Viscosity of calcium nitrate—calcium iodide hydrous melts

Z. KODEJŠ and I. SLÁMA

*Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences,
160 00 Prague*

Viscosity of highly concentrated aqueous solutions of a mixture of calcium nitrate and calcium iodide was investigated in the temperature interval 5—50°C and concentration range 5—20 mole % of salts in the system. It was found that viscosity of the ternary system is higher than viscosity of the binary system $Ca(NO_3)_2$—H_2O at comparable total concentration of salt. The values of viscosity of ternary systems $Ca(NO_3)_2$—CaX_2—H_2O, where $X = Cl$, Br, I, do not differ substantially at comparable conditions.

Была изучена вязкость высококонцентрированных водных растворов смеси нитрата кальция и иодида кальция в интервале температур 5—50°С и концентраций 5—20 мол. % соли в системе. Вязкость тройной системы выше вязкости двойной системы $Ca(NO_3)_2$—H_2O при сравнительной общей концентрации соли. Значения вязкостей тройных систем $Ca(NO_3)_2$—CaX_2—H_2O, где $X = Cl$, Br, I, значительно не отличаются при сравнительных условиях.

The aim of this work is the determination of the temperature and concentration dependence of viscosity of calcium nitrate—calcium iodide hydrous melts. This paper closes a series of studies [1—4] dealing with transport properties of the system $Ca(NO_3)_2$—CaX_2—H_2O, where X stands for Cl, Br, I. The data enable us to evaluate the influence of anionic composition on the viscosity of the above ternary system.

Experimental

For the preparation of solutions $Ca(NO_3)_2 \cdot 4H_2O$, anal. grade (Lachema, Brno) and $CaI_2 \cdot 4H_2O$ (Merck) were used. Solutions were prepared by mixing weighted amounts of both substances and of water. The content of calcium was checked by a chelatometric analysis and it is expressed as mole fraction $x = n_{Ca}/(n_{Ca} + n_{H_2O})$, where n_{Ca}, n_{H_2O} are the amounts of substance of calcium salts and of water, respectively, in solution. Error in the determination of mole fraction of calcium did not exceed 1%.

Kinematic viscosity (v) was measured by Ultrasonic viscometer Unipam Type 505 with precision ±2%. Results of this work are discussed on the basis of dynamic viscosity (η) which was calculated from the experimentally determined values of kinematic viscosity and density of investigated samples [4]. Viscosity of solutions was measured in the temperature interval 5—50°C. Sections of ternary system characterized by ionic fraction y 0.1; 0.2; 0.3; 0.4; 0.5 were investigated and the mole fraction x ranged from 0.05 to 0.17 ($y = n_i/(n_{NO_3} + n_i)$).

Results and discussion

An extensive set of experimental data was described by eqn (*1*) approximating the dependence of viscosity on temperature at constant x and y

$$\ln \eta = a + b/T + c/T^2 \tag{1}$$

where T is temperature (K) and a, b, c are the empirical parameters. Values of the parameters were calculated using the method of least squares and they are presented in Table 1.

Concentration dependence of viscosity at a given temperature was described by the relationship

$$\ln \eta = a_1 + a_2x + a_3x^2 + a_4x^3 \tag{2}$$

where x is the mole fraction of salts in the system and a_1—a_4 are the empirical parameters. The values of these parameters which were obtained by the least-square method on the basis of the values of viscosity interpolated at chosen temperature from eqn (*1*) are summarized in Table 2.

The relationships which have been used in previous works [5, 6] for the description of the temperature-concentration dependence of viscosity could not be used in this case because the fit to the experimental data was unsatisfactory.

On the basis of viscosity values calculated according to eqn (*2*) the influence of the replacement of nitrate ions by iodide ions on the viscosity of the system was evaluated. In Fig. 1 plot of the relative viscosity η_r as a function of content of iodide ions in the melt at different temperatures and constant total concentration of calcium salts in the system is given. Relative viscosity is defined as a ratio of viscosity of the ternary system $Ca(NO_3)_2$—CaI_2—H_2O and viscosity of the system $Ca(NO_3)_2$—H_2O [7] at the identical temperature and total concentration of salts. It follows that despite of considerable scatter of data the viscosity of the ternary system is higher than that of the binary system. Ratio of viscosities of solutions of calcium iodide and calcium nitrate at $x = 0.083$ and temperature 25°C equals 0.97 [8]. Influence of the replacement of nitrate ions by iodide ions is the more expressive the higher is the concentration of salts in solution and therefore also higher its viscosity. This observation can be explained by the diminishing influence

