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Structure of the melts of the systems MF–M_2SO_4, where M is Li, Na, K

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Abstract

The densities of the melts in the systems MF–M_2SO_4 (where M is Li, Na, K) were measured using the method of hydrostatic weighing. From the volume properties point of view the investigated systems exhibit almost ideal behaviour which indicates that the congruently melting compounds Na_3FSO_4 and K_3FSO_4, which are formed in the systems NaF–Na_2SO_4 and KF–K_2SO_4, respectively, exhibit a low thermal stability and at melting they undergo a considerable thermal dissociation. The degree of the thermal dissociation was calculated on the basis of both the thermodynamic analysis of the phase diagrams and the volume properties of the investigated systems. It was found that the degree of thermal dissociation of Na_3FSO_4 at the melting point attains the value $\alpha_0 = 0.71$ while that of K_3FSO_4 is $\alpha_0 = 0.78$. The dissociation enthalpies calculated on the basis of the density values are $\Delta_{\text{dis}}H(Na_3FSO_4) = 40.2\ \text{kJ mol}^{-1}$ and $\Delta_{\text{dis}}H(K_3FSO_4) = 24.1\ \text{kJ mol}^{-1}$.

INTRODUCTION

In the binary systems of alkali metal fluorides and other salts of alkali metals, such as sulphates, chromates, molybdates, tungstates and transition metal fluorides, complex compounds such as Na_3FSO_4, K_3FMoO_4, K_3TiF_7, K_3ZrF_7, are formed. At melting these compounds often undergo a more or less extended thermal dissociation, in some cases they even melt incongruently. Evidence of such behaviour may be found, for example, in refs. 1 and 2.

M_3FSO_4 compounds, where M = Na, K also belong to this group. The thermal stability of these compounds obviously depends on the chemical nature of the alkali metal present. The analogous compound Li_3FSO_4 is not formed in the system LiF–Li_2SO_4, probably due to the strong polarization

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ability of the lithium cation. From the phase equilibrium study of Kleppa and Julsrud [3] and the calorimetric measurements of the enthalpies of mixing performed by Hatem et al. [4] of these systems it follows that their behaviour is almost ideal.

The phase diagrams of the system $MF–M_2SO_4$ (where M is Li, Na, K) were studied by Kleppa and Julsrud [3]. These authors found that the system $LiF–Li_2SO_4$ is a simple eutectic system with the coordinates of the eutectic point of 41 mol% LiF and the eutectic temperature of 531.2°C.

In the system $NaF–Na_2SO_4$ the congruently melting additive compound Na_3FSO_4 with the melting point of 785.2°C is formed. This compound divides the system into two simple eutectic systems with the coordinates of the eutectic points of 26 mol% NaF and 748.2°C in the subsystem $Na_2SO_4–Na_3FSO_4$ and 59 mol% NaF and 780.1°C in the subsystem $Na_3FSO_4–NaF$.

As in the previous case the additive compound K_3FSO_4 with the congruent melting point of 875.2°C is formed in the system $KF–K_2SO_4$. The coordinates of the eutectic point of the subsystem $K_2SO_4–K_3FSO_4$ are 41 mol% KF and 870.1°C while for the subsystem $K_3FSO_4–KF$ the respective values are 83 mol% KF and 777.7°C. From the course of the liquidus curves of the last two systems it may be assumed that both additive compounds undergo considerable thermal dissociation at melting.

In the present work the densities of the melts have been measured and the volume properties of the molten systems $MF–M_2SO_4$ have been studied to obtain more information on their thermodynamic behaviour. The density values have been employed in the calculation of the degree of the thermal dissociation of the additive compounds M_3FSO_4 and are compared with those obtained from the thermodynamic analysis of the phase diagrams of the investigated systems.

PROCEDURE

With regard to the thermal dissociation of the additive compounds M_3FSO_4, the calculation of the equilibrium composition of the molten mixtures $MF–M_2SO_4$ can be based on the following procedure.

Let us consider an arbitrary mixture of $(1-x)$ mole of the substance MF and x mole of the substance M_2SO_4, in which the additive compound M_3FSO_4 is formed. For $x < 0.5$ a maximum number of x mole of M_3FSO_4 can be formed in the mixture. In the case of the thermal dissociation of the substance M_3FSO_4 according to the scheme

$$M_3FSO_4 \rightleftharpoons MF + M_2SO_4 \qquad (1)$$

with the dissociation degree α, the resulting amounts of the components in the mixture can be expressed as

$$x(\mathrm{MF}) = 1 - 2x + \alpha x$$

$$x(\mathrm{M_2SO_4}) = \alpha x$$

$$x(\mathrm{M_3FSO_4}) = x(1 - \alpha)$$

The total amount of substance of all components then will be $1 - x + \alpha x$. Consequently, the mole fractions of components are expressed by the equations

