Variation of Transport Properties as Functions of Temperature and Composition in Glass-forming Melts — An Isoenergic Equation

Nurul ISLAM,* Satendra KUMAR, and Kunwar Pal SINGH
Department of Chemistry, Aligarh Muslim University, Aligarh 202001, India
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Measurements of density, ρ, viscosity, η, and electrical conductance, Λ, in glass-forming molten mixtures of manganese(II) chloride–tetrabutylammonium bromide were made as functions of temperature and composition. The non-Arrhenius temperature dependence of transport properties has been discussed in terms of equations based on the free-volume model. Composition dependence of viscosities has been explained satisfactorily through a parabolic equation, $\eta=p+qN+rN^2+sN^3$, where p, q, r, and s are the empirical parameters and N is the mole fraction of the solute. The minimum in the viscosity isotherms has been observed at $N=-q/2r$. A better applicability of isoenergic equation, $Y(=\phi$ or $\Lambda)=(A_{0Y}-Q_{1Y}N)c^{-1/2}(T_{0(0)}+Q_2N)^{-1/2}\exp[-k_{1Y}/(T_{0(0)}+Q_2N)-(c-1)]$ over an isothermal equation (both based upon free volume model) in explaining the transport process in all the glass-forming melts has been emphasized.

Temperature dependence of transport properties starting from very high temperatures where it is of Arrhenius' type passes through the middle region from T_g to $2T_g$ where it becomes of non-Arrhenius' type, and once again it is of Arrhenius' type at low temperatures. Such dependence in the middle region has been studied by several workers in terms of equations based upon free-volume and configurational entropy models; of these based upon the former are

$$Y = A_{1Y}T^{-1/2}\exp[-k_{1Y}/(T-T_0)], \quad (1)$$

$$Y = A_{2Y}\exp[-k_{2Y}/(V-V_0)], \quad (2)$$

where symbols have their usual significances. Equally important composition dependence has been described by considering the variation of the empirical parameters, A_Y and T_Y with concentration of these equations. Angell[1,2] proposed an isothermal equation by assuming A_Y and k_Y as composition independent and only T_0 varying linearly with concentration, which is of the form

$$Y = A_{1Y}T^{-1/2}\exp[-k_{1Y}/Q_2(N_0\delta-N)], \quad (3)$$

where N is the concentration in mol%, Q_2 is the slope of T_0 *versus* N plots, and N_0, the characteristic composition at which the isothermal temperature, T becomes the glass transition temperature, T_g of the system. Recently, a linear decrease of A_{1Y} terms[3,4] with composition has been observed and Eq. 3 was modified[5] accordingly in order to account for that, and is of the form

$$Y = (A_{0Y}-Q_{1Y}N)T^{-1/2}\exp[-k_{1Y}/Q_2(N_0-N)]. \quad (4)$$

Q_{1Y} is the negative slope of A_Y *versus* N plots and A_{0Y} the preexponential term for the pure solvent. This equation was satisfactorily employed to explain the composition dependence of transport properties of several molten salt mixtures.[5,6] However, such an isothermal equation may only be employed within the temperature limits ranging between the T_0's of the solvent and the solute. Beyond this range N_0 will have values which are either less than zero or more than 100 mol% and such values may not have any physical meaning whatsoever. To overcome these difficulties an expression based upon configurational entropy model was suggested in an earlier paper,[7] in which the use of isentropic condition, $c=T/T_0$ was made based upon the definition of configurational entropy[8] as $S_c=\Delta C_p \ln(T/T_0)$ where ΔC_p is the difference in heat capacities of liquid and glassy state. Assuming ΔC_p as almost composition invariant at equal values of T/T_0, the entropy may also be considered as constant. However, we remain unable to give sufficient support to this assumption that ΔC_p is compostiion independent. Therefore, another modified expression based upon free volume model has been suggested here to explain more satisfactorily the composition dependence of transport properties of glass-forming melts. Tetrabutylammonium bromide–$MnCl_2$ system has been selected here for further studies of such behavior. The system under consideration is of importance, as its viscosities show an abnormal composition dependence. Such behavior of viscosity has been explained through a parabolic equation as well as modified free-volume expression.

