

THEORIES OF VISCOSITY APPLIED TO IONIC LIQUIDS

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I. INTRODUCTION

Most theories of viscosity have been applied to systems consisting of covalent molecules and to molten metals (see, in general, references 1, 6, 16, 17, 25, 27, 35, 36, 45), whereas systems composed predominantly of ions have received only occasional attention (3, 9, 24, 30, 38, 39, 46). Ionic liquids are important from a theoretical point of view, since the forces operating in such systems, being mainly of Coulomb character, are better understood than those between covalent molecules. Moreover, ionic liquids or molten salts represent simplified models for the slags which concern the metallurgist, although there will be considerable differences in behavior between systems containing simple anions, as in molten alkali halides, and those involving large complex anions, as in silicate melts.

The neglect of ionic liquids in discussions on the liquid state in general is partly due to the dearth of experimental data, but this has been supplemented by recent work on the electrical conductivity (9, 29), molar volume (11), viscosity (8, 29), and surface tension (13). A number of results obtained from these investigations have a direct bearing on, and may serve to illustrate, theoretical concepts of viscosity.

The term "ionic liquid" requires some qualification. There is probably no liquid which is completely electrovalent in character. Pauling (40) assigns a small degree of covalency even to solid sodium chloride, and the amount of covalency in liquids such as molten silver chloride, lead chloride, and cadmium chloride is probably greater, although the degree of covalency in the case of silver halides has probably been overestimated by some authors. The relatively high electrical conductivity (29), high surface tension (13), small molar volume (11), and small expansion coefficient (11) in the molten state suggest a predominantly ionic character.

II. RELATIONS BETWEEN THE VISCOSITY OF LIQUIDS AND THEIR
 SPECIFIC VOLUME

A. One-component systems

One of the most notable features of the viscosity of liquids is the high temperature coefficient of this property; nevertheless Batchinski (6) considered that the proper independent variable to which the viscosity (η) of a liquid should be related is not the temperature but the specific volume (v). He showed that experimental data are frequently satisfied by the expression

$$\eta = \frac{B}{v - b}$$

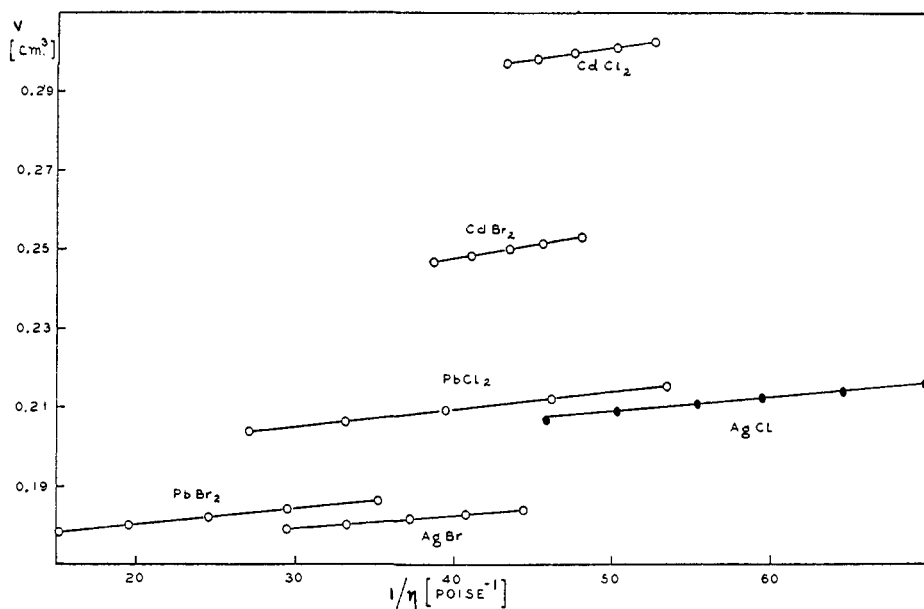


FIG. 1. Variation of fluidity with specific volume for several molten salts

where B and b are constants, the latter bearing some analogy to the covolume of the van der Waals equation.

Batchinski tested this equation for about eighty organic liquids and found that, except for "associated" liquids, it represents experimental data very well over a temperature range of about 100°C. The test is carried out by plotting fluidity, $\phi = 1/\eta$, against the specific volume, a straight line representing the experimental results if equation 1 is satisfied. Figure 1 shows a number of such curves for molten salts (8, 11, 29) and indicates that equation 1 satisfies the experimental data on the viscosity and the specific volume of molten salts to within 1 per cent over ranges of temperature of up to 200°C.

Later Macleod (35) used a physical model to arrive at essentially the same conclusion as Batchinski. He assumed that for molecular liquids (the only

class considered) the viscosity should be a function of the free space within the liquid. Since decrease in the free space in a liquid indicates an increase in the cohesive forces between the molecules, such a change will lead to an increase in viscosity. Macleod assumes that the viscosity of a liquid depends on a factor characteristic of the liquid but independent of temperature for normal liquids, and on a factor involving the free space in the liquid.

Macleod's expression relating viscosity and free space according to these principles is

$$\eta x^A = B \quad (2)$$

where x is the free space per unit volume and A and B are constants. We may, however, write the free space in the liquid as the specific volume minus a constant, i.e., $(v - b')$, and obtain:

$$\eta = B/x^A = B/(v - b')^A \quad (3)$$

As A in Macleod's equation is close to unity for most normal molecular liquids, Batchinski's equation (equation 1) satisfies experimental results over short ranges

TABLE 1
Comparison of b and b' with specific volume of solid at the melting point

	b'	b	v (SOLID AT MELTING POINT)
Ethyl iodide*.....	0.437	0.457	0.416
Acetone*.....	1.046	1.070	1.032

* Data by Batchinski (6) and Macleod (35).

of temperature. The constants A and b' in equation 3 can be determined only by a method of approximations.

Batchinski assumed that the viscosity of a liquid becomes infinite at the freezing point and hence reasoned that the constant in equation 1 should be equal to the specific volume of the solid at this temperature. However, he found that, in cases where data on the specific volume of the solid at the melting point were available, the value of b determined from equation 1 was higher than the experimentally determined specific volume of the solid at the melting point. This may be partly explained by Batchinski's original postulate that the viscosity of a liquid depends only upon its specific volume. The fact that the exponent A in the Macleod equation (equation 2) is not exactly unity suggests that this assumption is not strictly valid. If values of b' rather than of b are calculated (i.e., making allowance for the value of A in equation 3), there is a closer correspondence with the specific volume of the solid at the melting point (table 1).

Since measurements over a long temperature range are necessary to determine A and b' with any accuracy, the agreement between b'_{Macleod} and $v_{\text{m.p.}}$ is quite good. Unfortunately, data on the volume of the solid inorganic salts at the melting point are not available.

Although both Batchinski and Macleod have considered in some detail the magnitude and properties of the free space in liquids, the other constant (B in equations 1 and 2) has received little attention. This constant represents the variation of fluidity with volume at constant pressure:

$$\left(\frac{dv}{d\phi}\right)_p = B$$

Both authors attempted to related B to the molecular weight, Macleod attributing any variation in the linear proportionality to association.

