# Temperature and Composition Dependences of Transport Processes in Glass-forming Molten Mixtures of $Zn(NO_3)_2 \cdot 6.27H_2O$ and $CoCl_2$

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Density, viscosity, and electrical conductivity of glass-forming mixtures of zinc nitrate hexahydrate and anhydrous cobalt chloride were measured as functions of temperature and concentration. Non-Arrhenius temperature dependence of equivalent conductance, $\Lambda$ and fluidity, $\phi$ has been discussed in terms of a three parameter equation derived from Adam-Gibbs model. A linear correlation has been obtained between the preexponential parameter, $A_Y$ and the ideal glass transition temperature, $T_0$. The composition dependence of $\Lambda$ and $\phi$ has been described by the expression derived from the Adam-Gibbs equation on the criteria of constant $T/T_0$, where $T$ is the absolute temperature, and a modification to this expression has been made. An attempt has been made to describe the concentration dependence of $\Lambda\eta$ product in terms of modified Adam-Gibbs equation.

Much attention has been paid to describe the variation in mass transport properties of glass-forming melts with temperature. In doing so, several empirical and theoretical expressions[1-5] have been developed. On the other hand, expressions for describing the concentration dependence of transport properties are still in the process of development. In recent communications,[3,6,7] such expressions by modifying the basic equations for explaining the temperature dependence of transport behaviors of mixtures of molten salts have been proposed. The purpose of the present investigation on $Zn(NO_3)_2 \cdot 6.27H_2O$–$CoCl_2$ glass-forming melts is to test the applicability of these concentration-dependent equations and to improve them accordingly. Importance of selecting such systems has been discussed elsewhere.[3]

## Experimental

Zinc nitrate hexahydrate (BDH; mp 36.4 °C) was used as solvent in molten state and the solute, anhydrous cobalt chloride was added to it at about 50 °C, to prepare mixtures of molten salts of several concentrations. Anhydrous cobalt chloride was prepared[8] from the recrystallized hexahydrate salt using purified thionyl chloride (Riedel). Water of crystallization of hydrated zinc nitrate was estimated volumetrically[9] before using in sample preparation. The ratio $H_2O/Zn^{2+}$ was found to be 6.27. Accuracy of such an analysis was checked by taking hydrated calcium nitrate of known $H_2O/Ca^{2+}$ ratio and was found to be within $\pm 0.01$.

Densities were measured using pycknometer of 0.01 ml divisions. Viscosities and electrical conductivities were measured with calibrated Cannon-Ubbelohde viscometer[10] ($\beta = 6.26$ cSt/s) and a Philips Model PR 9500 conductance bridge along with capillary-type cell[11] (cell constant= 758.5 $cm^{-1}$ at 25 °C), respectively. Overall accuracy of these measurements were estimated to be better than $\pm 2.5\%$. Measurements were made in a descending as well as in an ascending order of temperature ranging between 298 to $358 \pm 0.02$ K.

## Results and Discussion

It may be interesting to compare the extent of dissolution of $CoCl_2$ in molten $Zn(NO_3)_2 \cdot 6.27H_2O$ and $Cd(NO_3)_2 \cdot 4.1H_2O$.[7] Anhydrous $CoCl_2$ dissolves up to approximately 30 mol % in the former and approximately 12 mol % in the latter case. The difference in the solubilities of $CoCl_2$ in these molten solvents may be due to the presence of associated species like $MNO_3^+$, where $M = Cd^{2+}$ and $Zn^{2+}$. Addition of anhydrous solute to the above hydrated melts appear to facilitate the formation of $MNO_3^+$ species through the dehydration of an equivalent amount of hydrated cations, $M(H_2O)_n^{2+}$. The maximum solubility of $CoCl_2$ may refer to the optimum concentration of $MNO_3^+$ obtained. Accordingly, higher solubility of $CoCl_2$ in $Zn(NO_3)_2 \cdot 6.27H_2O$ than in $Cd(NO_3)_2 \cdot 4.1H_2O$ is inferred to a higher association constant for $ZnNO_3^+$ than for $CdNO_3^+$ species. Furthermore, difference in the number of water molecules coordinated to the metallic cations may also be responsible for the difference in solubilities of $CoCl_2$ in these solvents.

