

The Viscosity of the Fused Salts Mixtures (KCl-LiCl and KCl-NaCl Systems)

By

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Isotherms of viscosity against molar compositions have been investigated over extended temperature ranges for the systems KCl-LiCl and KCl-NaCl and the activation energy for viscous flow are calculated with Eyring's theory.

The activation energy showed negative deviation from additivity in KCl-LiCl system, but in KCl-NaCl system the activation energy showed positive deviation from additivity in the range of 0~40 mol % NaCl and showed negative deviation in the range of 40~100 mol % NaCl.

These deviations are caused by the interaction between different types of molecules or ion pairs in the liquid mixture.

1. Introduction

The viscosity of the fused salts mixture has been investigated by J. Kendall¹⁾, E. Heymann, H. Bloom²⁾ and others³⁾⁻⁶⁾, both from the practical standpoint of wanting to be able to predict the viscosity of fused salts mixture from the properties of the pure components and from the theoretical viewpoint of wishing to gain a clearer insight into the behavior of liquid mixtures.

It has been recognized that viscosity-composition curves are not simple functions of composition, they may have a maximum, a minimum, neither, or both.

One of the early equations, and certainly one of the most popular concerning the viscosity of a liquid to temperature is

$$\eta = A \exp (E_{\text{vis}}/RT) . \quad (1)$$

- A : constant
- E_{vis} : activation energy for viscous flow
- R : gas constant
- T : absolute temperature
- η : viscosity of fused salt

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H. Eyring⁷⁾ added theoretical significance in the equation in the following form:

$$\eta = (\lambda_1 h / \lambda_2 \lambda_3 \lambda^2) \exp (\Delta G / RT) \quad (2)$$

- λ : distance between two equilibrium positions for viscous flow
 λ_1 : distance between two layers of molecules
 λ_2 : mean distance between two adjacent molecules in the moving layer in the direction at a right angle to the direction of the motion
 λ_3 : distance between neighboring molecules in the same direction of motion
 h : Planck constant
 ΔG : activation energy

Although λ is not necessarily equal to λ_1 , the two quantities are of the same order of magnitude, and if, as a first approximation, they are taken to be identical, and the product $\lambda_1 \lambda_2 \lambda_3$ is approximately the volume inhabited by a single molecule in the liquid state, equation (2) may be written as;

$$\eta = (Nh/V) \exp (\Delta G / RT) = B \exp (E_{\text{vis}} / RT) \quad (3)$$

or
$$\eta / \rho = (Nh/M) \exp (\Delta G / RT) = B' \exp (E_{\text{vis}} / RT) \quad (4)$$

- N : Avogadro number
 V : molar volume
 M : molar weight
 ρ : density of fused salt
 B, B' : constant

From equation (4) we calculated the values of activation energy for viscous flow of fused salts.

We investigated the viscosity of fused KCl-LiCl and KCl-NaCl mixtures which are the basic components of fused salts electrolyte and fluxes for welding or brazing of aluminum and its alloys.

The isotherms of viscosity against molar compositions were determined over extended temperature ranges for these systems and the value of activation energy for viscous flow was calculated.

2. Apparatus and Experimental Procedure

The viscosity of fused KCl-LiCl and KCl-NaCl systems were measured by the damped oscillating disc method⁸⁾ at temperatures 700°~900°C. The ex-

perimental apparatus is shown in Fig. 1. The platinum disc (30 mm diameter and 2 mm thickness) is suspended from stainless steel wire (0.3 mm diameter and 1,060 mm long). This platinum disc is immersed into the fused salt, which is contained in a platinum dish (95 mm diameter and 45 mm depth). In the several preliminary experiments with aqueous solutions of H_2SO_4 in various concentrations,

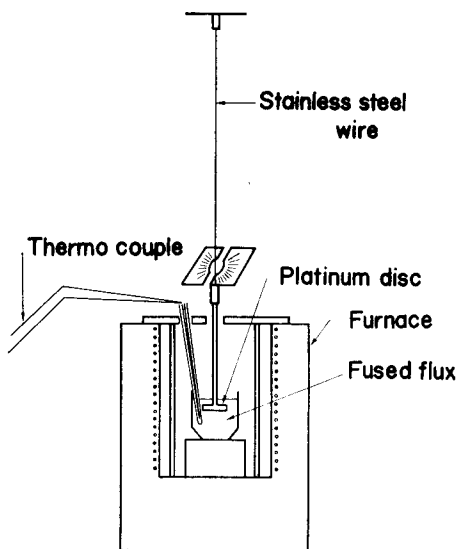


Fig. 1. Apparatus for determination of viscosity.

