# Temperature and concentration dependence of viscosity of $Mg(NO_3)_2$–$H_2O$ systems

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Densities and viscosities of aqueous magnesium nitrate solutions are measured as functions of temperature and composition. The temperature dependence of viscosity is described by the Vogel–Tammann–Fulcher (VTF) equation. By accounting quantitatively for the concentration dependences of all three parameters involved in the VTF equation an improved isothermal equation is obtained, it describes satisfactorily the concentration dependence of viscosity.

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On a mesuré, en fonction de la température et de la composition, les densités et les viscosités de solutions aqueuses de nitrate de magnésium. On décrit l'effet de la température sur la viscosité à l'aide de l'équation de Vogel–Tammann–Fulcher (VTF). En tenant compte quantitativement de l'effet de la concentration sur chacun des trois paramètres impliqués dans l'équation de VTF, on obtient une équation isotherme appropriée qui décrit d'une façon satisfaisante l'effet de la concentration sur la viscosité.

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## Introduction

It is known that in electrolyte solutions all empirical expressions (1–3) fail to explain the concentration dependence of viscosity at higher concentrations. At these concentrations, the viscosity data satisfactorily fit only Vand's (4) and similarly derived equations (5–8) but it is not clear why they work as well as they do.

One of the approaches being used to obtain an isothermal equation for explaining the concentration dependence of transport properties in glass-forming molten mixtures (9–11) is by substituting the empirical concentration dependences of the three parameters, $A$, $B$, and $T_0$, in the VTF equation (12)

$$[1] \quad \eta = AT^{1/2} \exp B/(T - T_0)$$

where $\eta$ is the viscosity and $T$ is the absolute temperature.

Angell and Bressel (13) extended this approach used in glass-forming molten mixtures to the $Ca(NO_3)_2$–$H_2O$ system and interestingly found that a Vand's type equation could be derived from eq. [1]. However, in getting the isothermal equation from [1] the concentration dependence of $A$ was completely ignored and that of $B$ was partly considered. Therefore, it is possible to improve the isothermal equation obtainable from eq. [1] by accounting appropriately for the concentration dependences of the $A$ and $B$ parameters of electrolyte solutions.

In an earlier paper (14) we derived eq. [1] from the Adam–Gibbs equation (15) after proper substitution for the temperature dependence of configurational heat capacity. Such a study has provided expressions for $A$ and $B$ according to which

$$[2] \quad A = A_0 \exp(-B_1/C_1T_0)$$

and

$$[3] \quad B = (B_1/C_1)(1 - C_2T_0/C_1)$$

$A_0$, $B_1$, $C_1$, and $C_2$ are all constant parameters for a particular system. $C_1$ is the difference in the heat capacities of glass and liquid at $T_0$. $C_2$ is the difference in the slopes of the plots of heat capacity versus $T$ for the glassy and liquid states. From eqs. [2] and [3] it is apparent that a quantitative description for the concentration dependences of $A$ and $B$ is possible.

In this paper we have studied the viscosities of aqueous magnesium nitrate solutions with concentration ranging from dilute to saturation point with a view to obtain an improved isothermal equation by incorporating, in light of eqs. [2] and [3], the concentration dependences of $A$ and $B$ also.

## Experimental

BDH(analar) grade magnesium nitrate hexahydrate was used in preparing all solutions. The water used was doubly distilled in a quartz distilling unit. The exact concentrations were volumetrically determined at 25°C by the EDTA titration method. Solutions having concentrations ranging between 0.0917*m* (*m* = molality) and 6.3682*m* (nearly the saturation point at 50°C) were studied.

The viscosity measurements were made using a Hoppler BH-2 falling ball viscometer with an accuracy of 0.5%. In this viscometer, since the solution was sealed, the loss of water at high temperatures was prevented. The densities, $\rho$, of the solutions required for calculating their viscosities were measured accurate to 0.01% using a calibrated pycnometer.

All measurements were made in a thermostated water bath of stability ±0.02° (Ultra Thermostat type NBE) and at temperatures ranging from 17 to 89°C.