Experimental

Tetrabutylammonium bromide (Fluka) was used as solvent in molten state and anhydrous $MnCl_2$[9] as solute. The experimental techniques used and the precision of measurements are similar to those reported earlier.[7,10] Also the ranges of composition and temperature measurements are the same as reported in a previous paper.[7]

Results and Discussion

The measured densities of the system under investigation have been least-squares fitted to a linear function of the form $\rho=a-bT$ (K) and the values of computed parameters are given in Table 1.

TABLE 1. COMPUTED PARAMETERS FOR DENSITY EQUATION, $\rho(\mathrm{gm/cm^3}) = a-bT(\mathrm{K})$ OF TBAB[a]-$MnCl_2$ MELTS

Mn^{2+} mol %	a (gm/cm^3)	$b\times10^3$	Std dev in ρ
5.00	1.2650	0.6420	0.54×10^{-3}
10.07	1.2611	0.5841	0.31×10^{-3}
15.09	1.3057	0.6331	0.67×10^{-3}
19.66	1.3250	0.6275	0.22×10^{-3}
25.04	1.3398	0.6099	0.19×10^{-3}
30.14	1.3806	0.6558	0.39×10^{-3}

a) TBAB=tetrabutylammonium bromide.

Table 2. Equivalent conductance (cm^2 $equiv^{-1}$ ohm^{-1}) and fluidity (P^{-1})[a] data of TBAB-$MnCl_2$ melts

T (K)	mol % of Mn^{2+}					
	5.00	10.07	15.09	19.66	25.04	30.14
373.0	0.3399 (0.8624)	0.3287 (1.0279)	0.2056 (0.8672)	0.1641 (0.8171)	0.1267 (0.5994)	0.1060 (0.5326)
378.0	0.4181 (1.0778)	0.4022 (1.1640)	0.2486 (1.0784)	0.2083 (1.0009)	0.1587 (0.7960)	0.1256 (0.6482)
383.0	0.5052 (1.3150)	0.4690 (1.4277)	0.2936 (1.3184)	0.2488 (1.2146)	0.1910 (0.9775)	0.1539 (0.7897)
388.0	0.5947 (1.5966)	0.5579 (1.7244)	0.3445 (1.5834)	0.3003 (1.4699)	0.2322 (1.1713)	0.1853 (0.9426)
393.0	0.7159 (1.9524)	0.6490 (2.1064)	0.3981 (1.9056)	0.3545 (1.7677)	0.2744 (1.3995)	0.2212 (1.1318)
398.0	0.8469 (2.4006)	0.7532 (2.5231)	0.4592 (2.2662)	0.4163 (2.1494)	0.3177 (1.6724)	0.2588 (1.3485)
403.0	1.0006 (3.0020)	0.8499 (3.0357)	0.5264 (2.7310)	0.4822 (2.5394)	0.3746 (2.0083)	0.3014 (1.6138)
408.0	1.1582 (3.7455)	0.9740 (3.6777)	0.6160 (3.2888)	0.5629 (2.9780)	0.4427 (2.3519)	0.3450 (1.9017)
413.0	1.3327 (4.6168)	1.1395 (4.4609)	0.6994 (3.9097)	0.6497 (3.4781)	0.5095 (2.6634)	0.4028 (2.2045)

a) Fluidity data are within parentheses.

