Viscosities of Some Binary Mixtures between
$MgCl_2$, $CaCl_2$ and AlkCl

D. DUMAS,* B. FJELD, K. GRJOTHEIM and H. A. ØYE

*Institutt for uorganisk kjemi, Norges tekniske høgskole, Universitetet i Trondheim,
N-7034 Trondheim-NTH, Norway*

The viscosity, η, of the following binary molten mixtures has been determined mainly in the temperature range 750° to 850°C by the method of an oscillating sphere: $CaCl_2 - NaCl$, $CaCl_2 - KCl$, $MgCl_2 - CaCl_2$, $MgCl_2 - LiCl$, $MgCl_2 - NaCl$, $MgCl_2 - KCl$, $MgCl_2 - RbCl$, and $MgCl_2 - CsCl$. Values for the excess Gibbs energy of activation for viscous flow have been calculated according to the equation

$$\Delta G^{E\ddagger} = RT[\ln \eta - (X_1 \ln \eta_1 + X_2 \ln \eta_2)]$$

The results have been interpreted in terms of bond strength, complex formation, and ionization of the partially covalent $MgCl_2$ liquid lattice. The relevance of the present investigation to the industrial electro-winning of magnesium is discussed.

Experimental determination of the viscosities of binary mixtures between $MgCl_2$, $CaCl_2$, and alkali chlorides were undertaken. This was part of a general study of physico-chemical properties of molten salt systems of interest in magnesium electrolysis. These systems are also of interest in developing a better understanding of the behaviour of ionic mixtures.

The viscosities of the salt mixtures studied are in the range $0.01 - 0.03$ poise. In our opinion, the best method for measuring viscosities of these very hygroscopic melts is the torsional pendulum method. The theory and utilization of this method is described in detail by Dumas *et al.*[1]

EXPERIMENTAL

Apparatus. The apparatus was that described by Dumas *et al.*[1] Further trials with thinner torsional wires were conducted in order to increase the period of the pendulum swing, but proved unsuccessful since poor stability resulted even with careful pretreating in a hydrogen atmosphere.[2]

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* Present address: Societé des Électrodes et Refractoires Savoie, Savoie, 10, Rue de l'Industrie, (69) Veissieux, France.

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Chemicals. The following chemicals were used: *p.a.* NaCl, KCl, RbCl, CsCl, and $MgCl_2$, from Merck, Darmstadt (Germany), and *p.a.* LiCl and $CaCl_2$, from Baker (USA).

The NaCl, KCl, RbCl, and CsCl were dried under vacuum for 12 h, melted under a nitrogen atmosphere and cooled slowly. Only clear crystals were picked out and used for the experiments. Anhydrous $MgCl_2$, $CaCl_2$, and LiCl were treated with HCl gas, melted and filtered.[3]

Procedure. The salt crystals were mixed mechanically in a dry-box. The crystals were then placed in a pyrex container fitted with a valve which allowed the transfer of salt to the viscosity crucible without exposure to air (see Fig. 4 in Ref. 1). This transfer mechanism was also used for adding LiCl, NaCl, and KCl to the first prepared melts in order to change the composition. However, this procedure was found to be unsatisfactory for RbCl and CsCl. When using this procedure, neither salt mixed properly with the firstly prepared melts. This was probably due to the high density of RbCl and CsCl. To obtain proper mixing, therefore, the mixtures were premelted in a quartz ampule obtaining mixing by convective flow caused by uneven heating. For each temperature at least three separate experiments were run to determine the damping of the pendulum. This was done to detect possible erroneous results in the delicate manual apparatus.

Calculation of the viscosity. The method of calculating the viscosity from the measurements was essentially the same as used before.[1]

The amplitude values of both sides were read from a scale for every second period. However, in the present investigation a computer program was used to smooth the amplitude values as a function of the oscillation number. The computer program took into account that each set of opposite readings differed by half a period and discarded automatically all amplitudes which deviated by more than 0.1 cm (about 0.5 % of the maximum amplitude). The typical number of discarded readings were between 1 and 5 out of about 40. The smoothing procedure also gave the arbitrary equilibrium position. This was different for each experiment.