508

Table 1

Values of the parameters of eqn (*1*) obtained for different values of mole fractions x and y

x	a	$b \cdot 10^{-3}$	$c \cdot 10^{-5}$	Average D	N
		$y = 0.1$			
0.0554	$-$ 8.4320	0.33368	1.7633	1.9	11
0.0780	$-$ 5.1233	$-$ 2.0943	6.1643	1.2	12
0.114	2.9154	$-$ 7.0621	14.609	0.6	11
0.141	9.6833	$-$ 11.670	23.221	1.1	11
0.166	15.897	$-$ 15.601	30.392	0.7	11
0.195	50.214	$-$ 36.714	63.921	1.6	12
		$y = 0.2$			
0.0569	$-$ 11.604	1.9160	$-$ 0.41789	1.6	10
0.0890	$-$ 6.0116	$-$ 1.7691	6.1495	2.3	10
0.144	6.6652	$-$ 10.066	21.323	1.3	11
0.167	23.235	$-$ 20.572	38.800	3.7	9
0.210	86.054	$-$ 13.377	32.465	2.4	10
		$y = 0.3$			
0.0558	$-$ 5.0230	$-$ 2.1758	5.8210	1.1	10
0.0822	$-$ 5.7352	$-$ 1.6939	5.4392	1.2	11
0.115	$-$ 1.3566	$-$ 4.5071	10.722	0.6	11
0.143	$-$ 0.31851	$-$ 5.6055	14.070	1.0	11
0.166	2.0222	$-$ 7.9031	19.795	1.6	12
0.187	17.298	$-$ 17.124	34.678	1.8	12
		$y = 0.4$			
0.0533	$-$ 2.8706	$-$ 3.4986	7.7322	0.9	11
0.0773	$-$ 2.5941	$-$ 3.6146	8.2706	1.0	10
0.110	3.2542	$-$ 7.3143	14.940	1.5	12
0.140	$-$ 4.3850	$-$ 3.0302	10.163	1.6	10
0.169	5.5147	$-$ 10.223	24.305	1.1	11
		$y = 0.5$			
0.0549	$-$ 12.473	2.2696	$-$ 0.91614	1.3	10
0.0789	$-$ 8.8921	0.02915	2.9852	1.0	12
0.112	$-$ 6.8149	$-$ 1.3923	6.2766	1.7	10
0.141	$-$ 5.3603	$-$ 2.5579	9.5885	1.0	11
0.172	3.9267	$-$ 9.1235	22.515	0.8	11

$D = 100 \left| (\eta_{exp} - \eta_{calc}) / \eta_{exp} \right|$.

N is the number of experimental points used for evaluation of parameters in eqn (*1*).

of water-like structure and increasing influence of quasi-lattice structure. Then the specific properties of ions more affect properties of the system.

Investigation of the electrical conductivity of this system furnished somewhat

Table 2

Values of the parameters of eqn (2)

Temperature °C	a_1	a_2	a_3	a_4	Average D
		$y = 0.1$			
5	−3.5091	−57.263	626.55	−1123.3	1.3
15	−3.4431	−63.623	665.68	−1306.8	0.4
25	−3.5243	−65.156	662.98	−1349.7	0.6
35	−3.7251	−62.744	626.23	−1277.8	1.2
45	−4.0228	−57.112	561.74	−1112.2	1.8
		$y = 0.2$			
5	−5.4842	−11.006	274.90	−197.01	0.1
15	−5.7540	−6.5648	210.55	−91.709	1.3
25	−5.8918	−6.4328	192.46	−104.50	1.8
35	−5.9211	−9.8122	212.17	−213.44	1.6
45	−5.8612	−16.052	262.76	−400.59	0.8
		$y = 0.3$			
5	−4.8195	−28.910	382.40	−388.05	2.6
15	−5.3035	−20.799	308.90	−295.41	1.8
25	−5.7932	−11.480	222.07	−140.92	1.1
35	−6.2844	−1.2347	124.91	62.991	1.3
45	−6.7739	9.7088	19.872	306.23	2.3
		$y = 0.4$			
5	−6.4505	20.168	−94.901	1235.2	0.8
15	−6.3020	7.3094	39.830	677.62	0.7
25	−6.2676	−0.57854	124.69	290.63	1.6
35	−6.3262	−4.3669	168.39	45.071	1.8
45	−6.4608	−4.7700	178.06	−83.019	1.6
		$y = 0.5$			
5	−6.6293	22.645	−104.49	1192.0	1.6
15	−6.4399	10.722	8.4527	734.55	1.1
25	−6.3674	2.8017	83.522	408.59	0.8
35	−6.3905	−1.8067	127.26	191.81	0.5
45	−6.4919	−3.6714	145.03	65.851	0.3