The temperature dependence of measured densities of $Zn(NO_3)_2 \cdot 6.27H_2O$–$CoCl_2$ systems was found to be linear (*cf.* Table 1). The fluidity, $\phi$ and equivalent conductance, $\Lambda$ show non-Arrhenius temperature behaviors in the range 298 to 358 K (*cf.* Table 2). These data can be expressed by the following expression,[5] when the exponential parameter, $k_Y$ is almost constant:

$$Y = A_Y \exp\left[-k_Y/T \ln (T/T_0)\right], \tag{1}$$

where, $Y = \phi$ or $\Lambda$ and $A_Y$, $k_Y$, and $T_0$ are empirical parameters. The values of the best fit parameters obtained in the condition described above are displayed in Table 3 along with standard deviation in $Y$. Plots of $\log Y$ *vs.* $1/T \ln (T/T_0)$ (Fig. 1) show linear relationship indicating the applicability of the above equation to the present system.

The values of $A_\phi$ and $A_\Lambda$ decrease linearly with increasing composition of $CoCl_2$, whereas $T_0$ increases (Fig. 2). Such variations in $A_\phi$, $A_\Lambda$, and $T_0$ are in accordance with the explanations given earlier.[3,6,12]

Based on the nature of composition dependences of $A_Y$ and $T_0$, they may be correlated[13] as

$$A_Y = \alpha - \beta T_0, \tag{2}$$

where $\alpha = A_{0Y} + T_{0(0)} Q_{1Y}/Q_{2Y}$, and $\beta = Q_{1Y}/Q_{2Y}$. $A_{0Y}$ and $T_{0(0)}$ are the values of $A_Y$ and $T_0$ for the pure solvent, respectively. $Q_{1Y}$ and $Q_{2Y}$ are the slopes of the linear plots (Fig. 2) of $A_Y$ and $T_0$ *versus* composition, respectively. Such an observation may be visualized through the inverse relationship[6] between preexponential factor, $A_Y$ and the rigidity of the system and also the direct dependence[3,14] of ideal glass transition

Table 1. Computed parameters for density equation, $\rho(\mathrm{g\,cm^{-3}}) = a - bT(\mathrm{K})$ of $\mathrm{Zn(NO_3)_2{\cdot}6.27H_2O\text{-}CoCl_2}$ melts

| $Co^{2+}$ mol % | $a$ g cm$^{-3}$ | $b \times 10^3$ | Std dev in $\rho$ | $V_m$ cm$^3$ mol$^{-1}$ |
|---|---|---|---|---|
| 0.00 | 2.1848 | 1.1553 | $0.94\times10^{-3}$ | 166.92 |
| 5.11 | 2.2117 | 1.1903 | $0.56\times10^{-3}$ | 160.67 |
| 10.14 | 2.2158 | 1.1757 | $0.47\times10^{-3}$ | 155.17 |
| 15.30 | 2.2241 | 1.1557 | $0.38\times10^{-3}$ | 149.12 |
| 20.52 | 2.2235 | 1.1236 | $0.23\times10^{-3}$ | 143.50 |
| 25.32 | 2.2616 | 1.1861 | $0.37\times10^{-3}$ | 137.71 |
| 30.20 | 2.2528 | 1.1290 | $0.33\times10^{-3}$ | 132.56 |