and fused KCl, we found that the damped oscillation of the disc gave logarithmic decrement to satisfy the condition for measuring viscosity, and the precision of measurement was found adequate with thin fluid whose number of oscillations (n) is given 20~50 between the initial torsion angle of 90° and the final torsion angle of 10° . The relation between the number of oscillation (n) and the viscosity (η) is shown by the following equation.

$$2.915/(n-1) = 1.0 \times 10^{-2}(\eta\rho)^{1/2} - 3.3 \times 10^{-4}(\eta\rho) + 1.3 \times 10^{-5}(\eta\rho)^{3/2} \quad (5)$$

where ρ is the density of fluid measured by the platinum sinker method.

3. Results

The variation in viscosity with both temperature and molar composition for the systems KCl-LiCl and KCl-NaCl are shown in tables 1 and 2. The isotherms of viscosity and molar volume of these systems plotted against molar fraction of KCl in the mixture are shown in Fig. 2 and 3, together with activation energy for viscous flow.

Table 1. Viscosity and activation energy for viscous flow of KCl-LiCl system.

Composition (mol %)		Temperature (°C)	Viscosity (centi poise)	Activation energy for viscous flow calc. with eq. (4) (K cal/mol.)
KCl	LiCl			
100	0	835	1.21	5.55
		790	1.37	
80	20	850	1.16	3.75
		810	1.23	
		790	1.27	
60	40	830	1.15	2.88
		810	1.23	
		790	1.27	
41	59	830	1.15	3.09
		810	1.19	
		790	1.23	
30	70	810	1.15	3.16
		790	1.19	
		690	1.44	
0	100	810	1.17	3.50
		790	1.21	
		742	1.30	

Table 2. Viscosity and the activation energy for viscous flow of KCl-NaCl system.

Composition (mol %)		Temperature (°C)	Viscosity (centi poise)	Activation energy for viscous flow calc. with eq. (4) (K cal/mol)
KCl	NaCl			
100	0	835	1.21	5.55
		790	1.37	
79	21	791	1.03	8.88
		766	1.13	
		727	1.40	
59	41	787	1.03	8.57
		760	1.12	
		719	1.39	
35	56	786	1.02	9.06
		762	1.12	
		720	1.38	
27	73	786	1.01	8.26
		764	1.11	
0	100	845	1.02	13.25
		829	1.12	

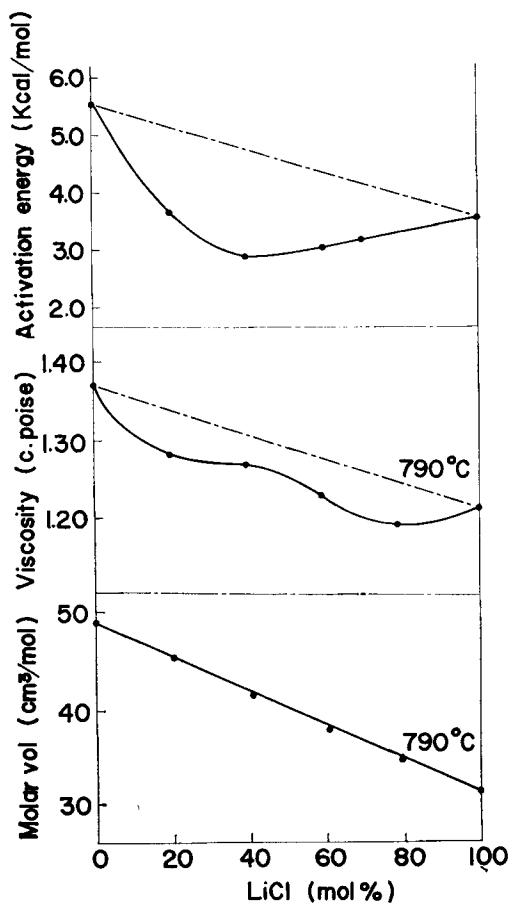


Fig. 2. Molar volume, viscosity and activation energy for viscous flow of KCl-LiCl system.

