

Temperature and concentration dependence of the viscosity of calcium nitrate—calcium bromide hydrous melts

Z. KODEJŠ and I. SLÁMA

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

Received 28 September 1979

Viscosity of highly concentrated aqueous solutions of calcium nitrate and calcium bromide mixtures was determined in the temperature interval 278—323 K and concentration range 5—25 mole % of salts in the system. The viscosity values ranged in broad interval 1×10^{-3} —25 Pa s. The influence of ratio of nitrate and bromide ions of the studied system is discussed.

Была определена вязкость сильно концентрированных водных растворов смесей нитрата и бромидов кальция в диапазоне температур 278–323 К и при концентрациях 5–25 мол. % солей в системе. Найденные значения вязкости находились в широком интервале значений 1×10^{-3} –25 Па с. Взаимное отношение нитратных и бромидных ионов в системе изменялось и обсуждается влияние этих изменений на вязкость системы.

Aqueous melts can be characterized as melts containing water in amount which is not sufficient to form complete hydration shells about ions. These melts contain, besides configurations corresponding to stoichiometric hydrates, also series of different clusters with lower or higher content of water. Viscosity data reveal information on structure of particles constituting solution and interactions among them. This information in connection with models used for description of molten salts helps us to understand the properties and behaviour of electrolytes in the concentration range in which their structure is determined rather by ionic interactions disturbed by water molecules than by structure of hydrogen bridges disturbed by ionic charges [1]. The aim of this work is to elucidate the influence of the addition of further component, namely of calcium bromide, to the binary system $\text{Ca}(\text{NO}_3)_2\text{--H}_2\text{O}$ on viscosity of the mixture. This paper is continuation of the previous studies [2—4].

Experimental

Samples were prepared from anal. grade chemicals — $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Lachema, Brno) and $\text{CaBr}_2 \cdot x\text{H}_2\text{O}$ (Merck) — by the method described earlier [3]. The required ratio of

bromide and nitrate ions was obtained by weighing both basic solutions and the concentration of calcium ions in each sample was determined by chelatometry.

The kinematic viscosity ν was determined with precision $\pm 2\%$ by Ultrasonic viscometer Unipam type 505. Temperature dependence of viscosity was calculated in the temperature range 278–323 K on the basis of ca. 10 experimental points. Mole fractions of salts in the system varied in the range 0.05–0.2. The mole fraction is defined as $x = n_{\text{Ca}}/(n_{\text{Ca}} + n_{\text{H}_2\text{O}})$. For elucidating the influence of ratio of both salts on viscosity the sections of ternary system were studied. These sections are characterized by the value of ionic fraction $y = n_{\text{Br}}/(n_{\text{Br}} + n_{\text{NO}_3})$ which assumes values 0.1, 0.2, 0.3, 0.4, 0.5 and limiting value for the binary system $\text{CaBr}_2\text{--H}_2\text{O}$. Density of the studied systems, knowledge of which is necessary for calculation of dynamic viscosity (η), was calculated from data published in [5]. The values of dynamic viscosity are in units Pa s.

Results and discussion

If we wish to appreciate the influence of composition of the system on its properties and to summarize in concise form extensive set of experimental data it is necessary to choose relationships which are able to describe dependence of viscosity on the studied parameters with sufficient accuracy.

For the description of temperature dependence of viscosity (η) a series of relationships was proposed. Discussion of their applicability for the region of highly concentrated solutions and melts was carried out by *Horsák* [6]. In a narrow interval the empirical polynomial approximation

$$\ln \eta = a + b/T + c/T^2 \quad (1)$$

can be recommended. T is the temperature (K) and a , b , c are the empirical constants. This equation is the simplest possible nonarrhenian approximation of temperature dependence of viscosity. From other relationships Fulcher equation [6] is often used

$$\ln \eta = A + B/(T - T_0) \quad (2)$$

This equation has very good fitness to experimental data in broader interval than eqn (1) and it can be derived theoretically on the basis of free volume theory [7] or configurational entropy [8]. However, the calculated parameters A , B , T_0 of eqn (2) are too sensitive to the studied temperature range and to dispersion of experimental data about fitted curve, which can be regarded as a disadvantage of the equation. With respect to this disadvantage the experimental data were treated using eqn (1). Values of parameters a , b , c corresponding to given composition are summarized together with the result of fitness test in Table 1.