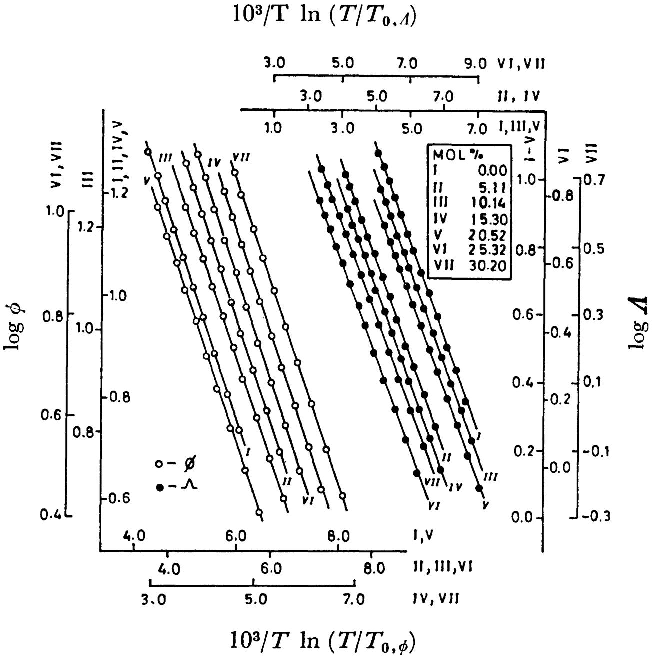

Fig. 1. Plots of log $Y$ vs. $1/T \ln (T/T_0)$ for $\mathrm{Zn(NO_3)_2{\cdot}6.27H_2O\text{-}CoCl_2}$ melts.

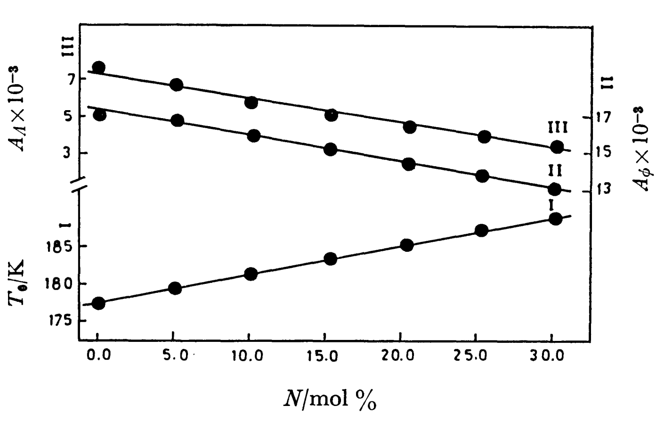

Fig. 2. Variation of $T_{0Y}$ (average of $T_{0,\phi}$ and $T_{0,\Lambda}$, and $A_Y$ ($A_\phi$ for II and $A_\Lambda$ for III) with composition for $\mathrm{Zn(NO_3)_2{\cdot}6.27H_2O\text{-}CoCl_2}$ melts.

temperature, $T_0$ upon the rigidity of the system, *i.e.* upon the coulombic interactions or cohesive energy[14] of the system. The rigidity of the system under investigation may increase with increase in concentration of $CoCl_2$ which is responsible for the variation of

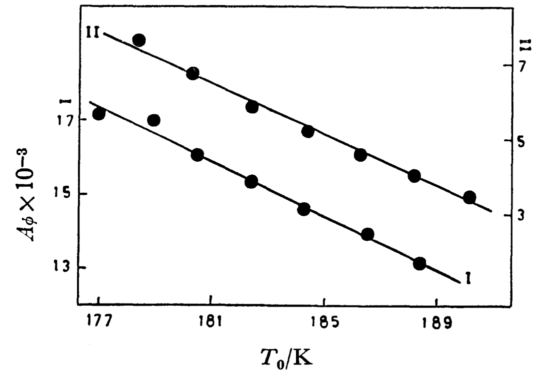

Fig. 3. Plots of $A_\phi$ and $A_\Lambda$ vs. $T_{0Y}$ (average of $T_{0,\phi}$ and $T_{0,\Lambda}$) for $\mathrm{Zn(NO_3)_2{\cdot}6.27H_2O\text{-}CoCl_2}$ melts.

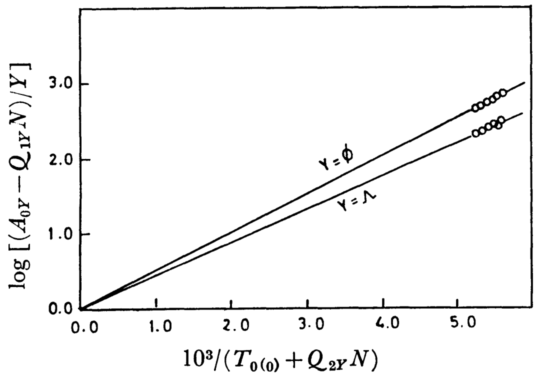

Fig. 4. Plots of $\log [(A_{0Y}-Q_{1Y}N)/Y]$ vs. $1/(T_{0(0)}+Q_{2Y}N)$ for $\mathrm{Zn(NO_3)_2{\cdot}6.27H_2O\text{-}CoCl_2}$ melts.

