# THE TEMPERATURE AND CONCENTRATION DEPENDENCE OF VISCOSITY AND THE CONCENTRATION DEPENDENCE OF GLASS TRANSITION TEMPERATURE FOR THE SYSTEM CALCIUM NITRATE–POTASSIUM NITRATE–WATER

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The temperature and concentration dependence of viscosity of the system calcium nitrate–potassium nitrate–water was studied in the temperature range −20 to +75°C for concentrations given by ionic fractions of the potassium salt of 0·1, 0·2, 0·3, 0·4, and 0·5. The mole fraction of the salts was within the range 0·047 to 0·238. The temperature and concentration dependence of viscosity has been correlated with empirical equations. An equation describing the temperature and concentration dependence of viscosity has been proposed on the basis of the variation of glass transition temperature with concentration.

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In developing models allowing to predict the behaviour of hydrated melts over a wide temperature range, it is essential to know how the viscosity of the system varies with temperature and concentration.

From the analyses advanced by Turnbull[1] and Uhlmann[2] it follows that the knowledge of the viscosity at the melting point and of its derivative allows one to derive conclusions about the supercooling ability of the liquid. Another factor determining the stability of a solution below the temperature of liquidus is the nucleation frequency which is strongly dependent upon viscosity. Obviously, the viscosity and the supercooling ability of a system are closely related.

On the other hand, the supercooling ability significantly extends the temperature region of the existence of the liquid state where the viscosity exhibits departures from the Arrhenian behaviour. In this connection, the need arises to establish relations describing the viscosity or fluidity over wide temperature and concentration ranges.

The aim of the present work was to propose a relation involving a reasonable number of constants, which would describe the variation of viscosity of a ternary system over wide temperature and concentration ranges, with special regard to the region of highly concentrated solutions.

As a model, we have chosen the system calcium nitrate–potassium nitrate–water which shows a great tendency to supercooling, thus allowing experimental data on viscosity to be measured over a wide temperature range.

## EXPERIMENTAL

Samples for the viscosity measurements were prepared in the same way as described earlier[3,4] so that required values could be reached of the quantities $Z$ and $X$ defined as

$$Z = n_{K^+}/(n_{Ca^+} + n_{K^+})$$

and

$$X = (n_{Ca(NO_3)_2} + n_{KNO_3})/(n_{Ca(NO_3)_2} + n_{KNO_3} + n_{H_2O}) \, ,$$

where $n_{K^+}$, $n_{Ca^{2+}}$, $n_{Ca(NO_3)_2}$, $n_{KNO_3}$. and $n_{H_2O}$ are the mole numbers of potassium ions, calcium ions, calcium nitrate, potasium nitrate, and water, respectively. The concentrations will henceforth be expressed either by mole percent of the salts ($X$ . 100), or by the mole fractions of calcium nitrate, $X_1$, and potassium nitrate, $X_2$, defined by the relations $X_1 = (1 - Z) X$ and $X_2 = ZX$.

Viscosities were measured on a commercial Höppler viscosimeter (Prüfgerate-Werk Medingen) allowing measurements over a range from $10^{-5}$ to $10^2$ Pa.s with an accuracy of 0·1—1%. The measuring tube of the viscosimeter was thermostatted in an alcohol bath. The temperature of the measurements ranged from —20°C, or, alternatively, from the lowest temperature at which the sample still did not show crystallization, to +75°C. The temperature was measured by a platinum resistance thermometer with an accuracy of ±0·01°C. The temperature of the thermostatting medium was kept to within better than ±0·04°C. The densities necessary for the viscosity calculations were taken from previous papers[3-5].

The concentration of water in the samples was determined prior and after measurement by chelatometric titration of calcium using a Kalkon indicator.

