August, 1980] © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **53**, *2371—2375 (1980)* 2371

Concentration Dependence of Flow Properties of Molten Salt Systems

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(Received December 15, 1979)

The concentration dependence of fluidities and conductances of molten calcium nitrate tetrahydrate-MNCS ($M=Na^+$ or NH_4^+) systems was quantitatively explained by the isoenergetic and isoentropic equations essentially based on the Vogel-Tammann-Fulcher (VTF) and the Configurational Entropy Model (CEM) equations. The pre-exponential terms of the VTF and the Doolittle's equations were found to depend linearly on the values of the corresponding parameters, *i.e.*, T_0, the zero mobility temperature and those of V_0, the molar intrinsic volume at T_0, respectively. The linear interdependence of the two thermodynamic parameters, T_0 and V_0 on each other has been demonstrated. In addition to the linear dependence of the corrected energy of activation, E_{cor} on V_0, a physically meaningful linear dependence of E_{cor} on T_0 has also been demonstrated.

A solute experiences strong interionic effects due to the close proximity of charged species even in extremely dilute solutions of molten salts as is the case with very concentrated electrolytes. This renders such solutions to behave differently from those of the aqueous solutions. Attention has recently been drawn to the fact that the great majority of solutions which reach concentrations approaching their maximum solubility become very viscous on cooling to their melting temperatures and may readily supercool to the vitreous state.[1–4] This has led to the examination of relaxation processes in glass-forming melts in order to have greater insight into the nature of the transport behaviour in highly concentrated solutions and to provide new empirical description for the concentration dependence of such properties.

In order to achieve this aim Angell[2] transformed the Vogel-Tammann-Fulcher (VTF) equation[5] to an isothermal expression for the variation of transport properties with concentration by assuming the pre-exponential, A_Y, and the exponential, k_Y, parameters as concentration independent while taking only the T_0 as varying linearly with concentration. The resulting expression is of the form,

$$Y = A_Y T^{-1/2} \exp\,[-k_Y/Q_Y(N_0-N)], \tag{1}$$

where Y stands for the fluidity, $\phi=\eta^{-1}$, or the conductance, A, Q_Y (denoted by Q_{2Y} in Eq. 2) is the slope of the linear plot of T_0 *versus* N being in mol% and is given as,

$$T_0 = T_{0(0)} \pm Q_{2Y}N \tag{2}$$

The parameter N_0 is the characteristic concentration at which the isothermal temperature, T becomes the glass transition temperature T_g of the system, *i.e.*, the concentration at which the particle mobilities would fall to zero at the isothermal temperature. Recent studies on a large varieties of molten salt systems[6–8] have revealed that the parameter A_Y also varies linearly with concentration and may be expressed as,

$$A_Y = A_{0Y} \pm Q_{1Y}N, \tag{3}$$

in which Q_{1Y} represents the slope of the plot of A_Y *versus* N and A_{0Y} is the value of A_Y for the pure solvent. By accounting for such a dependence of A_Y Eq. 1 was modified[8] to

$$Y = (A_{0Y} \pm Q_{1Y}N)\,T^{-1/2} \exp\,[-k_Y/Q_{2Y}(N_0-N)]. \tag{4}$$

The above isothermal equation has been satisfactorily employed to explain the concentration dependence of transport properties of many molten salt mixtures. The limitations of this equation may, however, be pointed out. This equation has been found to be meaningfully applicable only within the T_0 values of the two components of the melts. If we try to go beyond this range of temperature the values of N_0 will be either less than zero or more than 100 mol% which are physically meaningless. For example, in the case of $Ca(NO_3)_2 \cdot 4.09H_2O$–$Cd(NO_3)_2 \cdot 4.07H_2O$[6] melts the T_0 values of the solvent and that of the solute range between 205 and 193 K. Therefore, the concentration dependence of transport properties obtained above 205 K cannot be explained by such an isothermal equation. Similar difficulties arise in applying the above isothermal equation to the mixtures of alkali metal nitrates in molten $Cd(NO_3)_2 \cdot 4H_2O$[9] and $Ca(NO_3)_2 \cdot 4H_2O$.[10] In view of such an inherent difficulty with Eq. 4 another expression based on the VTF equation was obtained[11] at equal values of T/T_0 ($=c$). This results in an isoenergetic equation,