$A_Y$ terms with $T_0$ linearly but inversely. Linear plots of $A_{Y(=\phi\text{ or }\Lambda)}$ *versus* $T_0$ (an average of $T_{0,\phi}$ and $T_{0,\Lambda}$ has been taken) (Fig. 3) further emphasize the validity of Eq. 2.

To describe the composition dependence of transport processes, an isoenergetic equation was suggested in earlier publication[6] based upon the Vogel-Tammann-Fulcher equation. However, Eq. 1 which is based upon Adam-Gibbs model is more satisfactory in describing the physical changes in the properties of fused salts and supercooled liquids. In view of this notion Eq. 1 was modified recently[7] by considering $T_0$ as the basis for the corresponding temperature, $T$ and at $T/T_0=\text{constant}=c$, to

$$Y = A_Y \exp\left[-k_Y/T_0 c \ln c\right], \tag{3}$$

and by substituting the linear variations[6] of $A_Y$ and $T_0$ we obtain

$$Y = (A_{0Y}-Q_{1Y}N) \exp\left[-k_Y/(T_{0(0)}+Q_{2Y}N)c \ln c\right], \tag{4}$$

where the symbols have their usual significances. To test the applicability of Eq. 4, the values of $Y(=\phi$ or $\Lambda)$ at constant, $c=1.5$ were calculated from Eq. 3 and were in turn least-squares fitted to Eq. 4. Computer fitted values of empirical constants, $A_{0Y}$, $T_{0(0)}$, $Q_{1Y}$, and $Q_{2Y}$ are given in Table 4. The linearity of the plots of $\log[(A_{0Y}-Q_{1Y}N)/Y]$ *versus* $1/(T_{0(0)}+Q_{2Y}N)$ which pass through origin (Fig. 4) supports the feasibility of Eq. 4. However, it may be noted that Eq. 4 is not capable of correlating directly the measured transport data with the composition. A prior calculation of the transport property at constant $c$ value is

TABLE 2. EQUIVALENT CONDUCTANCE ($cm^2\,equiv^{-1}\,\Omega^{-1}$) AND FLUIDITY[a)] ($P^{-1}$) DATA AS A FUNCTION OF TEMPERATURE FOR $Zn(NO_3)_2\cdot6.27H_2O$-$CoCl_2$ MELTS