The amplitudes remaining from the smoothing procedure were used to calculate the damping, δ, according to the procedure used by Dumas *et al.*[1]

RESULTS

Control experiments were performed with H_2O, KNO_3 and KCl. The results are given in Table 1. These values deviate less than 0.7 % from the literature values.[1,4,5] The viscosities for the binary mixtures as functions of temperature and composition are given in Figs. 1 − 8. If measurements at 800°C were not performed the curves in Figs. 1 − 8 were extrapolated to this temperature. A comparison between the results at 800°C are given in Figs. 9 and 10.

The platinum sphere of the pendulum had to be remachined after use in LiCl-melts. At the same time minor rearrangements in the apparatus were made.

Table 1. Observed viscosities compared with literature values for H_2O,[9] KNO_3,[10] and KCl.[6]

Compound	Temp. °C	Viscosity, cP	
		This work	Lit. values
	14.7	1.151	1.152
H_2O	17.7	1.078	1.073
	19.6	1.026	1.022
	362.0	2.352	2.342
KNO_3	374.8	2.477	2.487
	397.0	2.106	2.092
KCl	819.7	0.930	0.935
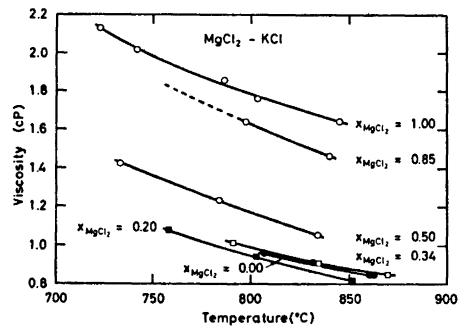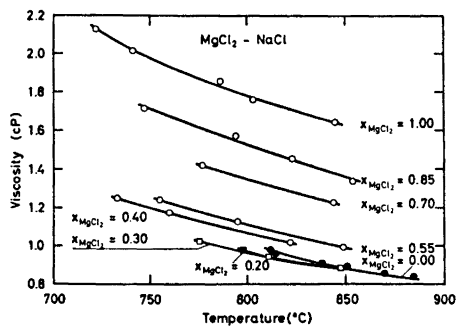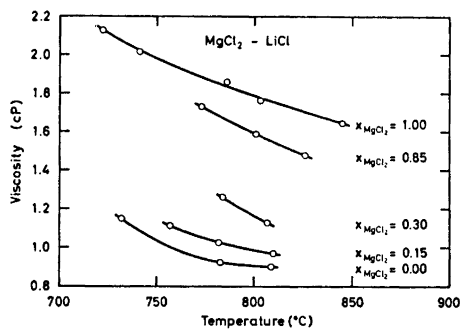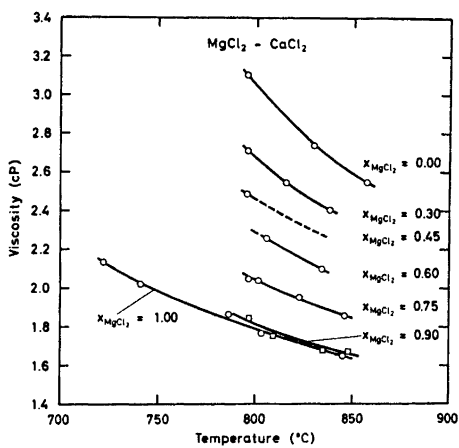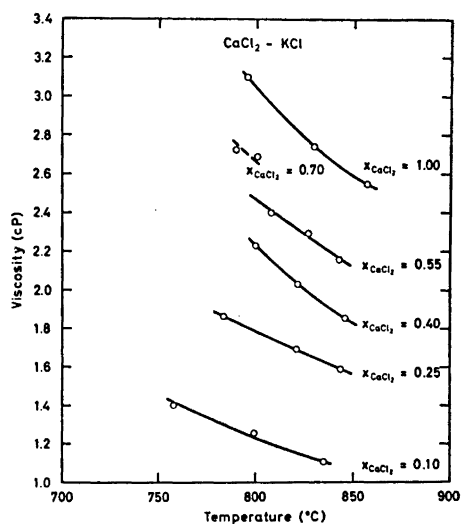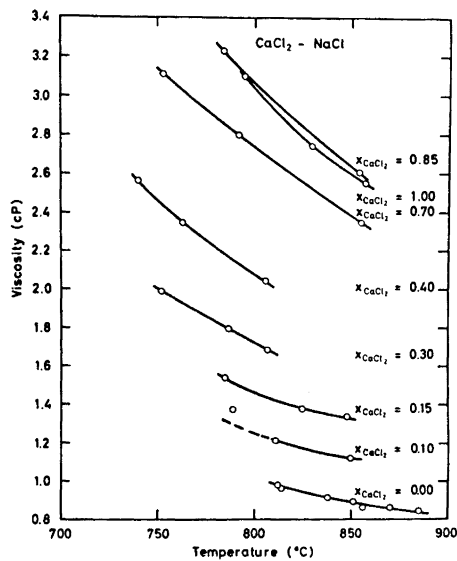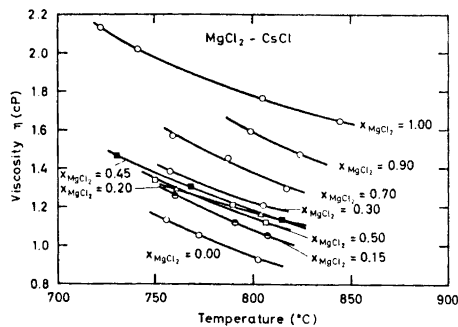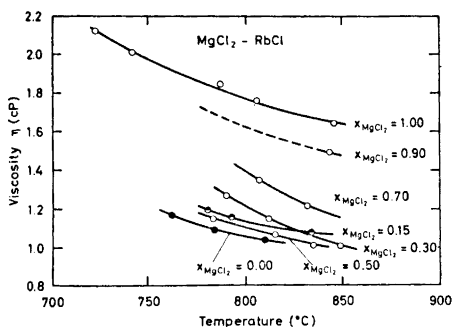
Figs. 1 — 8. Shear viscosity of the molten binary systems: $CaCl_2 - NaCl$, $CaCl_2 - KCl$, $MgCl_2 - CaCl_2$, $MgCl_2 - LiCl$, $MgCl_2 - NaCl$, $MgCl_2 - KCl$, $MgCl_2 - RbCl$ and $MgCl_2 - CsCl$.