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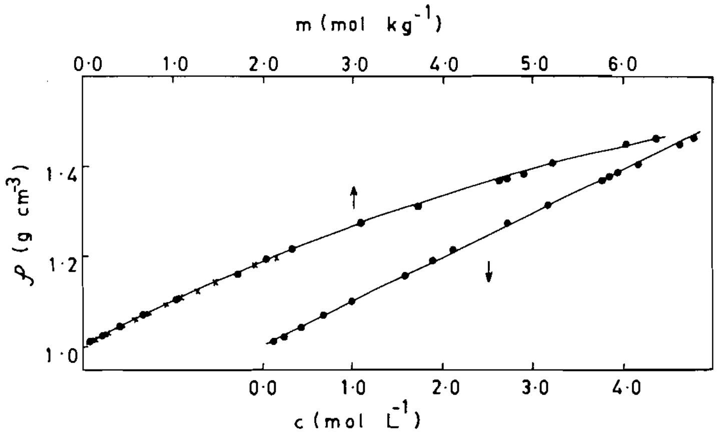


FIG. 1. Plots of densities of $Mg(NO_3)_2$–$H_2O$ systems at 20°C versus molality and molarity of $Mg(NO_3)_2$ (●, observed; ×, reported).

## Results and discussion

The measured densities of the magnesium nitrate solutions are found to be linear functions of temperature (Table 1) whereas their dependence on molality does not exhibit a linear relationship. Surprisingly, for the dependence of density on molarity, $c$ is found to be linear in the concentration range studied. Such dependences of ρ on concentration are illustrated in Fig. 1 by plotting ρ versus $m$ and ρ versus $c$ isotherms at 20°C. From Fig. 1 it may also be noted that the reported values (16) of densities of a few magnesium nitrate solutions at 20°C are in good agreement to within ±0.3% of the present values.

The measured viscosities of aqueous magnesium nitrate solutions are presented as Arrhenius plots in Fig. 2. The non-Arrhenius temperature dependences of η are therefore least-squares fitted to eq. [1]. The values of the parameters $A$, $B$, and $T_0$ so obtained are listed in Table 2.

TABLE 1. Parameters of the density equation $\rho = a - bt(°C)$

| $m$ (mol kg$^{-1}$) | $a$ | $b \times 10^4$ | Std. dev. in ρ, $\sigma \times 10^4$ |
|---|---|---|---|
| 0.0917 | 1.0214 | 4.6154 | 0.9282 |
| 0.2297 | 1.0346 | 4.3443 | 0.7162 |
| 0.4243 | 1.0559 | 4.5686 | 0.9182 |
| 0.6753 | 1.0816 | 5.1671 | 0.7699 |
| 1.0524 | 1.1170 | 5.2511 | 0.8032 |
| 1.7055 | 1.1714 | 5.2673 | 1.5334 |
| 2.0428 | 1.2047 | 5.4326 | 1.4241 |
| 2.3300 | 1.2310 | 5.7854 | 1.6654 |
| 3.1050 | 1.2884 | 5.9078 | 2.0046 |
| 3.7251 | 1.3289 | 6.2154 | 1.0309 |
| 4.6299 | 1.3828 | 6.0195 | 1.8120 |
| 4.7091 | 1.3906 | 6.1908 | 1.8578 |
| 4.8578 | 1.4002 | 5.8546 | 1.1534 |
| 5.2393 | 1.4227 | 6.4114 | 1.3185 |
| 6.0371 | 1.4671 | 8.0131 | 1.3727 |
| 6.3682 | 1.4801 | 8.1530 | 1.3131 |

It is clear from several studies (2, 8) that the viscosity of an electrolytic solution is governed by two types of interactions occurring in the solution, viz., ion–ion and ion–solvent. The contribution to viscosity from ion–ion interaction is described by a $c^{1/2}$ term and that due to ion–solvent or solute–solvent interaction shows an exponential dependence on concentration. It has been observed empirically that the contribution of the $c^{1/2}$ term is significant only at very low concentrations whereas at higher concentrations the exponential term due to the solute–solvent interaction dominates. Therefore, the variations occurring in the values of $A$, $B$, and $T_0$ as a function of concentration are considered to be governed predominantly by the solute–solvent interactions. Accordingly, an attempt has been made here to correlate first the variations produced in $T_0$ with the hydration phenomenon.