| $T$/K | $Co^{2+}$/mol % | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0.00 | 5.11 | 10.14 | 15.30 | 20.52 | 25.32 | 30.20 |
| 298.0 | 2.2018 | 1.8449 | 1.6788 | 1.3715 | 1.2240 | 0.9611 | 0.8067 |
| 303.0 | 2.7154 | 2.3135 | 2.0531 | 1.7029 | 1.5276 | 1.2051 | 1.0328 |
| 308.0 | 3.2798<br>(5.4731) | 2.7556<br>(4.9810) | 2.4909<br>(4.6869) | 2.0827<br>(4.1956) | 1.8662<br>(3.7626) | 1.4782<br>(3.0931) | 1.2743<br>(2.7808) |
| 313.0 | 3.9155<br>(6.4785) | 3.2549<br>(5.9617) | 2.9833<br>(5.6028) | 2.5202<br>(5.0615) | 2.2446<br>(4.5593) | 1.7959<br>(3.7968) | 1.5472<br>(3.4258) |
| 318.0 | 4.5834<br>(7.7262) | 3.7962<br>(7.1376) | 3.5126<br>(6.7591) | 2.9672<br>(6.1107) | 2.6862<br>(5.5353) | 2.1515<br>(4.6526) | 1.8564<br>(4.2229) |
| 323.0 | 5.3085<br>(9.1206) | 4.4806<br>(8.4339) | 4.1153<br>(8.0108) | 3.4909<br>(7.2884) | 3.1459<br>(6.6203) | 2.5729<br>(5.5541) | 2.2050<br>(5.0849) |
| 328.0 | 6.1060<br>(10.445) | 5.0947<br>(9.7106) | 4.7611<br>(9.2242) | 4.0522<br>(8.4380) | 3.6636<br>(7.6614) | 2.9771<br>(6.4863) | 2.5991<br>(5.9803) |
| 333.0 | 6.9042<br>(11.963) | 6.0133<br>(11.209) | 5.4336<br>(10.702) | 4.6645<br>(9.7868) | 4.2118<br>(8.8910) | 3.4580<br>(7.5625) | 2.9925<br>(7.0034) |
| 338.0 | 7.8650<br>(13.611) | 6.7256<br>(12.809) | 6.0507<br>(12.183) | 5.2374<br>(11.217) | 4.7756<br>(10.207) | 3.9350<br>(8.8178) | 3.4046<br>(8.1453) |
| 343.0 | 8.8010<br>(15.340) | 7.5293<br>(14.464) | 6.8128<br>(13.779) | 5.8140<br>(12.709) | 5.4010<br>(11.687) | 4.4454<br>(10.055) | 3.8546<br>(9.3439) |
| 348.0 | 9.8035<br>(17.166) | 8.4858<br>(16.280) | 7.6675<br>(15.477) | 6.5285<br>(14.331) | 5.8786<br>(13.176) | 4.9597<br>(11.554) | 4.3251<br>(10.654) |
| 353.0 | 10.788<br>(19.186) | 9.4167<br>(18.194) | 8.4510<br>(17.313) | 7.2951<br>(15.981) | 6.5210<br>(14.819) | 5.4885<br>(12.985) | 4.7842<br>(11.917) |
| 358.0 | 11.802 | 10.189 | 9.3328 | 8.0861 | 7.2206 | 6.0014 | 5.2936 |

a) Fluidity data are within parentheses.

TABLE 3. COMPUTED PARAMETERS FOR EQ. 1 FOR THE FLUIDITY AND EQUIVALENT CONDUCTANCE DATA OF $Zn(NO_3)_2\cdot6.27H_2O$-$CoCl_2$ MELTS

| $Co^{2+}$ / mol % | $A_\phi$ | $k_\phi$ | $T_{0,\phi}$ | Std dev in $\phi$ | $A_\Lambda$ | $k_\Lambda$ | $T_{0,\Lambda}$ | Std dev in $\Lambda$ |
|---|---|---|---|---|---|---|---|---|
| 0.00 | 340.54 | 685.01 | 180.00 | 0.055 | 161.52 | 639.51 | 180.80 | 0.024 |
| 5.11 | 337.04 | 684.00 | 181.99 | 0.049 | 144.99 | 642.52 | 182.00 | 0.068 |
| 10.14 | 324.54 | 680.00 | 183.06 | 0.036 | 128.97 | 631.03 | 183.20 | 0.031 |
| 15.30 | 312.99 | 681.26 | 184.50 | 0.024 | 116.59 | 635.60 | 184.48 | 0.035 |
| 20.52 | 299.51 | 680.96 | 186.00 | 0.044 | 103.81 | 622.00 | 186.24 | 0.044 |
| 25.32 | 287.35 | 690.21 | 188.00 | 0.061 | 92.14 | 625.01 | 188.30 | 0.031 |
| 30.20 | 268.96 | 681.00 | 189.97 | 0.026 | 80.89 | 616.07 | 190.20 | 0.015 |

TABLE 4. COMPUTED PARAMETERS FOR EQ. 4 ($c=1.5$) FOR THE FLUIDITY[a)] AND EQUIVALENT CONDUCTANCE OF $Zn(NO_3)_2\cdot6.27H_2O$-$CoCl_2$ MELTS

| $A_{0Y}$ | $Q_{1Y}$ | $k_Y$/K | $T_{0(0)}$/K | $Q_{2Y}$ | Std dev in $Y$ |
|---|---|---|---|---|---|
| 161.24 | 2.624 | 631.68 | 178.69 | 0.322 | 0.064 |
| (350.30) | (2.483) | (689.30) | (180.30) | (0.320) | (0.035) |

a) Parameters for fluidity are within parentheses.

