

# Viscosity of the concentrated aqueous solutions of calcium chloride and nitrate

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Viscosity of the highly concentrated aqueous solutions of a  $\text{Ca}(\text{NO}_3)_2$ — $\text{CaCl}_2$  mixture with the ionic ratio  $\text{NO}_3^-/\text{Cl}^-$  equal to 1.5 and 2.33, respectively, was followed in the temperature interval 278—328 K. The concentration of the solutions varied from 5 mole % up to 23 mole %. A number of the examined solutions were in a metastable supersaturated state. The selection of a convenient equation for the description of the temperature and concentration dependence of the viscosity of the solutions is discussed.

Была исследована вязкость концентрированных водных растворов  $\text{Ca}(\text{NO}_3)_2$ — $\text{CaCl}_2$  с ионным отношением  $\text{NO}_3^-/\text{Cl}^-$  1,5 и 2,33 в температурном интервале 278—328 К. Концентрацию растворов изменяли в пределах от 5 мол. % до 23 мол. %. Ряд исследуемых растворов находился в пересыщенном метастабильном состоянии. Обсуждается проблема подходящего выбора уравнения для описания температурной и концентрационной зависимости вязкости растворов.

The viscosity of a solution is one of the properties affecting the course of the nucleation and crystallization. Therefore, it is studied not only for purely theoretical reasons but also with respect to the crystallization which is an important industrial process. The knowledge of the size of particles in the solutions of electrolytes is important for a better understanding of the nature of the crystallization itself and it is the viscosity which can provide valuable information as one of the transport characteristics.

The aim of this work was to study the viscosity of concentrated solutions of calcium nitrate and chloride in the temperature range both above and below the liquidus temperature and to verify the applicability of the equations usually used for the description of the temperature dependence of viscosity. The system calcium nitrate—calcium chloride—water was chosen as the substances are readily available and the solutions can be rather easily supercooled. The formation and a relative stability of the supercooled solutions enabled us to follow their viscosity in the metastable state. The solutions of the two salts with a common cation were chosen for the verification of the effect of anions on the behaviour of solutions in a metastable state since many data on the viscosity of the solutions of calcium nitrate have been reported for the same concentration and temperature range [1—3]. However, the study of such effects will require a thorough comparison of various systems, hence this paper may be regarded only as a presentation of the achieved experimental data.

## Experimental

Samples were prepared from reagent grade calcium nitrate tetrahydrate and calcium chloride. Both the substances were dissolved in a minimum necessary amount of water, their solutions were analyzed and mixed in a calculated ratio. The prepared solution was filtered through a fritted glass (S3) to remove all mechanical impurities, which may act as nucleation and crystallization centres. The samples with required concentrations were prepared from the basic solution through a dilution or evaporation. The concentration of Ca(II) ions in the individual samples was determined by chelatometry.

The viscosity of the solutions was determined using a commercial Höppler viscosimeter BH 2 with an accuracy of  $\pm 0.5\%$  over the range 0.002–0.25 Pa s and  $\pm 1\%$  over the range 0.25–50 Pa s. The determined viscosities are expressed in the Pascal second units.

The viscosimetric tube was thermostated by a water jacket connected with an ultrathermostat. The temperature of the jacket was maintained constant within  $\pm 0.1$  K and measured with a mercury thermometer. The reproducibility of a series of three successive measurements performed in five minutes intervals was considered as a criterion of the achieved temperature equilibrium between the measured solution and the water jacket. For the determination of the temperature dependence, the viscosity of the samples was measured at 6 temperatures in the range 278–328 K.

The density of the solutions, required for the viscosity calculation, was determined in the range 293–328 K by the method proposed by *Ewing* and *Mikovsky* [4]. The temperature dependence of the density was very well approximated by the quadratic equation

$$\rho = a + b t + c t^2$$

The coefficients of this function for individual samples were determined from the experimental density values by the least squares method.

## Results and discussion

The temperature dependence of the viscosity ( $\eta$ ) or fluidity ( $\varphi$ ) of diluted aqueous solutions, having viscosity of the same order as that of water, is usually described by the Arrhenius equation in the form

$$\varphi = A \exp(-E/RT), \quad (1)$$

where  $A$  and  $E$  are empirical constants,  $R$  and  $T$  have their usual meaning.

Eqn (1) is not obeyed in more concentrated solutions where the condition of the constancy of the apparent activation energy  $E$  in the whole temperature interval is not met. The temperature dependence of  $E$  was discussed among others by *Moynihan* [2], who pointed out that, e.g. for concentrated solutions of calcium nitrate, the values of  $E$  vary from 30 kJ mol<sup>-1</sup> for solutions with a comparatively low viscosity up to 250 kJ mol<sup>-1</sup> for very viscous metastable solutions with the same concentration.

In this viscosity region, the Fulcher equation was proposed for the description of the temperature dependence

$$\varphi = k_1 \exp[k_2/(T - T_0)] \quad (2)$$

as well as the Vogel—Tamman—Fulcher equation

$$\varphi = k_3 T^{-1/2} \exp [k_4/(T - T_0)]. \quad (3)$$

Symbols  $k_1$ — $k_4$  and  $T_0$  denote empirical constants. Some authors [1, 5] look upon the value of the parameter  $T_0$  as a temperature corresponding to the zero free volume in the liquid.