$$\begin{aligned} Y = {} & (A_{0Y} \pm Q_{1Y}N)c^{-1/2}(T_{0(0)} \pm Q_{2Y}N)^{-1/2} \\ & \times \exp\,[-k_Y/(T_{0(0)} \pm Q_{2Y}N)(c-1)]. \end{aligned} \tag{5}$$

Similarly, such behaviours may also be quantitatively explained in terms of the essentially configurational entropy model,[12)]

$$Y = (A'_{0Y} \pm Q'_{1Y}N) \exp\,[-k'_Y/(T_{0(0)} \pm Q_{2Y}N)c \ln c]. \tag{6}$$

Some of the melts employed for this purpose have inherent glass-forming ability while others are induced by the presence of high concentrations of solute. In the latter category, the solubility of solutes, namely transition metal salts, in a given molten salt solvent depends upon several factors, *e.g.*, the ease of ionization, complex ion forming ability and their energetics, solvation, equilibria among several chemical species, *etc.* Furthermore, these molten salt mixtures could either be grouped as ideal with respect to the intrinsic volume, $V_{0,i}$ as well as to the zero mobility temperature, $T_{0,i}$ or as non-ideal. The former is marked by the absence of reactions involving complex-ion formation while the latter seems to have been caused by the presence of either tetrahedral or octahedral complex-ions as a result of pronounced interactions among the components of the melts.

The purpose of this paper is to examine the ability of generalized Eqs. 5 and 6 to explain the concentration dependence of the transport properties without being restricted by the T_0 values of the two components and the role of the relevant parameters including the derived ones in understanding the successive variations in their behaviour with concentration.

The mixed molten salt systems, calcium nitrate tetrahydrate–ammonium thiocyanate and calcium nitrate tetrahydrate–sodium thiocyanate have been selected for the present investigation. In addition to these melts, reported[12,13] data on the concentration dependence of the flow processes in the cases of non-ideal melts containing either tetrahedral or octahedral complex-ions have also been analysed.

Experimental

Calcium nitrate tetrahydrate (BDH; mp 42.7 °C) was used as solvent in the molten state. Ammonium thiocyanate (BDH; mp 149.6 °C) and sodium thiocyanate (BDH; mp 287 °C, recrystallized twice from double distilled water) were used as solutes.

Samples were prepared in a thermostated paraffin bath at about 333 K. During the samples' preparation all the chemicals were handled with extra care in an atmosphere of pure and dry nitrogen. Several samples of different concentrations were prepared. Calcium nitrate tetrahydrate was found to dissolve approximately 60 mol% of ammonium thiocyanate, and 24 mol% of sodium thiocyanate.

Density measurements were made using a calibrated dilatometer of approximately 6.0 ml capacity with graduated stem of 0.01 ml divisions. The viscosities of the melts were determined with the help of a Cannon-Ubbelohde[14] type viscometer (viscometer constant, 6.26 cSt/s). The conductance measurements were made with conductivity bridge of Philips Model PR 9500 type. The cells used were of capillary-type[15,16] of cell constant values as 542 cm^{-1} and 730 cm^{-1} at 298 K.

Densities, viscosities, and conductivities were measured within ±0.3%, ±0.1%, and ±1.5% accuracy, respectively, in a thermostated paraffin bath of ±0.1 °C thermal stability under dry nitrogen atmosphere.