Temperature Dependence of Fluidities and Conductances. The conductance and fluidity data (Table 2) show non-Arrhenius temperature dependence and therefore least-squares fitted to Eqs. 1 and 2. The empirical parameters of these Eqs. along with standard deviations in $\ln \phi$ and $\ln \lambda$ are given in Table 3. Linear plots (Fig. 1) of $\log(\phi T^{1/2})$ and $\log(\lambda T^{1/2})$ *versus* $1/(T-T_0)$ show the applicability of Eq. 1 to explain the temperature dependence. Further, the plots of ϕ and λ *versus* $(V-V_0)$ were found to be non-linear signifying the inability of the Hildebrand equation,[11] $Y(=\phi$ or $\lambda)=B(V-V_0)/V_0$, to explain the transport behavior in the present system. However, linear plots (Fig. 2) of $\log \phi$ and $\log \lambda$ *versus* $1/(V-V_0)$ demonstrate a better fit of these data to Doolittle Eq. 2. Empirical parameters of this equation are given in Table 3 along with standard deviations in $\ln \phi$ and $\ln \lambda$.

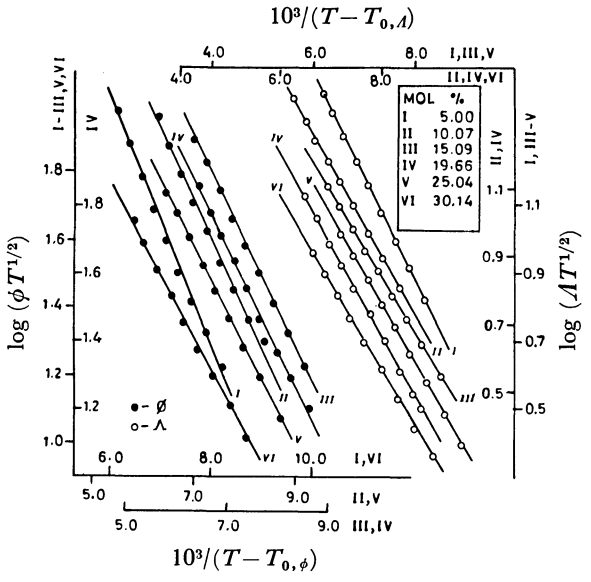

Fig. 1. Plots of $\log(YT^{1/2})$ *vs.* $1/(T-T_0)$ for TBAB-$MnCl_2$ melts.

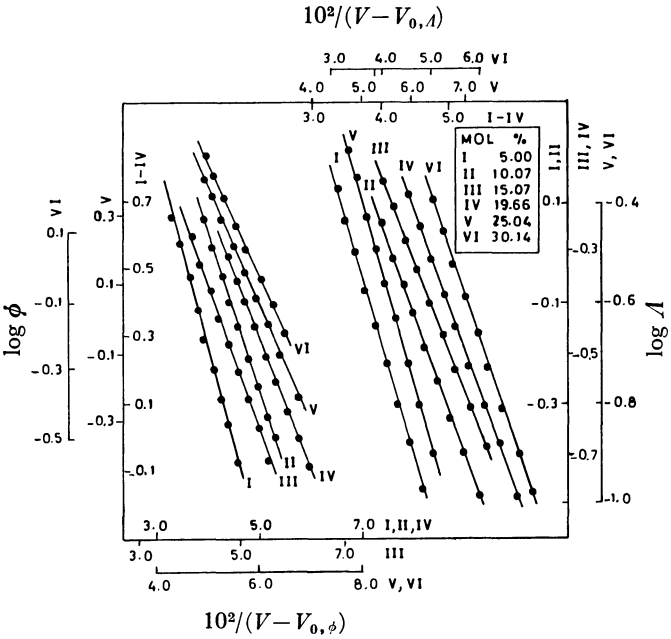

Fig. 2. Plots of $\log Y$ *vs.* $1/(V-V_0)$ for TBAB-$MnCl_2$ melts.