A general discussion of the sources of error was given by Dumas *et al.*[1] Although some errors have been reduced with the more exact measurement of the sphere dimensions and through computer treatment of the data we still consider $\pm 2 \%$ to be a reasonable estimate for the standard deviation.
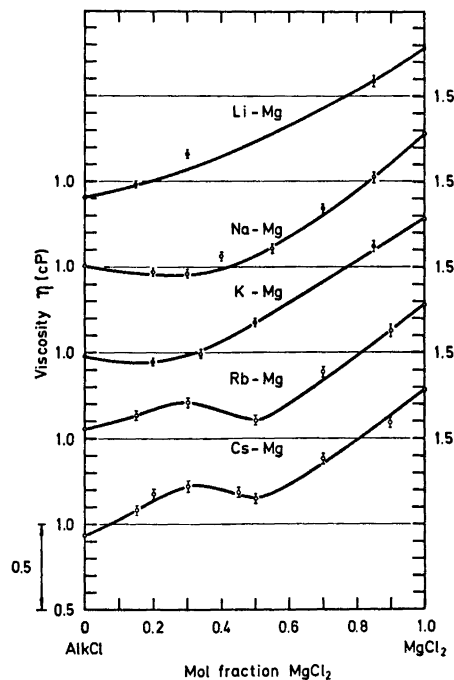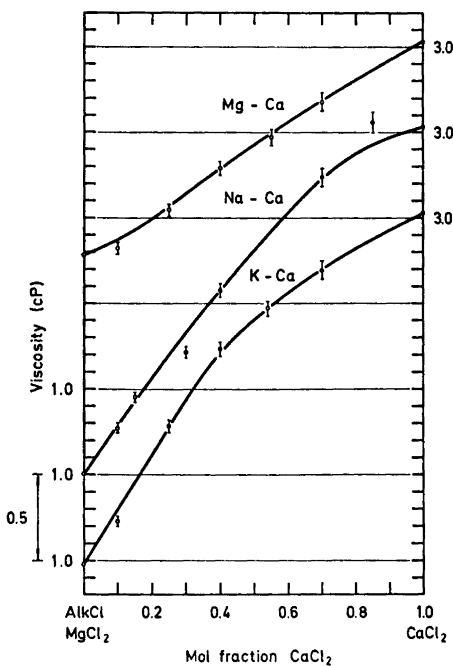