## RESULTS

In order to establish the temperature dependence of viscosity at individual $X$ and $Z$, the measured viscosity values were correlated with the Fulcher equation

$$\ln \eta = A + B/(T - T_0) \, , \qquad (1)$$

where $A$, $B$. and $T_0$ are the constants, with $T_0$ having the meaning of the glass transition temperature at infinitely slow cooling, $\eta$ is the viscosity in Pa.s, and $T$ is the absolute temperature. The constants of Eq. (1) and the confidence intervals for the individual $X$ and $Z$ are summarized in Table I. All the statistical computations were performed adopting a significance level of 0·05.

The irregular variation in the parameters of Eq. (1) as a function of concentration, as well as the broad confidence intervals for these parameters, is caused by flat minima of the sums of the squares of deviations. Consequently, one and the same set of experimental data may be described, within the limits of experimental error, by several sets of parameters.

This shortcoming may be eliminated if besides the criterion of the minimum of the sum of squares of deviations a continuous function specifying the variation of the parameters for subsets of data with differing concentrations is involved in the optimization of the parameters of the Fulcher equation (1).

TABLE I

Temperature dependence of viscosity. Constants of Eq. (*1*)

| $X$ | $T_0$, K | $A$ | $B \cdot 10^{-2}$ | Average relative error % |
|---|---|---|---|---|
| $Z = 0·1$ | | | | |
| 0·1972 | 204·5 ± 7·9 | −8·225 ± 0·485 | 6·08 ± 0·99 | 1·23 |
| 0·1667 | 192·7 ± 9·2 | −8·281 ± 0·408 | 5·68 ± 0·94 | 1·00 |
| 0·1379 | 161·0 ± 44·1 | −9·076 ± 1·417 | 6·92 ± 4·20 | 1·90 |
| 0·1127 | 159·2 ± 11·2 | −9·012 ± 0·303 | 5·91 ± 0·91 | 0·51 |
| 0·0746 | 136·3 ± 65·8 | −9·667 ± 1·551 | 6·51 ± 5·19 | 0·90 |
| 0·0527 | 144·7 ± 19·1 | −9·483 ± 0·369 | 5·19 ± 1·22 | 0·47 |
| $Z = 0·2$ | | | | |
| 0·2062 | 194·7 ± 13·5 | −8·683 ± 0·712 | 6·52 ± 1·61 | 1·92 |
| 0·1672 | 185·2 ± 8·8 | −8·609 ± 0·342 | 5·64 ± 0·84 | 0·87 |
| 0·1447 | 177·7 ± 10·7 | −8·710 ± 0·346 | 5·33 ± 0·90 | 0·73 |
| 0·1130 | 168·9 ± 9·6 | −8·844 ± 0·247 | 4·87 ± 0·69 | 0·44 |
| 0·0791 | 189·7 ± 33·4 | −8·292 ± 0·699 | 2·76 ± 1·63 | 1·77 |
| 0·0527 | 147·7 ± 105·0 | −9·228 ± 1·870 | 4·54 ± 6·03 | 2·68 |
| $Z = 0·3$ | | | | |
| 0·2174 | 199·4 ± 3·0 | −8·386 ± 0·240 | 5·46 ± 0·42 | 1·64 |
| 0·1613 | 191·7 ± 1·4 | −8·281 ± 0·070 | 4·28 ± 0·13 | 0·42 |
| 0·1412 | 185·5 ± 2·9 | −8·447 ± 0·097 | 4·20 ± 0·22 | 0·28 |
| 0·1112 | 180·6 ± 2·4 | −8·607 ± 0·066 | 3·84 ± 0·16 | 0·17 |
| 0·0779 | 183·2 ± 10·3 | −8·493 ± 0·260 | 2·98 ± 0·58 | 1·02 |
| 0·0531 | 163·3 ± 19·3 | −9·086 ± 0·428 | 3·80 ± 1·14 | 1·09 |
| $Z = 0·4$ | | | | |
| 0·2381 | 207·1 ± 1·9 | −8·043 ± 0·105 | 4·70 ± 0·20 | 0·35 |
| 0·1980 | 200·5 ± 2·0 | −8·127 ± 0·082 | 4·14 ± 0·17 | 0·27 |
| 0·1684 | 187·6 ± 3·9 | −8·473 ± 0·129 | 4·37 ± 0·30 | 0·29 |
| 0·1403 | 188·1 ± 5·0 | −8·461 ± 0·146 | 3·74 ± 0·34 | 0·36 |
| 0·0974 | 198·6 ± 4·6 | −8·284 ± 0·112 | 2·48 ± 0·23 | 0·37 |
| 0·0762 | 190·5 ± 12·6 | −8·462 ± 0·269 | 2·55 ± 0·60 | 0·73 |
| 0·0474 | 133·5 ± 50·7 | −9·772 ± 0·974 | 5·48 ± 3·32 | 1·20 |
| $Z = 0·5$ | | | | |
| 0·2342 | 202·2 ± 18·6 | −8·082 ± 0·570 | 4·24 ± 1·35 | 0·55 |
| 0·1898 | 186·8 ± 2·0 | −8·476 ± 0·047 | 4·40 ± 0·13 | 0·03 |
| 0·1706 | 176·2 ± 12·9 | −8·718 ± 0·295 | 4·71 ± 0·85 | 0·20 |
| 0·1318 | 183·7 ± 3·8 | −8·588 ± 0·080 | 3·56 ± 0·21 | 0·10 |
| 0·1053 | 209·6 ± 6·8 | −8·043 ± 0·143 | 1·93 ± 0·28 | 0·41 |
| 0·0754 | 141·8 ± 54·9 | −9·670 ± 1·025 | 5·36 ± 3·50 | 0·86 |
| 0·0505 | 139·0 ± 6·0 | −9·947 ± 0·115 | 5·44 ± 0·39 | 0·11 |