Both Eqs. 1[12] and 2[13] based upon the free volume approach are similar to one another. The parameter A_{2Y} of Doolittle Eq. is expected to depend on composition as in the case of A_{1Y} of free-volume model. Similarly k_{2Y} in the exponential term is related to k_{1Y} as being composition independent. Moreover, values of $T_{0,\phi}$ and $T_{0,\Lambda}$ and $V_{0,\phi}$ and $V_{0,\Lambda}$ obtained from Eqs. 1 and 2, respectively, are very close to one another thereby indicating the thermodynamic nature of glass transition temperature, T_0 and intrinsic volume, V_0 rather than kinetic. $k_\phi \approx 700$ K and $k_\Lambda \approx 600$ K seem

Table 3. Computed parameters for Eqs. 1 and 2 for the fluidity[a] and equivalent conductance data of TBAB-$MnCl_2$ melts

Mn^{2+} mol %	A_{1Y}	k_{1Y} (K)	$T_{0,Y}$ (K)	Std dev in ln Y	A_{2Y}	k_{2Y}	$V_{0,Y}$ (cm^3/mol)	Std dev in ln Y
5.00	1121.40 (7658.50)	605.20 (712.00)	253.54 (253.24)	0.054 (0.095)	57.66 (436.29)	111.59 (136.13)	283.10 (283.14)	0.017 (0.056)
10.07	1000.80 (7252.40)	596.20 (702.69)	255.62 (255.68)	0.018 (0.054)	33.37 (250.50)	84.97 (102.80)	271.70 (271.62)	0.016 (0.053)
15.09	748.60 (6802.70)	606.80 (697.60)	257.64 (257.75)	0.036 (0.032)	18.34 (212.21)	81.00 (99.04)	255.69 (255.78)	0.017 (0.030)
19.66	651.40 (6300.60)	602.25 (687.21)	259.67 (259.73)	0.014 (0.035)	25.80 (176.98)	83.87 (89.25)	243.50 (243.60)	0.011 (0.022)
25.04	522.60 (5505.70)	604.08 (699.50)	260.38 (260.34)	0.018 (0.037)	26.21 (137.58)	83.76 (79.49)	229.89 (230.90)	0.014 (0.017)
30.14	414.40 (4812.30)	590.00 (695.80)	262.64 (262.34)	0.020 (0.070)	13.39 (96.14)	69.66 (76.17)	217.34 (217.08)	0.017 (0.024)

a) Fluidity data are within parentheses.

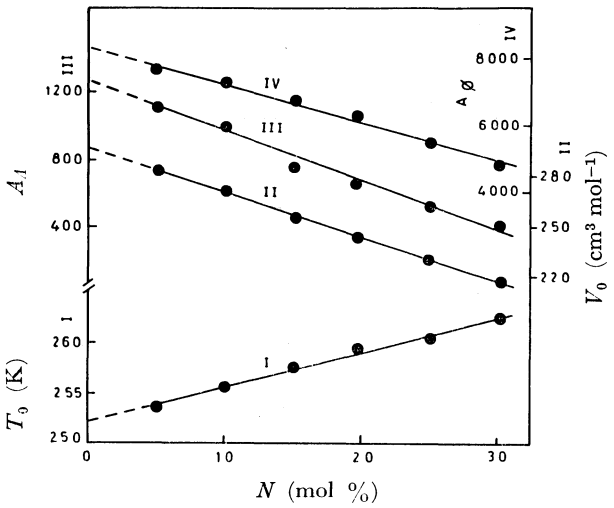

Fig. 3. Variation of T_{0Y}, $V_{0,\phi,A}$, and A_{1Y} with composition for TBAB-$MnCl_2$ melts.

to be very close to the values assigned to them as being universal constants.

The values of the preexponential factors of both Eqs. 1 and 2 decrease linearly with concentration (Fig. 3). Although there is a marked difference in the magnitude of A_Y terms of these equations which may be due to the absence of $T^{-1/2}$ in the preexponential term in Eq. 2. According to Cohen and Turnbull,[14] the A_Y terms may be expected to show direct dependence on $r/m^{1/2}$, where r and m are the effective radius and mass, respectively of the component particles of the system. In the present system there is a decrease in average molar mass by the addition of $MnCl_2$ to the molten TBAB, hence one can predict an increase in A_Y terms with increase in [$MnCl_2$]. However, an opposite trend has been obtained in the variation of A_Y with composition and may be represented as

$$A_Y = A_{0Y} - Q_{1Y}N, \tag{5}$$

where A_{0Y} is the value of the preexponential term for the pure solvent and Q_{1Y} gives the negative slopes of A_Y *versus* N plots.