$$x(\mathrm{MF}) = \frac{1 - 2x + \alpha x}{1 - x + \alpha x}$$

$$x(\mathrm{M_2SO_4}) = \frac{\alpha x}{1 - x + \alpha x} \tag{2}$$

$$x(\mathrm{M_3FSO_4}) = \frac{x(1 - \alpha)}{1 - x + \alpha x}$$

Assuming the ideal behaviour of the solutions, the equilibrium constant of eqn. (1) can be written as

$$K = \frac{\alpha_o^2}{1 - \alpha_o^2} = \frac{\alpha(1 - 2x + \alpha x)}{(1 - \alpha)(1 - x + \alpha x)} \tag{3}$$

where α_o is the dissociation degree of pure $\mathrm{M_3FSO_4}$. A similar expression for the equilibrium constant can be derived for $x > 0.5$

$$K = \frac{\alpha[x - (1 - \alpha)(1 - x)]}{(1 - \alpha)[x + \alpha(1 - x)]} \tag{4}$$

By means of eqns. (3) and (4) it is possible to calculate the degree of thermal dissociation α of $\mathrm{M_3FSO_4}$ for any arbitrarily selected value of α_o and, after inserting the calculated value α into eqns. (2), to obtain the values of the equilibrium mole fractions of the individual components. In the calculation it was assumed that in the given temperature range of the liquidus the equilibrium constant does not change with temperature. Introducing the values of the equilibrium mole fractions of the individual components, $x(i)$, into the LeChatelier–Shreder equation, the values of the temperature of primary crystallization of components, $T_{\mathrm{pk}}(i)$, may be calculated, and so it may be possible to draw the hypothetical liquidus curves of the investigated systems corresponding to the appropriate value of the degree of dissociation α_o. The melting temperatures of the hypothetical undissociated compounds $\mathrm{M_3FSO_4}$ for the given equilibrium composition were calculated from the experimentally determined melting temperatures of these compounds.

The criterion for the selection of the correct value of the degree of dissociation α_o, is the best fit between the experimental and calculated liquidus temperatures according to the condition

$$\sum_{i=1}^{n} [T_{pk}(i, \text{exp}) - T_{pk}(i, \text{cal})]^2 = \text{min} \tag{5}$$

The experimentally determined phase diagrams from Kleppa and Julsrud [3] were taken for the calculation. Data for the temperatures and enthalpies of melting of pure components were taken from JANAF Tables [5], and the corresponding values for M_3FSO_4 were taken from refs. 6 and 7 ($\Delta_f H(Na_3FSO_4) = 69\ \text{kJ mol}^{-1}$, $\Delta_f H(K_3FSO_4) = 86\ \text{kJ mol}^{-1}$).

In the determination of the degree of thermal dissociation of the additive compounds M_3FSO_4, based on the volume properties, the theoretical density of the melts has been calculated according to the equation

$$\rho(\text{cal}) = \left[\frac{w(MF)}{\rho(MF)} + \frac{w(M_2SO_4)}{\rho(M_2SO_4)} + \frac{w(M_3FSO_4)}{\rho(M_3FSO_4)}\right]^{-1} \tag{6}$$

where $w(i)$ and $\rho(i)$ are the equilibrium mass fraction and the densities of the components i, respectively, $\rho(M_3FSO_4)$ being the hypothetical density of the undissociated molten compound M_3FSO_4 at a given temperature. For each selected value of the equilibrium constant (eqns. (3) and (4)) and for a selected hypothetical density of undissociated molten M_3FSO_4, a set of theoretical density values has been obtained for each initial composition of the melt. Here again, the criterion of the correctness of the selection was the condition

$$\sum_{i=1}^{n} [\rho(i, \text{exp}) - \rho(i, \text{cal})]^2 = \text{min} \tag{7}$$

EXPERIMENTAL

The density of the melts of the systems $MF–M_2SO_4$ was measured by means of the Archimedean method. The platinum sphere with a diameter of 20 mm suspended on a platinum wire ($d = 0.3$ mm) has been used as the measuring body. The dependence of the volume of the sphere on the temperature was determined by calibration using molten NaCl and KCl. The experimental error of the density measurement did not exceed 0.2%. The detailed description of the measuring device used is given in ref. 8.

The measurements were performed on cooling within a temperature range of about 150 K, the lower limit of this interval being 10–20°C above the temperature of primary crystallization of the respective samples.