Hydration of the solute particles will cause the system to lose some of its configurational degrees of freedom, thereby resulting in a decrease of the configurational entropy, $S_c$, of the system. As the concentration increases $S_c$ will therefore keep on decreasing. Since $T_0$ is the temperature at which $S_c$ becomes zero, $T_0$ must increase with increase in concentration. Accordingly, $T_0$ can be related to the probability, $p$, of finding a solvent particle in the hydration shells of the solute particles which, of course, increases by increasing concentration because $p = nm/55.51$ where $n$ is the total hydration number of the solute. Consequently, the values of $T_0$ are drawn against $m$ and a linear plot is obtained (Fig. 3$a$), reflecting the dependence of $T_0$ on the hydration phenomenon of the solute. The observed

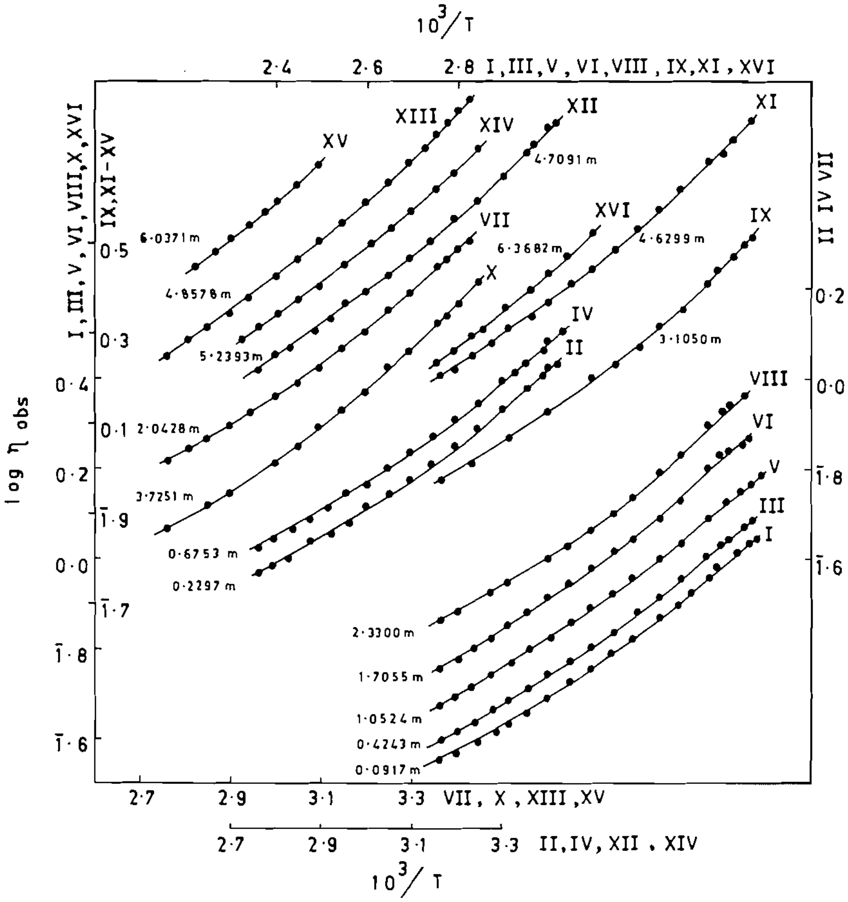
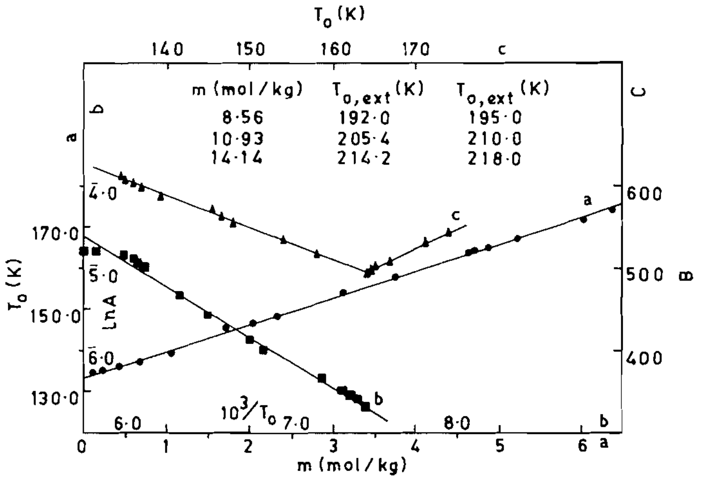