An alternative explanation may be accorded for such a change in A_Y terms. According to Maxwell

$$Y = \frac{1}{\tau G}, \tag{5}$$

where τ is the relaxation time of the flowing entities and G is the rigidity modulus of the system. Using Eyring's expression, Eq. 6 may be written as

$$Y = \frac{1}{G\tau_0} \exp\left[-E_Y/RT\right], \tag{7}$$

in which τ_0 is the period of vibration of the flowing entity in its equilibrium position and E_Y is the activation energy for the transport process. R and T have their usual significances. Comparing Eqs. 1 and 7 we may obtain

$$A_{1Y} = \frac{T^{1/2}}{\tau_0 G}. \tag{8}$$

The above expression implies that A_Y is a function of rigidity of the system and as the concentration increases the rigidity of the system may increase. Moreover, the transition probability decreases with increasing concentration, in other words, the relaxing species will vibrate for a longer time in its equilibrium position with an increase in concentration. Accordingly, this may account for the linear decrease of A_Y terms with increasing [$MnCl_2$]. Further, the larger value for the slope of the linear plot of A_ϕ *versus* N than that of A_A *versus* N implies that A_ϕ decreases more rapidly than A_A with increase in concentration. Therefore, conductance appears to be less prone to the change in rigidity of the system than the fluidity.

In the system under investigation as well as in a variety of other[3,5,12,15] systems T_0 shows a linear relationship with mol % of solute (Fig. 3) which may be expressed as

$$T_0 = T_{0(0)} + Q_2N, \tag{9}$$

where $T_{0(0)}$ is the glass transition temperature for the pure solvent and Q_2 is the slope of T_0 *versus* N plot. This linear increase of T_0 with composition can be explained by considering that T_0 depends upon coulombic interactions or cohesive energy of the system.[12] The interactions increase with increase in [Mn^{2+}] thereby increasing T_0 values. In other words, an increase in T_0 with an increase in [$MnCl_2$] may be

Table 4. Computed parameters for Eqs. 10 and 11 for Walden product of TBAB–$MnCl_2$ melts

Mn^{2+} mol %	A_3	k_3 (K)	$T_{0,\Lambda\eta}$ (K)	Std dev in $\Lambda\eta$	A_4	k_4	$V_{0,\Lambda\eta}$ (cm^3/mol)	Std dev in $\Lambda\eta$
5.00	0.1679	102.85	253.21	0.049	0.1559	20.59	283.20	0.043
10.07	0.1410	103.45	255.57	0.047	0.1269	18.50	271.70	0.035
15.09	0.0947	105.64	257.43	0.021	0.0852	18.87	255.58	0.023
19.66	0.0887	105.74	259.54	0.052	0.1436	6.15	243.60	0.011
25.04	0.0854	108.37	260.42	0.056	0.1438	5.28	230.80	0.011
30.14	0.0837	106.74	262.54	0.061	0.1473	4.46	217.10	0.009

attributed to an increase in net cohesion in the system due to complex formation which leads to an eventual supercooling to glassy state. Therefore, it appears that in the absence of crystallization, addition of an excess amount of solute to any ionic solution results in glass formation and a sharp increase in viscosity may result, and such a concentration will be the glass transition composition, N_0. Also the linear increase in $T_{0,Y}$ with increase in [$MnCl_2$] may be due to the decrease in average mass of the system with the addition of $MnCl_2$ to TBAB melts.[7] Moreover, the values of $V_{0,\phi}$ and $V_{0,\Lambda}$ (Fig. 3) appear to decrease with increase in [$MnCl_2$] which may be due to the close packing of the system.