Furthermore, this procedure enables one to develop an equation describing the temperature and concentration dependence of viscosity for the system under study.

First, we tried to express the concentration dependence of the parameter $T_0$. This quantity is known to be closely related to the glass transition temperature, $T_g$, which is accessible to experimental determination. It has been established[6] that the two quantities vary in a similar manner, and that the glass transition temperature is usually by 5 to 20 K higher than $T_0$. It is also known that for a number of salts, $T_g$ varies linearly with concentration. On these grounds, the following additive linear relationship was proposed for the description of the variation of $T_g$ with the concentrations of salts in a ternary system:

$$T_g = T_{g0} + T_{g1}X_1 + T_{g2}X_2 \,, \qquad (2)$$

where $T_{g0}$, $T_{g1}$, and $T_{g2}$ are the constants, with $T_{g0}$ having the meaning of the glass transition temperature of pure water.

In order to test the applicability of this equation, the polynomial regression method was used to fit a set of 72 experimental data[7-9] to the equation, and all the constants were calculated. The fitted lines are shown in Fig. 1.

The fit can be improved, though the improvement is not of great significance, by introducing another term into Eq. (2) so that $T_g$ is now related to concentration by the equation

$$T_g = T_{g0} + T_{g1}X_1 + T_{g2}X_2 + T_{g12}(X_1X_2)^{1/2} \,. \qquad (3)$$

The parameters of Eqs (2) and (3) are listed in Table II, along with the standard deviation, $s_p$, of the parameters, and the standard deviation, $s$, of the fit.

Investigation of the concentration dependence of the parameter $B$ of the Fulcher equation revealed that unlike some binary systems for which this parameter in the analogous Vogel–Tamman–Fulcher equation may be considered linearly dependent on concentration[6], such linear relation does not apply to ternary systems. In fitting the set of the $B$ constants from Table I to various types of functions, the best fit was obtained using the relation

$$B = B_0 + B_1X_1 + B_2X_2 + B_{11}X_1^2 + B_{22}X_2^2 + B_{12}X_1X_2 \,, \qquad (4)$$

where $B_0$, $B_1$, $B_2$, $B_{11}$, $B_{22}$, and $B_{12}$ are constants.

Analysis of the temperature dependence of viscosity in the system under study indicated that the parameter $A$ of the Fulcher equation is most likely independent of concentration, or dependent on it only very slightly.