Table 1. Equivalent conductance (10^4 Λ, Sm^2 equiv^{-1}) and fluidity (10^{-1} ϕ, N^{-1} m^2 s^{-1}) data as a function of temperature for molten (a) $Ca(NO_3)_2 \cdot 4.23H_2O$–$NH_4NCS$ and (b) $Ca(NO_3)_2 \cdot 4.1H_2O$–NaNCS systems

T/K	(a) NH_4^+/mol%						
	0.00	10.11	20.02	30.35	40.48	51.30	63.42
313.0	1.25 (1.246)	1.18 (1.110)	1.08 (1.201)	1.42 (1.338)	1.71 (1.413)	2.06 (1.814)	2.51 (2.477)
318.0	1.62 (1.600)	1.44 (1.394)	1.35 (1.587)	1.65 (1.724)	2.09 (1.789)	2.49 (2.330)	2.94 (3.063)
323.0	1.88 (2.005)	1.75 (1.761)	1.66 (1.976)	1.95 (2.164)	2.50 (2.200)	2.93 (2.841)	3.39 (3.696)
328.0	2.25 (2.454)	2.10 (2.200)	1.97 (2.484)	2.34 (2.699)	3.03 (2.950)	3.31 (3.408)	4.07 (4.425)
333.0	2.63 (2.974)	2.48 (2.599)	2.32 (3.030)	2.71 (3.154)	3.60 (3.415)	3.82 (4.132)	4.45 (5.218)
338.0	3.13 (3.570)	2.92 (3.154)	2.67 (3.634)	3.12 (3.777)	4.15 (3.926)	4.27 (4.814)	5.07 (6.099)
343.0	3.58 (4.370)	3.36 (3.766)	3.14 (4.273)	3.57 (4.466)	4.78 (5.004)	4.93 (5.660)	5.79 (7.018)
348.0	4.05 (4.907)	3.85 (4.388)	3.55 (4.977)	4.17 (5.155)	5.46 (5.867)	5.36 (6.416)	6.47 (7.885)
353.0	4.54 (5.664)	4.41 (5.121)	4.03 (5.741)	4.61 (5.949)	6.14 (6.700)	5.99 (7.334)	7.17 (8.872)

T/K	(b) Na^+/mol%					
	0.00	5.58	10.28	16.02	20.13	24.84
313.0	0.98 (1.017)	0.89 (0.991)	0.56 (0.925)	0.51 (0.903)	0.50 (0.811)	—
318.0	1.22 (1.333)	1.09 (1.299)	0.75 (1.219)	0.65 (1.180)	0.64 (1.082)	—
323.0	1.46 (1.675)	1.34 (1.650)	0.94 (1.555)	0.81 (1.512)	0.80 (1.399)	0.72 (1.337)
328.0	1.75 (2.078)	1.64 (2.052)	1.09 (1.944)	0.99 (1.894)	0.98 (1.766)	0.89 (1.732)
333.0	2.14 (2.545)	2.04 (2.522)	1.30 (2.407)	1.19 (2.341)	1.18 (2.187)	1.08 (2.159)
338.0	2.19 (3.080)	2.40 (3.053)	1.61 (2.923)	1.42 (2.866)	1.40 (2.679)	1.28 (2.653)
343.0	2.57 (3.659)	2.77 (3.641)	1.81 (3.487)	1.61 (3.421)	1.59 (3.222)	1.50 (3.190)
348.0	2.94 (4.286)	3.21 (4.268)	2.01 (4.096)	1.87 (4.035)	1.85 (3.783)	1.75 (3.770)
353.0	3.38 (4.998)	3.66 (4.970)	2.39 (4.772)	2.19 (4.702)	2.10 (4.436)	2.01 (4.418)

a) Fluidity data are within parentheses.

Results and Discussion

The waters of hydration in the melts were determined by the method[17] of comparison of densities.

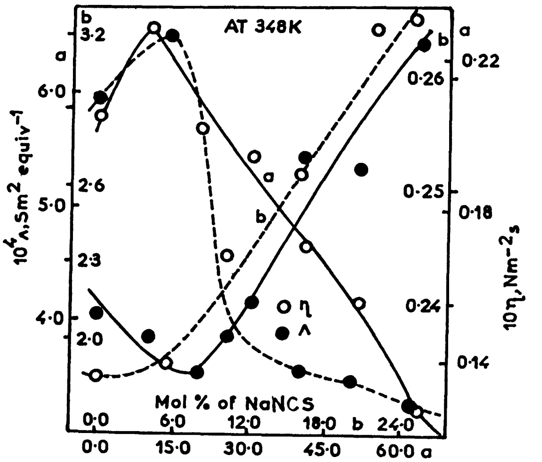

Fig. 1. Viscosity and conductance isotherms for molten (a) $Ca(NO_3)_2 \cdot 4.23H_2O$–$NH_4NCS$ and (b) $Ca(NO_3)_2 \cdot 4.1H_2O$–NaNCS systems.