*Tweer* [6] investigated the viscosity of the molten calcium nitrate—potassium nitrate mixture as far as to the proximity of the glass transition temperature, *i.e.* up to the viscosity of the order  $10^{13}$  Pa s, and he proved that the Fulcher equation does not hold for highly viscous solutions. Thus this equation does not describe satisfactorily the temperature dependence of the viscosity in all the concentration region. The delimitation of the validity range of eqns (2) and (3) is important especially with respect to an accurate determination of the parameter  $T_0$ , if we intend to compare its value with the experimentally determined glass transition temperature  $T_g$ . The parameters of eqns (2) and (3) calculated from the experimental data satisfying the assumptions of validity of the Arrhenius equation, are only empirical values and they cannot be interpreted theoretically anyway. Furthermore, due to the scattering of the experimental data, the correlation of these data by eqn (2) or (3) yields sometimes a physically unreal value of the parameter  $T_0$ .

We examined the viscosity of the concentrated solutions of calcium nitrate and chloride characterized by the ionic ratio  $\text{NO}_3^-/\text{Cl}^-$  equal to 2.33 and 1.5, respectively. The viscosity was measured in the concentration range 5—23 mole % of the salt and the temperature interval 278—328 K. The experimentally determined viscosities ranged from 0.001 to 100 Pa s. For the characterization of the anionic composition of the solutions, we used the anionic fraction  $y = n_1/(n_1 + n_2)$  where  $n_1$  and  $n_2$  denote the material amount of  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$ , respectively.

The fit of eqns (1—3) with the experimental data was verified by calculating their parameters and the relative deviations of the calculated and experimental values by means of the relationship  $\Delta = |\varphi_{\text{exp}} - \varphi_{\text{calc}}|/\varphi_{\text{exp}}$ . The average values of the relative deviations (in %) are listed in Table 1 for all the solutions studied. Table 1 shows an obvious deviation of the highly concentrated solutions from the Arrhenius relationship. The fit of eqns (2) and (3) is identical in the region investigated. A three parameters equation was also used for the correlation of the temperature dependence of the fluidity

$$\ln \varphi = a + b/T + c/T^2 \quad (4)$$

Eqn (4) is advantageous with respect to a more simple calculation of its parameters though this advantage may vanish if a computer is used for processing the data. However, the comparison of the results in Table 1 shows that not even eqn (4) is quite convenient for the description of the temperature dependence in a

Table 1

Comparison of the experimental and calculated values

Molar fraction of salt $x$	Average relative deviation, %			
	Arrhenius	Fulcher	V.T.F.	Polyn.
			$y = 0.3$	
0.0527	1.2	0.5	0.5	0.6
0.0804	1.7	0.8	0.8	0.8
0.116	1.8	0.4	0.3	0.3
0.148	4.9	1.0	1.0	1.4
0.174	8.1	0.5	0.5	0.8
0.211	15.9	0.9	0.9	2.2
0.235 <sup>a</sup>	10.2	1.8	1.8	2.4
			$y = 0.4$	
0.0529	1.4	1.2	1.2	1.2
0.0758	2.0	0.8	0.8	0.9
0.102	2.4	0.4	0.4	0.4
0.140	4.0	0.7	0.7	0.9
0.166	7.0	0.4	0.4	0.9
0.199	13.0	1.4	1.4	2.5
0.216	17.2	0.8	0.9	2.1

a) Experimental temperature interval 298—328 K.

broad range of the viscosity values although, in comparison with eqn (1), its better fit is obvious.

With respect to the mentioned comparison, the Arrhenius equation (1) may be regarded applicable only for the solutions with a viscosity comparable to that of water. For more viscous solutions, empirical eqn (4) can be used in a limited range (ca. up to 1 Pa s). Eqns (2) and (3) are applicable in all the followed range of the viscosities ( $10^{-3}$ — $10^2$  Pa s). A better fit of the experimental and calculated values can be achieved using a higher polynomial order than in eqn (4). When the 3rd polynomial order was applied to the series characterized by  $y = 0.4$ , the average relative deviation did not exceed 0.72. However, the aim of our work was mainly to compare the applicability of the three parameters equations.

Since the presentation of a large number of the experimental data was considered to be superfluous, only parameters of eqn (2) are listed in Table 2 for the individual solutions.

