A Viscosity-Temperature Study for a Glass-Forming-Non Aqueous Electrolyte: Zinc Bromide in Ethyl Acetate

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The low temperature behavior of solutions of zinc bromide in ethyl acetate has been studied by viscosity measurements and differential thermal analysis. It is shown that the solutions go through a glass transition at temperatures between 100 K and 220 K. With decreasing temperature, $\eta(T)$ behaves first Arrhenius-like and then obeys the Fulcher relation. A reduction of the viscosity with respect to that of the pure solvent (η_s) gives a family of curves converging to one point at high temperature; if moreover $\ln(\eta/\eta_s)$ is plotted vs. the inverse of the reduced temperature T/T_g, T_g being the glass transition temperature, the plots coincide within 5% for all solutions. A simple relation between the reduced viscosity and the lone entropy is found, since one obtains $\mathrm{d}\ln(\eta/\eta_s)/\mathrm{d}(T_g/T) = \alpha(T_g/T - T_g)$. Comparison is made with the Adam-Gibbs model. The properties of these glass-forming electrolytes are assumed to be due to a "granular" structure which becomes quasi-polymeric at high concentration.

I. Introduction

It is well known that concentrated aqueous electrolytes, especially multivalent electrolytes, (or molten salts) can become glasses. But often crystallization occurs during cooling before the glassy state is reached. Numerous studies have been carried out in this respect: measurements of heat capacities and fusion entropies [1, 2], conductivities [3–5], electrical relaxation [6] and viscosities [7–10]. Very little, however, is known about non aqueous electrolyte solutions except the zinc chloride – pyridinium chloride system, which has been extensively studied by Easteal and Angell [11].

We present here a viscosity study on zinc bromide in ethyl acetate. Due to the low dielectric constant of the solvent ($\varepsilon = 6.09$ at room temperature), the dominating interactions in this system are interionic whereas the ion-solvent interactions are less important, contrary to aqueous electrolytes. Indeed, recent investigations on this system *at room temperature* have shown that the salt is associated and forms probably small ionic chains at high concentrations [12–15]. Three distinct concentration ranges have been previously identified from the concentration-dependence of the transport and thermodynamic properties [13, 16]: at low solute mole fraction ($x < 0.1$), the medium would be characterized by a dilute solution of small ionic particles (association of tetrahedral cells of $[\mathrm{ZnBr_4}]_n^=$ with $n \cong 2$), the remaining zinc-ions being "lost" in the solvent, i.e. solvated by the acetate molecules. This structure gives rise to a regular increase of the molar conductivity and viscosity with adding solute, whereas the partial molar volume of the salt, $\bar{V}$, remains equal to that calculated for $(\mathrm{ZnBr_4})^=$ cells; then, for $0.1 < x < 0.3$, the mean distance between the complex ions becomes such that they begin to form bigger aggregates, which produces a sharp increase of the viscosity and volume $\bar{V}$ (this latter reaches the molar volume of the crystalline anhydrous salt). A consequence of this cluster formation is a decrease of the molar conductivity. The concentration and the size of these small ionic particles are such that one obtains a "halo" on the small angle X-ray scattering patterns; their size would be nearly 10 Å [16]. A third behavior is observed for the very concentrated solutions ($0.3 < x < 0.42$): at this stage, the mean distance between the small ionic aggregates is of the same order of magnitude as their size. This quasi-melt structure is probably the origin of the very high viscosity ($\cong 147 \cdot 10^{-3}\,\mathrm{Pa \cdot s}$ at 293 K); moreover, the partial molar volume $\bar{V}$ of the solute becomes equal to that of the molten salt [13]. This structure gives an intensity maximum in the small angle X-ray scattering patterns for a scattering

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vector $s = (10\,\text{Å})^{-1}$. Thus, we have here a disordered system of small charged ionic clusters in which crystallization does not occur, probably due to repulsive coulombic forces, very similar to glass forming liquids. Indeed, with decreasing temperature, glass-transitions are found in nearly the whole concentration range ($0.06 < x < 0.42$). For that reason, the low temperature phase diagram has been determined and the viscosity has been measured for several samples of different concentrations. The experimental data coincide well at low temperature with the Vogel-Tammann-Fulcher equation (VTF relation) [17]. Nevertheless, the temperature dependence of the viscosity will be explained in the light of the Adam-Gibbs theory [18], which seems to be one of the most fruitful models for the interpretation of the temperature-dependence of relaxation phenomena arising near a glass-transition. Indeed, it is believed that the main process involved in the glass transition region of super-cooled liquids corresponds to a great increase of the molecular relaxation times associated with a decrease in the number of configurations available for the system; in that point of view, the glass temperature T_g is considered as being the temperature below which relaxation times are too long to permit the establishment of equilibrium in the time scale of the experiment.

II. Experimental

High purity anhydrous zinc bromide was used (Fluka A.G., Buchs S.G., Switzerland). The salt was dried under vacuum for several days and then transferred into a dry box and weighed. Very pure commercial ethyl acetate was used without further purification (E. Merck, Darmstadt, Germany, Ref. 863). The concentration of the solutions was determined by atomic absorption titration.