FIG. 2. Plots of log η versus $1/T$ for $Mg(NO_3)_2$–$H_2O$ systems.



| m (mol/kg) | $T_{0,ext}$ (K) | $T_{0,ext}$ (K) |
|---|---|---|
| 8·56 | 192·0 | 195·0 |
| 10·93 | 205·4 | 210·0 |
| 14·14 | 214·2 | 218·0 |

FIG. 3. Plots of ln $A$, $B$, and $T_0$ versus $1/T_0$, $T_0$, and $m$, respectively, for $Mg(NO_3)_2$–$H_2O$ systems.

TABLE 2. Parameters of eq. [1] for the viscosity of $Mg(NO_3)_2–H_2O$ systems (viscosity range in parentheses)

| $m$ (mol $kg^{-1}$) | Temperature range (°C) and viscosity range (cP) | $A \times 10^3$ | $B$ | $T_0$ (K) | Std. dev. in $\ln \eta$ |
|---|---|---|---|---|---|
| 0.0917 | 16.4–89.0<br>(1.11–0.36) | 1.2263 | 614.62 | 134.5 | $1.31 \times 10^{-3}$ |
| 0.2297 | 19.5–89.0<br>(1.08–0.37) | 1.3246 | 607.00 | 135.0 | $1.23 \times 10^{-3}$ |
| 0.4243 | 17.0–89.0<br>(1.22–0.39) | 1.4194 | 602.99 | 136.0 | $8.30 \times 10^{-4}$ |
| 0.6753 | 18.0–89.0<br>(1.28–0.42) | 1.5474 | 596.77 | 137.0 | $5.90 \times 10^{-4}$ |
| 1.0524 | 15.5–89.0<br>(1.53–0.47) | 1.7865 | 585.42 | 139.3 | $3.30 \times 10^{-4}$ |
| 1.7055 | 17.6–89.0<br>(1.87–0.57) | 2.0927 | 547.02 | 145.7 | $1.56 \times 10^{-3}$ |
| 2.0428 | 18.9–89.0<br>(2.04–0.66) | 2.4980 | 561.54 | 146.5 | $1.96 \times 10^{-3}$ |
| 2.3300 | 18.2–89.0<br>(2.31–0.72) | 2.7977 | 554.24 | 148.0 | $2.08 \times 10^{-3}$ |
| 3.1050 | 17.0–89.0<br>(3.26–0.94) | 3.7373 | 533.81 | 154.0 | $1.60 \times 10^{-3}$ |
| 3.7251 | 16.4–89.0<br>(4.11–1.16) | 4.7852 | 516.49 | 158.0 | $1.16 \times 10^{-3}$ |
| 4.6299 | 17.0–89.0<br>(5.91–1.61) | 7.0307 | 492.38 | 164.0 | $4.80 \times 10^{-4}$ |
| 4.7091 | 19.7–89.0<br>(5.82–1.68) | 7.2028 | 495.05 | 164.5 | $3.50 \times 10^{-4}$ |
| 4.8578 | 18.8–89.0<br>(6.58–1.79) | 7.4559 | 500.90 | 165.0 | $5.40 \times 10^{-4}$ |
| 5.2393 | 35.0–89.0<br>(5.16–2.06) | 7.9671 | 508.96 | 167.0 | $4.80 \times 10^{-4}$ |
| 6.0371 | 50.0–81.5<br>(4.73–2.81) | 8.1115 | 530.15 | 171.5 | $9.24 \times 10^{-4}$ |
| 6.3682 | 50.0–89.4<br>(5.32–2.74) | 7.9414 | 542.63 | 174.0 | $1.26 \times 10^{-3}$ |