Since the fluidity of a liquid is likely to depend on the free space and also on the size of the unit of flow, it would seem preferable to relate B to the latter quantity rather than to the molecular weight. If the free space of two liquids increases by the same amount on increase of temperature, we should expect the liquid with the smaller units of flow to show a greater increase in fluidity than the liquid with the larger units of flow. Provided little change occurs in the dimensions of the molecules themselves on increase of temperature, the same relation is likely to hold for the specific volume, i.e., the increase of fluidity with specific volume is likely to be greatest for those liquids containing the smallest units of flow:

$$\left(\frac{d\phi}{dv}\right)_p \propto \frac{1}{\text{size of flow unit}}$$

or

$$\left(\frac{dv}{d\phi}\right)_p = B \propto \text{size of flow unit}$$

Thus B should be proportional to the size of the flow unit rather than to the molecular weight. These last two quantities are not necessarily proportional, since a very symmetrical molecule may have a smaller effective geometric size than an unsymmetrical molecule of lower molecular weight

Table 2 shows values taken from Batchinski's paper (6), illustrating the variation of B as we ascend an homologous series; in such a series both the molecular weight and the size of the flow unit will increase as additional carbon atoms are added. Only for each separate series does B increase with the molecular weight. The fact that B for methyl iodide is less than for methyl sulfide, for example, indicates that it is not proportional to the molecular weight. On the other hand, the effective size of the methyl sulfide molecule $[(\text{CH}_3)_2\text{S}]$ is likely to be greater than that of the methyl iodide molecule (CH_3I) , which would be consistent with the smaller value of B shown by the latter compound.

Section B of table 2 shows values of B for several molten salts. Although there is little difference between the values of B as we pass from chloride to bromide of one cation, owing probably to the small difference in ionic radii, the value of B changes by a greater amount as we pass from potassium nitrate to sodium nitrate, where the difference in the radii of the unlike ions is much greater. Moreover, it appears that nitrates have greater values for B than halides, owing to the large difference in effective size between the halide and the nitrate ions.

It is noteworthy that the value of B for cadmium chloride is much greater than for lead chloride, although the radius of Cd^{++} is smaller than that of Pb^{++} . This is consistent with the assumption, supported by measurements of electrical conductivity and surface tension (12), that cadmium chloride contains auto-complexes in the liquid state.

TABLE 2
 $B \times 10^6$ for various liquids
Part A

<i>n</i> -Pentane.....	612	Methyl sulfide.....	544
<i>n</i> -Hexane.....	647	Ethyl sulfide.....	631
<i>n</i> -Heptane.....	654	Acetone.....	491
<i>n</i> -Octane.....	665	Methyl ethyl ketone.....	493
		Diethyl ketone.....	506
		Methyl <i>n</i> -propyl ketone.....	507
Ethyl bromide.....	399	Diethyl ether.....	571
<i>n</i> -Propyl bromide.....	445	Di- <i>n</i> -propyl ether.....	609
Methyl iodide.....	284	Methyl formate.....	543
Ethyl iodide.....	348	Ethyl formate.....	567
<i>n</i> -Propyl iodide.....	394	<i>n</i> -Propyl formate.....	576
Part B*			
Lead chloride.....	380	Cadmium chloride.....	620
Lead bromide.....	390	Cadmium bromide.....	645
Silver chloride.....	350	Potassium nitrate.....	960
Silver bromide.....	380	Sodium nitrate.....	880

* Values for the lead, silver, and cadmium halides are calculated from data by Bloom, Harrap, and Heymann (8) and by Harrap and Heymann (29), and those for the alkali nitrates from data by Dantuma (15).

B. Two-component systems

Macleod (36) has also discussed mixture laws for viscosity. According to Macleod, if we assume that a change in the volume of a liquid results in an n -fold change in its viscosity, i.e., if the viscosity is primarily determined by the volume, then if the molar volume isotherms of a two-component liquid system show deviations from additivity on mixing, the viscosity isotherms should deviate from additivity by an n -fold quantity in the opposite direction. This is likely to be valid for nonpolar or weakly polar organic liquids. If a contraction occurs on mixing two such liquids, it will be the result mainly of an increase in the closeness of packing. That is, a change in volume on mixing probably indicates a corresponding change in free volume.

In the case of liquids which are strongly polar and capable of hydrogen bond formation, the position is made complex because of the possibility of the forma-

tion of more or less permanent association complexes, i.e., a change in the size of the units of flow. With ionic liquids there may be, in addition, a change in the degree of covalency on mixing, an increase in covalency leading to an *increase* in the specific volume, and hence a change in specific volume on mixing may not be due solely to a packing effect. Anomalies of this type are illustrated most strikingly by the system lead chloride-cadmium chloride. The molar volume isotherms for this system show negative deviations from additivity (11), yet the viscosity isotherms also show negative deviations (29). Because of these anomalies we shall consider only those molten salt systems whose molar volume isotherms are additive.

In formulating an expression for the viscosity of a mixture in terms of the viscosities of the pure components Macleod assumes that, after mixing, the viscosity of each component undergoes a change dependent on the change in its free space on mixing and its molar concentration. Assuming also that the exponent A in equation 2 is equal to unity, Macleod expresses these ideas in the form

$$\eta = \eta_1 N_1 \frac{x_1}{x} + \eta_2 N_2 \frac{x_2}{x} \quad (4)$$

where η_1 and η_2 are the viscosities of components 1 and 2, N_1 and N_2 their molar fractions, x_1 and x_2 their free spaces, and η and x the viscosity and free space of the mixture. Provided the molar volumes are additive, Macleod gives the last-named quantity as

$$x = x_1 V_1 + x_2 V_2 \quad (5)$$

where V_1 and V_2 are the volume fractions of each component.

Equation 4 indicates that the viscosity of a mixture can be calculated from a knowledge of the free spaces and viscosities of the pure components. It was found to satisfy experimental data on organic liquid mixtures to a high degree of accuracy, provided no change in volume occurred on mixing.

Equation 4 has been tested for a number of molten salt systems whose molar volume isotherms are additive (table 3). The values of x were calculated from equation 5, using for x_1 and x_2 the corresponding values of $(v - b)/v$ for the pure components; the latter were computed from the data shown in figure 1, assuming the validity of Batchinski's equation.

Table 3 shows that equation 4 holds well for molten salt systems whose molar volume isotherms are additive.

C. Note on electrical conductivity and volume

It is interesting to apply the arguments of Batchinski and Macleod to electrical conductivity. Bloom and Heymann (9) have shown that the mechanisms of ionic migration and viscous flow in molten salts are very different. Viscous flow always involves a configurational change of both cations and anions, whilst the conductivity is usually mainly determined by the migration of one ionic species, the cations in the case of alkali and silver halides and the anions in the

case of bivalent metal chlorides. In the case of the alkali halides, this mechanism for ionic migration is demonstrated by the fact that the equivalent conductivity decreases markedly as we follow the series lithium chloride, sodium chloride, potassium chloride, rubidium chloride, i.e., on change of cation for the same anion, whilst there is little variation on change of anion for the same cation, *viz.*, potassium chloride, potassium bromide, potassium iodide.

TABLE 3
Viscosity isotherms calculated from equation 4
CdCl₂-CdBr₂ (600°C.)

