Concentration Dependence of Transport Properties of Glass-forming Melts

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Synopsis. The Vogel-Tammann-Fulcher (VTF) equation has been derived from the Adam-Gibbs (AG) model after accounting for the empirical nature of the temperature dependence of configurational heat capacity. An expression for describing the concentration dependence of the preexponential parameter of the VTF equation and another two-parameter isothermal equation for describing such dependences of transport properties are obtained. The applicability of the newly derived equations has been verified using the data available for several hydrate melts. The present study emphasizes the view that the glass transition temperature controls the concentration dependence of transport properties of glass-forming melts.

A large amount of literature[1-8] on the transport properties of binary molten systems containing at least one component as the hydrated salt has been accumulated. The temperature dependence of the transport properties of all such molten salt systems has been described in terms of the VTF equation

$$Y = A_y T^{-1/2} \exp[-B_y/(T-T_{oy})], \quad (1)$$

where Y is the transport property, either fluidity (ϕ) or equivalent conductance (Λ). T is the absolute temperature. A_y, B_y, and T_{oy} are the three constant parameters. Empirically these three parameters have been found to have dissimilar types of concentration dependence. B_y remains almost independent of concentration in binary molten systems containing either anhydrous or hydrated salts (or both). The ideal glass transition temperature, T_{oy} has been found to vary linearly with concentration in almost all the binary melts studied.

On the other hand, the dependence of A_y parameter on concentration is comparatively less understood and the nature of this dependence is found to be inconsistent in the various systems studied. For instance, studies made by Islam and coworkers[4-7] have revealed a linear dependence of A_y on concentration. Instead, Moynihan *et al.*[3] observed a linear variation of $\ln A_y$ with concentration in the molten mixture of calcium nitrate tetrahydrate and cadmium nitrate tetrahydrate and this trend was found to be contrary to the be havior expected from the free volume model.[9]

The objective of this paper is therefore to obtain an analytical expression to describe the observed trend in the variation of A_y with concentration and then to derive an isothermal equation for representing the concentration dependence of fluidity and conductance of binary mixture containing hydrate melt or melts. The approach adopted to achieve this is to insert the temperature dependence of heat capacity in the AG equation.[10]

Derivation of the New Isothermal Equation. As adopted by others,[11-13] in the absence of a rigorous theoretical description for the variation of heat capacity, C_p of molten salt systems with temperature, an alternative approach to account for the temperature dependence of configurational heat capacity, ΔC_p would be to take into cognizance the general trend in the empirical behavior of C_p with T. It is interesting to note from the reported heat capacity data for hydrate melts[14] and molecular liquids[12,15] that their C_p exhibits a linear dependence on T in the glassy as well as liquid regions. Accordingly, ΔC_p may be written as

$$\Delta C_p = \Delta C_o + \Delta C_1(T-T_o), \quad (2)$$

where $\Delta C_o = C_{ol} - C_{og}$ and $\Delta C_1 = C_{1l} - C_{1g}$. C_{ol} is the extrapolated heat capacity of the melt at T_o, C_{1l} is the slope of the linear variation of melt heat capacity with T, C_{og} is the heat capacity of the corresponding glass at T_o, C_{1g} is the slope of the linear variation of glass heat capacity with temperature. It may be noted that ΔC_1 becomes a negative, zero, or positive term depending upon the relative rates of change (linear) of C_p of mels and glass with T. For example, in $Ca(NO_3)_2 \cdot 4H_2O$,[14] $Cd(NO_3)_2 \cdot 4H_2O$,[14] $Mg(OAc)_2 \cdot 4H_2O$,[14] *o*-terphenyl,[12,15] *o*-benzylphenol,[12] and phenyl salicylate[12] ΔC_1 is found to be a negative quantity and Eq. 2 resembles with the function used for ΔC_p by Laughlin and Uhlmann[12] as well as with one of the probable functiont suggested by Privalko.[13] Substituting Eq. 2 in the AG equation[10] and then by making a few approximations, we get for Y an expression of the form

$$Y = A_{1y} T^{-1/2} \exp(B_{1y}/T_{oy}) \times \exp[-B_{1y}(1-\Delta C_1 T_{oy}/\Delta C_2)/(T-T_{oy})], \quad (3)$$

where A_{1y} and B_{1y} are constant parameters and $\Delta C_2 = \Delta C_o - \Delta C_1 T_o$. It is interesting to find that Eq. 3 is similar to the VTF equation and comparison of Eqs. 1 and 3 gives

$$A_y = A_{1y} \exp(B_{1y}/T_{oy}), \quad (4)$$

$$\text{and } B_y = B_{1y}[1-(\Delta C_1/\Delta C_2)T_{oy}]. \quad (5)$$

The empirical fact that B_y remains almost independent of concentration appears to imply that in molten salt systems the term $\Delta C_1/\Delta C_2$ is proportional to $1/T_{oy}$. By taking into account in Eq. 3 the constancy of B_y and the linear variation of T_{oy} with mole fraction of the solute, x, we obtain an isothermal expression for describing the concentration dependence of Y which approximates after neglecting the higher powers of x to

$$Y = A_y^* \exp(\pm Q_y^* X), \quad (6)$$

A_y^* and Q_y^* are empirical constants. The negative sign of the exponent in Eq. 6 is valid when T_o increases with x and the positive sign corresponds to the case of T_o decreasing with x.

