + a_2m^2 + a_3m^3. \quad (19)$$

We notice that this form is in excellent agreement with our results, and the independence of molality of temperature gives coefficients  $a_i$  depending only on temperature (table 5). Plotting  $a_i(T)$  versus reciprocal absolute temperature shows a linear behaviour (figure 7), and  $a_0(T)$  is in a good agreement with the logarithm of viscosity of pure water given in the literature [23].

#### 4. Conclusion

In the present work we have determined densities and shear viscosities of cerium (III) nitrate aqueous solutions as functions of molality for different temperatures. The choice of salt was based on the important ion–ion and ion–solvent interaction due to the significant cation size and high valency. The density data show a quadratic dependence on concentration

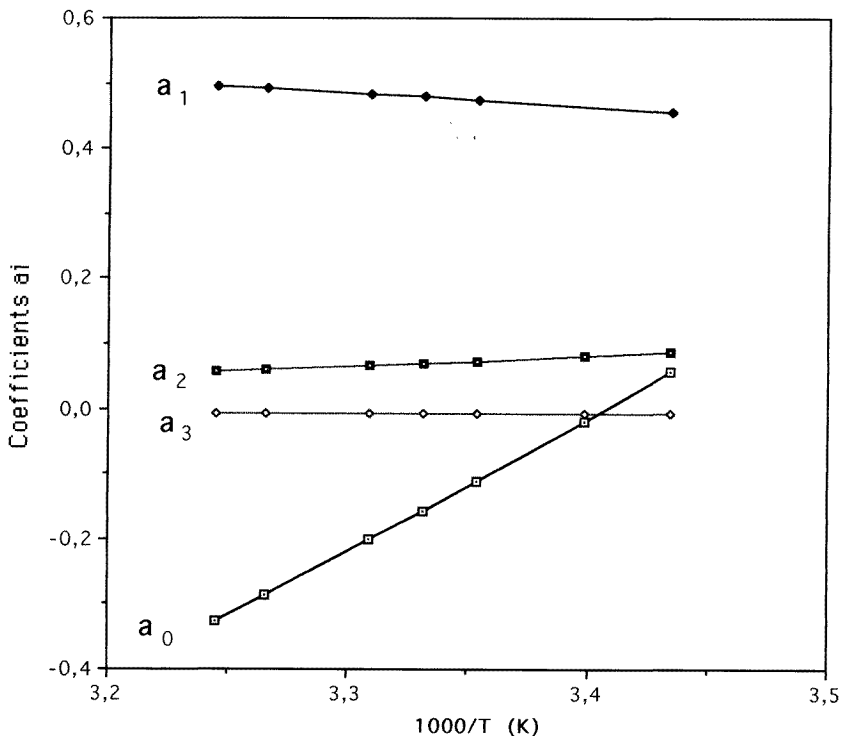


**Figure 6.** A plot of the logarithm of the shear viscosity as a function of the molality at different temperatures.

**Table 5.** The variation of the coefficients  $a_i$  (equation (19)) with temperature.

$T$ ( $^{\circ}\text{C}$ )	$a_0$	$a_1$	$a_2$	$a_3$
18	0.055 74	0.456 35	0.087 99	-0.008 57
21	-0.018 52	0.464 86	0.081 77	-0.008 15
25	-0.112 78	0.475 31	0.073 29	-0.007 52
27	-0.157 47	0.479 02	0.069 93	-0.007 28
29	-0.201 48	0.483 13	0.066 46	-0.007 03
33	-0.285 59	0.491 44	0.059 34	-0.006 46
35	-0.326 11	0.494 77	0.056 17	-0.006 21

up to  $3.5 \text{ mol kg}^{-1}$ . Kinematic viscosity increases exponentially with concentration. At  $25 \text{ }^{\circ}\text{C}$  the shear viscosity  $\eta$  is in agreement with the literature for the dilute region in the framework of the Jones–Dole approximation. The magnitude of the coefficient  $B$  shows a strongly hydrated electrolyte aqueous solution and allows estimation of the hydration number of Ce(III) in the dilute region. This value is in agreement with those obtained by self-diffusion and conductimetric methods. The extension model, using the volume fraction or the effective rigid molar volume, is an excellent representation of the viscosities of these rare-earth concentrated aqueous solutions but diverges in very concentrated regions (in the neighbourhood of saturation). This very sharp rise of  $\eta$  due essentially to strong ion–solvent–ion interactions induces us to propose an expression with the independent variables



**Figure 7.** A plot of the coefficients  $a_i$  ( $i = 0, 1, 2, 3$ ) versus the reciprocal of the absolute temperature.

molality and temperature. The cubic form in terms of the molality is in excellent agreement with all of the data determined, and has coefficients depending linearly on the absolute temperature over the whole range. We conclude that for subsequent study in the framework of critical binary mixtures (already treated in dilute solutions for optical properties), the effect of salt in high concentrations is to maintain the classical behaviour versus absolute temperature in aqueous solutions.

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