MOLE FRACTION OF CdBr ₂	VOLUME FRACTION* OF CdBr ₂	α (CALCULATED)	η (CALCULATED)	η^\dagger (OBSERVED)	DEVIATION IN PER CENT
0.000	0.000	0.1191		0.0232	
0.252	0.294	0.1105	0.0239	0.0239	0
0.445	0.488	0.1048	0.0244	0.0242	1
0.725	0.768	0.0967	0.0251	0.0250	0.5
1.000	1.000	0.0899		0.0258	

PbCl₂-PbBr₂ (510°C.)

MOLE FRACTION OF PbCl ₂	VOLUME FRACTION* OF PbCl ₂	α (CALCULATED)	η (CALCULATED)	η^\dagger (OBSERVED)	DEVIATION IN PER CENT
0.000	0.000	0.0609		0.0354	
0.247	0.217	0.0591	0.0372	0.0372	0
0.436	0.404	0.0576	0.0385	0.0381	1
0.769	0.738	0.0549	0.0413	0.0420	2
1.000	1.000	0.0527		0.0495	

AgCl-AgBr (500°C.)

MOLE FRACTION OF AgCl	VOLUME FRACTION* OF AgCl	α (CALCULATED)	η (CALCULATED)	η^\dagger (OBSERVED)	DEVIATION IN PER CENT
0.000	0.000	0.0733		0.0284	
0.200	0.180	0.0753	0.0267	0.0266	0.5
0.400	0.369	0.0775	0.0251	0.0250	0.5
0.599	0.567	0.0798	0.0236	0.0234	1
0.732	0.705	0.0814	0.0222	0.0226	2
1.000	1.000	0.0849		0.0207	

* Calculated from density data by Boardman, Dorman, and Heymann (11).

† Data by Bloom, Harrap, and Heymann (8) and by Harrap and Heymann (29).

Boardman (10) has calculated on geometric grounds the size of the holes through which a cation in an alkali halide melt must pass during migration and has found that the conductivity of the molten alkali halides at corresponding temperatures (10 per cent above the melting point in degrees absolute) is roughly proportional to the size of the interstices between the ions. The treatment assumes that the ions are not deformed and that the melts are pure cation conductors. When these conditions are not fulfilled, as in the lead and cadmium halides, calculations are much more difficult.

If the general principles underlying this treatment are correct, it may be assumed that the conductivity of such melts depends upon the free volume, and one might therefore expect the validity of an equation expressing proportionality between specific conductivity (κ) and free volume ($v - b''$), similar to the viscosity equation of Batchinski, *viz.*,

$$\kappa = a (v - b'') \quad (6)$$

where a is a constant. The free volume ($v - b''$) of equation 6 cannot be expected to be the same as that given by Batchinski's equation, since the unit of viscous flow is likely to be the ion pair, whereas the unit of ionic migration is the single ion, a much smaller unit.

Figure 2, showing plots of κ against v for several molten salts, reveals that equation 6 satisfies experimental data very well over temperature ranges of approximately 100°C., but considerable deviations occur over wider ranges of temperature. This suggests that the free volume is not the only factor determining conductivity.

III. RELATIONS BETWEEN VISCOSITY AND TEMPERATURE

A. Activation energy and configurational change

Exponential relations between viscosity and temperature of the type

$$\eta = A'e^{B'/RT} \quad (7)$$

were first put forward by de Guzman (16) and Dunn (17); A' and B' are constants. A more detailed theory, leading to a similar exponential relation, is due to Andrade (1), who suggested that transfer of momentum in liquids takes place by means of molecules, which are in adjacent layers, and which possess a certain critical energy, coming into contact for a finite time. By utilizing the Boltzmann distribution equation for the relation between temperature and the fraction of molecules possessing the necessary potential energy to effect this temporary union, Andrade also deduced an equation of the form:

$$\eta = A'e^{B'/RT}$$

Andrade's somewhat artificial model was used by Panchenkov (38), who has obtained for the viscosity of a liquid a remarkable equation which contains no empirical constants. Using this equation, Panchenkov has been able to calculate the viscosities of molecular liquids, including associated liquids, with an accuracy of about 20 per cent. The agreement between calculated and experimental (4) values for the viscosity of molten sodium chloride is less satisfactory. However, a knowledge of critical volumes and pressures is necessary to apply the Panchenkov equation; since values for these quantities are either unknown or of very doubtful accuracy for molten salts, Panchenkov's equation cannot be usefully applied to this class of liquids.

An attempt is also being made by Telang (44) to derive an equation which contains no arbitrary constants and which relates the viscosity of a liquid to

temperature. The treatment uses the theory of absolute reaction rates (cf. Section III, B) but is not yet sufficiently developed, nor are the requisite data available to apply it to molten salts.

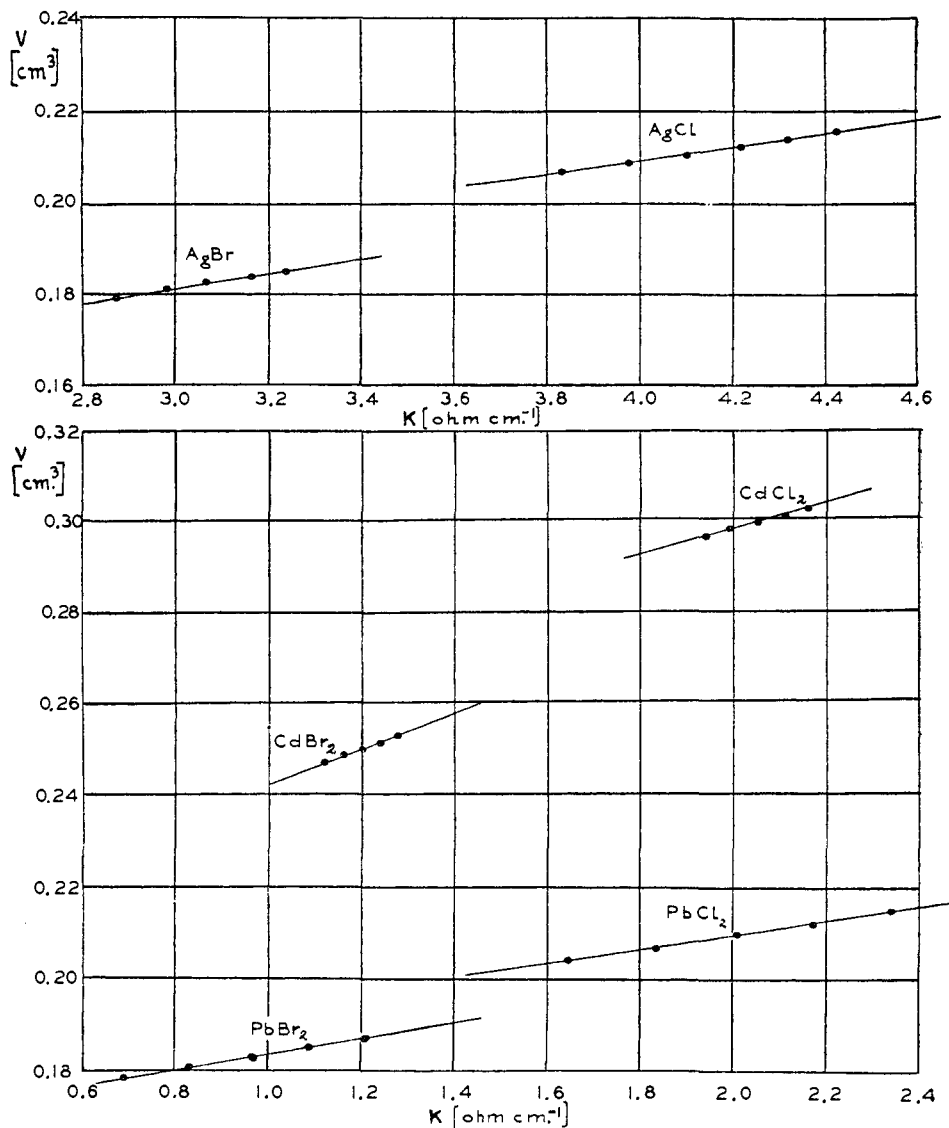


FIG. 2. Variation of specific conductivity with specific volume for several molten salts