Temperature Dependence of Walden's Product. The temperature dependence of Walden's product, $\Lambda\eta$ may be represented through expressions[5] essentially based upon Eqs. 1 and 2 of the form

$$\Lambda\eta = A_3 \exp\left[k_3/(T-T_0)\right], \tag{10}$$

and

$$\Lambda\eta = A_4 \exp\left[k_4/(V-V_0)\right], \tag{11}$$

where A_3, k_3, A_4 and k_4 are empirical constants. The best fit values of these parameters are given in Table 4. The simultaneous representation of the temperature dependences of Λ and η appears to be more sound due to their interdependent nature.

The temperature dependence of $\Lambda\eta$ product may also be expressed satisfactorily by Frenkel's equation[16]

$$\Lambda^n\eta = \text{constant}, K. \tag{12}$$

This is apparent from its recent application to the $\Lambda\eta$ products of $CoCl_2$–$Ca(NO_3)_2.3.91H_2O$ molten mixtures.[5] Computed parameters for Eq. 12 are given in Table 5 for the present system. Here n is the ratio of E_ϕ/E_Λ, which is found to be greater than one. It may be further emphasized that failure of Walden's rule in molten salts may be due to the higher activation energies for viscous flow than ionic and is likely due to the difference in the availability of the species for relaxation in the two processes.

Table 5. Computed parameters for Eq. 12 for the products of Λ and η of TBAB-$MnCl_2$ melts

Mn^{2+} mol %	n	ln K	Std dev in ln η
5.00	1.2223	1.1219	0.031
10.07	1.2328	1.3068	0.035
15.09	1.2319	1.7886	0.009
19.66	1.0764	1.7041	0.018
25.04	1.0713	1.7292	0.017
30.14	1.0635	1.7522	0.015

Composition Dependence of Fluidities and Conductances. A regular decrease in electrical conductance with increase in composition is observed (Table 2) which may be attributed to the removal of more mobile anions as a result of complex formation and simultaneous decrease in free volume. While an increase in fluidity is observed as the concentration of $MnCl_2$ increases from ≈5 to ≈10 mol % and then decreases with further increase in concentration. The minimum at ≈10 mol % of Mn^{2+} appears to flatten as the temperature increases (Fig. 4). Such an unexpected trend in the viscosity isotherms has earlier[3] been observed in the molten TBAI+$CoCl_2$ systems. Similar abnormal behavior of viscosity as well as conductance isotherms has also been reported in several other binary molten mixtures.[15,17,18]

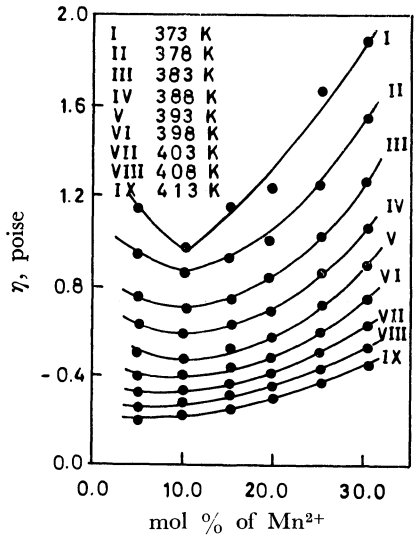

Fig. 4. Viscosity, η isotherms for TBAB–$MnCl_2$ melts.

The decrease in the viscosity in concentration range up to ≈10 mol % of $MnCl_2$ may be attributed to the decrease in electrostatic force holding a solvent ion-pair together due to the presence of free metal ions in its neighborhood. Such a dissociation with increase in concentration of solute at constant temperature depends upon the number of free metal ions and the thermal energy of the solvent.[19] The minimum in the viscosity isotherms corresponds to a point where dissociation is maximum. Furthermore, when the dissociation of solvent molecules (TBAB) increases

with increase in [$MnCl_2$], the solvent anions, *i.e.*, Br^- ion formed in this way form a complex species with the free metal ion as $MnBr_4^{2-}$, the presence of which has been supported by its ligand-field bands.[10] The complex species formed associates with the solvent cation, Bu_4N^+. Such a simultaneous complexation and association at higher concentrations may increase the viscosity of the system from ≈0.1 to ≈0.30 mole fraction of $MnCl_2$. This abnormal nature of viscosity isotherms has been empirically described by least-squares fitting the data to a polynomial equation of the form