The shear viscosities were measured with the rotating viscosimeters RM15T and RM30 (Contraves A.G. Zurich, Switzerland). The low temperature measurements were carried out in an anhydrous ethanol bath, the temperature of which was controlled within 0.1 K by a colora TK thermostat and measured with a calibrated platinum resistance probe. The experiments were performed in a glove-bag under N_2 atmosphere. In such circumstances, the accuracy is better than 2–3%.

The temperatures of the glass-transitions have been determined with a D.T.A. apparatus (Mettler T.A. 2000 – Switzerland). For two samples, the specific heat variations have been obtained with a Perkin Elmer Differential Scanning Calorimeter (D.S.C.) from 130 K to 300 K.

As the glass transition temperature may depend on the thermal history of the sample [19, 20], the transition-temperatures have been taken at the mid-point of the rising part of the D.T.A. curve during the *first* cooling and the first heating at a rate of 5 K/min, except for the concentration $x = 0.21$ (second temperature run – see below). Cooling and heating runs have been performed also at various rates (5, 10, 20, 40 K/min), but no *typical* differences have been found: the T_g-values coincided within 1%.

For the viscosity measurements, the solutions have been cooled very slowly since, for each experimental point, the temperature was maintained constant during more than half an hour before reading. The T_0-temperature, calculated from the viscosity data (V.T.F. relation), have been compared with those given by D.T.A. during first cooling, though such a determination is thought to be less accurate than during heating. In such circumstances, one remains always in the liquid phase and gets near the vitreous transition with always $T > T_g$.

III. Results

A) Differential thermal analysis

The liquid mixtures can be cooled slowly to the glassy state in a big concentration range without crystallization ($0.06 < x <$ saturation). But on heating some glasses crystallize, particularly the dilute samples the structure of which is probably similar to that of pure ethyl acetate. Indeed, this later has a well defined melting point and does not exhibit a vitreous state. On the phase diagram given in Fig. 1, the three concentration ranges previously observed at room temperature [13, 16] are obvious:

(i) $0.06 < x < 0.14$. The transition occurs at very low temperature during cooling at constant rate. The hypothetical glass transition of pure solvent can be determined by extrapolation of the data; one obtains $T_g \cong 105$ K.

(ii) $0.14 < x < 0.29$. T_g increases sharply with concentration. Moreover we have noted that some

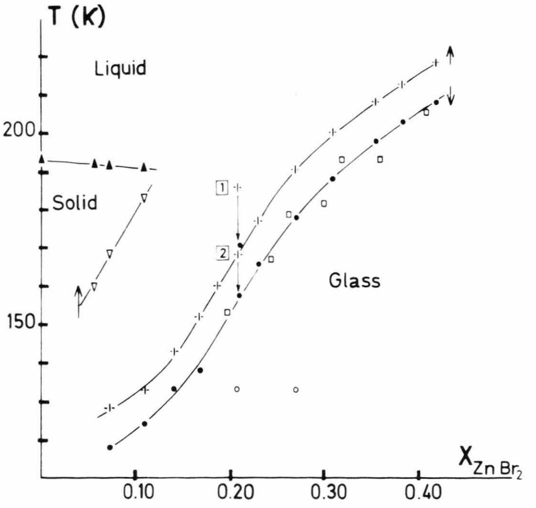

Fig. 1. Phase diagram of the zinc bromide-ethyl acetate system. First glass-transition: + heating (D.T.A.); ● cooling (D.T.A.); □ cooling (viscosimetry). Second glass transition: ○ cooling (D.T.A.); crystallization: ▽ beginning (heating); ▲ fusion (heating).
①: anomalous behavior of the $x = 0.21$ sample during first run;
②: normal behavior of this sample during the second run.

samples show an endothermic transformation at very low temperature (= 133 K). This concentration range can be considered as a transition region between the dilute solutions, where T_g has a tendency to increase with salt addition, and the very concentrated mixtures, where T_g would have a tendency to decrease. Indeed, at the inflexion point, $x = 0.21$, an anomalous behaviour of T_g is observed during the first temperature run: the T_g value is ~ 9 K bigger than that of the nearby mixtures. This anomaly disappears at the second temperature run as shown on Figure 1.

(iii) $0.29 < x < 0.42$. T_g increases more slowly. The ΔC_p, measured by D.S.C. for the sample $x = 0.408$, is found to be 77.66 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, for one mole of mixture (Figure 2).

Moreover, the existence of a hysteresis in temperature, $\Delta T = 9$ K, practically independent of the salt concentration and of the rate of the temperature runs, must be noted, cf. Figs. 1 and 3.

B) Viscosity

The log η vs. T^{-1} plots are given in Figure 4.