For the despriction of the temperature dependence of the density the linear equations in the form

$$\rho = a - bt \tag{8}$$

TABLE 1

Values of the coefficients a and b in the equation $\rho = a - bt$ for the melts of the investigated systems MF–M_2SO_4

Composition		$a/\mathrm{g\,cm^{-3}}$	$b \times 10^4/\mathrm{g\,cm^{-3}\,°C^{-1}}$	$s \times 10^4/\mathrm{g\,cm^{-3}}$
x(MF)	$x(M_2SO_4)$			
LiF–Li_2SO_4				
0.0	1.0	2.353	4.070	1.8
0.2	0.8	2.331	4.090	4.1
0.4	0.6	2.314	4.100	3.2
0.6	0.4	2.281	4.002	2.8
0.8	0.2	2.245	4.104	4.7
1.0	0.0	2.224	4.902	1.9
NaF–Na_2SO_4				
0.0	1.0	2.585	6.400	3.8
0.2	0.8	2.565	6.009	1.9
0.4	0.6	2.530	5.505	4.9
0.6	0.4	2.504	5.106	3.7
0.8	0.2	2.521	5.215	3.6
1.0	0.0	2.521	5.100	2.5
KF–K_2SO_4				
0.00	1.00	2.352	4.808	5.3
0.25	0.75	2.421	5.491	8.2
0.50	0.50	2.463	6.206	2.2
0.75	0.25	2.446	6.200	2.9
1.00	0.00	2.468	6.509	3.7

were used, where ρ is the density in g cm^{-3} and t is the temperature in °C. The values of the constants a and b are given together with the standard deviations of approximation in Table 1. From the measured density values the molar volumes and the excess molar volumes of the investigated systems at 900 and 1000°C were calculated.

RESULTS AND DISCUSSION

The density isotherms in the systems MF–M_2SO_4 (Table 2) increased monotonically with increasing content of M_2SO_4. From the values of the excess molar volumes, it follows that these systems differ only little from the ideal behaviour, as was found in ref. 3. However, the excess molar volumes are positive in all systems investigated, which is in contradiction with the finding in ref. 3, where the enthalpies of mixing in the NaF–Na_2SO_4 and KF–K_2SO_4 systems have different sign. The course of the molar volume change is not affected by the formation of the compounds M_3FSO_4, which indicates considerable thermal dissociation of these compounds. The

TABLE 2

Values of the density, molar volume and excess molar volume of the investigated melts of the system $MF-M_2SO_4$

Composition $x(M_2SO_4)$	$\rho/g\,cm^{-3}$		$V_m/cm^3\,mol^{-1}$		$V_{ex}/cm^3\,mol^{-1}$	
	900°C	1000°C	900°C	1000°C	900°C	1000°C
$LiF-Li_2SO_4$						
0.0	1.783	1.734	14.55	14.96	0.00	0.00
0.2	1.876	1.835	22.79	23.30	0.08	0.03
0.4	1.921	1.881	31.00	31.66	0.13	0.08
0.6	1.945	1.904	39.25	40.09	0.23	0.21
0.8	1.963	1.922	47.45	48.46	0.27	0.27
1.0	1.987	1.946	55.34	56.50	0.00	0.00
$NaF-Na_2SO_4$						
0.0	2.009	1.945	20.90	21.59	0.00	0.00
0.2	2.024	1.964	30.63	31.57	0.13	0.17
0.4	2.035	1.980	40.31	41.43	0.21	0.22
0.6	2.044	1.993	49.90	51.18	0.21	0.16
0.8	2.052	2.000	59.48	61.03	0.19	0.20
1.0	2.062	2.011	68.89	70.64	0.00	0.00
$KF-K_2SO_4$						
0.00	1.882	1.817	30.87	31.97	0.00	0.00
0.25	1.888	1.826	46.15	47.72	0.62	0.83
0.50	1.904	1.842	61.00	63.06	0.80	1.24
0.75	1.927	1.872	75.37	77.58	0.50	0.84
1.00	1.946	1.901	89.53	91.66	0.00	0.00

values of the equilibrium dissociation constants, degrees of dissociation and densities of the molten undissociated compounds M_3FSO_4 at 900 and 1000°C are summarized in Table 3. As shown by the dissociation degree values, both congruently melting compounds undergo pronounced thermal dissociation on melting. The respective Li_3FSO_4 compound is almost fully dissociated and does not form a dystectic point in the phase diagram. Based on the dependence of the equilibrium dissociation constant on temperature, the values of the enthalpies of dissociation $\Delta_{dis}H(Na_3FSO_4) = 40.2\ kJ\,mol^{-1}$ and $\Delta_{dis}H(K_3FSO_4) = 24.1\ kJ\,mol^{-1}$ have been calculated, which is in both cases a substantial part of the enthalpy of fusion. The dissociation enthalpy of the hypothetical compound Li_3FSO_4 is $\Delta_{dis}H(Li_3FSO_4) = 50.5\ kJ\,mol^{-1}$.