concentration dependence of $T_0$ can therefore be written as

$$[4] \quad T_0 = T_0(0) + Q_1 m$$

where $T_0(0)$ refers to the $T_0$ value of the pure solvent and $Q_1$ is the slope. The least-squares fitted (standard deviation in $T_0 = 0.64$) values of $T_0(0)$ and $Q_1$ are found to be 133.48 K and 6.4441 K $mol^{-1}$ kg, respectively. It may be noted that the value 133.48 K for $T_0$ of water is in agreement with the glass transition temperature, $T_g$ (139 K) reported for amorphous solid water (17). Moreover, the reported (9) $T_0$ values of a few concentrated $Mg(NO_3)_2–H_2O$ systems based on their equivalent conductance data are in agreement to within ±5 K of the values of $T_0$ obtained by extrapolating the plot of $T_0$ versus $m$ (Fig. 3$a$) to the corresponding concentrations.

After accounting quantitatively for the concentration dependence of $T_0$, that of $A$ can easily be described in light of eq. [2]. A plot of $\ln A$ versus $1/T_0$ is made (Fig. 3$b$) and it is found to be linear. The linearity of such a plot envisages the applicability of eq. [2] for describing the concentration dependence of $A$ and also reveals that the $B_1/C_1$ value is fairly constant in the concentration range studied. The least-squares fitted (standard deviation in $\ln A = 0.09$) values of $\ln A_0$ and $B_1/C_1$ are found to be 2.3022 and 1208.2, respectively.

On the other hand, the $B$ parameter, without showing a monotonous variation, decreases initially with increase in concentration up to 4.63$m$ and

TABLE 3. Parameters of eq. [6] for the viscosity of $Mg(NO_3)_2$–$H_2O$ systems

| $T$ (K) | Concentration range (mol $kg^{-1}$) and viscosity range (cP) | $A_0'$ | $b'$ | $c' \times 10^3$ | Std. dev. in ln η |
|---|---|---|---|---|---|
| 298.0 | 0.0917–4.6299<br>(0.9086–4.8009) | 0.8775 | 0.3284 | 8.1356 | $1.14 \times 10^{-2}$ |
| | 0.0917–4.8578<br>(0.9086–5.5503) | 0.8820 | 0.3166 | 11.6670 | $1.56 \times 10^{-2}$ |
| 308.0 | 0.0917–4.6299<br>(0.7366–3.7642) | 0.7180 | 0.3106 | 10.4715 | $7.6 \times 10^{-3}$ |
| | 0.0917–5.2393<br>(0.7366–5.1554) | 0.7225 | 0.2967 | 14.3718 | $1.24 \times 10^{-2}$ |
| 323.0 | 0.0917–4.6299<br>(0.5692–2.7998) | 0.5581 | 0.2911 | 12.4280 | $1.03 \times 10^{-2}$ |
| | 0.0917–6.3682<br>(0.5692–5.3209) | 0.5476 | 0.3218 | 6.5556 | $2.71 \times 10^{-2}$ |