The studied solutions exhibited a pronounced temperature as well as concentration dependence. Angell [1] used a correlation of the parameter  $T_0$  with the solution composition for the description of the isothermal concentration dependence of the fluidity. Such a procedure is rather inconvenient with regard to the broad reliability interval of the parameters of eqn (3), which is reflected also in the

Table 2

Values of the parameters of eqn (2)

Molar fraction of salt $x$	$k_1 \cdot 10^{-4}$	$k_2 \cdot 10^{-2}$	$T_0$	Relative deviation, %	
				average	maximum
		$y = 0.3$			
0.0527	3.4036	- 8.2639	113.4	0.49	1.46
0.0804	1.2645	- 6.2618	145.7	0.77	1.79
0.116	1.5106	- 8.0527	150.0	0.40	0.76
0.148	0.64638	- 6.5731	187.2	0.99	2.14
0.174	1.0359	- 8.0855	193.3	0.45	0.98
0.211	2.8704	-10.530	203.5	0.89	2.38
0.235	49.245	-16.696	194.1	1.80	4.53
		$y = 0.4$			
0.0529	1.5851	- 5.6432	142.6	1.16	2.07
0.0758	1.3505	- 6.4076	141.0	0.83	2.48
0.102	1.1562	- 6.8179	153.0	0.40	1.18
0.140	1.1300	- 7.6385	171.3	0.67	1.42
0.166	9.99038	- 7.8211	188.0	0.38	1.05
0.199	0.6723	- 9.2847	202.7	1.35	2.52
0.216	5.4140	-11.963	202.4	0.83	2.28

Table 3

Values of the parameters of eqn (5)

Temperature K	$a_1$	$a_2$	$a_3 \cdot 10^{-2}$	$a_4 \cdot 10^{-3}$	Relative deviation, %	
					average	maximum
			$y = 0.3$			
278.15 <sup>a</sup>	6.1235	- 7.6982	-0.81525	-0.50164	0.69	1.7
288.15	6.6422	-14.783	-0.27512	-0.48058	1.85	3.8
298.15	6.9779	-17.352	-0.10311	-0.40167	2.42	5.1
308.15	7.2126	-17.688	-0.11118	-0.30223	2.48	5.2
318.15	7.3825	-16.740	-0.22271	-0.19467	2.25	4.7
328.15	7.5096	-15.067	-0.39257	-0.008578	1.87	3.8
			$y = 0.4$			
278.15	8.1576	-68.596	4.6657	-1.9876	4.00	7.2
288.15	8.2150	-61.339	3.8928	-1.6068	3.76	7.5
298.15	8.2596	-55.059	3.2615	-1.3083	3.31	7.0
308.15	8.2936	-49.504	2.7273	-1.0660	2.79	6.2
318.15	8.3193	-44.523	2.2644	-0.86402	2.23	5.2
328.15	8.3385	-40.014	1.8561	-0.69215	1.69	4.1

 a) Experimental concentration interval  $x = 0.05-0.21$

expression for the concentration dependence. The sensitivity of the parameters of eqn (2) with respect to the interval of the experimental viscosity values was discussed by *Moynihan* [2]. For calcium nitrate tetrahydrate, the values of the parameter  $T_0$  ranged from 185 to 207 K depending on the chosen interval.

We verified the effect of the variance of the experimental values for one of the examined solutions ( $y = 0.3$ ,  $x = 0.11$ ). A change in one of the six experimental viscosity values by 3% resulted in the change of the parameter  $T_0$  by 14 K. For this reason we did not investigate the concentration dependence of the parameter  $T_0$  or the parameters of eqn (4) and rather preferred searching for the functional dependence of the fluidity values upon the concentration at chosen temperatures. Since the experimental values were not measured at predetermined temperatures, the starting values for the evaluation of the concentration dependence had to be calculated. The Fulcher equation (2) was used with the parameters listed in Table 2. The coordinate system  $\ln \varphi - x$  appeared to be the most convenient for the expression of the concentration dependence, where  $x$  denotes the concentration expressed as molar fraction of the salt. Values of the parameters of equation

$$\ln \varphi = a_1 + a_2 x + a_3 x^2 + a_4 x^3 \quad (5)$$

are given in Table 3 for some chosen temperatures together with calculated deviations. This procedure enabled us to calculate the viscosity of a solution at any concentration and temperature in the region investigated. Fig. 1 shows the course of the concentration dependence in one series of experiments and the consistency of the experimental values with the calculated ones.

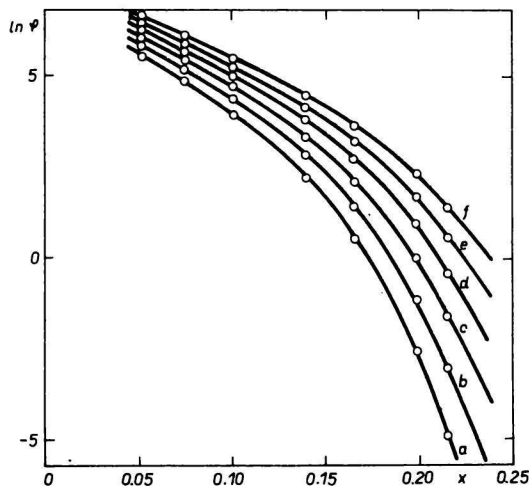


Fig. 1. The concentration dependence of the fluidity  $[(\text{Pa s})^{-1}]$  at chosen temperatures.  $y = 0.4$ ,  $x$  — molar ratio of the salt, temperatures [K]: a) 278.15; b) 288.15; c) 298.15; d) 308.15; e) 318.15; f) 328.15.

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