$D = 100|(\eta_{exp} - \eta_{calc})/\eta_{exp}|.$

different results [4]. It was found that conductivity of the ternary system is higher than conductivity of the binary system $Ca(NO_3)_2$—H_2O at lower values of mole fraction x, while at higher concentrations of salts in solution the exchange of nitrate by iodide ions results in a decrease of conductivity. This phenomenon was
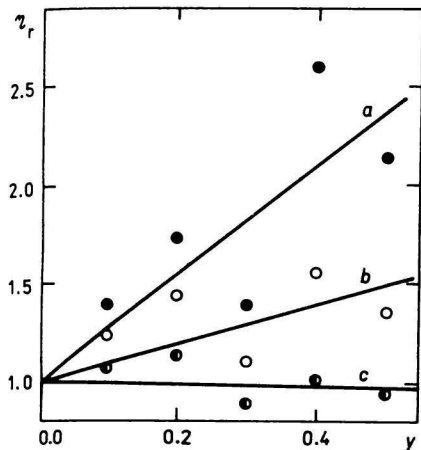
Fig. 1. Dependence of relative viscosity on composition.
Temperature 5°C.
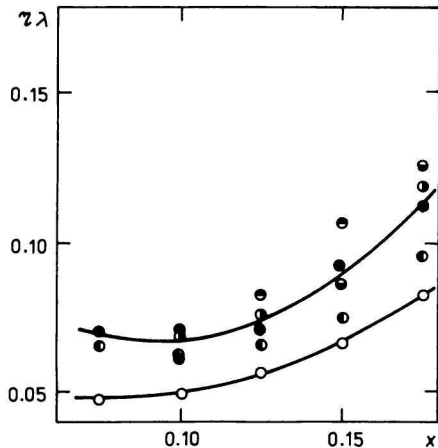*a*) $x = 0.16$; *b*) $x = 0.14$; *c*) $x = 0.10$.

Fig. 2. Dependence of the value of product of viscosity and electrical conductivity (Pa s S cm^2 mol^{-1}) on the concentration of salts in solution at different anionic composition.
Temperature 25°C.
○ $y = 0$; ● $y = 0.1$; ◑ $y = 0.2$;
◐ $y = 0.3$; ◒ $y = 0.4$; ◓ $y = 0.5$.

explained by a contradictory influence of decreasing size of building particles of solution and of association equilibria between calcium ions, nitrate ions, and water molecules.

Mutual comparison of viscosity and electrical conductivity can be done on the basis of the value of product $\eta\lambda$ which is a function of both temperature and concentration of salt. The values of the product are presented in Fig. 2 as a function of total concentration of salt. Values of the product for ternary system are higher than values for the corresponding binary system. However, the shape of the dependence is preserved, *i.e.* increasing concentration of salt influences more markedly viscosity than conductivity. The dependence between replacement of nitrate ions by iodide ions (y) and the product of viscosity and conductivity was not observed.

The comparison of influence of different halide ions on viscosity of ternary system is illustrated in Fig. 3. In the region of concentrated solutions the influence of all three halide ions is similar and replacement of nitrate by halide ions results in an increase of viscosity. The influence of the replacement of nitrate ions by halide ions (Cl, Br, I) can be readily explained taking into account difference in size of these particles. Size of ionic diameters is discussed in numerous papers in connection with structural interpretation of thermodynamic properties. Even if
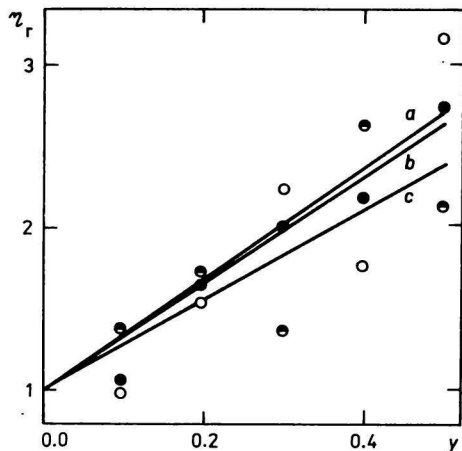
Fig. 3. Comparison of the influence of replacement of nitrate ions by halide ions on viscosity of the system $Ca(NO_3)_2$—CaX_2—H_2O. Temperature 5°C; $x = 0.16$.
a) ○ X = Cl; *b*) ● X = Br; *c*) ◒ X = I.