then increases (Table 2). The plot of $B$ versus $T_0$ is shown in Fig. 3*c*. According to eq. [3] the decrease in value of $B$ is attributable to the increase in value of $T_0$ as concentration increases. The linearity of the plot (Fig. 3*c*) implies that $C_2/C_1$ is almost constant up to 4.63*m*. Both $C_1$ and $C_2$ have been found by Angell and Tucker (18) to decrease with increasing concentration for electrolyte solutions. Therefore, the constancy of $C_2/C_1$ must be due to the same rates of decrease of $C_1$ and $C_2$ up to 4.63*m*, whereas the observed increase in $B$ beyond 4.63*m* appears to be attributable to the fact that, at these concentrations, the value of $C_2$ becomes very low. It may be governing the value of $C_2T_0/C_1$, causing a decrease in the value of this ratio with increase in concentration. These trends of $C_2/C_1$, viz., constancy up to 4.63*m* and then decrease, are also verified by calculating its values with the knowledge of $B$, $T_0$, and $B_1/C_1$ from the slope of Fig. 3*b*. This kind of behaviour of $B$ appears to imply a structural change around 4.63*m* which may be a transition to quasi-crystalline structure.

With the concentration dependences of $A$, $B$, and $T_0$ having been discussed, it is now possible to describe quantitatively the overall concentration dependence of η by the expression

$$[5] \quad \eta = A_0T^{1/2} \exp\left\{\frac{B_0[1 - Q_2(T_0(0) + Q_1m)]}{T - (T_0(0) + Q_1m)} - \frac{B_0}{T_0(0) + Q_1m}\right\}$$

where $B_0 = B_1/C_1$ and $Q_2 = C_2/C_1$. The values of $B_0$ and $Q_2$ are, of course, different below and above 4.63*m*. By approximating $1/[T - T_0(0) - Q_1m]$ to $[1 + Q_1m/(T - T_0(0))]/(T - T_0(0))$ and $1/(T_0(0) + Q_1m)$ to $[1 - Q_1m/T_0(0)]/T_0(0)$, eq. [5] can be reduced to a simple isothermal expression of the form

$$[6] \quad \eta = A_0' \exp(b'm + c'm^2)$$

where $A_0'$, $b'$, and $c'$ are constants at a particular temperature. In fact, $A_0'$, $b'$, and $c'$ will have different values below and above 4.63*m*. However, an attempt has been made to fit the viscosity data to eq. [6] in both concentration ranges 0.0917*m* to 4.6299*m* and 0.0917*m* to saturation point. It is apparent from Table 3 that in both concentration ranges the least-squares fittings are equally satisfactory. Moreover, the linearity of the plot of log η versus $b'm + c'm^2$ (Fig. 4) also reinforces the applicability of eq. [6] in explaining the concentration dependence of viscosity in the entire concentration range studied.

Finally, it is interesting to find that by neglecting the contribution of the $c'm^2$ term eq. [6] can be brought to the form of Vand's (4) as well as Angell

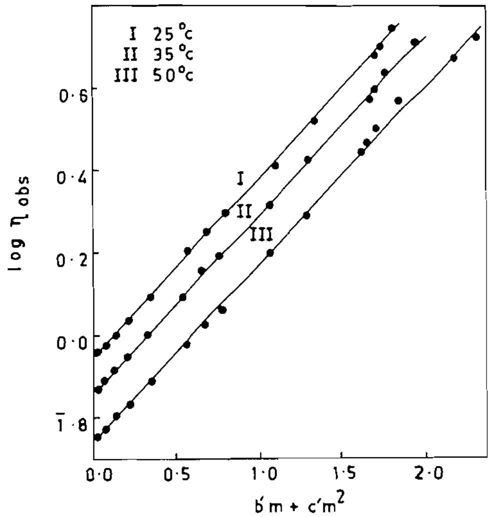


FIG. 4. Plots of log η versus $b'm + c'm^2$ for $Mg(NO_3)_2$–$H_2O$ systems (I: $b' = 0.3166$, $c' = 11.6670 \times 10^{-3}$; II: $b' = 0.2967$, $c' = 14.3718 \times 10^{-3}$; III: $b' = 0.3218$, $c' = 6.5556 \times 10^{-3}$).

and Bressels' (13) equations using the relations of $m$ with molarity and mol%. It may, therefore, be concluded that eq. [6] is an improved isothermal equation for describing the composition dependence of viscosity in aqueous solutions.

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