Numerous other equations relating viscosity and temperature have been proposed on empirical or semiempirical grounds (reviewed by Srinivasan and Prasad (43a)). Recently the viscosity of a liquid has been related to its reduced temperature in equations of Jones and Bowden (31a) and Thomas (44a). How-

ever, in the absence of reliable data on the critical temperatures of molten salts, these equations cannot be applied to this class of liquid.

B. Theories of Frenkel and Eyring and their application

One of the earlier and most fully developed of the specific models for the process of viscous flow and for the liquid state in general is that of Frenkel (21, 22, 23). This author emphasizes the similarity in properties between liquid and solid rather than between liquid and gas, especially at temperatures well below the critical temperature, mainly on the following grounds: The increase in volume on melting is relatively small (order of 10 per cent) when compared to that occurring on vaporization; the latent heat of fusion is of the order of $\frac{1}{3}$ to $\frac{1}{10}$ the latent heat of evaporation at the normal boiling point; the specific heat of solids is only slightly changed on fusion; if the effect of the application of a shear force is considered, it can be shown that there is no fundamental difference in the effects on solids and liquids. According to Frenkel, fusion probably consists of a discontinuous loss of distant (long-range) order characteristic of a crystalline structure, the local (short-range) order being retained. Thus, on this basis, the change in structure on melting is probably less drastic than has often been pictured.

Frenkel explains the sharp increase in fluidity on fusion in broad outline by assuming that the fluidity of a body, that is, its complete yielding to shearing stress, implies the possibility of the individual displacement of its molecules, which in turn requires a certain amount of free volume within the liquid. In crystalline bodies the amount of free volume is relatively small, being realized in the form of a number of vacant sites and a general expansion of the lattice. The sudden 10 per cent increase in volume on fusion is sufficient to provide room for individual displacements of molecules from one equilibrium position to another, the two equilibrium positions being separated by a potential barrier.

Frenkel calculates the speed of self-diffusion in such a liquid model. Developing this further, he calculates the effect of the application of an external force to the liquid system and obtains an exponential expression relating viscosity and temperature similar to that mentioned above (equation 7). However, although his equation represents the temperature coefficient of viscosity very well, the value of the preexponential factor (A' in equation 7), as calculated from his final equation, is approximately 100- to 1000-fold that determined from experimental data. Moreover, the preexponential factor contains a temperature term and should therefore vary with temperature. Frenkel attempts to explain this discrepancy by assuming that the activation energy varies inversely with temperature. Data on normal organic liquids as well as on molten salts do not, however, reveal a variation of the activation energy with temperature sufficient to satisfy Frenkel's equation. It therefore appears that Frenkel's theory is too simplified.

Frenkel also considers the nature of the free space in the liquid. In crystalline bodies we are dealing with two kinds of holes constituting the free space. Firstly, there are the interstices between the constituents of the crystal lattice; secondly,

the vacant sites in the lattice itself. In the liquid state any distinction between the two types of holes becomes meaningless. Frenkel considers as holes in the liquid any gap between the spheres of influence of the constituent molecules, the holes having no definite size or shape. It is interesting that this concept coincides with that of Macleod, who assumed that the free space effective in viscous flow is equal to the total volume minus the volume of the spheres of influence of the molecules.

In the case of molten salts it is difficult to decide whether the free space consists of gaps between individual ions, or between ion pairs considered as a whole. However, since the unit of flow is likely to be the ion pair and since ionic liquids satisfy equation 1 relating viscosity and free volume, it seems likely that the amount of free space controlling viscous flow in molten salts is that between ion pairs rather than between single ions.

It is interesting to compare the basic ideas and development of Frenkel's model with those of Eyring and coworkers (18, 19, 20, 25, 34). Although Eyring builds his model of a liquid on the basis of its similarity to the solid state, he also likens it to the gas phase and uses the methods of statistical mechanics as applied to this phase, chiefly the theory of absolute reaction rates.

Whereas Frenkel treats his model in terms of oscillations of molecules about their equilibrium positions, Eyring's school relates the liquid to the gas phase by the analogy that, just as a gas is assumed to consist of molecules moving in an empty space, so a liquid may be regarded as composed of holes moving about in matter. The free volume is regarded as being distributed in the liquid as small discrete cavities.

According to Roseveare, Powell, and Eyring (43), a liquid is best considered as a solid to which a large number of equilibrium positions or holes have been added. These workers consider that the expansion of a solid on melting, and also the expansion of a liquid on increase of temperature, arises almost entirely from the introduction of new equilibrium positions into the solid-state lattice. However, this seems to us to imply rather too strongly that order in the liquid state is of a long-range nature. This is not borne out by x-ray analysis. According to Prins and Fonteyne (42), although there may be short-range order in the liquid, it probably does not extend at the most beyond a few tens of molecular diameters even if the molecules are polar.

Viscous flow, according to Eyring, is assumed to take place by the activated jumping of an aggregate composed of one or more molecules from an initial normal configuration to a second normal position, the two being separated by an intermediate activated state.

In the absence of an external shearing force on the liquid, it is reasonable to assume that the potential barriers involved are symmetrical. However, if an external shearing force is now applied to the liquid, the height of the barrier with respect to molecules on the side from which the force originates will be effectively lowered because of the energy they gain from the applied force, whilst the height of the barrier on the other side will be effectively increased by an equal amount. The symmetry of the molecules passing backwards and forwards over

the barrier will therefore be destroyed, more molecules passing in one direction than the other, and hence viscous flow will take place.

After making certain assumptions as to the partition function in the liquid state, Eyring's final equation is

$$\eta = 1.09 \times 10^{-3} \cdot \frac{M^{1/2} \cdot T^{3/2}}{v^{2/3} \Delta E_{\text{vap}}} \cdot e^{\Delta E_{\text{vis}}/RT} \quad (8)$$

where M is the molecular weight, v is the molar volume, and ΔE_{vap} ($= \Delta H_{\text{vap}} - RT$) is the energy of vaporization. It would appear at first sight that the pre-exponential term in equation 8 is temperature dependent. However, Ewell (18) has shown that this is not the case and that the preexponential term is sensibly independent of temperature.

TABLE 4
Values of $\Delta E_{\text{vap}}/\Delta E_{\text{vis}} = n$ for molten salts

SALT	ΔE_{vis}	ΔE_{vap}^*	n
	kcal./mole	kcal./mole	
NaCl.....	9.1†	37.7	4.2
NaBr.....	8.0†	34.5	4.3
KCl.....	7.4†	35.5	4.8
KBr.....	8.0†	33.5	4.2
PbCl ₂	6.7‡	32.5	4.9
PbBr ₂	6.2‡	30.2	4.8
CdCl ₂	4.0‡	31.8	7.9
AgCl.....	2.9‡	44.7	15.3

* Data by Kelley (32).