High temperature range ($T > 255$ K)

The viscosities of all the mixtures have a typical Arrhenius behavior. The apparent activation energies, for the viscous flow, U_{app}, evaluated from the $\ln \eta$ vs. T^{-1} slopes, increase with solute concentration in the way shown on Figure 5. They must be compared to the energies calculated from the slopes of the $\ln \eta$ vs. concentration curves. Indeed, according-

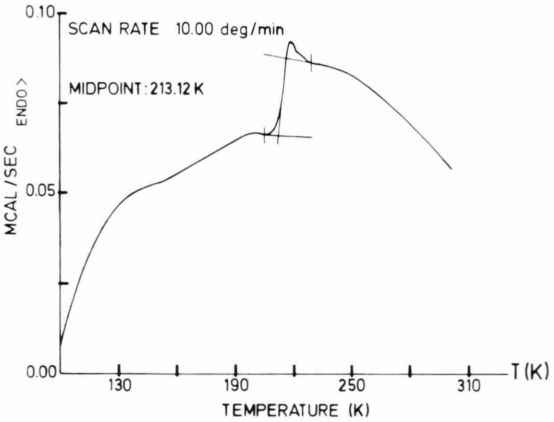

Fig. 2. D.S.C. heating curve for a concentrated sample ($x = 0.40$). The sample is quenched from room temperature to liquid nitrogen before heating at 10 K/min.

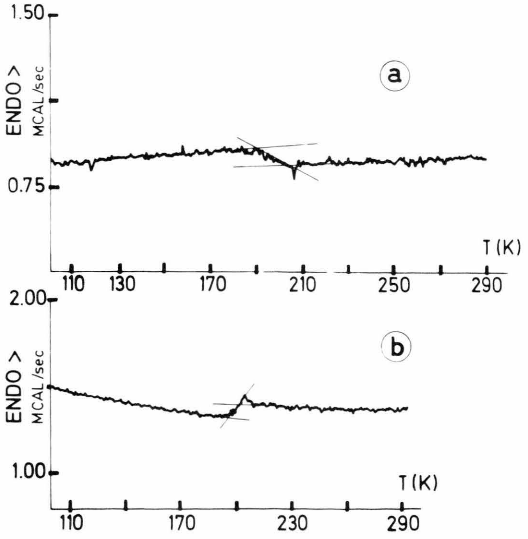

Fig. 3. Complete D.S.C. run at a rate of 10 K/min ($x = 0.36$). a) cooling curve, b) heating curve. ENDO〉: direction of endothermic transitions.

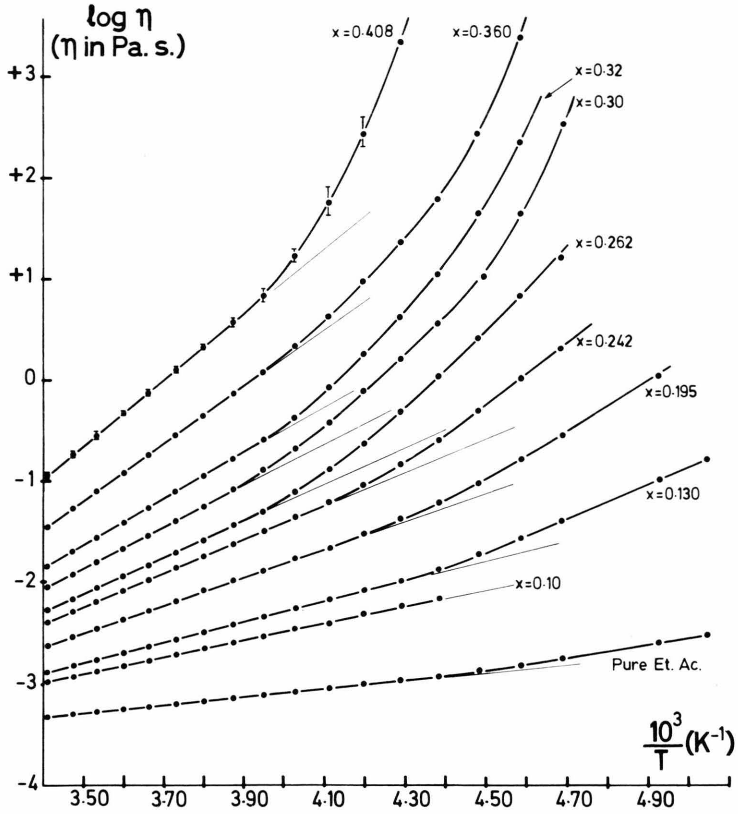

Fig. 4. ln η vs. T^{-1} plots for various $ZnBr_2$-Et.Ac. mixtures.

ing to [13], the composition dependence of the viscosity at 293 K is such that:

(i) $x < 0.16$: $\ln \eta = -\ 7.66 + \ 7.25\, x$,
(ii) $0.16 < x < 0.29$: $\ln \eta = -\ 8.50 + 12.5\, x$,
(iii) $0.29 < x < 0.42$: $\ln \eta = -\ 12.26 + 25\, x$.

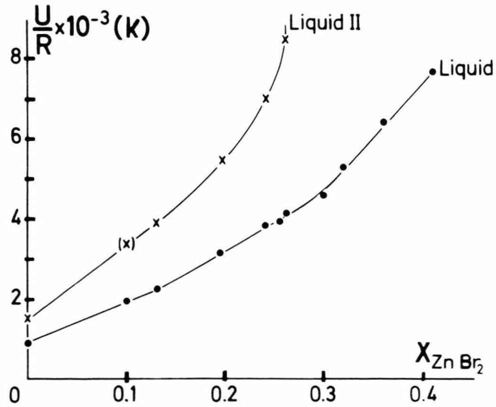

Fig. 5. Apparent activation energies, (U_{app}/R) (K) for various salt concentrations. Liquid I: Arrhenius behavior at high temperature. Liquid II: Quasi-Arrhenius behavior at low temperature of the dilute solutions.