necessary and in order to remove this difficulty an alternative expression may be written as

$$Y = (A_{0Y} - Q_{1Y}N)\exp\{-k'_Y/T\ln[T/(T_{0(0)}+Q_{2Y}N)]\}. \qquad (5)$$

The measured fluidity and equivalent conductance data at all concentrations were least-squares fitted to Eq. 5 and reasonably good fits were obtained. The values of empirical parameters, $A_{0Y}$, $k'_Y$, $T_{0(0)}$, $Q_{1Y}$, and $Q_{2Y}$ are given in Table 5 and were found to be very close to those obtained from the corresponding plots. Furthermore, linear plots (Fig. 5) of $\log[(A_{0Y}-Q_{1Y}N)/Y]$ *versus* $1/T\ln[T/(T_{0(0)}+Q_{2Y}N)]$ provide graphical support to the validity of Eq. 5. Thus, we are able to describe satisfactorily the composition dependence of transport processes without depending upon the measurements as a function of temperature in the entire range of composition.

Having examined the individual behaviors of viscosity and electrical conductivity, their simultaneous representation may similarly be analysed. Walden's rule, $\Lambda\eta$=constant, fails to hold good in the cases of molten salt systems and is found to change both with temperature and concentration. The temperature dependence of $\Lambda\eta$ product for the system under investigation may quantitatively be described by the relations,[3,6)]

$$\Lambda\eta = A_1\exp[B_1/(T-T_0)] \qquad (6)$$

Table 5. Computed parameters for Eq. 5 for the fluidity[a)] and equivalent conductance of $Zn(NO_3)_2 \cdot 6.27H_2O$-$CoCl_2$ melts

| $A_{0Y}$ | $Q_{1Y}$ | $k_Y$/K | $T_{0(0)}$/K | $Q_{2Y}$ | Std dev in ln $Y$ |
|---|---|---|---|---|---|
| 162.9±1.1 | 2.66±0.004 | 631.4±0.50 | 178.5±0.04 | 0.324±0.001 | 0.055±0.007 |
| (345.2±1.0) | (2.37±0.002) | (686.3±0.41) | (177.3±0.09) | (0.328±0.001) | (0.0396±0.004) |

a) Parameters for fluidity are within parentheses.

Table 6. Best-fit parameters for Eqs. 6 and 7 for $\Lambda\eta$ product of $Zn(NO_3)_2 \cdot 6.27H_2O$-$CoCl_2$ melts

| $Co^{2+}$ mol % | $A_1$ | $B_1$ | $T_{0,\Lambda\eta}$ | Std dev in $\Lambda\eta$ | $A_2$ | $B_2$ | $V_{0,\Lambda\eta}$ | Std dev in $\Lambda\eta$ |
|---|---|---|---|---|---|---|---|---|
| 0.00 | 0.4714 | 32.00 | 177.84 | 0.0037 | 0.4850 | 2.7148 | 152.75 | 0.0038 |
| 5.11 | 0.4341 | 30.00 | 179.80 | 0.0050 | 0.4487 | 2.4000 | 147.01 | 0.0050 |
| 10.14 | 0.3756 | 45.00 | 181.40 | 0.0035 | 0.3901 | 3.5928 | 142.30 | 0.0035 |
| 15.30 | 0.3464 | 46.00 | 183.33 | 0.0038 | 0.3588 | 3.5000 | 137.20 | 0.0037 |
| 20.52 | 0.3329 | 50.00 | 185.30 | 0.0056 | 0.3409 | 3.7348 | 132.50 | 0.0056 |
| 25.32 | 0.3071 | 55.00 | 187.50 | 0.0055 | 0.3278 | 3.6343 | 127.00 | 0.0053 |
| 30.20 | 0.2867 | 56.00 | 189.20 | 0.0028 | 0.2947 | 3·8543 | 122.70 | 0.0028 |