† Data by Ward (46).

‡ Data by Harrap and Heymann (29).

Eyring (25) has also postulated that, during the activated transfer of a molecule from one equilibrium position to another, that is, while viscous flow is taking place, the activated state of the molecule requires a volume larger than that required by the initial state. Since this additional volume necessitates the creation of a new hole in the liquid (not necessarily the full size of the molecule), then, according to Eyring, the energy of activation for viscous flow, ΔE_{vis} , which represents the work done in creating this hole, should be some fraction of the energy of vaporization, ΔE_{vap} , the work necessary to create a hole of molecular size in the liquid.

From data on a large number of molecular liquids, Eyring found that for nonpolar molecules of spherical symmetry the ratio $\Delta E_{\text{vap}}/\Delta E_{\text{vis}} = n$ is in the neighborhood of 3, whereas for polar molecules n is nearer 4. In Ewell's opinion (18), the value of n should be characteristic of the form of the unit of flow. If the value of n for any liquid is significantly greater than 3 or 4, the unit of flow is considerably less than the unit of evaporation and *vice versa*.

Table 4 shows values of n for several molten salts. Since ΔE_{vap} varies slightly with temperature, values for this quantity are taken at temperatures approximating to those at which the corresponding viscosity data were obtained.

With the exception of cadmium chloride and silver chloride, the value of n is close to 4, similarly to that found for polar molecular liquids. On Ewell's reasoning, it would appear that the unit of flow is the same as the unit of evaporation for most ionic liquids, probably the ion pair.

The anomalous value for cadmium chloride is probably due to the fact that different "bonds" are broken during the processes of evaporation and viscous flow (*cf.* Section III, D and Grunberg and Nissan (26, 27)). This may be interpreted in terms of the likelihood that in the liquid state cadmium chloride exists to a certain extent in the form of autocomplexes which are dissociated on vaporization. Autocomplex formation is unlikely in the case of silver chloride, however (*cf.* reference 12), and no explanation can be offered for the anomalous value of n for this liquid.

An equation for the *free energy* of activation of viscous flow was derived by Roseveare, Powell, and Eyring (43):

$$\Delta G_{vis} = RT \ln (v\eta/hN) \quad (9)$$

They found a relation between this quantity and the energy of vaporization

$$\Delta E_{vap}/\Delta G_{vis} = 2.45$$

to hold within narrow limits for approximately one hundred liquids. It can be shown, however, that equation 9 does not satisfy experimental data and must be modified to contain another constant. Equation 9 may be transformed to give:

$$R \ln (v\eta) - R \ln (hN) = \Delta G_{vis}/T \quad (10)$$

Since R , h , and N are constants, if $R \ln (v\eta)$ is plotted against $1/T$, the resultant curve should be linear and its slope should give ΔG_{vis} . For all liquids tested, both molecular and ionic, the plot of $R \ln (v\eta)$ against $1/T$ is linear over a considerable range of temperature, but the intercept on the $R \ln (v\eta)$ axis is considerably different from $R \ln (hN)$, the gradient values of ΔG_{vis} differing from those calculated from equation 9 by as much as 50 per cent in many cases (table 5). Moreover, the values of ΔG_{vis} calculated from equation 9 vary with temperature, whereas the gradient values show no such variation. This fact has also been pointed out, using a somewhat different approach, by van Velden (45) and Ketalaar, de Vries, van Velden, and Kooy (33).

This suggests that another constant must be inserted in equations 9 and 10. It can be shown that this constant is related to that which must be inserted into the preexponential factor of the original viscosity equation (equation 8) in order that it should satisfy experimental data. Ewell and Eyring (19) found that the values for the preexponential factor of equation 8 calculated by inserting numerical values for the various physical quantities contained in it differed from the experimental values by a factor of 2 to 4. This discrepancy suggests that some fundamental consideration is not taken into account in the development of the viscosity equation. The explanation may lie in the assumption of the formation of temporary "double molecules" during flow, as suggested by

Ewell and Eyring (19), instead of the "unimolecular process" suggested originally.

It can be shown that the value of ΔE_{vis} for water (calculated from data in *International Critical Tables* (31)) varies with temperature; this is attributed by Eyring to the breaking of structural bonds in water as the temperature is raised. On the other hand, according to Eyring, the value of ΔG_{vis} calculated from equation 9 shows no such abnormality; furthermore, the value of the ratio $\Delta E_{vap}/\Delta G_{vis}$ for water is stated to be normal (i.e., 2.45). This is interpreted on the basis of ΔE_{vis} containing a term for the entropy of activation for viscous flow,

TABLE 5
Values of ΔG_{vis} for ionic and molecular liquids

LIQUID	TEMPERATURE	ΔG_{vis} (EQUATION 10)	ΔG_{vis} (GRAPE)
	°C.	kcal./mole	kcal./mole
Chloroform.....	0	2.67	1.52
	20	2.75	1.52
	40	2.84	1.52
	60	2.92	1.52
Acetone.....	0	2.30	1.40
	30	2.40	1.40
	50	2.47	1.40
Methyl acetate.....	0	2.67	1.74
	20	2.73	1.74
Benzene.....	10	2.87	2.24
Carbon tetrachloride.....	0	3.12	2.24
n-Hexane.....	0	2.62	1.51
Methyl propyl ketone.....	30	2.89	1.73
CdCl ₂	680	10.5	3.60
	600	10.4	3.60
CdBr ₂	600	10.8	4.0
PbCl ₂	620	10.5	6.2
PbBr ₂	520	9.7	5.9
AgCl.....	560	4.3	2.6
AgBr.....	520	8.6	2.9

suggesting that the entropy of the activated state is greater than that of the initial state. However, as mentioned before, conclusions based on values of ΔG_{vis} calculated from equation 9 are highly doubtful. ΔG_{vis} calculated from the plot of $R \ln(\eta\nu)$ vs. $1/T$ for water is not independent of temperature, as Eyring assumes, the curve obtained being far from linear.

C. Free space or breaking of bonds as determining factors for viscosity?

Powell, Roseveare, and Eyring (41) have considered the interesting question of whether it is the breaking of bonds or whether it is the free space available in the liquid which is the factor determining the viscosity of a liquid. The Batchinski-MacLeod relations suggest that the free space is the important factor. If such were the case, the apparent energy of activation for viscous flow at con-

stant volume, as defined by $(d(R \ln \eta)/d(1/T))_v$, would be expected to be a small fraction of that at constant pressure, since under conditions of constant volume the free space would not be expected to alter appreciably with temperature.

Fortunately, experimental data on the effect of pressure and temperature on the viscosities of a number of molecular liquids are available (14). For non-polar liquids, the energy of activation at constant volume is only a very small fraction of that at constant pressure, indicating that for these liquids the free space is, in fact, the important factor.

However, for associated or hydrogen-bonded liquids, it is found that the energy of activation at constant volume is a large fraction of that at constant pressure, showing that for this class of liquids the breaking of the hydrogen bond is an important factor. For these liquids the energy of activation also varies with temperature, probably owing to the breakdown of the hydrogen-bonded structure on increase of temperature.