Fig. 9. Viscosities of the binary mixtures $CaCl_2 - NaCl$, $CaCl_2 - KCl$, and $CaCl_2 - MgCl_2$ at 800°C.

Fig. 10. Viscosities of the systems $MgCl_2 - AlkCl$ at 800°C.

DISCUSSION

Definition of ideality. Rice et al.[6] in their discussion of viscosity of simple liquids define an ideal binary mixture as a mixture where the compounds have the same energy interaction parameter, ε, and the same rigid core diameter, σ. They point out that the Eyring theory [7,8] then leads to linear additivity of the fluidity, $\phi = 1/\eta$. The Rice-Alnatt theory,[9] however, gives linear additivity of the viscosity, while other theories give more complex behaviour.[6]

None of these theories, however, can be used in the present case. For example, our mixtures of molten salts are far from being ideal in this sense since ε and σ are not the same for each component. It is, therefore, necessary to resort to more semi-empirical theories in order to correlate the data we obtained.

The temperature dependence of high-viscosity fluids is often best represented by a Vogel-type equation,[10] involving a temperature parameter T_0 related to the glass transition temperature,[11]

$$\log \eta = a + \frac{b}{T - T_0} \tag{1}$$

where a and b are constants.

For low-viscosity molten salts at temperatures far from the glass-transition temperature, the temperature dependence of the viscosity is best given by an Arrhenius-type function [11]

$$\eta = A \, e^{B/T} \tag{2}$$

where A and B are constants. This equation follows from the Eyring theory,[7,8]

$$\eta = A \, e^{\Delta G^{\ddagger}/RT} = A \, e^{[(\Delta H^{\ddagger}/RT) - (\Delta S^{\ddagger}/R)]} \tag{3}$$

where $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are, respectively, the Gibbs energy, the enthalpy, and the entropy of activation for viscous flow.

By introducing $A = Nk/V$, where N is the number of atoms, k is the Boltzmann's constant and V is the volume, we obtain

$$\eta = (Nk/V) \, e^{\Delta G^{\ddagger}/RT} \tag{4}$$

The temperature dependence of the viscosity given by the Arrhenius function is appropriate for our results.

The viscosity of ideal mixtures, assuming no enthalpy or volume change on mixing, has been studied by several authors.[12] Negative deviations from linear additivity of the viscosity are found. The results are often satisfactorily described by the Arrhenius rule,[13]

$$\ln \eta = X_1 \ln \eta_1 + X_2 \ln \eta_2 \tag{5}$$

where X_1 and X_2 represent mol fractions. Arrhenius originally recommended the use of mass fractions. Use of volume fraction has also been suggested.[14,15] Eqn. (5) can be justified theoretically from the rate theory by assuming the following linear additivity of the interaction parameters

$$\Delta H^{\ddagger} = X_1 \Delta H_1^{\ddagger} + X_2 \Delta H_2^{\ddagger} \tag{6}$$

$$\Delta S^{\ddagger} = X_1 \Delta S_1^{\ddagger} + X_2 \Delta S_2^{\ddagger} \tag{7}$$

and by assuming the pre-exponential factor in eqn. (4) to be equal for the two components. Eqn. (5) can be considered then as the definition of an ideal mixture, but it leads to a different ideality in viscosity than the equations given by Rice *et al.*[6]

Linear additivity of viscosity itself will only be fulfilled in eqn. (5) if $\eta_1 = \eta_2$, and then η is independent of composition. For $\eta_1 \neq \eta_2$ a negative deviation from linear additivity of the viscosity is ideal according to this definition. For example, the deviation for an equimolar mixture is 13 % if the two viscosities differ by a factor of 3.