$$\eta = p + qN + rN^2 + sN^3, \quad (13)$$

where p, q, r, and s are empirical constants, using POLRG computer program. This computer program is similar to that reported by Easteal and Hodge[17] and can fit the data to polynomials up to seventh degree. The computed values of the empirical constants are presented in Table 6 along with the standard deviation from the observed η. It is apparent from the table that in most of the cases the polynomial is quadratic and the expected minimum at the mole fraction, $N=-q/2r$ fairly coincides with those of the viscosity isotherms, *viz.* ≈0.1 (Fig. 4).

The conventional activation eneriges, E_ϕ and E_A were computed from the corresponding derivatives of Eq. 1. A regular decrease in activation energies, E_ϕ and E_A with temperature was obtained which may be due to the thermal expansion of the system thereby decreasing the interionic forces or, in other words, lowering the height of the potential energy barrier for the flow processes.

Table 6. Computed parameters for Eq. 13 for the viscosity of TBAB-$MnCl_2$ melts

T (K)	p	q	r	s	Std dev in η
373.0	1.6613	−14.160	87.76	−127.01	0.047
378.0	1.0632	−3.666	17.49	—	0.014
383.0	0.8673	−2.928	14.11	—	0.012
388.0	0.7199	−2.521	12.13	—	0.009
393.0	0.5859	−2.009	9.93	—	0.008
398.0	0.4592	−1.164	5.53	4.85	0.010
403.0	0.3486	−0.454	2.26	7.44	0.006
408.0	0.2970	−0.731	3.56	4.75	0.009
413.0	0.2282	−0.434	3.95	—	0.005

On the other hand, an abnormal behavior in the composition dependence of E_ϕ has been observed. E_ϕ decreases initially with an increase in the concentration of $MnCl_2$ and passes through a minimum at ≈10 mol % of $MnCl_2$ and then increases with further increase in [$MnCl_2$] as observed in the case of Bu_4NI–$CoCl_2$ melts.[3] The decrease in activation energy for viscous flow up to ≈10 mol % may be due to the dissociation of solvent molecules which results in an ease to viscous flow. Furthermore, the increase in E_ϕ following minimum may be due to the complexation and association as discussed above. However, at equal values of T/T_0 the corrected activation energies ($E_Y + 1/2RT$) of the molten salt systems may be considered as constant,[2,20] which may be termed as an isoenergic condition. Therefore, the fluidities and conductances may be plotted *versus* composition at constant T/T_0 values. The significance of such plots is that a better quantitative illustration of the composition dependence of transport properties may be made at equal T/T_0 values by accounting for the composition dependence of individual parameters in Eq. 1. At T/T_0=constant, c, Eq. 1 becomes

$$Y = A_{1Y}(cT_0)^{-1/2} \exp\left[-k_{1Y}/T_0(c-1)\right]. \quad (14)$$

The values of fluidities and equivalent conductances at constant T/T_0 ratios ranging from 1.4 to 2.1 were calculated from Eq. 14 and are in turn least-squares fitted to the equation obtained by substituting the linear variations of A_Y and T_0 with composition, in Eq. 14 as

$$Y = (A_{0Y} - Q_{1Y}N)c^{-1/2}(T_{0(0)} + Q_2N)^{-1/2} \exp\left[-k_{1Y}/(T_{0(0)} + Q_2N)(c-1)\right]. \quad (15)$$

Table 7. Computed parameters for Eq. 15 (c=1.4 to 2.1) for the fluidities[a] and equivalent conductances of TBAB-$MnCl_2$ melts