For molten salts no data are available on the effect of pressure on viscosity; consequently the energy of activation at constant volume cannot be calculated. However, the fact that molten salts satisfy the Batchinski-MacLeod relation over quite long ranges of temperature, and also the fact that the activation energy (ΔE_{vis}) at constant pressure varies little with temperature—in contradistinction to hydrogen-bonded liquids—suggests that the free space is the important factor controlling the variation of their viscosity with temperature.

D. Activation energy of viscosity and cohesion

The theories of Frenkel and Eyring are developed from specific models and employ rigorous mathematical treatment. Little use has been made of Frenkel's equation in the present discussion, since several conclusions from it (temperature-variability of the preëxponential term and the postulate of an activation energy which varies strongly with temperature) are obviously not in accordance with experimental facts. Eyring's theory has been applied by a number of investigators. However, closer scrutiny of the work reveals appreciable variations of the original model in the interpretation of experimental data, and the treatment must be regarded as semiempirical.

Ward (46) first introduced the plausible idea that ΔE_{vis} is the energy necessary to break certain bonds during the configurational change occurring in viscous flow. His treatment is based on a theory by Bernal (7) which connects the free energy of a liquid with its coördination number. Ward's ideas were further developed by Barrer (2, 3), who regards the ions in an ionic liquid *at rest* as coördinated to a certain extent with those of opposite sign, as they are in the crystalline state. According to Barrer, the activation energy of viscous flow may be regarded as the energy which the system must absorb in order to break down this coördination *before* viscous flow can occur. The extra energy required for the breakdown of this coördination in ionic liquids results in their having higher values of ΔE_{vis} than nonpolar molecular liquids. An analogous relation has been drawn between hydrogen-bonded liquids and nonpolar liquids, the former class having higher values of ΔE_{vis} than the latter.

A similarity between the configurational changes taking place during fusion and viscous flow has previously been postulated by de Guzman (16) on the basis of a rough correspondence between the values of ΔE_{vis} and the latent heat of fusion (ΔH_{fus}) for molecular liquids. Table 6 shows that for molten salts also ΔH_{fus} is of the same order of magnitude as ΔE_{vis} .

For a number of compounds ΔE_{vis} (as defined by $R d(\ln \eta)/d(1/T)$) is not constant but decreases with increasing temperature. Ward has attributed this to a change in coordination. This concept is particularly useful in the case of hydrogen- and hydroxyl-bonded liquids such as water and the lower fatty acids and alcohols. Here the variation of ΔE_{vis} with temperature is attributed by Ward (46) and Eyring (cf. 25) to the breakdown of these structural bonds in the liquid as the temperature is increased. In none of the molten salts investigated by us does ΔE_{vis} vary with temperature. This is understandable, as with alkali halides there is no variation in coordination and bond type with temperature. In the case of the silver halides and the cadmium and lead halides, which possess some

TABLE 6
Comparison of ΔH_{fus} and ΔE_{vis} for molten salts

SALT	ΔH_{fus} *	ΔE_{vis}	SALT	ΔH_{fus}	ΔE_{vis}
	<i>kcal./mole</i>	<i>kcal./mole</i>		<i>kcal./mole</i>	<i>kcal./mole</i>
NaCl.....	7.2	9.1	NaNO ₃	3.7	3.7
KCl.....	6.4	7.4	KNO ₃	2.6	4.4
AgCl.....	3.1	2.9	PbCl ₂	5.7	6.7
AgBr.....	2.4	3.1			

* Data by Ward (46).

degree of covalency, the variations over the temperature ranges under investigation are probably too small to cause a noticeable variation of ΔE_{vis} .

The concepts mentioned above are semiempirical and less specific than those of Eyring, but appear to have a more general applicability in view of the absence of a rigorous mathematical theory of the liquid state. Their usefulness emerges clearly from an investigation by Grunberg and Nissan (26, 27). These authors have made the interesting observation that for unassociated molecular liquids the work of cohesion (W_c) as determined from the surface tension (γ) is very similar in magnitude to ΔE_{vis} . The work of cohesion per mole as defined by Harkins and Cheng (28) is calculated from the relationship

$$W_c = 2 \times 2.39 \times 10^{-8} \gamma V^{2/3} N^{1/3}$$

where V is the molar volume and N is Avogadro's number. The approximate equality of W_c and ΔE_{vis} suggests that the number of bonds broken (per mole) during the surface formation and viscous flow is nearly the same. For "associated" and hydrogen-bonded liquids ΔE_{vis} is greater than W_c ; Grunberg and Nissan attribute this to the fact that structural bonds are broken during viscous flow. On the other hand, W_c does not include the energy increment charac-

terizing the breaking of these bonds, since the latter quantity is calculated from equilibrium values of the surface tension and will contain no energy increments due to "dissociation" of associated complexes or clusters.¹ If a dynamic surface tension were determined, W_c calculated from this value would be greater than from the equilibrium value and would contain energy increments of "cluster bond energy." The difference between W_c and ΔE_{vis} for hydrogen-bonded liquids is therefore due to the fact that W_c is determined statically, whilst ΔE_{vis} is determined dynamically.

Grunberg and Nissan have also compared W_c with the energy of vaporization (ΔE_{vap}). For most nonassociated liquids the ratio $\Delta E_{vap}/W_c$ is between 3 and 4. They have shown that this ratio is to be expected for liquid systems of molecules with an arrangement of high symmetry. They consider the number of bonds which must be broken (per molecule) on surface formation and on evaporation for arrangements conforming to tetrahedral, octahedral, cubic body-centered, cubic close-packing, and hexagonal close-packing types, and find that in these cases values for $\Delta E_{vap}/W_c$ of between 3 and 4 are to be expected. For associated liquids, however, provided the vapor is unassociated, they find $\Delta E_{vap}/W_c$ to be greater than 4, since ΔE_{vap} contains increments of energy necessary to break the structural bonds, whilst W_c does not contain these increments. The fact that values of the ratio $\Delta E_{vap}/\Delta E_{vis}$ lie between 3 and 4 for normal liquids and that somewhat smaller values are obtained for associated liquids, as originally found by Eyring, also conforms to these ideas.

Table 7 shows values of W_c , ΔE_{vap} , ΔE_{vis} , and their ratios, calculated for molten salts.

The values of $\Delta E_{vap}/W_c$ are of the same order as those for associated liquids, to which molten salts are similar in some respects owing to the continuous electrostatic forces which extend throughout the liquid. This field of force is of higher symmetry for the alkali halides than for lead and cadmium halides. However, an extension of the concept of Grunberg and Nissan to ionic liquids encounters difficulties because, unlike molecular liquids, the kinetic unit in the liquid and in the vapor state may not be the same. With cadmium chloride and lead chloride we probably have a proportion of molecules in the liquid, and the kinetic unit in the vapor is probably the molecule, with appreciable polarity of binding. "Clusters" of ions are also likely to be present in all these salts in the liquid state (2, 3).