On the Application of Eqs. 5 and 7. To justify the suitability of Eq. 4 for describing the variation of A_y parameter with concentration, exemplary plots of $\ln A_y$ *versus* $1/T_{oy}$ using their reported values are drawn in Fig. 1 for some of the molten mixtures.[3,4b,5,6] The linearity of these plots justifies the validity of Eq. 4. Furthermore, on substituting the linear concentration dependence of T_o (decrease or increase) in Eq. 4 it approximates to (after

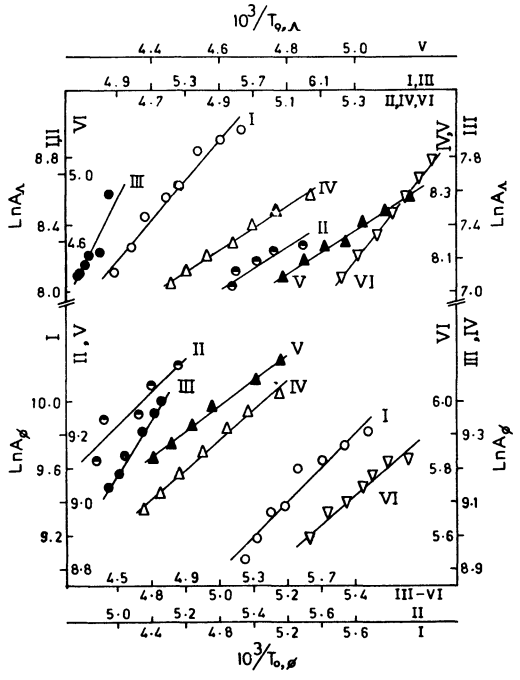

Fig. 1. Plots of $\ln A_y$ *versus* $1/T_{oy}$ for binary melts. The plots I to VI correspond to the six systems given in Table 1 and are in the same order.

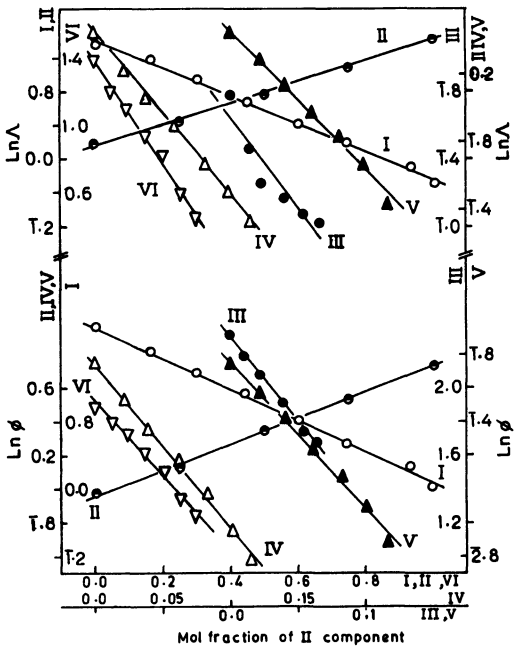

Fig. 2. Plots of $\ln Y$ *versus* mole fraction of the second component for binary melts. The plots I to VI correspond to the six systems given in Table 1 and are in the same order.

neglecting higher powers of x)

$$\ln A_y = A'_y \pm B'_y X, \quad (7)$$

where A'_y and B'_y are another set of constant parameters. It is interesting to find that Eq. 7 explains the empirical behavior of A_y with concentration in molten $Ca(NO_3)_2 \cdot 4.09H_2O + Cd(NO_3)_2 \cdot 4.07H_2O$ mixture which could not be explained[3] on the basis of the free volume model[9] as mentioned above.

To verify the applicability of Eq. 6, the reported fluidity and equivalent conductance data at 313 K for the various molten mixtures cited above are least-squares fitted to Eq. 6. The values of A_y^* and Q_y^* so obtained are listed in Table 1. It is apparent from Table 1 and from the linearity of the plots of $\ln Y$ *versus* x (Fig. 2) that Eq. 6 describes satisfactorily the concentration dependences of transport properties of binary molten mixtures containing hydrate melts. It is worthwhile to note that the isothermal Eq. 6 has only two adjustable parameters unlike the cases with the expressions reported earlier.[4b,16,17] The applicability of Eqs. 4 and 6 also reinforces the view that the concentration dependence of transport properties of binary melts is completely governed by the behavior of the ideal glass transition temperature with concentration.

Table 1. Best-fit parameters for Eq. 6 for the fluidity and equivalent conductance of glass-forming melts

Melt	A_y^*	Q_y^*	Std. dev. in $\ln Y$
$Zn(NO_3)_2 \cdot 6.33H_2O + Ca(NO_3)_2 \cdot 4.1H_2O$	1.9401	−1.8714	0.029
	(1.4351)	(−1.6966)	(0.046)
$Ca(NO_3)_2 \cdot 4.09H_2O + Cd(NO_3)_2 \cdot 4.07H_2O$	−0.0498	0.7681	0.017
	(−0.2163)	(0.6215)	(0.012)
$Ca(NO_3)_2 \cdot 3.91H_2O + CoCl_2$	−0.1054	−9.8721	0.020
	(−0.3662)	(−10.6646)	(0.106)
$Cd(NO_3)_2 \cdot 4.1H_2O + NiCl_2$	0.7641	−10.0624	0.020
	(0.4589)	(−9.6243)	(0.016)
$Cd(NO_3)_2 \cdot 4.1H_2O + CoCl_2$	0.7797	−9.0010	0.036
	(0.4891)	(−8.4575)	(0.042)
$Zn(NO_3)_2 \cdot 6.27H_2O + CoCl_2$	1.9078	−2.1327	0.038
	(1.3715)	(−3.0096)	(0.033)

Parameters for equivalent conductance are within the parentheses.

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