The fluidities and conductances of the systems (Table 1) under investigation are found to change quite markedly with concentration (Fig. 1). The viscosity of a system is determined mainly by the bulky or less mobile entities while the ions of higher mobilities appear to be mainly responsible for the conductance behaviour. Therefore, both are expected to show an opposite trend in their behaviour with concentration as has actually been found.

In the case of the system, $Ca(NO_3)_2 \cdot 4.23H_2O$–$NH_4NCS$ fluidity and conductance both increase with increase in concentration of NH_4NCS. In this melt the hydrated solvent cation, $Ca(H_2O)_4^{2+}$ seems to be less mobile than the added solute cation, NH_4^+. Therefore, on adding NH_4NCS we are increasing the concentration of the conducting NH_4^+ ions which increase the conductance value with $[NH_4^+]$. It may, however, be pointed out that in the cases of ideal systems the resultant viscosities of the mixtures of molten salts may also depend upon the respective values of the two components. The above fact may be responsible for the increase in fluidity with $[NH_4^+]$. Both fluidity and conductance decrease with increase in the concentration of solute for the system, $Ca(NO_3)_2 \cdot 4.1H_2O$–NaNCS. Here the substitution of less mobile Na^+ for $(1/2)Ca^{2+}$ appears to be responsible for the decrease in the conductance value with increase in [NaNCS]. Decrease in the viscosity with concentration may presumably be due to an increase in the compactness or rigidity of the system.

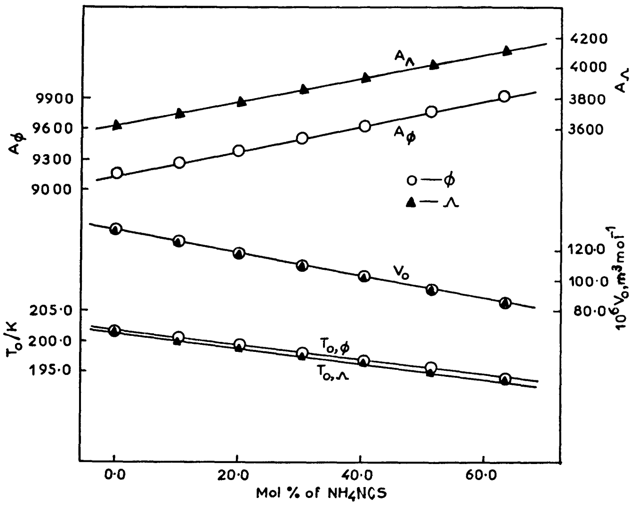

Fig. 2. Variation of A_Y, V_0, and T_0 with $[NH_4NCS]$ in molten $Ca(NO_3)_2 \cdot 4.23H_2O$–$NH_4NCS$ system.

In order to analyse the concentration dependence of fluidities and conductances the data were first least-squares fitted to the VTF and the CEM equations. The values of the parameters A_Y, A_Y', and T_0 thus obtained gave linear plots (Fig. 2) with N as expected from Eqs. 2 and 3.

Having examined the linear concentration variations of A_Y, A_Y', and T_0 the fluidities and conductances were

Table 2. Computed parameters of Eq. 5 for the equivalent conductance and the fluidity of molten salt mixtures

Melt	c	A_{0Y}	Q_{1Y}	k_Y	$T_{0(0)}$	Q_{2Y}	Std dev in ln Y
$Ca(NO_3)_2 \cdot 4.23H_2O$–$NH_4NCS$	1.7	3620.0 (9140.0)	7.720 (12.29)	567.0 (672.0)	201.3 (201.7)	0.104 (0.125)	0.019 (0.006)
$Ca(NO_3)_2 \cdot 4.1H_2O$–NaNCS	1.7	3300.0 (8357.0)	16.12 (19.48)	580.0 (670.0)	203.6 (203.9)	0.210 (0.205)	0.035 (0.004)

a) Parameters for the fluidity data are within parentheses.