estimation of the size of ionic diameters on the basis of transport properties furnishes diverse data according to investigated transport process [9], the relations between ions are preserved. Therefore we can use for explanation of our results the values of ionic diameters which were obtained using different methods. Crystal radii of the ions in question are as follows: $Ca^{2+} - 99$ pm, $Cl^- - 181$ pm, $Br^- - 196$ pm, $I^- - 216$ pm, $NO_3^- - 264$ pm [10]. Value of the ionic radius of nitrate ion is rather questionable and different authors report very different values. On the basis of investigation of fused salts [11] this value was determined to be 231 pm while scaled particle theory [9] yielded the value 196 pm. All presented values were used in discussion of structural arrangement and thermodynamic properties. At discussion of transport properties one should consider also hydration of ions and the corresponding effect of increase of size of particles. According to *Nightingale* [10] all ions discussed in this paper are hydrated in diluted solutions and the pair NO_3—H_2O is the weakest from all possible interactions ion—dipole. The values of effective diameters of hydrated ions are presented as follows: $Ca^{2+} - 412$ pm, $Cl^- - 332$ pm, $Br^- - 330$ pm, $I^- - 331$ pm, $NO_3^- - 335$ pm. However, situation is somewhat more complicated by the fact that in the most concentrated systems ($x = 0.2$) only 4 water molecules correspond to 3 ions originating formally from dissociation of calcium nitrate and, therefore, hydration cannot be considered from the point of view of diluted solutions. Rather it can be assumed that cations are hydrated preferably and that values of crystal radii play considerable role.

In agreement with the previous conclusions [3] and making certain simplification it can be stated that the increase in viscosity, which results due to the replacement of nitrate by halide ions, is a consequence of new arrangement which is more resistant against shear tension. This arrangement is caused by replacement of

unsymmetric nitrate ions by symmetric halide ions having smaller diameter. The differences in diameters of halide ions do not have more pronounced effect. In diluted solutions the effect of replacement is not so remarkable because the water-like structure prevails and the radii of hydrated anions are very similar. Simplification of this interpretation consists in that only geometrical relations in solution are considered and the differences in ability of different halide ions to form associates with calcium ions are not taken into account. The assumption about the preferential hydration of cations is supported by the results of study of viscosity in the system $Ca(NO_3)_2$—KNO_3—H_2O [12]. It was found that replacement of Ca^{2+} ions by potassium ions results in a decrease of viscosity. If we take into account the size of effective diameter of hydrated potassium ion 331 pm and its crystal radius 133 pm [10] then this trend can be readily understood.

References

1. Kodejš, Z., Horsák, I., and Sláma, I., *Rev. Roum. Chim. 24*, 293 (1979).
2. Kodejš, Z., Sláma, I., and Novák, J., *Chem. Zvesti 30*, 439 (1976).
3. Kodejš, Z. and Sláma, I., *Chem. Zvesti 34*, 335 (1980).
4. Novák, J. and Sláma, I., *Collect. Czech. Chem. Commun. 45*, 1639 (1980).
5. Sláma, I. and Kodejš, Z., *J. Solution Chem. 8*, 801 (1979).
6. Kodejš, Z., Novák, J., and Sláma, I., *Chem. Zvesti 35*, 515 (1981).
7. Bressel, R. D., *Ph.D. Thesis.* Purdue University, Lafayette, 1972.
8. Rakowsky, F. and Garrett, A. B., *J. Electrochem. Soc. 101*, 117 (1954).
9. Masterton, W. L., Bolocofsky, D., and Lee, T. P., *J. Phys. Chem. 75*, 2809 (1971).
10. Nightingale, E. R., *J. Phys. Chem. 63*, 1381 (1959).
11. Emi, T. and Bockris, J. O'M., *J. Phys. Chem. 74*, 159 (1970).
12. Skokánek, M., *CSc. Thesis.* Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague, 1979.

Translated by P. Fellner