For the description of temperature–concentration dependence of viscosity at the constant value of ionic fraction y the following equation was used

$$\ln \eta = A_1 + (B_1 + B_2x)/(T - T_1 - T_2x) \quad (3)$$

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

x	a	$b \cdot 10^{-3}$	$c \cdot 10^{-5}$	D %	N
$y = 0.1$					
0.0535	-10.339	0.7209	1.6626	0.1	5
0.0722	- 4.1080	- 3.1716	8.0596	0.3	6
0.115	- 3.1382	- 3.9023	10.464	0.2	6
0.147	0.005374	- 6.2621	15.685	1.3	6
0.172	10.876	-13.305	27.947	0.9	5
0.225 ^a	29.421	-27.249	55.979	1.1	5
$y = 0.2$					
0.0772	11.913	-11.570	19.238	2.5	9
0.109	3.9326	- 7.5228	14.947	1.5	10
0.137	8.5452	-10.777	21.418	1.6	11
0.155	1.6522	- 7.3098	18.037	0.7	10
0.184	13.406	-15.439	33.171	1.0	11
0.210 ^a	29.886	-26.776	53.877	2.4	9
$y = 0.3$					
0.0784	- 4.8208	- 2.1826	6.1494	1.3	11
0.112	3.4279	- 7.3695	15.098	1.1	11
0.145	6.9442	- 9.9387	20.835	2.0	11
0.167	19.496	-18.282	35.485	2.5	11
0.192 ^a	69.682	-50.282	87.727	2.3	8
0.201	26.003	-24.055	48.896	3.1	10
$y = 0.4$					
0.0561	-15.186	4.1736	- 3.8908	1.3	8
0.0769	- 4.7605	- 2.4546	6.8977	1.2	9
0.111	- 4.0487	- 3.0807	8.9885	1.0	11
0.168	18.608	-18.019	35.530	0.7	8
0.192	20.713	-20.538	42.575	1.3	10
$y = 0.5$					
0.0784	- 0.63212	- 4.5869	9.5307	1.1	10
0.109	1.0308	-11.367	20.886	0.9	12
0.142	19.249	-17.300	31.792	1.9	11
0.162	16.395	-16.730	33.637	1.3	11
0.191 ^a	51.447	-38.903	70.225	0.5	7
$y = 1.0$ (CaBr ₂ -H ₂ O)					
0.0562	- 2.3494	- 3.8451	8.1094	0.6	12
0.0783	-12.529	- 2.1453	-0.12412	0.9	12
0.103	- 8.8783	0.23862	2.9573	0.3	11
0.121 ^b	-11.959	2.2824	0.15105	0.7	7
0.130 ^c	- 9.3460	0.26168	4.0720	0.7	6

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

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

Experimental temperature interval: a) 288—323 K; b) 298—323 K; c) 308—333 K.

Its suitability had been proved on several systems [9]. In our case, however, there were great differences in values of parameters of eqn (3) calculated for given value of anionic fraction y . Therefore, in this work, for the final treatment of temperature–concentration dependence a modified procedure was used. According to this procedure the denominator in eqn (3) is derived from eqn (2) which describes temperature dependence of viscosity. The concentration dependence of parameter T_0 was approximated by linear function of mole fraction of salts in the system. As it follows from theoretical studies [7, 8], the parameter T_0 can be regarded as ideal temperature of glass transition and its connection with the temperature of glass transition T_g which can be determined experimentally had been discussed by Angell [10]. In coordinates $T-x$ eqn (3) can be represented as a set of radiating lines which are actually isoviscosity curves. The concentration dependence of T_g is also a linear function of concentration expressed by mole fraction x [11] and it represents the isoviscosity line for viscosity value 10^{12} Pa s [12, 13]. The value of experimentally determined temperature of glass transition depends partially on the rate of cooling and the ideal temperature of glass transition T_0 should be about 5–20 K lower than is the value determined experimentally. Therefore the concentration dependence of T_0 in eqn (3) was replaced by concentration dependence of T_g using experimentally accessible parameters T'_1 and T'_2 and correction parameter C_1 characterizing the difference between T_0 and T_g