We may write these relations as follows:

$$\text{for given } T \text{ (293 K)}, \quad \ln \eta = b + \frac{U_0}{RT} x \ ;$$

$$\text{for given } x, \quad \ln \eta = a + \frac{U_{app}}{R} \frac{1}{T} \ .$$

The U_{app} and U_0 – values are summarizes in Table 1; both energies are in the same order of magnitude. Thus, an increase of solute concentration would have the same effect on the viscosity as a decrease of temperature.

If $\ln(\eta/\eta_s)$ is plotted vs. T^{-1}, η_s being the viscosity of the pure solvent at temperature T, one obtains a family of curves which converge at high temperature to a common point A, provided $x > 0.10$ (cf. Figure 6). Such a convergence was also observed for the recently studied $LiClO_4$ – Et. Ac. System [21]. The coordinates of this point are in our case $\ln(\eta/\eta_s)_A = -0.10$ and $T_A^{-1} = 2.55 \cdot 10^{-3}\ K^{-1}$ i.e. $T_A = 392$ K. Hence the viscosity obeys the simple

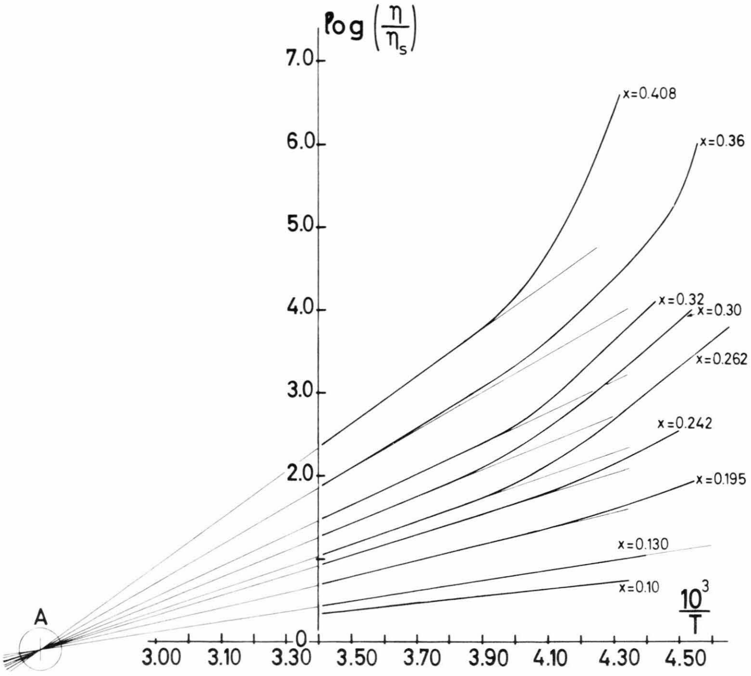

Fig. 6. $\ln(\eta/\eta_s)$ vs. T^{-1} plots. η_s = viscosity of the solvent at temperature T.

relation, provided $T > 255$ K:

$$\ln(\eta/\eta_s) - \ln(\eta/\eta_s)_A = \frac{U(x)}{R}\left[\frac{1}{T} - \frac{1}{T_A}\right];$$

as

$$\ln(\eta/\eta_s)_A \cong 0 \; \ln(\eta/\eta_s) \cong \frac{U(x)}{R}\left[\frac{1}{T} - \frac{1}{T_A}\right].$$

Table 1. Comparison of activation energies for one mole. U_{app} is obtained from Arrhenius plots, U_0 from isothermal concentration-viscosity variations.

x	$\frac{U_{app}}{R} \cdot 10^{-3}$ (K)	$\frac{U_0}{R} \cdot 10^{-3}$ (K)
0.408	7.70	7.32
0.36	6.40	
0.32	5.30	
0.30	4.60	
0.262	4.15	3.66
0.258	4.00	
0.242	3.80	
0.195	3.15	
0.130	2.25	2.12
0.10	1.95	
Pure acetate	0.93	

U_{app}: calculated from the $\ln\eta$ vs. T^{-1} curves.
U_0: calculated from the $\ln\eta$ vs. x curve at 293 K.

Low temperature range ($T < 255$ K)

The viscosities of the dilute solutions still show quasi-Arrhenius behavior but with changes in the activation energies near 255 K (Liquids II of Figure 5). However the data are better fitted by using the Vogel-Tammann-Fulcher (V.T.F.) relation [17]:

$$\ln\eta = \ln\eta_0 + B_F/(T - T_0)\,, \tag{2}$$

B_F being a constant and T_0 an empirical parameter corresponding to the "ideal" glass-transition temperature, which reflects the forces of cohesion in the liquid [22]. The B_F and T_0 parameters have been obtained by differentiation of $\ln\eta$ with respect to T^{-1} [23]: the slope and the intercept of a plot of:

$$\left(\frac{d\ln\eta}{dT^{-1}}\right)^{-1/2} = B_F^{-1/2} - T_0\,B_F^{-1/2}\,T^{-1} \tag{3}$$

yields B_F and T_0; then η_0 is calculated directly from the experimental data. The results are summarized in Table 2. A comparison of the T_0-parameter evaluated from the viscosity data with the T_g-temperature obtained by D.T.A. experiments reveals that both temperatures are nearly equal, if we take the T_g-value during first cooling ($T_g \downarrow$). This equality must be pointed out since it has been shown that