Table 7. Computed parameters for Frenkel equation for the product of equivalent conductance and viscosity of $Zn(NO_3)_2 \cdot 6.27H_2O$-$CoCl_2$ melts

| $Co^{2+}$ mol % | $n$ | ln $K$ | Std dev in $\eta$ |
|---|---|---|---|
| 0.00 | 1.0541 | 0.4411 | 0.006 |
| 5.11 | 1.0471 | 0.5546 | 0.009 |
| 10.14 | 1.0736 | 0.5581 | 0.007 |
| 15.30 | 1.0772 | 0.6347 | 0.008 |
| 20.52 | 1.0884 | 0.6354 | 0.012 |
| 25.32 | 1.0869 | 0.6947 | 0.011 |
| 30.20 | 1.0977 | 0.7536 | 0.006 |

and,

$$\Lambda\eta = A_2 \exp\,[B_2/(V - V_0)], \tag{7}$$

essentially based upon the "Vogel-Tammann-Fulcher" (VTF) and the "Doolittle" equations, respectively. The empirical parameters $A_1$, $B_1$, $A_2$, and $B_2$ are the resultant of those for the individual $\Lambda$ and $\eta$ values in the VTF and the Doolittle equations. $V$ is the molar volume and $V_0$ is the intrinsic volume at the ideal glass transition temperature, $T_0$. The values of the best-fit parameters for Eqs. 6 and 7 are given in Table 6. The computed values of the parameters $T_{0,\Lambda\eta}$ and $V_{0,\Lambda\eta}$ were in good agreement with those obtained independently from fluidity and conductance data, *i.e.*, $T_{0,\phi,\Lambda}$ and $V_{0,\phi,\Lambda}$ values, respectively, emphasizing further the thermodynamic nature of these parameters.

Moreover, the nature of $\Lambda\eta$ product may also be explained by Frenkel equation, $\Lambda^n\eta$=constant, $K$, where $n$ is the ratio of activation energies for the viscous and the conductance flows, $E_\eta/E_\Lambda$. The least-squares fitted values of the parameters for this equation are given in Table 7.

An attempt has been made here to understand the composition dependence of the Walden product. It is worthy to note a monotonous decrease in $\Lambda\eta$ with increasing composition (Fig. 6) and is different from the behavior reported in $Ca(NO_3)_2 \cdot 3.91H_2O + CoCl_2$ and in $(C_4H_9)_4NI + CoCl_2$ melts.[3,15)] As equivalent conductance decreases with increasing the composition of $CoCl_2$, the variation of $\Lambda\eta$ product of the present system seems to be mainly determined by the value of $\Lambda$. However, as the concentration increases the amount of decrease in $\Lambda\eta$ lessens thereby reflecting the contribution of viscosity as well.

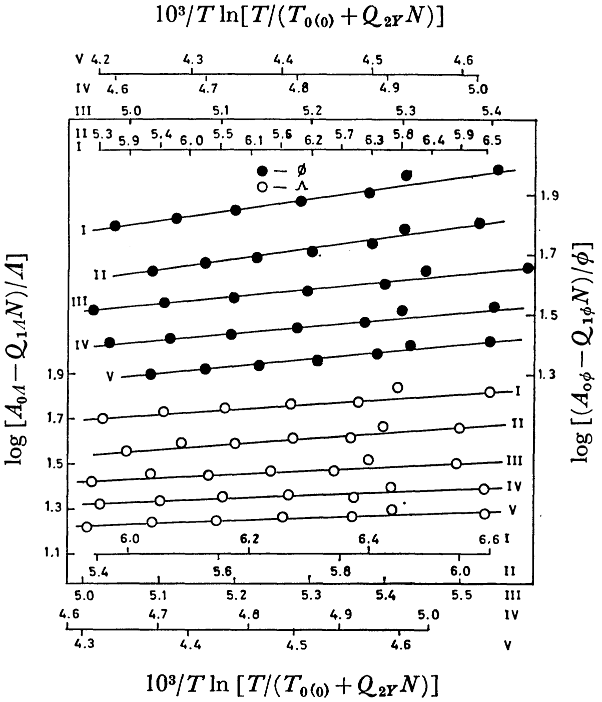

Fig. 5. Plots of $\log\,[(A_{0Y} - Q_{1Y}N)/Y]$ *vs.* $1/T \ln\,[T/(T_{0(0)} + Q_{2Y}N)]$ for $Zn(NO_3)_2 \cdot 6.27H_2O$-$CoCl_2$ melts (I: 308 K, II: 318 K, III: 328 K, IV: 338 K, V: 348 K).