In view of the above conclusions, the Fulcher equation was modified into the form

$$\ln \eta = A + \frac{B_0 + B_1X_1 + B_2X_2 + B_{11}X_1^2 + B_{22}X_2^2 + B_{12}X_1X_2}{T - T_0^0 - T_1^0X_1 - T_2^0X_2}, \qquad (5)$$

which was fitted by the regression method to a set of 531 experimental data on viscosity for the systems calcium nitrate–potassium nitrate–water and calcium nitrate–water[5]. Modification of this equation by introducing both the function $A = A_0 + A_1X_1 + A_2X_2$ and Eq. (*3*) for $T_0$ did not result in any significant reduction

TABLE II

Constants of Eqs (*2*) and (*3*)

| Eq. | $T_{g0}$ | $s_{p0}$ | $T_{g1}$ | $s_{p1}$ | $T_{g2}$ | $s_{p2}$ | $T_{g12}$ | $s_{p12}$ | $s$ |
|---|---|---|---|---|---|---|---|---|---|
| (*2*) | 135·7 | 1·2 | 403·9 | 7·8 | 61·8 | 10·4 | — | — | 3·10 |
| (*3*) | 135·8 | 0·9 | 413·0 | 6·5 | 195·7 | 23·3 | −122·2 | 19·8 | 2·51 |

TABLE III

Constants of Eq. (*5*)

| Parameter | Parameter value | $s_p$ | Parameter | Parameter value | $s_p$ |
|---|---|---|---|---|---|
| | | optimization of 10 parameters | | | |
| $A$ | −9·08 | 0·05 | $B_{22}$ | −2 846 | 550 |
| $B_0$ | 326 | 10 | $B_{12}$ | 2 224 | 750 |
| $B_1$ | 2 161 | 38 | $T_0^0$ | 134·4 | 1·5 |
| $B_2$ | 452 | 70 | $T_1^0$ | 321·7 | 5·3 |
| $B_{11}$ | 806 | 180 | $T_2^0$ | 70·4 | 12 |
| | | optimization of 9 parameters using $T_0^0 = 120$ K | | | |
| $A$ | −9·46 | 0·03 | $B_{22}$ | −3 205 | 626 |
| $B_0$ | 416 | 5 | $B_{12}$ | 1 793 | 854 |
| $B_1$ | 2 352 | 37 | $T_0^0$ | 120 | — |
| $B_2$ | 482 | 82 | $T_1^0$ | 368·9 | 2·0 |
| $B_{11}$ | −405 | 142 | $T_2^0$ | 85·0 | 13·6 |

in the error. With respect to the given limits of experimental accuracy, the additional parameters proved to be statistically insignificant or on the borderline of significance.

The parameters of Eq. (*5*) are listed in Table III, together with the standard deviations, $s_p$, of the parameters. The standard deviation of the fit $s = 0{\cdot}06896$. The fits of the sets of experimental data to the equation are illustrated in Figs 2–7 in which the same scale has been used.

## DISCUSSION

It can be seen from Fig. 1 that, to a first approximation, the assumption of the linear dependence of $T_g$ on the concentration of individual salts is well fulfilled. In practically all cases, the deviations from the linear fit, with a standard deviation of 3·1 K, are comparable with the accuracy of the employed experimental methods which is usually within ±4 K.

In addition to the fitting procedure, the applicability of Eq. (*2*) can be tested by extrapolation to zero salt concentration. In our case, the $T_g$ value for water comes out to be 135 ± 3·5 K. Although the extrapolation is relatively long, the resulting value is in very good agreement with the values 127 ± 4 K and 139 K obtained by Miller[10] and Sare[7], respectively.

Similar comparison between our value of $T_0$ for water (134 ± 3 K) and the literature values is much more difficult on account of considerable spread in the data (from 143 K to 200 ± 20 K (ref.[7,11–13])). This is due to the fact that the obtained value of the parameter $T_0$ strongly depends on the temperature range covered by the experimental data and on the length over which the data have been extrapolated.