Table 2. Best calculated parameters for the Fulcher plots of the temperature-viscosity behavior. B' is obtained by taking $T_0 = T_g\downarrow$. *Less accurate estimated values since crystallization have occured at low temperature.

x	B_F (K)	T_0 (K)	η_0 (Pa · s)	$T_g\downarrow$ (K)	$T_g\uparrow$ (K)	B'_F (K) (taking $T_0 \equiv T_g\downarrow$)
0.408	390	205	$2.31 \cdot 10^{-3}$	206	216.5	346 within 6%
0.362	320	193	$8.75 \cdot 10^{-3}$	198	209.5	
0.320	(309)*	193	$1.08 \cdot 10^{-3}$	191	202	
0.300	(475)	182	$1.6 \cdot 10^{-4}$	186	197.5	443 within 5%
0.262	424	179	$1.8 \cdot 10^{-4}$	176	188	
0.242	486	167	$1.0 \cdot 10^{-4}$	169	182	
0.195	432	155	$1.6 \cdot 10^{-4}$	151	163	
0.130			$1.0 \cdot 10^{-5}$	130	139	788

the T_g's depend on the heating or cooling rate [24], i.e. on the thermal history of the glass, and that usually $T_g \neq T_0$. But here we have $T_0 \cong T_g\downarrow$, and the relation (2) becomes identical to

$$\ln \eta = \ln \eta_0 + B'_F/(T - T_g)\downarrow . \tag{4}$$

The B'_F values calculated from (4), taking $T_0 = T_g\downarrow$, are 346 K within 6% in the high concentration range ($0.30 < x < 0.42$), 446 K within 5% in the intermediate range ($0.19 < x < 0.30$) and 788 K in the low concentration range. Such a difference may be due to solvent-effects. If $\ln \eta/\eta_s$ is plotted vs. $T_g\downarrow/T$, the family of curves of Figs. 4 and 6 reduce to a single curve within 5% as shown in Figure 7. (A similar normalization has been observed when the activation energies of numerous simple organic liquids and various molten oxides are plotted vs. T_g/T [25]).

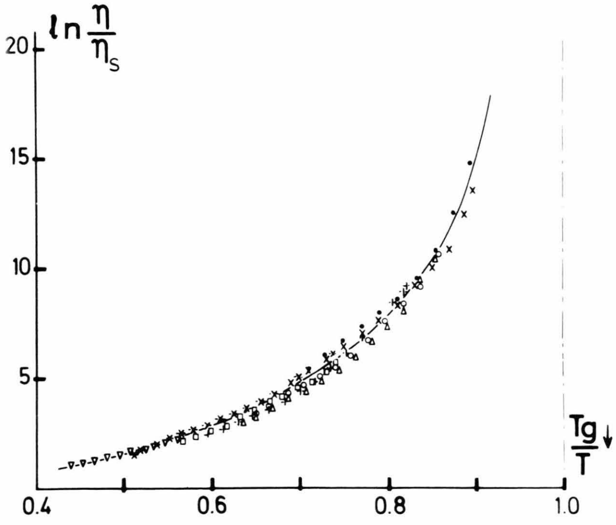

Fig. 7. Normalization of the viscosity-temperature data: $x = 0.40$ (●), 0.36 (×), 0.32 (○), 0.30 (△), 0.262 (+), 0.242 (□), 0.195 (*), 0.130 (▽).

IV. Discussion

From various experiments carried out on these solutions [13, 16, 35], they can be considered as "suspensions" of small ionic clusters in the solvent; the viscosity would be a function of the fraction of volume occupied by the particles [26, 27] or of an average "free volume" per "bead"; such a model would be similar to that developped by Cohen and Turnbull for simple liquids giving glasses [28] which is still valid at high temperature and becomes formally equivalent to that of Arrhenius as noted by the authors themselves. So, one would explain the similar part played by temperature and dilution (at least for $T > 255$ K) in the viscosity behavior.

Nevertheless the temperature-dependence of the viscosity would be explained better in the light of the Adam-Gibbs theory since the glass transition is a second order phase transition, i.e. a cooperative phenomenon.

Indeed, Adam and Gibbs [18], in their theory define a "cooperatively rearranging region" as being a subsystem of the sample which can rearrange into another configuration independently of its environment. The size of this region would depend on the configurational entropy of the liquid and is reciprocally dependent on the potential barrier hindering the rearrangement. The average transition probability of the "cooperatively arranging region" is shown to be a function of the entropy of configuration of the liquid. As this probability is reciprocally related to the relaxation time, a direct consequence of this model is that the temperature-viscosity variations can be expressed by:

$$\ln \eta = B_G/TS_c + \text{const.} \tag{5}$$

Here, S_c is the configurational entropy, i.e. the difference between the entropy of the liquid at the temperature T and that of glass at the ideal glass transition temperature $T_0 \cdot S_c$ would vanish at $T = T_0$ since there would be only one available configuration. The "critical · size" of the region and the potential barrier hindering the rearrangements are involved in the value of the constant B_G. A consequence of this theory would be that the slope of the Arrhenius plots of the viscosity must be proportional to the reciprocal of the configuration-entropy, if this last quantity is kept constant [4, 29]. But S_c changes with temperature. Adam and Gibbs, remarking that the specific heat of glass forming liquids is approximately independent of temperature and that $S_c = 0$ at $T = T_0$, have obtained the following relation for the S_c variations:

$$S_c = \Delta C_p \ln (T/T_0)\,, \tag{6}$$

ΔC_p being the difference in specific heat between the liquid and the glass at the transition-temperature [4, 18]. Since we have always $T/T_0 > \frac{1}{2}$, the logarithm in (6) may be expanded:

$$\ln (T/T_0) \sim 1 - (T_0/T)$$

and S_c becomes equal to

$$S_c = \Delta C_p (T - T_0)/T\,. \tag{7}$$

From (5) one deduces

$$\ln \eta = \text{cte} + \frac{B_G}{\Delta C_p (T - T_0)}\,. \tag{8}$$

If the Fulcher relation takes its origin in the Adam-Gibbs theory, the constant B_F of (2) must be equal to $B_G/\Delta C_p$.

In order to precise the behavior of $\ln (\eta/\eta_s)$ against T_g/T, the $(\mathrm{d} \ln (\eta/\eta_s)/\mathrm{d}\,(T_g/T))$ function has been calculated for the mean curve of the Figure 7. This derivative has been plotted as a function of $(1 - T_g/T)^{-1}$. The result is a straight line, as is displayed in Figure 8. Indeed we have

$$\mathrm{d} \ln (\eta/\eta_s)/\mathrm{d}\,(T_g/T) = \alpha T_g/(T - T_g) \tag{9}$$

with $\alpha = 10$, independent of concentration, whereas the "apparent" activation energy at the equilibrium configuration is given by

$$\mathrm{d} \ln (\eta/\eta_s)/\mathrm{d}T^{-1} = B_F (T/(T - T_g))^2 - \beta\,, \tag{10}$$

β being the activation energy of the pure solvent. B_F depends on the concentration range [1: $x < 0.16$; 2: $0.16 < x < 0.30$; 3: $0.30 < x < 0.42$]. Relation (10) may be compared to the expression of the "apparent" activation energy calculated at constant entropy by Macedo and Napolitano for B_2O_3 [29] who reach similar conclusions.

The integration of (9) gives

$$\ln \left(\frac{\eta}{\eta_s}\right) = 10 \left[\frac{T - T_g}{T} - \ln \frac{T - T_g}{T}\right] + \text{const}\,. \tag{11}$$

The constant in (11), evaluated from the experimental data, is equal to +10. Thus

$$\ln \frac{\eta}{\eta_s} = 10 \left[1 + \frac{T - T_g}{T} - \ln \frac{T - T_g}{T}\right]. \tag{12}$$

This relation is different from that of Adam-Gibbs since the variables are the reduced temperature and viscosity. It appears as being applicable for *all the mixtures* in the *whole studied temperature range*. Is it still verified at lower temperatures, as $T \rightarrow T_g$, in which case (12) would give

$$\ln (\eta/\eta_s) \sim -10 \ln ((T - T_g)/T_g)?$$

The answer is difficult since these viscosity-measurements have been carried out quite far from the glass transition temperature; it is not impossible that, as one is getting near the vitreous state, the temperature-viscosity behaviour will be different. Indeed, it is well known that the semi-empirical relation of Fulcher is usually followed by glass-forming-liquids in a shear-viscosity range such that $\eta \lesssim 10^3$ Pa · s and that, for higher viscosities, the behavior often returns to a quasi Arrhenius type [9, 24, 29, 30], i.e., the viscosity increases more slowly as the temperature decreases. Unfortunately, our technique does not allow to measure the shear viscosity very near the glass transition temperature.

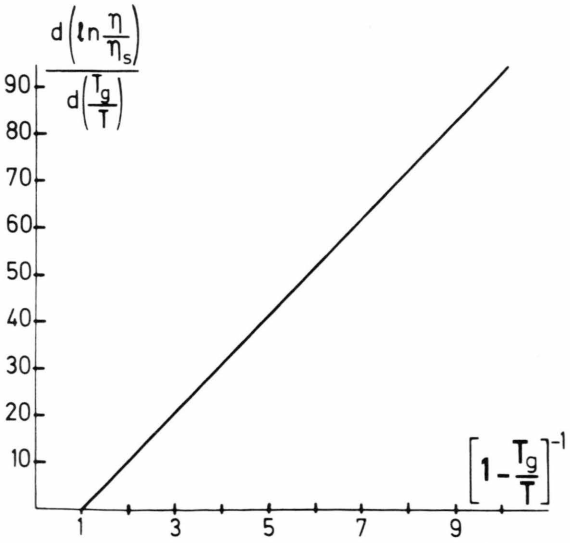

Fig. 8. Plot of $\mathrm{d} \ln (\eta/\eta_s)/\mathrm{d}\,(T_g/T)$ vs. $(1 - T_g/T)^{-1}$.