For non-ideal mixtures a natural expansion of the linear additivity of the interaction parameters must include an excess viscous Gibbs energy of activation:

$$\eta = \frac{Nk}{V} \exp \left(\frac{X_1 \Delta G_1^{\ddagger} + X_2 \Delta G_2^{\ddagger} + \Delta G^{E\ddagger}}{RT} \right) \tag{8}$$

$$\ln \eta = X_1 \ln \eta_1 + X_2 \ln \eta_2 + \frac{\Delta G^{E\ddagger}}{RT} \tag{9}$$

The excess viscous Gibbs energy of activation, $\Delta G^{E\ddagger}$, must be zero for X_1 or $X_2 = 0$. The simplest equation in which $\Delta G^{E\ddagger}$ fulfills this necessary boundary conditions is

$$\Delta G^{E\ddagger} = X_1 X_2 b^{\ddagger} \tag{10}$$

This is analogous to the form of ΔG^{E} for regular solutions

$$\Delta G^{E} = \Delta H_{mix} = X_1 X_2 b \tag{11}$$

The viscosity can then be given as

$$\ln \eta = X_1 \ln \eta_1 + X_2 \ln \eta_2 + \frac{X_1 X_2 b^{\ddagger}}{RT} \tag{12}$$

An equation of the type given as eqn. (9) was first proposed by Powell *et al.*[16] However, they unjustifiedly used the thermodynamic excess Gibbs energy. An experimental correlation between the excess parameter $b^{\ddagger}$ in eqn. (12) and enthalpy has been established experimentally.[17,18] The correlation yields for regular solutions, eqn. (11), a $b^{\ddagger}$ which is opposite in sign from b in accordance with intuitive reasoning from a bond force concept. Increasing the bond forces in the mixture, $b < 0$, leads to a positive excess viscosity, $b^{\ddagger} > 0$. This simple concept will, however, break down for large negative deviations caused by the formation of complexes as the viscosity is not expected to be related directly to the bond strength within the complex. In cases with complex formation or association, Bondi recommends interpretation in terms of the complexes formed.[11]

Pure molten chlorides. Our data for LiCl, RbCl, and $CaCl_2$ at 800°C are in agreement with the values reported by Janz *et al.* in a recent National Bureau of Standards Circular.[19] Our value for KCl is 11 % lower and our value for CsCl is 6 % higher than the values they present. For NaCl a severe discrepancy is found; our value is nearly 50 % lower.
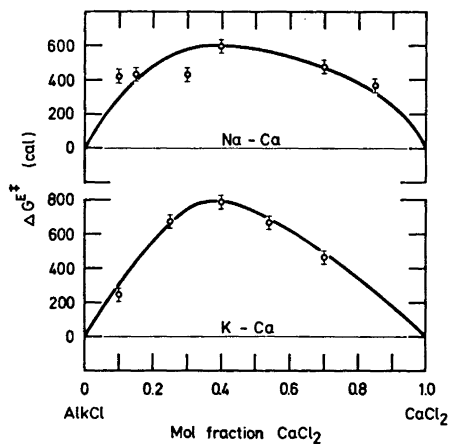
Fig. 11. Excess viscous Gibbs energy of activation, $\Delta G^{E\ddagger}$, from eqn. (9) for the systems: $CaCl_2 - NaCl$ and $CaCl_2 - KCl$.
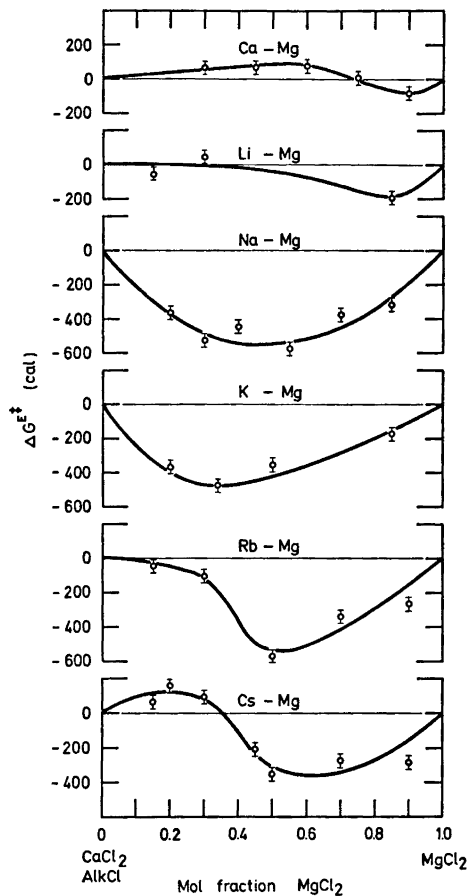
Fig. 12. Excess viscous Gibbs energy of activation, $\Delta G^{E\ddagger}$, from eqn. (9) for the systems: $MgCl_2 - CaCl_2$, $MgCl_2 - LiCl$, $MgCl_2 - NaCl$, $MgCl_2 - KCl$, $MgCl_2 - RbCl$ and $MgCl_2 - CsCl$.