Table 3. Computed parameters of Eq. 6 for the equivalent conductance and the fluidity of molten salt mixtures

Melt	c	A'_{0Y}	Q'_{1Y}	k'_Y	$T_{0(0)}$	Q_{2Y}	Std dev in ln Y
$Ca(NO_3)_2 \cdot 4.23H_2O$–$NH_4NCS$	1.7	50.10 (160.0)	0.945 (0.946)	586.2 (693.5)	201.3 (201.5)	0.122 (0.141)	0.035 (0.019)
$Ca(NO_3)_2 \cdot 4.1H_2O$–NaNCS	1.7	62.00 (180.0)	2.000 (0.530)	595.4 (694.7)	202.7 (204.0)	0.250 (0.190)	0.017 (0.017)

a) Parameters for the fluidity data are within parentheses.

Table 4. Parameters for density equation[a)] and molar volumes for molten salt systems

Melt	mol%	a	$b\times10^{-3}$	10^6V_m(m^3/mol) at 328 K
$Ca(NO_3)_2\cdot4.23H_2O$-NH_4NCS	NH_4^+			
	0.00	1.9635	0.7752	140.52
	10.11	1.9520	0.7841	131.93
	20.02	1.9185	0.7639	124.31
	30.35	1.8783	0.7451	116.53
	40.48	1.8424	0.7526	108.94
	51.30	1.7823	0.7054	100.60
	63.42	1.7035	0.6642	91.63
$Ca(NO_3)_2\cdot4.1H_2O$-$NaNCS$	Na^+			
	0.00	1.9813	0.7941	138.23
	5.58	1.9745	0.7884	133.53
	10.28	1.9782	0.8009	129.27
	16.02	1.9738	0.8014	124.35
	20.13	1.9704	0.7926	120.62
	24.84	1.9702	0.8002	117.03

a) The density equation is $10^{-2}\,\rho(\text{kg m}^{-3})=a-bT(\text{K})$.

least-squares fitted to Eqs. 5 and 6 at several values of constant T/T_0 ($=c$). The corresponding temperature, T lying in the experimental range and the value of c which gave reasonably good fits were selected. The values of the relevant parameters thus obtained along with the standard deviations in ln ϕ and ln A are listed in Tables 2 and 3. It should be noted that the computed values of the parameters A_{0Y}, Q_{1Y}, k_Y, Q_{2Y}, and $T_{0(0)}$ from Eq. 5 and those of A'_{0Y}, Q'_{1Y}, k'_Y, Q_{2Y}, and $T_{0(0)}$ from that of Eq. 6 are very close to those obtained from the corresponding plots (Fig. 2). Furthermore, the values of $T_{0(0)}$ obtained from Eqs. 5 and 6 are in good resemblance with those obtained by extrapolating the plots of T_0 *versus* N to zero mol% of solute in the respective melts.

It may be emphasized that the isoenergetic[18)] as well as an apparently isoentropic[19)] conditions used in the present systems satisfactorily represent the concentration dependence of viscosities and conductances in the glass-forming melts irrespective of the nature of the melt, whether they are ideal or non-ideal.[8)] However, the isoenergetic condition appears to have a direct experimental relevance as compared to that involving an apparently constant entropy (the latter, however, is far from constant). Such an analysis emphasizes further the importance of choosing T/T_0 as a better corresponding state for the comparison of liquid properties.