$$\ln \eta = A_1 + (B_1 + B_2x)/(T - T'_1 - T'_2x - C_1) \quad (4)$$

By treating the experimental data of sections differing in anion composition y we used the values of parameters T'_1 and T'_2 which had been determined in the previous work [11]. The calculated values of parameters of eqn (4) are presented in Table 2 together with data on fitness of the used approximation. The experimental data of the binary system $\text{CaBr}_2\text{-H}_2\text{O}$ were fitted to eqn (3) because the calculating procedure used for finding parameters of eqn (4) did not converge.

Table 2
Values of the parameters of eqn (4)

y	A	B_1	B_2	T'_1	T'_2	C	s
0.1	-9.357	434.2	2189	129	461	-24.1	0.029
0.2	-7.783	168.9	2355	127	464	- 4.1	0.076
0.3	-8.369	264.8	2585	126	493	-17.0	0.058
0.4	-7.969	216.1	2150	126	476	- 1.8	0.078
0.5	-8.170	199.1	2726	127	492	-10.9	0.042
1.0	-9.743	402.9	5370	99.4 ^a	78.5 ^a	—	0.038

a) Values of the parameters T_1 and T_2 of eqn (3).

s is the standard deviation of the dependent variable $\ln \eta$.

The influence of anion composition y was estimated after introducing the relative viscosity $\eta_r = \eta_{\text{tern}}/\eta_{\text{bin}}$ which expresses the ratio of viscosity of the ternary system $\text{Ca}(\text{NO}_3)_2 - \text{CaBr}_2 - \text{H}_2\text{O}$ and the binary system $\text{Ca}(\text{NO}_3)_2 - \text{H}_2\text{O}$ at constant temperature and total concentration of salts in the system. The binary system was chosen as a standard for comparison because the experimental data on the system are easily available in broad temperature and concentration range [14]. The results presented in Fig. 1 show the influence of addition of bromide ions when concentration x remains constant. It follows that despite of fairly high variation of results, the viscosity of ternary system is significantly higher than that of the binary system $\text{Ca}(\text{NO}_3)_2 - \text{H}_2\text{O}$. The higher is the salt concentration the higher is the increase of viscosity. The ratio of viscosities of both binary aqueous melts is presented in this figure as well. It seems to be a paradox in behaviour of ternary system because the replacement of nonspheric nitrate ions by spherically symmetrical halogenide ions results in an increase of viscosity. This antilubricant effect has been observed earlier in nonaqueous melts of nitrates and halogenides [15]. The increase of viscosity is the reflection of change in structural arrangement of the system. Decreasing number of water molecules in hydration shells of ions brings their intimate interaction. The difference in ionic radii of both anions asserts and closer packing of particles results in an increase of viscosity. Discussing structure and properties of aqueous melts, the anionic radii of hydrated ions estimated by *Nightingale* [16] ($\text{NO}_3^- - 335 \text{ pm}$, $\text{Br}^- - 330 \text{ pm}$) should be replaced by values which are close to crystallographic radii [17], *i.e.* $\text{NO}_3^- - 264 \text{ pm}$, $\text{Br}^- - 195 \text{ pm}$. This approach respects the opinions of preferential hydration of cations. This fact is also proved by decreasing of molar volume of mixtures when the nitrate ions are

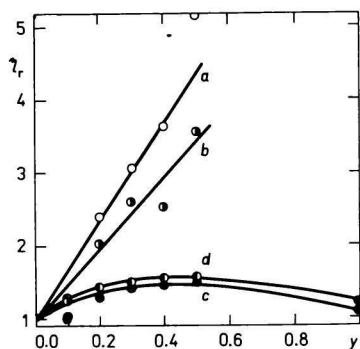


Fig. 1. Dependence of relative viscosity on temperature and composition.

a) $x = 0.18$, $T = 278.15 \text{ K}$; b) $x = 0.18$, $T = 298.15 \text{ K}$; c) $x = 0.12$, $T = 298.15 \text{ K}$; d) $x = 0.12$, $T = 318.15 \text{ K}$.