Nevertheless, the dielectric relaxation times of some polyalcohols have been measured recently in a temperature range very near to T_g [31]. The authors find that the τ_D's obey the relation

$$\ln\left(\frac{\tau_D}{\tau_A}\right) \cong 12.7\,\frac{T_0}{(T-T_0)}\,,$$

whereas the "activation energy for the isoentropic states", $\mathrm{d}\ln(\eta/\eta_s)/\mathrm{d}(T_g/T) = ``E''_{\text{iso}}$, evaluated for our system is such that $``E''_{\text{iso}} = 10\,T_g/(T-T_g)$, a very similar expression. As the shear relaxation time τ_{sh} is nearly equal to the dielectric relaxation time τ_D [31], the comparison between both results gives

$$``E''_{\text{iso}} \cong \ln(\tau_D/\tau_A) \cong \ln(\tau_{\text{sh}}/\tau_B)\,.$$

This would mean that the usual relation between τ_{shear} and η_{shear} is no more valid when $T \rightarrow T_g$.

Some information about the structure of the system can be obtained by observing the composition dependence of the glass-transition temperature [20, 32]. A comprehensive study of Lesikar [19] on numerous mixtures of liquids has shown that this composition dependence parallels qualitatively that of the excess enthalpy of mixing and that $\mathrm{d}T_g/\mathrm{d}x$ is a significant quantity. For example, a linear variation of T_g would suggest some simple form of mixing values [20, 33].

In our case, it is obvious that the glassy state properties of the solutions are principally due to solution-properties rather than to that of pure solvent or pure salt since neither of them seems to give easily a vitreous state. Thus, it appears difficult here to predict accurate values of T_g from relations such as that obtained by Gordon et al. [20] for simple binary solutions since they involve the glass-temperature-transitions of each pure component.

Nevertheless, thermodynamic considerations, derived from the approach made by Angell et al. [33, 34] may bring some help. Indeed these authors consider a thermodynamic cycle "through" the glass transition vs. concentration line, one half of the cycle being in the liquid and one half in the glass. They obtain a simple relation

$$\frac{\mathrm{d}T_g}{\mathrm{d}x} = -\frac{\Delta\left(\dfrac{\partial H}{\partial x}\right)_T}{\Delta C_p} \quad \text{for the enthalpy cycle}$$

and

$$\frac{\mathrm{d}T_g}{\mathrm{d}x} = -\,T_g\frac{\Delta\left(\dfrac{\partial S}{\partial x}\right)_T}{\Delta C_p} \quad \text{for the entropy cycle,}$$

where the Δ quantities represent the difference in solute partial molar enthalpy (entropy) variations between the liquid and the glass.

For our system, we have precised the T_g vs. concentration curve by plotting the derivative $\mathrm{d}T_g/\mathrm{d}x$ as a function of x, as shown on Figure 9. This function presents a big maximum for $x = 0.21$ and a change in the slope for $x = 0.3$. The Δ differences can be calculated for the concentrated sample of known ΔC_p, $x = 0.42$. As we observe an hysteresis in temperature for the transition, the enthalpy term does not change, since $\mathrm{d}T_g/\mathrm{d}x$ looks alike for cooling or heating runs, but the entropy cycle changes. Thus, we have

$$\Delta C_p = 77.66\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}},\quad \mathrm{d}T_g/\mathrm{d}x = 125$$

and

$$\Delta\,(\partial H/\partial x)_{T=T_g} = -\,9707\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}\,.$$

For the entropy term

$$\text{cooling}\quad T_g\!\downarrow\, = 208\ \mathrm{K}\,,$$
$$\Delta\,(\partial S/\partial x)_{T_g} = -\,47.12\ \mathrm{J\cdot mol^{-1}}\ \text{of}\ \mathrm{ZnBr_2}\,,$$
$$\text{heating}\quad T_g\!\uparrow\, = 218\ \mathrm{K}\,,$$
$$\Delta\,(\partial S/\partial x)_{T_g} = -\,44.53\ \mathrm{J\cdot mol^{-1}}\ \text{of}\ \mathrm{ZnBr_2}\,.$$

The change in the $\mathrm{d}T_g/\mathrm{d}x$ variations for $x = 0.30$ (Fig. 9) may be connected to a change in the mixing properties. Indeed, we can assume from previous experiments [13, 16] that the dilute solutions of this system would be analogous to suspensions of small aggregates of $\mathrm{ZnBr_2}$. These small "grains" would

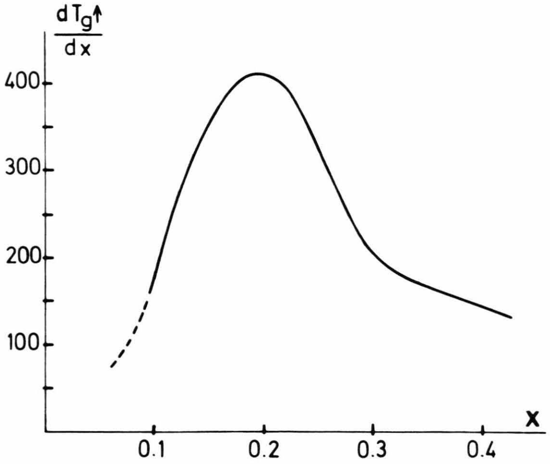

Fig. 9. Plot of $\mathrm{d}T_g\!\uparrow/\mathrm{d}x$ vs. x.

have a tendency to associate and to form chains at high concentration. Such a "granular" structure has been observed recently by electron microscope technics: indeed small ionic clusters are observed; their mean sizes are nearly 10 Å and they have a tendency to form chains [35]. Also we must note that a very compact structure of four or five tetrahedral cells $[ZnBr_4]^=$ joined by the faces can actually give an average grain-size of 10 Å [12, 13, 16].