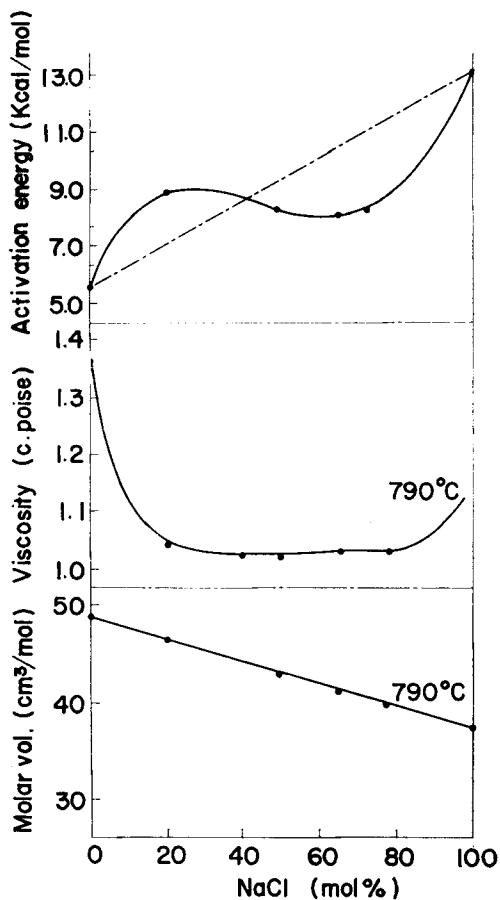


Fig. 3. Molar volume, viscosity and activation energy for viscous flow of KCl-NaCl system.

The isotherms of viscosity of KCl-LiCl system decrease with increasing LiCl in the mixture and a minimum value of viscosity was found at 68 mol % LiCl. The activation energy for viscous flow showed negative deviation from additivity and a minimum value was found in the range of 55~60 mol % LiCl.

The isotherms of viscosity against molar composition for the system KCl-NaCl showed negative deviation from additivity and a minimum value of viscosity was found at 70 mol % NaCl. The value of activation energy for viscous flow showed positive deviation from additivity in the range of 0~40 mol % NaCl and showed negative deviation in the range of 40~100 mol % NaCl.

4. Discussion

The phase diagrams for these systems⁹¹ indicate the simple eutectics. There is no evidence for the formation of complex ion in these systems¹⁰, and the molar volume of mixtures indicate a good agreement with the additivity of molar compositions.

In these systems, since there are two types of molecules in a mixture, we consider that the deviation of the activation energy for viscous flow from additivity is caused by the interaction between different types of molecules.

We consider a number of different encounters of a mixture, which consists of molecules of types A and B, (in these systems they are ion pairs of K^+Cl^- , Li^+Cl^- and Na^+Cl^-) some of which are shown in Fig. 4¹¹.

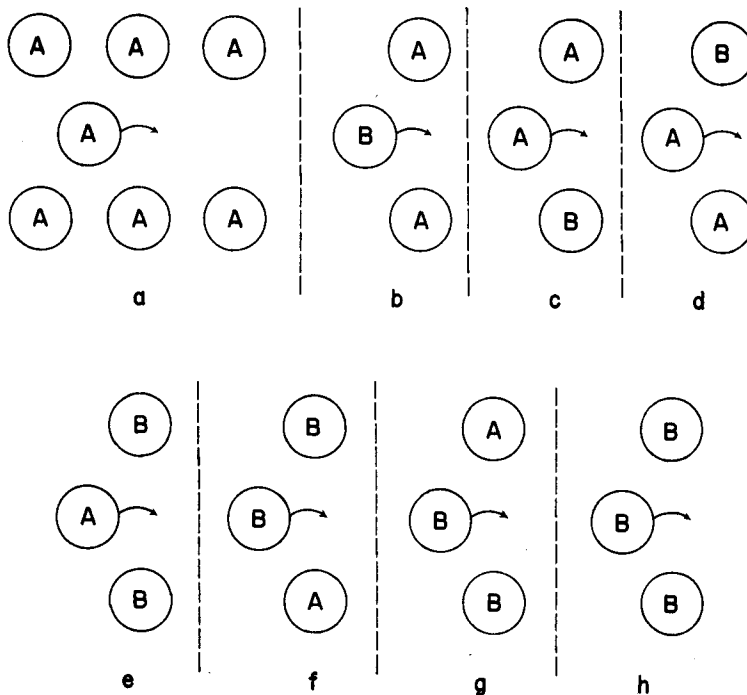


Fig. 4. The type of viscosity interaction in a binary mixture (three body model)

The types of interaction considered in these cases are only three bodied and are all in one plane. The type of interaction shown in Fig. 4(a) would correspond to the activation energy E_A , that is, for pure component A, the interaction 4 (h) would correspond to the activation energy E_B , that is, for pure component B, interactions of types (b), (c) and (d) all correspond to two molecules of type A and

one of type B. One would expect the activation energy of types (c) and (d) to be identical.