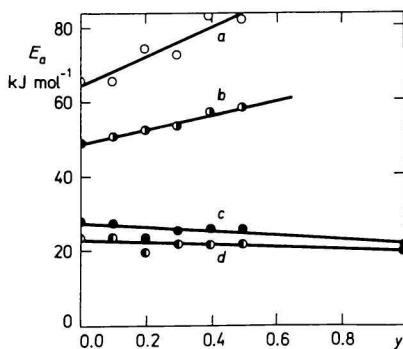


Fig. 2. Dependence of activation energy on temperature and composition.

a) $x = 0.18$, $T = 278.15 \text{ K}$; b) $x = 0.18$, $T = 298.15 \text{ K}$; c) $x = 0.12$, $T = 298.15 \text{ K}$; d) $x = 0.12$, $T = 318.15 \text{ K}$.

replaced by bromide ions. This decrease of volume is in accordance with calculated values of molar volumes of both components [5] at infinitely low concentration of water: $\text{Ca}(\text{NO}_3)_2$ — $68.86 \text{ cm}^3 \text{ mol}^{-1}$, CaBr_2 — $56.64 \text{ cm}^3 \text{ mol}^{-1}$ at 0°C .

Activation energy of viscose flow, which is defined by the relation $E_a = R(\partial \ln \eta / \partial(1/T))$, can be regarded as a measure of stability of the system. The influence of anion composition of ternary system on this parameter was evaluated and the results are presented in Fig. 2. Two different tendencies can be seen. While at higher concentration of water the replacement of nitrate ions by bromide ions results in a decrease of activation energy, at lower concentration of water ($x > 0.14$) its value remarkably increases. One should take into account that at salt concentration $x = 0.2$, 4 moles of water correspond to 1 mole of salt and, therefore, water cannot be considered to be the medium in which the charged particles move. In this concentration range the moving particles are clusters which require higher activation energy than simple ions.

References

1. Braunstein, J., *Ionic Interactions*, Vol. 1, pp. 180—260. Academic Press, New York, 1971.
2. Kodejš, Z., Sláma, I., and Novák, J., *Chem. Zvesti* 30, 439 (1976).
3. Kodejš, Z., Horsák, I., and Sláma, I., *Rev. Roum. Chim.* 24, 293 (1979).
4. Malá, J., Novák, J., Kodejš, Z., and Sláma, I., *Collect. Czech. Chem. Commun.* 43, 183 (1978).
5. Kodejš, Z. and Sláma, I., *Collect. Czech. Chem. Commun.* 45, 17 (1980).
6. Horsák, I. and Sláma, I., *Chem. Listy* 73, 785 (1979).
7. Cohen, M. H. and Turnbull, D., *J. Chem. Phys.* 31, 1164 (1959).
8. Adam, G. and Gibbs, J. H., *J. Chem. Phys.* 43, 139 (1965).
9. Sláma, I. and Kodejš, Z., *J. Solution Chem.* 8, 801 (1979).
10. Angell, C. A. and Bressel, R. D., *J. Phys. Chem.* 76, 3244 (1972).
11. Malá, J. and Sláma, I., *Collect. Czech. Chem. Commun.* 44, 1877 (1979).
12. Tweer, H., Laberge, N., and Macedo, P. B., *J. Amer. Ceram. Soc.* 54, 121 (1971).
13. Ambrus, J. H., Moynihan, C. T., and Macedo, P. B., *J. Electrochem. Soc.* 119, 192 (1972).
14. Bressel, R. D., *Ph. D. Thesis*. Purdue University, Lafayette, 1972.
15. Rhodes, E., Smith, W. E., and Ubbelohde, A. R., *Trans. Faraday Soc.* 63, 1943 (1968).
16. Nightingale, E. R., *J. Phys. Chem.* 63, 1381 (1959).
17. Pauling, L., *Nature of the Chemical Bond*. Cornell University Press, Ithaca, N. Y., 1948.

Translated by P. Fellner