This analysis of our results must be compared to the works of B. Wunderlich [36] who found that glasses can be looked at as being built of "beads" which would be the elementary units arising in the glass transition phenomenon. Though the "bead" concept is very ambiguous, it has been used recently for inorganic glasses such as $ZnCl_2$ or B_2O_3 [37].

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[1] C. A. Angell and J. C. Tucker, J. Phys. Chem. **78,** 278 (1974).
[2] C. A. Angell and J. C. Tucker, J. Phys. Chem. **84,** 268 (1980).
[3] C. A. Angell, J. Phys. Chem. **70,** 3988 (1966).
[4] C. A. Angell, J. Phys. Chem. **70,** 2793 (1966).
[5] C. A. Angell and R. D. Bressel, J. Phys. Chem. **76,** 3245 (1972).
[6] F. S. Howell, R. A. Bose, P. B. Macedo, and C. T. Moynihan, J. Phys. Chem. **78,** 639 (1974).
[7] J. D. Pandey and A. D. M. David, J. Phys. Chem. **85,** 3151 (1981).
[8] R. Weiler, S. Blaser, and P. B. Macedo, J. Phys. Chem. **73,** 4147 (1969).
[9] H. Tweer, J. H. Simmons, and P. B. Macedo, J. Chem. Phys. **54,** 1952 (1971).
[10] J. H. Simmons and P. B. Macedo, J. Chem. Phys. **54,** 1325 (1971).
[11] A. J. Easteal and C. A. Angell, J. Phys. Chem. **74,** 3987 (1970).
[12] A. Sadoc, A. Fontaine, P. Lagarde, and D. Raoux, J. Amer. Chem. Soc. **103,** 6287 (1981).
[13] M. Nicolas and R. Reich, Nouv. J. Chimie **6** (10), 467 (1982).
[14] J. L. Glimois, Thesis, Nantes 1973.
[15] M. Nicolas and R. Reich, J. Phys. Chem. **85,** 2843 (1981).
[16] M. Nicolas and E. Dartyge, J. Amer. Chem. Soc. **104,** 7403 (1982).
[17] G. S. Fulcher, J. Amer. Ceram. Soc. **8,** 339 (1925).
[18] G. Adam and J. H. Gibbs, J. Chem. Phys. **43,** 139 (1965).
[19] A. V. Lesikar, J. Chem. Physics **66,** 4263 (1977).
[20] J. M. Gordon, G. B. Rouse, J. H. Gibbs, and W. M. Risen, J. Chem. Phys. **66** (11), 4971 (1977).
[21] G. Colin and R. Reich, private communication.
[22] C. A. Angell, J. Chem. Phys. **46,** 4673 (1967).
[23] For the differenciation, we have used a standard I.M.S.L. subroutine ICSVKU which fits the experimental data by a least square approximation (cubic spline – variable knots) and then gives the derivative taken on the smoothed value. The fitting is made within 2%.
[24] a) C. T. Moynihan, A. J. Easteal, and J. Wilder, J. Phys. Chem. **78,** 2673 (1974).
b) C. A. Angell, R. C. Stell, and W. Sichina, J. Phys. Chem. **86,** 1540 (1982).
[25] W. T. Laughlin and D. R. Uhlmann, J. Phys. Chem. **76,** 2317 (1972).
[26] A. Einstein, Ann. Physik **17,** 459 (1905).
[27] M. Mooney, J. Colloid Sci. **6,** 162 (1951).
[28] M. H. Cohen and D. Turnbull, J. Chem. Phys. **31,** 1164 (1959).
[29] P. B. Macedo and A. Napolitano, J. Chem. Phys. **49,** 1887 (1968).
[30] A. Campbell Ling and J. E. Willard, J. Phys. Chem. **72,** 1918 (1968).
[31] a) C. A. Angell and Smith, J. Phys. Chem. **86,** 3845 (1982).
b) R. Meister, C. J. Marhoeffer, R. Sciamanda, L. Cotter, and J. Litovitz, J. Appl. Physics **31,** (5), 854 (1960).
[32] A. V. Lesikar, J. Chem. Phys. **68** (7), 3323 (1978).
[33] C. A. Angell, J. M. Sare, and E. J. Sare, J. Phys. Chem. **82,** 2622 (1978).
[34] C. A. Angell and E. J. Sare, J. Chem. Phys. **52,** 1058 (1970).
[35] M. Nicolas and C. Colliex, to be published.
[36] a) B. Wunderlich, J. Phys. Chem. **64,** 1052 (1960).
b) M. Goldstein, J. Chem. Phys. **39,** 3369 (1963).
[37] V. P. Privalko, J. Phys. Chem. **84,** 3307 (1980).