For this reason, the check on the applicability of Eq. (*5*) was made by calculating values of the glass transition temperature, $T_g$. The calculation was based on the observation that at the glass transition temperature the viscosity of the solution has a value of $10^{12}$ Pa.s. Accordingly, $T_g$ values were calculated with this value substituted in Eq. (*5*).

Fig. 8 provides a comparison between the $T_g$ values calculated from Eq. (*5*) and those found experimentally. As is evident, the calculated values exhibit a systematic deviation amounting on the average to 5·6 K. Likewise, the $T_g$ value of 150 K obtained by extrapolation to zero salt concentration is by 15 to 20 K higher than the literature data. The discrepancies are likely due to the fact that the experimental data did not cover the low-concentration region and viscosities at temperatures near $T_g$.

The validity of this assumption was tested by restricting the calculation of the parameter $T_0^0$ of Eq. (*5*) to a set from which data measured at low concentrations and temperature were removed gradually. The $T_0^0$ values calculated at each step showed a clear tendency to increase.

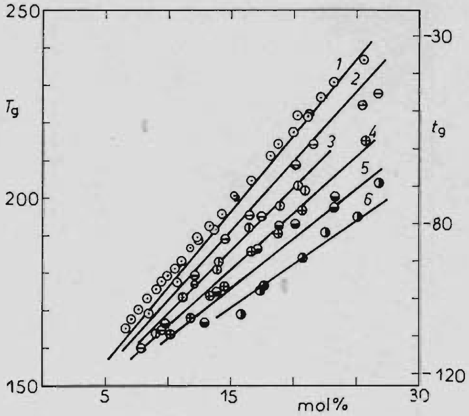

FIG. 1

Concentration dependence of glass transition temperature, $T_g$ (K), at various $Z$: *1* 0·0; *2* 0·1; *3* 0·2; *4* 0·3; *5* 0·4; *6* 0·5

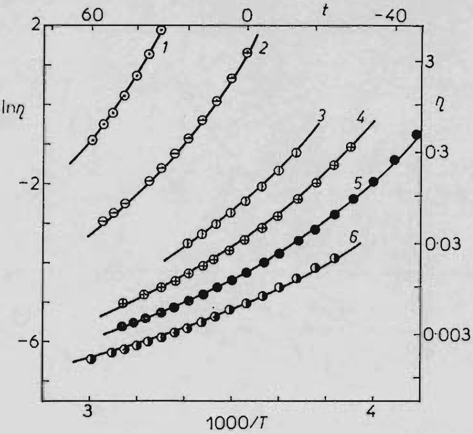

FIG. 2

Temperature dependence of viscosity, $\eta$(Pa.s), for $Z = 0{\cdot}0$ at various $X$: *1* 0·259; *2* 0·197; *3* 0·136; *4* 0·115; *5* 0·091; *6* 0·066

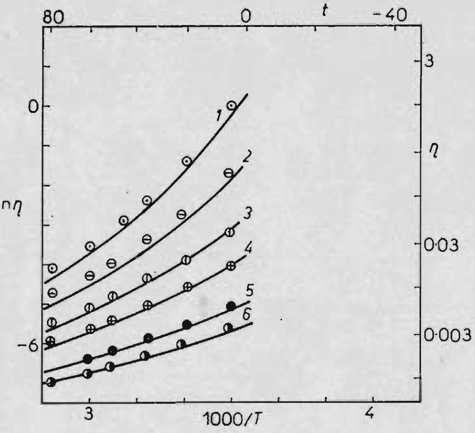

FIG. 3

Temperature dependence of viscosity, $\eta$(Pa.s), for $Z = 0{\cdot}1$ at various $X$: *1* 0·197; *2* 0·167; *3* 0·138; *4* 0·113; *5* 0·075; *6* 0·053