Our measured viscosity for $MgCl_2$ of 1.78 cP at 800°C [1] differs significantly from the often quoted literature value of 4 cP at the same temperature.[20] We also observed that our measured viscosities of the alkali chlorides remained almost constant throughout the series from LiCl to CsCl. The electrical conductivity of the alkali chlorides, however, decreases strongly from LiCl to CsCl.[19] Therefore, the Frenkel correlation [21] between the equivalent conductivity, Λ, and the viscosity, η, given by eqn. (13)

$$\Lambda^n \, \eta = \text{constant} \tag{13}$$

is not obeyed. The constant viscosity may be explained as a balance between decreasing bond forces and increasing cation size as one proceeds from LiCl to CsCl.

Binary chloride mixtures. In Figs. 11 and 12 are presented the excess Gibbs energy of activation, for viscous flow, $\Delta G^{E \neq}$, calculated from eqn. (9). For the systems $CaCl_2 - NaCl$ and $CaCl_2 - KCl$ a correlation between $\Delta G^{E \neq}$ and the thermodynamic enthalpy of mixing [22] is found. This is similar to what one observes for mixtures of organic liquids.[11] $\Delta G^{E \neq}$ and ΔH have opposite signs, and the value of $\Delta G^{E \neq}$ increases with an increasing negative ΔH. The correlation between $\Delta G^{E \neq}$ and ΔH_{mix} or ΔG^{E} breaks down, however, for systems containing $MgCl_2$. This is particularly true for the systems $MgCl_2 - NaCl$, $- KCl$, $- RbCl$, $- CsCl$ where large negative heats of mixing are observed,[23] while the excess Gibbs energy of activation for viscosity is mainly strongly negative.

It is possible to explain the deviation from the "ideal law", eqn. (5), in terms of the following three guiding principles. These three principles were also applied to our studies of conductivity,[3] density,[24] and surface tension.[25]

(i) For minor structural changes the interaction between the next nearest neighbours results in an exothermic mixing reaction (negative excess Gibbs energy of mixing) and a strengthening of the bond forces.

(ii) When cations with strong field strengths are present, the polarization of anions leads to the strengthening of bonds between this cation and the nearest neighbour anions at the cost of the other short-range cation-anion bonds. In the extreme case, complex formations result; for example, $MgCl_4^{2-}$.

(iii) Structural breakdown of the melts with partly covalent character occurs; for example for $MgCl_2$, resulting in the ionization of the lattice.