Furthermore, an interesting relationship for the dependence of A_Y on T_0 obtained[11)] by combining Eqs. 2 and 3,

$$A_Y = [A_{0Y}-(Q_{1Y}/Q_{2Y})T_{0(0)}] + (Q_{1Y}/Q_{2Y})T_0 \qquad (7)$$

is found (Fig. 3) to be applicable to the systems under investigation. This equation may be applied to any system in which A_Y and T_0 both vary linearly with concentration.

In view of the significance of another thermodynamic parameter, V_0 of Doolittle's equation[20)] in explaining the transport behaviour, variations in the values of the parameters A''_Y and V_0 with concentration have similarly been examined. The molar volumes were obtained from the corresponding densities (Table 4). The pre-exponential term A''_Y of Doolittle's equation like those of A_Y and A'_Y terms shows a linear dependence on concentration and is, therefore, expressed as,

$$A''_Y = A''_{0Y} \pm Q_{3Y}N, \qquad (8)$$

where A''_{0Y} is the value of A''_Y for the pure solvent and Q_{3Y} is the slope of the plot of A''_Y *versus* N. It is also apparent from the plots of V_0 *versus* N (Fig. 2) that the V_0 varies linearly with concentration and may similarly be represented as,

$$V_0 = V_{0(0)} \pm Q_{4Y}N, \qquad (9)$$

where $V_{0(0)}$ is the value of V_0 for the pure solvent and Q_{4Y} is the slope of the plot of V_0 *versus* N. Equations 8 and 9 may be combined to yield,

$$A''_Y = [A''_{0Y}\mp(Q_{3Y}/Q_{4Y})V_{0(0)}]\pm(Q_{3Y}/Q_{4Y})V_0 \qquad (10)$$

for the linear dependence of A''_Y on V_0.

Finally, combining Eqs. 2 and 9 a meaningful correlation between the two thermodynamic variables T_0 and V_0 may be obtained as,

$$T_0 = [T_{0(0)}\mp(Q_{2Y}/Q_{4Y})V_{0(0)}]\pm(Q_{2Y}/Q_{4Y})V_0. \qquad (11)$$

The Eqs. 7, 10, and 11 represent the linear dependence of A_Y on T_0, A''_Y on V_0, and T_0 on V_0, respectively, as has actually been found in the cases of ideal (Fig. 3)

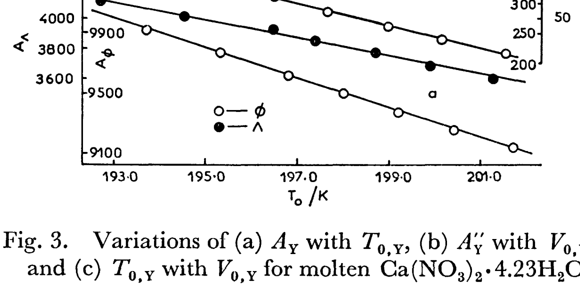

Fig. 3. Variations of (a) A_Y with $T_{0,Y}$, (b) A''_Y with $V_{0,Y}$, and (c) $T_{0,Y}$ with $V_{0,Y}$ for molten $Ca(NO_3)_2\cdot4.23H_2O$–NH_4NCS system.

as well as non-ideal systems containing either tetrahedral or octahedral complex-ions. The data for these parameters were least-squares fitted to the above derived equations and the computed values of the corresponding slopes and the intercepts are comparable with those obtained from the plots of A_Y, A''_Y, and T_0 against T_0, V_0, and V_0, respectively.

Furthermore, it is equally interesting to examine the relationship between the corrected activation energy, E_{cor} and T_0 value especially in view of their linear variations with concentration, *i.e.*, Eq. 2 and the following equation,

$$E_{cor} = E'_{cor} + Q_{5Y}N, \qquad (12)$$

where E'_{cor} is the intercept while Q_{5Y} is the slope of E_{cor} *versus* N plot. Thus, combining Eqs. 12 and 2, we get,

$$E_{cor} = [E'_{cor} \mp T_{0(0)}(Q_{5Y}/Q_{2Y})] + (Q_{5Y}/Q_{2Y})T_0, \qquad (13)$$

which suggests a linear increase in the corrected activation energies with T_0 as has actually been found (Fig. 4) in all the systems under investigation and also in those reported earlier.[12,13)]