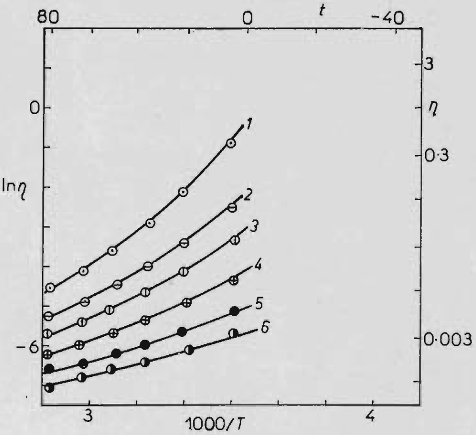

FIG. 4

Temperature dependence of viscosity, $\eta$(Pa.s), for $Z = 0{\cdot}2$ at various $X$: *1* 0·206; *2* 0·169; *3* 0·145; *4* 0·113; *5* 0·079; *6* 0·053

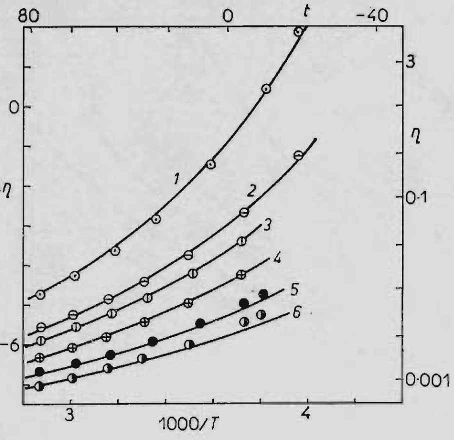

FIG. 5

Temperature dependence of viscosity, $\eta$(Pa.s), for $Z = 0{\cdot}3$ at various $X$: *1* 0·214; *2* 0·161; *3* 0·141; *4* 0·111; *5* 0·078; *6* 0·053

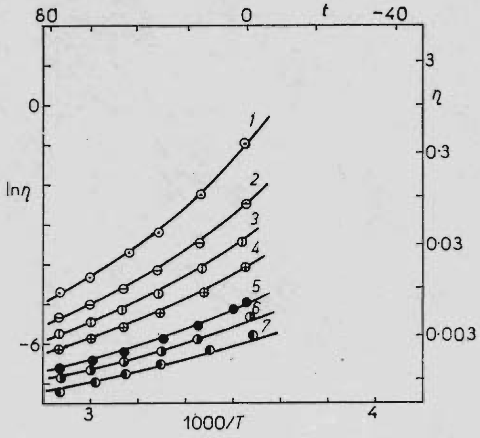

FIG. 6

Temperature dependence of viscosity, $\eta$(Pa.s), for $Z = 0{\cdot}4$ at various $X$: *1* 0·238; *2* 0·198; *3* 0·168; *4* 0·140; *5* 0·097; *6* 0·076; *7* 0·047

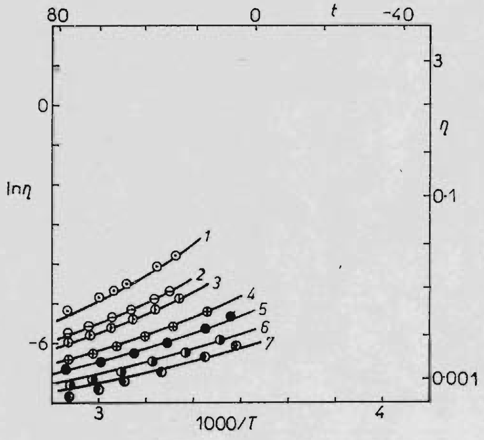

FIG. 7

Temperature dependence of viscosity, $\eta$(Pa.s), for $Z = 0{\cdot}5$ at various $X$: *1* 0·234; *2* 0·190; *3* 0·171; *4* 0·132; *5* 0·105; *6* 0·075; *7* 0·051