A comparison of the number of bonds broken on vaporization and surface formation by the method of Grunberg and Nissan meets therefore with difficulties. Applying Grunberg and Nissan's arguments, qualitative considerations would suggest that the number of "bonds" broken on evaporation multiplied by the energy terms characterizing each of these "bonds" is greater than on surface formation by a larger amount than for normal molecular liquids. Thus $\Delta E_{vap}/W_c$ is much greater than 4. The excess may be regarded as being due to

¹ This reasoning is only approximate, since the cluster in the bulk has a configuration very different from that in the surface, owing to the strong molecular orientation in the latter.

the energy required to break up "clusters" on vaporization. For reasons similar to those mentioned in connection with associated liquids, W_c calculated from the equilibrium surface tension of molten salts does not include energy increments due to "cluster bond energy."

For alkali halides ΔE_{vis} is greater than W_c , although the actual values may be in error owing to the uncertainty about ΔE_{vis} at high temperatures. If real, this signifies that more bonds have to be broken during viscous flow than during the formation of an equilibrium surface. Again, if we have clusters in the liquid at rest, ΔE_{vis} will contain the increments of "cluster bond energy," whilst W_c will not.

TABLE 7
Values of ΔE_{vis} , ΔE_{vap} , and W_c for several molten salts

SALT	TEMPERATURE	W_c^*	ΔE_{vis}	ΔE_{vap}	$\frac{\Delta E_{vis}}{W_c}$	$\frac{\Delta E_{vap}}{W_c}$	$\frac{\Delta E_{vap}}{\Delta E_{vis}}$
	°C.						
NaCl	850	5.1	9.1?	37.7	1.78?	7.4	4.2?
NaBr	800	5.3	8.0?	34.5	1.51?	6.5	4.3?
KCl	800	5.2	7.4?	35.5	1.42?	6.8	4.8?
KBr	800	5.0	8.0?	33.8	1.60?	6.8	4.2?
NaNO ₃	350	6.1	3.7		0.61		
KNO ₃	400	6.4	4.4		0.69		
AgCl	600	6.8	2.9	44.7	0.43	6.6	15.3
AgBr	600	6.4	3.1		0.48		
CdCl ₂	600	4.8	4.0	31.8	0.83	6.6	7.9
CdBr ₂	700	4.4	4.5		1.02		
PbCl ₂	600	7.6	6.7	32.5	0.88	4.3	4.9
PbBr ₂	600	7.8	6.2	30.2	0.80	3.9	4.9

* Data by Boardman, Palmer, and Heymann (13).

† ΔE_{vap} for cadmium bromide, silver bromide, sodium nitrate, and potassium nitrate cannot be determined, owing to decomposition at temperatures little above their melting points.

For the other salts, *viz.*, the alkali nitrates, silver halides, and lead and cadmium halides, W_c is greater than ΔE_{vis} , although for the lead and cadmium halides $\Delta E_{vis}/W_c$ is not far from unity, as for nonassociated molecular liquids. This means that the energy necessary for surface formation is appreciably greater than for viscous flow in the case of silver halides and alkali nitrates. This is the opposite to what is found for associated molecular liquids and demonstrates that the analogy between the two classes of liquids is very limited.

The value of $\Delta E_{vap}/\Delta E_{vis}$ is 4-5 in most cases, with the exception of silver chloride and cadmium chloride. In terms of Grunberg and Nissan's concept this would suggest that $\Delta E_{vap}/\Delta E_{vis}$ is largely determined by the coördination in the liquid, as it is with molecular liquids. According to this, the unit of flow, presumably much smaller than the "cluster," should be the same as the unit of vaporization. The ratio of 4-5 indicates that the short-range arrangement of the

ions follows either the cubic body-centered, cubic close-packing, or hexagonal close-packing system. This is compatible with the packing found in the solid state. Caution must be exercised, however, in view of the uncertainty of the values for ΔE_{vis} ,² for alkali halides. If these were appreciably smaller than the values given in table 7, $\Delta E_{vap}/\Delta E_{vis}$ might be as anomalous for alkali halides as it is for cadmium chloride. The large value of the ratio for cadmium chloride may be due to the fact that, owing to autocomplex formation in this molten salt, the unit of flow is the autocomplex, whilst the vapor consists of $CdCl_2$ molecules or triple ions; as a consequence more bonds have to be broken during vaporization than during viscous flow.³ The very large value of this ratio for silver chloride—15—so far defies explanation.

The approximate nature of all conclusions based on the concept by Grunberg and Nissan is realized on considering that ΔE_{vap} and ΔE_{vis} are total energies, whilst W_c is a free energy. The first two show little variation with temperature (except for hydrogen-bonded liquids), whilst W_c is strongly variable with temperature.

E. Viscosity of mixtures

When considering liquid mixtures, the viewpoints of the Frenkel and Eyring schools of workers differ little in broad outline.

According to Roseveare, Powell, and Eyring (43), if viscous flow consists of the movement of one molecule at a time from one equilibrium position to the next, and provided the two molecular species in the mixture do not interact, then the equation

$$\phi = N_1\phi_1 + N_2\phi_2 \quad (11)$$

where N_1 and N_2 are the molar fractions of the components, ϕ_1 and ϕ_2 their fluidities, and ϕ the fluidity of the mixture, may be expected to hold. This equation involves the assumption, however, that the energy of activation for viscous flow is the same in the mixture as in the pure components. It has been shown (29) that this condition is very nearly fulfilled in the systems silver bromide–silver chloride, lead bromide–lead chloride, and cadmium chloride–cadmium bromide, and figure 3 shows that the plot of fluidity against molar fraction for these systems is linear. On the other hand, the system silver chloride–lead chloride, where the activation energies of the individual components differ greatly from those in the mixtures, does not satisfy equation 11.

Other mixture laws have been derived using theoretical backgrounds by Frenkel (24) and Panchenkov (38). The discussions of these authors also assume that it is the activation energy for viscous flow rather than the viscosity which is primarily related to the composition. Roseveare, Powell, and Eyring (43)

² Also, values of ΔE_{vap} , determined by different investigators, vary by as much as 10 per cent. However, the values given by Kelley (32), quoted in table 7, are regarded as the most reliable ones.

³ The anomalous value of $\Delta E_{vap}/\Delta E_{vis}$ for cadmium chloride can be explained on the assumption of autocomplexes in the melt in terms of both Eyring's and Grunberg and Nissan's concepts.

assume that for ideal mixtures the energy of activation ΔE_{vis} is a linear function of the molar composition:

$$\Delta E_{vis}^M = N_1 \Delta E_{vis}^{11} + N_2 \Delta E_{vis}^{22} \quad (12)$$