As already pointed out, the deviation from logarithmic additivity for the systems $CaCl_2 - NaCl$ and $CaCl_2 - KCl$ is explained by the bond strength concept in (i). An increasing negative ΔH_{mix} leads to an increasingly positive excess viscosity. A polarization of Cl^- by Ca^{2+} might also be operative.[26] The near ideal viscosity behaviour of the systems $MgCl_2 - CaCl_2$ and $MgCl_2 - NaCl$ for $CaCl_2$ and $NaCl$ rich mixtures is explained by a small ΔH_{mix} [22,26] causing small changes in the bond forces during mixing.

The breakdown of the covalent structure of magnesium chloride, (iii), is demonstrated by the slightly negative deviations in viscosity from eqn. (5) for the systems $MgCl_2 - CaCl_2$ and $MgCl_2 - LiCl$, and the stronger, nearly constant, negative deviations in viscosity for the systems $MgCl_2 - NaCl$, $- KCl$, $- RbCl$, and $- CsCl$ for $MgCl_2$ rich mixtures.

The system $MgCl_2 - CsCl$ has the largest negative enthalpy of mixing [23] and the most pronounced tendency to form $MgCl_4^{2-}$. For the CsCl-rich mixtures a positive deviation from logarithmic additivity in viscosity is exhibited with a maximum near the stoichiometric composition Cs_2MgCl_4. The system $MgCl_2 - RbCl$ tends toward a positive deviation in viscosity near the stoichiometric composition Rb_2MgCl_4. This disappears for the systems $MgCl_2 - KCl$ and $MgCl_2 - NaCl$. Since formation of the stable entity $MgCl_4^{2-}$ is expected to lead to increased viscosity, it is surprising that this is not manifested by an excess positive viscosity for the KCl melts. Raman spectroscopy and previous thermodynamic studies have indicated $MgCl_4^{2-}$ formation in these melts.[28] The dif-

ference in behaviour between the NaCl and KCl systems in contrast with the RbCl and CsCl systems might give a clue to understanding of the kinetic stability of $MgCl_4^{2-}$. The relaxation time of $MgCl_4^{2-}$ may be so much shorter in the NaCl and KCl systems that it is not manifested in the viscosity.

Relevance of the present studies to the electrowinning of magnesium. One of the main objectives of this study was to clarify the effect of a change in composition and temperature on the viscosity of the industrially important magnesium electrolyte. Although the present study includes only binary systems, we can predict the viscosity behaviour of quaternary industrial electrolytes such as the mixture $MgCl_2 - CaCl_2 - NaCl - KCl$.

As mentioned above, the high viscosity of $MgCl_2$ reported in earlier literature [20] has been disproved. The viscosities we measured do not seem to be sensitive to structure. No sharp viscosity maximum as function of composition is found here as reported by Strelets et al.[20]

Although the viscosity of $MgCl_2$ is somewhat higher than that for NaCl and KCl, an increase of the $MgCl_2$ content in the industrially interesting range (5 to 15 mol %) actually results in a small lowering of the viscosity (Fig. 10).

Exchange of NaCl for KCl in an $MgCl_2 - CaCl_2 - NaCl - KCl$ mixture is expected to result only in very small changes in viscosity. This is due to the nearly equal viscosities of the pure salts and the similarities between the viscosity curves for the $MgCl_2 - NaCl$ and $MgCl_2 - KCl$ systems and for the $CaCl_2 - NaCl$ and $CaCl_2 - KCl$ systems (Figs. 9 and 10).

An increase in the $CaCl_2$ content of the quaternary mixture $MgCl_2 - CaCl_2 - NaCl - KCl$ is always expected to result in an increase in viscosity as shown in Fig. 9. The viscosity of pure $CaCl_2$ at 800°C is 3.03 cP. A lowering of the temperature by 50°C from 800 to 750°C will result in a viscosity increase of about 10 to 15 % for the melts studies (Figs. 1 – 8). One would, therefore, expect the $MgCl_2 - CaCl_2 - NaCl - KCl$ system to exhibit a similar behaviour.

We might conclude that the change in viscosity as a function of composition and temperature in the presently studied mixtures is relatively modest compared with viscosity changes in other important industrial liquids as for instance oils and high-polymer solutions.

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