They will be referred to as E_{AAB} , the activation energy for interaction (b) will be referred to as E_{ABA} . The interactions of types (f), (g) and (e) all correspond to one molecule of type A and two of type B, and activation energy for types (f) and (g) would be equal and designated by E_{ABB} , whereas type (e) may be designated by E_{BAB} .

In any binary mixture of mol fraction x_1 the fraction of type (a) in total occurrences would be x_1^3 , as long as the number of molecules of type A and B are distributed at random in the liquid.

Corresponding occurrences of the various type of interactions are listed in table 3;

Table 3. Type of interaction and its fraction of total occurrences.

Type of interaction	A-A-A	A-B-A	A-A-B B-A-A	B-A-B	A-B-B B-B-A	B-B-B
Fraction of total occurrences	x_1^3	$x_1^2x_2$	$2x_1^2x_2$	$x_1x_2^2$	$2x_1x_2^2$	x_2^3
Activation energy for viscous flow	E_A	E_{ABA}	E_{AAB}	E_{BAB}	E_{ABB}	E_B

The assumption made here of course is that probability for the interaction is dependent only on the concentration and not on the activation energy for viscous flow.

It may be assumed that an activation energy for viscous flow in mixture may be shown as follows;

$$E_M = x_1^3E_A + x_1^2x_2E_{ABA} + 2x_1^2x_2E_{AAB} + x_1x_2^2E_{BAB} + 2x_1x_2^2E_{ABB} + x_2^3E_B \quad (6)$$

Two additional assumptions are made at this point;

$$E_A = (E_{ABA} + 2E_{AAB})/3,$$

$$E_B = (E_{BAB} + 2E_{ABB})/3.$$

From these assumptions equation (6) can be written as;

$$E_M = x_1^2E_A + 3x_1^2x_2E_A + 3x_1x_2^2E_B + x_2^3E_B \quad (7)$$

We calculated the activation energy for viscous flow in the systems with Eq. (7) and from additivity of molar compositions.

Similarly using experimental data, the activation energy was calculated with Eq. (4). The results are shown in Table 4 and 5.

Table 4. Activation energy for viscous flow of KCl-LiCl system.

mol fraction		calc. from additivity (Kcal/mol)	calc. with eq. (7) (Kcal/mol)	calc. with eq. (4) (Kcal/mol)
KCl	LiCl			
1.00	0.00	5.55	5.55	5.55
0.80	0.20	5.15	3.75	3.75
0.60	0.40	4.75	2.98	2.88
0.41	0.59	4.32	3.03	3.09
0.30	0.70	4.08	3.16	3.16
0.00	1.00	3.50	3.50	3.50

Table 5. Activation energy for viscous flow of KCl-NaCl system.

mol fraction		calc. from additivity (Kcal/mol)	calc. with eq. (7) (Kcal/mol)	calc. with eq. (4) (Kcal/mol)
KCl	NaCl			
1.00	0.00	5.55	5.55	5.55
0.79	0.21	7.08	8.88	8.88
0.59	0.41	9.50	8.48	8.57
0.35	0.65	10.53	8.08	8.06
0.27	0.73	11.20	8.26	8.26
0.00	1.00	13.25	13.25	13.25

It can easily be seen that the values calculated with Eq. (7) are all in close agreement with those calculated with Eq. (4).

It may be therefore concluded that, the deviation of the values of activation energy for viscous flow from additivity of the molar compositions are caused by the interaction between different types of molecules or ion pairs in the liquid mixture.

5. Summary

We measured the viscosity of KCl-LiCl and KCl-NaCl systems by the damped oscillation method with platinum disc.

In the KCl-LiCl system, the isotherms of viscosity against molar compositions showed negative deviation from additivity and a minimum value of viscosity was found at 68 mol % LiCl. The activation energy for viscous flow showed negative deviation from additivity.

In the KCl-NaCl system, the isotherms of viscosity against molar compositions showed negative deviation from additivity and a minimum value of viscosity was found at 70 mol % NaCl. The activation energy showed positive deviation from additivity in the range of 0~40 mol % NaCl and showed negative deviation in the range of 40~100 mol % NaCl.

These deviations are caused by the interaction between different types of

molecules or ion pairs in the liquid mixture, and the activation energy for viscous flow of fused KCl-LiCl and KCl-NaCl mixtures may be represented by Eq. (7).

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