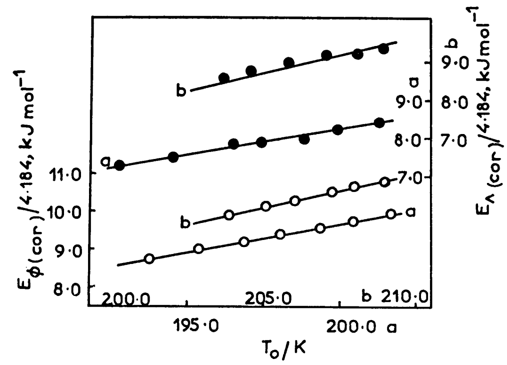

Fig. 4. Variation of E_Y with $T_{0,Y}$ for molten (a) Ca-$(NO_3)_2 \cdot 4.23H_2O$–NH_4NCS and (b) $Ca(NO_3)_2 \cdot 4.1H_2O$–NaCNS systems.

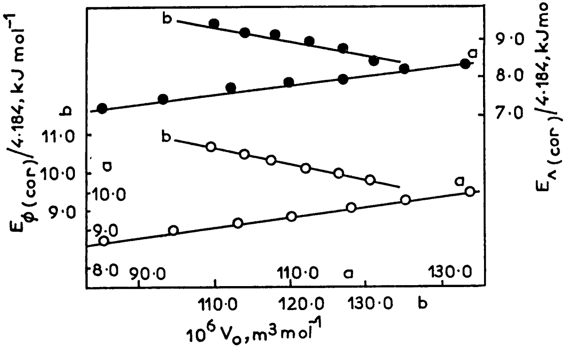

Fig. 5. Variation of E_Y with $V_{0,Y}$ for molten (a) Ca-$(NO_3)_2 \cdot 4.23H_2O$–NH_4NCS and (b) $Ca(NO_3)_2 \cdot 4.1H_2O$–NaNCS systems.

Similarly, in view of Eq. 11, E_{cor} may be expected to vary linearly with increase in the value of V_0 (Fig. 5) depending upon the sign in Eq. 11 for the dependence of T_0 on the V_0. Thus Eqs. 9 and 12 yield,

$$E_{cor} = [E'_{cor} \mp V_{0(0)}(Q_{5Y}/Q_{4Y})] \pm (Q_{5Y}/Q_{4Y})V_0. \qquad (14)$$

It may be noted that Eq. 13 always envisages the same trend in the behaviour of E_{cor} with T_0 and is also physically understandable.

The authors wish to thank Professor W. Rahman, Head of the Chemistry Department, for providing the facilities. The financial assistance from the Council of Scientific and Industrial Research (New Delhi) to one of us (A. A.) is gratefully acknowledged.

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5) The VTF equation is of the form,

$$Y = A_Y T^{-1/2} \exp[-k_Y/(T-T_0)]$$

where the terms have their usual significance.

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18) The corrected activation energies, E_{cor}, for conductance and viscous flows were obtained as, $E_{cor}/Rk_Y = [T/(T-T_0)]^2$ from the derivative of VTF equation. R is the gas constant and k_Y is the empirical constant. Now, if we take T_0 as basis for the corresponding temperature, T in fused salts, then at constant values of T/T_0 we have, $E_{cor} = [(T/T_0)/\{(T/T_0)-1\}]^2 Rk_Y$. Therefore, E_{cor} may have a constant value at equal T/T_0 values.

19) According to the CEM, the configurational entropy of the system is given as $S_c = \Delta C_p \ln(T/T_0)$ where ΔC_p is the difference in heat capacities for the liquid and the glassy state which may be regarded as almost invariant with concentration. Therefore, at equal values of T/T_0 the configurational entropy of the system may apparently be treated as constant.

20) The Doolittle's equation is of the form.

$$Y = A''_Y \exp[-k''_Y/(V-V_0)]$$

where V is the molar volume and V_0 is the molar intrinsic volume of the melt.