Equation 5 may be written as

$$\Lambda\eta = \left(\frac{A_{0\Lambda} - Q_{1\Lambda}N}{A_{0\phi} - Q_{1\phi}N}\right) \exp\left[\frac{k'_\phi - k'_\Lambda}{T \ln[T/(T_{0(0)} + Q_{2Y}N)]}\right] \tag{8}$$

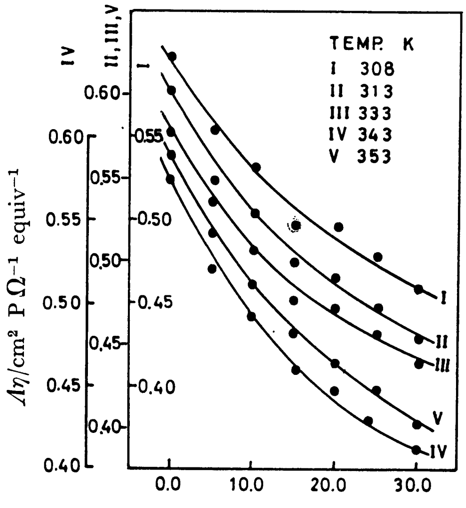

Fig. 6. Variation of $\Lambda\eta$ product with composition for $Zn(NO_3)_2 \cdot 6.27H_2O$–$CoCl_2$ melts.

for describing the composition dependence of $\Lambda\eta$ product. The ratios of the variation of $A_\Lambda$ and $A_\phi$ with $N$ seems to be almost independent of composition as the slopes of $A_\Lambda$ and $A_\phi$ *vs.* $N$ are nearly equal (Fig. 2). This indicates that the similar species are taking part in the processes of conductance and viscous flows as suggested earlier.[16] Adam and Gibbs[5] also suggested that identical species are responsible for the two kinds of flow. Therefore, the contribution of preexponential factor towards the variation of $\Lambda\eta$ with concentration seems to be negligible and Eq. 8 may be approximated to

$$\Lambda\eta = \left(\frac{A_{0\Lambda}}{A_{0\phi}}\right)\exp\left[\frac{k'_\phi - k'_\Lambda}{T\ln[T/(T_{0(0)}+Q_{2Y}N)]}\right]. \tag{9}$$

From above equation it is apparent that the difference in $k_Y$ terms is almost constant while the denominator of the exponential term decreases with increase in concentration at a given temperature thereby resulting in a monotonous increase in the $\Lambda\eta$ product which is contrary to the observed trend. Instead, the ratio of activation energies for flow processes, $E_\phi/E_\Lambda = n$ is greater than unity, also the value of $n$ increases with the increase in concentration of $CoCl_2$ may be responsible for the overall decrease of the $\Lambda\eta$ product with composition.

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13) The Linear variation of $A_Y$ and $T_0$ *vs.* $N$ may be represented as[3,6]

$$A_Y = A_{0Y} - Q_{1Y}N,$$

and

$$T_0 = T_{0(0)} + Q_{2Y}N.$$

On rearranging the equation for $T_0$ and substituting into the $A_Y$ equation, we have

$$\begin{aligned} A_Y &= A_{0Y} - \frac{(T_0 - T_{0(0)})}{Q_{2Y}}Q_{1Y} \\ &= A_{0Y} + \frac{T_{0(0)}Q_{1Y}}{Q_{2Y}} - \frac{Q_{1Y}}{Q_{2Y}}T_0, \\ A_Y &= \alpha - \beta T_0. \end{aligned}$$

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