Volues of c	A_{0Y}	Q_{1Y}	k_{1Y} (K)	$T_{0(0)}$ (K)	Q_2	Std dev in ln Y
1.4	1278.0	27.52	607.8	251.5	0.368	0.098
	(8229.0)	(103.20)	(703.8)	(251.2)	(0.375)	(0.097)
1.5	1282.0	28.08	607.7	251.6	0.365	0.089
	(8241.0)	(103.70)	(703.4)	(251.3)	(0.374)	(0.081)
1.6	1285.0	28.44	608.2	251.6	0.366	0.084
	(8244.0)	(104.50)	(704.6)	(251.4)	(0.373)	(0.070)
1.7	1272.0	28.07	608.5	251.4	0.364	0.079
	(8246.0)	(104.80)	(703.6)	(251.2)	(0.374)	(0.062)
1.8	1275.0	28.36	608.7	251.6	0.362	0.076
	(8248.0)	(104.60)	(704.6)	(251.3)	(0.375)	(0.057)
1.9	1270.0	28.20	608.5	251.7	0.363	0.073
	(8243.0)	(105.20)	(700.0)	(251.4)	(0.370)	(0.053)
2.0	1268.0	28.20	608.2	251.6	0.367	0.071
	(8245.0)	(106.60)	(702.8)	(251.4)	(0.374)	(0.049)
2.1	1272.0	28.40	609.6	251.5	0.364	0.070
	(8243.0)	(106.20)	(703.8)	(251.3)	(0.373)	(0.047)

a) Parameters for fluidity are within paratheses.

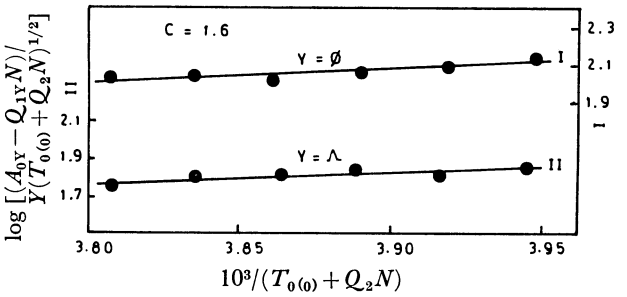

Fig. 5. Plots of $\log[(A_{0Y}-Q_{1Y}N)/Y(T_{0(0)}+Q_2N)^{1/2}]$ *vs.* $1/(T_{0(0)}+Q_2N)$ for TBAB-$MnCl_2$ melts.

Reasonably good fits were obtained at different c values and the computed values of the parameters are given in Table 7. The successful applicability of Eq. 15 to explain composition dependence of transport properties in the system under investigation may be emphasized by linear plots (Fig. 5) of $\log[(A_{0Y}-Q_{1Y}N)/Y(T_{0(0)}+Q_2N)^{1/2}]$ *versus* $1/(T_{0(0)}+Q_2N)$ which pass through the origin. The computer fitted values of the parameters A_{0Y}, Q_{1Y}, k_{1Y}, Q_2, and $T_{0(0)}$ were found to be very close to those obtained from the corresponding plots (Fig. 3). Thus the value of $T_{0(0)}$ obtained from Eq. 15 is in good resemblance with that obtained by extrapolating the plot of T_0 *versus* N to zero mol% of $MnCl_2$.

It may be concluded that the isoentropic conditions used in the earlier paper[7] [TBAX (X=Cl, I)-$MnCl_2$ systems] and the isoenergic conditions used in the present system, satisfactorily represent the composition dependence of viscosities and conductances in the glass-forming melts irrespective of the geometry of the complex species present. However, the latter conditions seem to be more satisfactory because of having sound experimental base and may be employed over wide range of temperature without depending on the T_0's of the solvent and solute.

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20) The corrected activation energies, E_{corr}, for conductance and viscous flows were obtained as $E_{corr}/Rk_{1Y}=[T/(T-T_0)]^2$ from the derivatives of Eq. 1, where R is the gas constant and k_{1Y} is the empirical constant in Eq. 1. If we take T_0 as the corresponding temperature scale instead of absolute temperature, T then at the constant value of T/T_0 we have $E_{corr}/Rk_{1Y}=[(T/T_0/(T/T_0-1)]^2$. Therefore, E_{corr}/Rk_{1Y} may have a constant value at equal T/T_0 values.