Figure 1 shows the phase diagram of the system $NaF-Na_2SO_4$ according to ref. 3 and the liquidus curves calculated for the value of the equilibrium dissociation constant of compound Na_3FSO_4, $K_{dis}(Na_3FSO_4) = 1.017$, the corresponding values of the degree of dissociation and the hypothetical melting temperature of the undissociated compound Na_3FSO_4 being $\alpha_o = 0.71$ and $T_{f,nd}(Na_3FSO_4) = 1368\ K$. The standard deviation of ap-

TABLE 3

Values of the equilibrium constants, the degree of thermal dissociation, the hypothetical densities of undissociated compounds M_3FSO_4 and the standard deviations of approximation in the theoretical density calculation

Compound	$t/°C$	K	α_o	$\rho/g\,cm^{-3}$	$s \times 10^3/g\,cm^{-3}$
Li_3FSO_4	900	4.263	0.90	1.85	3.7
	1000	6.402	0.93	1.80	4.5
Na_3FSO_4	900	1.286	0.75	2.01	0.8
	1000	1.778	0.80	1.95	0.9
K_3FSO_4	900	1.367	0.76	1.83	1.5
	1000	1.660	0.79	1.72	1.3

proximation is 2.9 K, which shows good agreement between the two sets of data and the correctness of the thermodynamic model employed. The determined value of the degree of dissociation is consistent with values $\alpha_0(900°C) = 0.75$ and $\alpha_0(1000°C) = 0.80$ determined by analysis of the volume properties.

Figure 2 shows the phase diagram of the system $KF–K_2SO_4$ according to ref 3. The best fit between the experimental and calculated liquidus curves has been obtained for the value of the equilibrium dissociation constant of K_3FSO_4, $K_{dis}(K_3FSO_4) = 1.367$ with the corresponding value of the degree of dissociation $\alpha_o = 0.76$ and the hypothetical melting temperature of the undissociated additive compound $T_{f,nd}(K_3FSO_4) = 1475$ K. The standard deviation of approximation was determined to be 8 K. The value of the degree of dissociation of K_3FSO_4 is consistent with the values

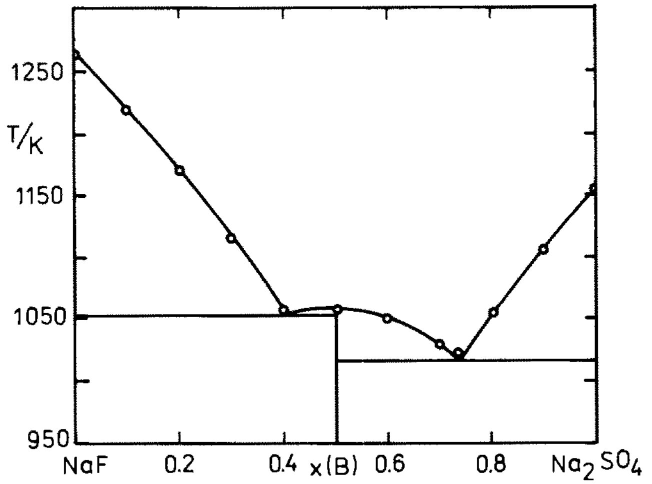

Fig. 1. Comparison of the calculated and experimentally determined phase diagram of the system $NaF–Na_2SO_4$. O, experimental [3]; —, calculated.

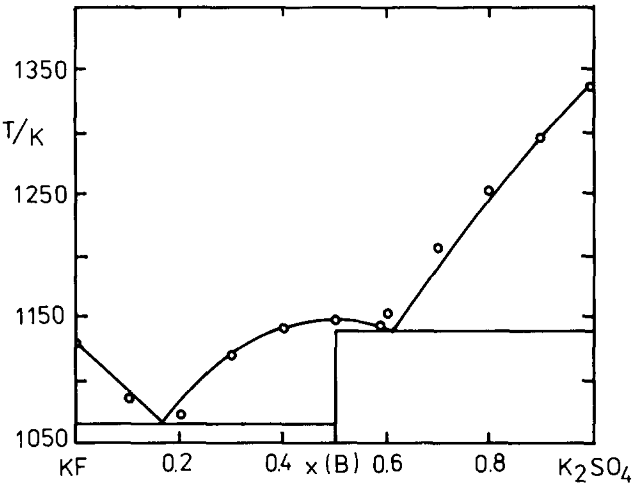

Fig. 2. Comparison of the calculated and experimentally determined phase diagram of the system KF–K_2SO_4. ○, experimental [3]; ——, calculated.

$\alpha_0(900°C) = 0.76$ and $\alpha_0(1000°C) = 0.79$ determined by analysis of the volume properties.

From the calculated value of the degrees of dissociation it follows that the thermal stability of the additive compounds depends on the chemical nature of the alkali metal cation present. In the presence of the lithium cation the repulsive forces of both anions present are so strong that formation of the additive compound does not occur. Both sodium and potassium cations soften these repulsive forces, which leads to the formation of dystectic points in phase diagrams.

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