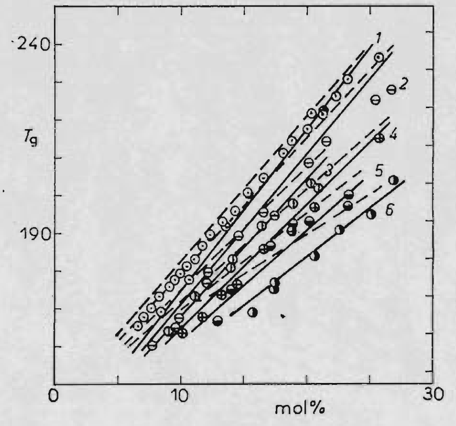

FIG. 8

Comparison of experimental and calculated $T_g$ values (K) at various $Z$: *1* 0·0; *2* 0·1; *3* 0·2; *4* 0·3; *5* 0·4; *6* 0·5; ----- $T_0^0 = 134{\cdot}4$; —— $T_0^0 = 120$ K

As the constant $T_0^0$ is not experimentally accessible, and the literature data based on long extrapolations differ considerably from one another, it may be, in a sense, considered an adjustable parameter. It turns out that on changing $T_0^0$ by 10 K and recalculating the remaining parameters, the fit of Eq. (*5*) is only slightly impaired, with the standard deviation increasing from $6{\cdot}90 \,.\, 10^{-2}$ to $7{\cdot}12 \,.\, 10^{-2}$. By properly adjusting the parameter $T_0^0$, it is possible to obtain an average deviation between calculated and experimental $T_g$ values which is just within the limits of experimental accuracy. For the system under study, the optimum $T_0^0$ value, at which the calculated and experimental $T_g$ values agree with each other, is approximately 120 K.

If we now set $T_0^0$ equal to 120 K and recalculate the constants of Eq. (*5*) by optimization technique, we obtain the set of parameters which is given in Table III.

The calculation of $T_g$ for water from Eq. (*5*) using the above parameters and assuming a value of $10^{12}$ Pa.s for the viscosity at $T_g$, leads to a value of 121·3 K which is in agreement with published data. Using Eq. (*5*), the constants from Table III and $T_0^0 = 120$ K, $T_g$ and $T_0$ for the non-aqueous system calcium nitrate–potassium nitrate with a composition of 38·1 mol % $Ca(NO_3)_2$ are found to be 331 K and 314 K, respectively. The values quoted in the literature are 329 K (ref.[14]) for $T_g$ and 316 K (ref.[15]) for $T_0$. The $T_g$ values calculated from Eq. (*5*) using the constants from Table III ($T_0^0 = 120$ K) and the viscosity value of $10^{12}$ Pa.s are compared with the experimental values in Fig. 8.

In view of the very good agreement between the calculated and experimental data, it seems reasonable to conclude that the proposed equation not only satisfactorily describes the ternary system in the studied temperature and concentration ranges, but can be applied to the nonaqueous system as well.

## REFERENCES

1. Turnbull D.: Contemp. Phys. *10*, 673 (1969).
2. Uhlmann D. R.: J. Non-Cryst. Solids *7*, 337 (1970).
3. Skokánek M.: *Thesis*. Institute of Inorganic Chemistry, Prague 1979.
4. Skokánek M., Sláma I.: This Journal, in press.
5. Skokánek M., Sláma I.: Chem. Zvesti *35*, 35 (1981).
6. Bressel R. D.: *Thesis*. Purdue University, Lafayette, Indiana 1970.
7. Sare E. J., Angell C. A.: J. Sol. Chem. *2*, 53 (1973).
8. Sare E. J.: *Thesis*. Purdue University, Lafayette, Indiana 1971.
9. Malá J., Sláma I.: This Journal *45*, 1896 (1980).
10. Miller A. A.: Science *163*, 1325 (1968).
11. Bernini V., Fittipaldi F., Ragozzino E.: Nature (London) *224*, 910 (1969).
12. Korsin L., Drost-Hansen W., Millero F. J.: J. Phys. Chem. *73*, 34 (1969).
13. Miller A. A.: J. Chem. Phys. *38*, 1568 (1963).
14. Dietzel A., Pogel M. J.: Proceedings of the 3rd International Glass Congress, Venice 1953, p. 219.
15. Angell C. A.: J. Phys. Chem. *68*, 1917 (1964).

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