If a change in intermolecular potential occurs on mixing, it is suggested that a

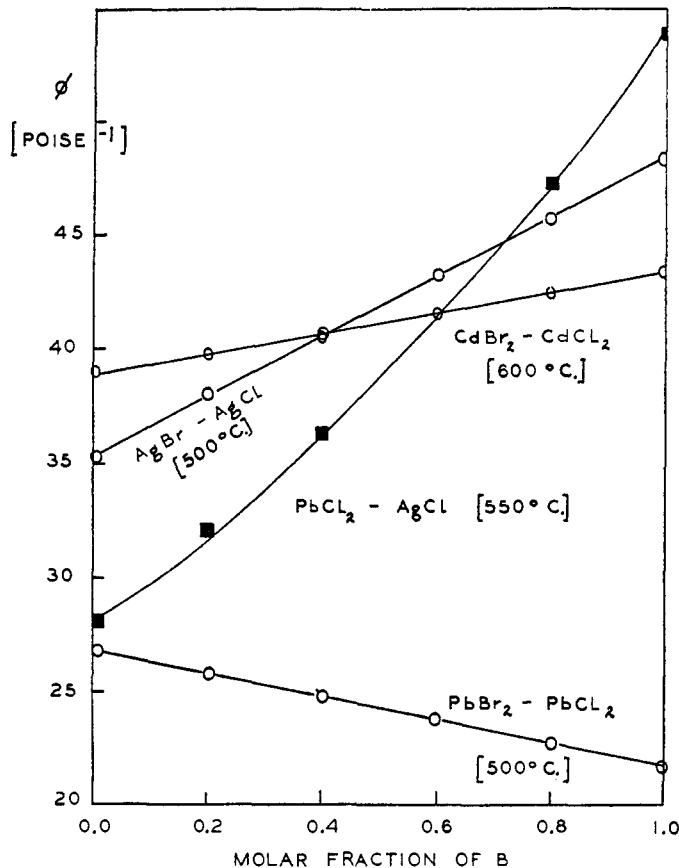


FIG. 3. Isotherms of fluidity *vs.* molar composition for several molten salt systems whose molar volume isotherms are linear.

further activation energy term ΔE_{vis}^{12} be added, giving:

$$\Delta E_{vis}^M = N_1 \Delta E_{vis}^{11} + N_2 \Delta E_{vis}^{22} + \Delta E_{vis}^{12} \quad (13)$$

Furthermore, Roseveare, Powell, and Eyring suggest that the term ΔE_{vis}^{12} should be related to the heat of mixing, since both quantities reflect the change in intermolecular potential on mixing; that is, ΔE_{vis}^{12} should be positive when the heat of mixing is positive and *vice versa*. This is qualitatively borne out for molecular liquid mixtures for which data are available (43).

Reference to figures 4 and 5 shows ΔE_{vis} plotted against molar composition

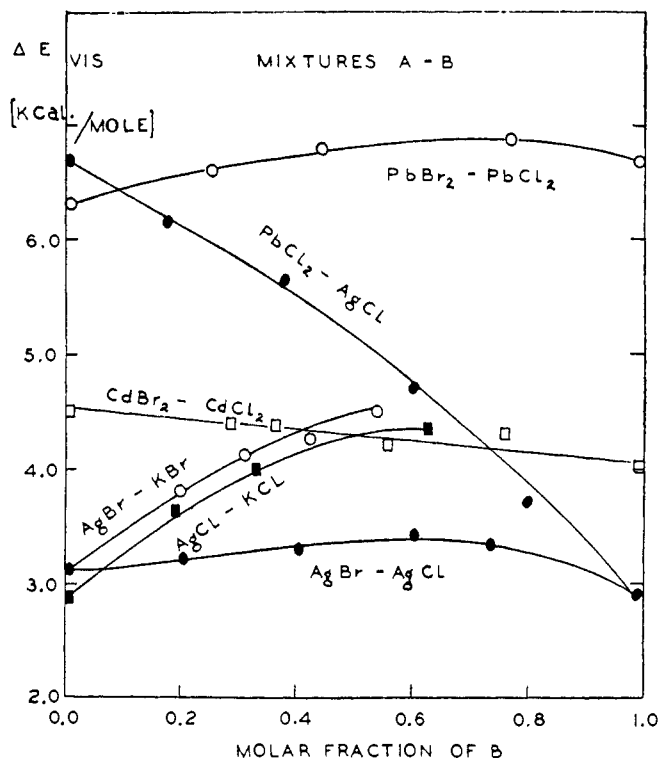


Fig. 4. Variation of activation energy of viscous flow with molar composition for several molten salt systems whose molar volume isotherms are linear.

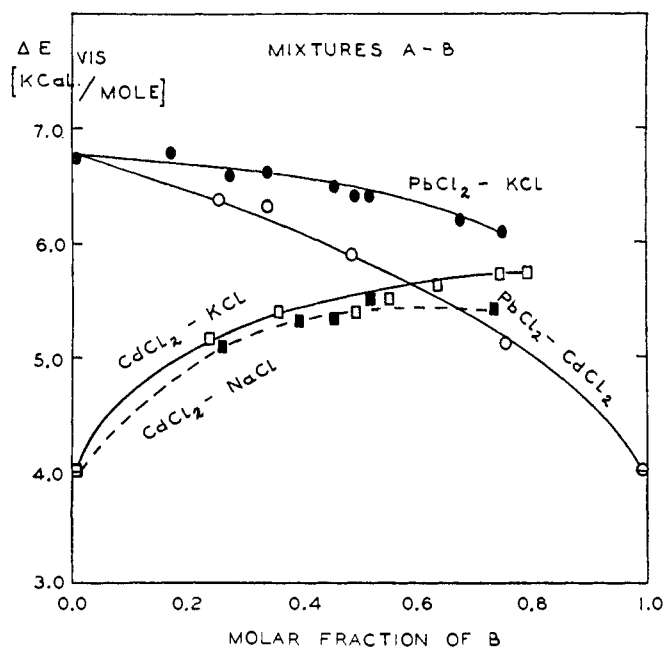


Fig. 5. Variation of activation energy of viscous flow with molar composition for several molten salt systems whose molar volume isotherms show deviations from additivity.

for the molten salt systems silver chloride-silver bromide, cadmium chloride-cadmium bromide, lead chloride-lead bromide, silver chloride-potassium chloride, and silver bromide-potassium bromide, and also for the systems lead chloride-potassium chloride, cadmium chloride-potassium chloride, cadmium chloride-sodium chloride, and lead chloride-cadmium chloride (8, 29). The curves so obtained exhibit slight to moderate positive deviations from additivity. On the interpretation of Roseveare, Powell, and Eyring, this would correspond to a positive heat of mixing. Unfortunately, no experimental determinations of heats of mixing for molten salt systems are available. For the systems lead chloride-potassium chloride, cadmium chloride-potassium chloride, and possibly cadmium chloride-sodium chloride, a positive heat of mixing, in view of the complex-ion formation which occurs in these mixtures, is plausible.

Frenkel (24) and Panchenkov (39) have both related the activation energy for viscous flow with the molar composition by a quadratic function of the type

$$\Delta E_{vis}^M = N_1^2 \Delta E_{vis}^{11} + N_2^2 \Delta E_{vis}^{22} + 2N_1 N_2 \Delta E_{vis}^{12} \quad (13a)$$

where ΔE_{vis}^{12} is a supplementary energy term expressing the effect of interaction between components 1 and 2.

None of these workers remarks, however, that any mixture law of the type represented by equations 13 and 13a must be qualified if expansion or contraction in volume, that is, a change in free volume, occurs on mixing. This is particularly important in the case of molten salt systems, where volume expansion takes place when "complex"-ion formation in the mixture occurs, e.g., the systems lead chloride-potassium chloride and cadmium chloride-potassium chloride (11). The complex formation is indicated by strong minima in the isotherms of equivalent conductivity (9), yet the viscosity isotherms do not show maxima as might be expected but reveal only slight negative deviations from additivity. It will be shown in another publication (29) that this can be understood only on considering the variation of both the intermolecular potential and the free space on mixing, although the two quantities are to a certain extent interdependent.

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