mit to make $R \cong 0$, then the Eqs. (20) and (21) have to be solved by successive approximations, starting with $R = 0$ for the first approximation of ϱ and λ, then computing R from Eq. (19) in order to obtain the second approximation, etc. The rate constants k_s, k_d may finally be determined from Eqs. (6) – (8).

Conclusions

1. By the extension of COHEN's theory to separating columns with successive exchange between three fluids it is posible both to determine the dependence of the mole fractions on the height of the column from known values of the rate constants, and to compute the rate constants if the values of the mole fractions at the ends of the column are known.

2. The specific feature of columns with successive exchange between three fluids consists in the height dependence of the mole fractions in the form of two exponential terms with unequal exponents. Excepting a zone situated at the bottom of the column, $z \cong 0$, the mole fractions vary along the column so that the ratio of the driving forces remain constant.

On the Dissociation of Silver, Thallium and Zinc Sulphates in Some Molten Nitrates *

P. FRANZOSINI, C. SINISTRI, and G. FLOR

Institute of Physical Chemistry, University of Pavia, Italy

(Z. Naturforschg. **21 a**, 749—752 [1966]; received 21 February 1966)

The cryoscopic behaviour of Ag, Tl and Zn sulphates in a number of molten univalent nitrates has been investigated. Ag_2SO_4 appears to be thoroughly ionized in $LiNO_3$ and partially ionized in KNO_3; Tl_2SO_4 thoroughly in Li, Na and Ag nitrates; $ZnSO_4$ thoroughly in $LiNO_3$ and partially in Na, K and Ag nitrates.

The present paper aims at inquiring the ionization of some sulphates when dissolved in molten nitrates having suitable characteristics, and of which heats of fusion and cryoscopic constants were already well known[1]. The solutions of Ag_2SO_4 in $LiNO_3$ and KNO_3, of Tl_2SO_4 in $LiNO_3$, $NaNO_3$, and $AgNO_3$ and of $ZnSO_4$ in $LiNO_3$, $NaNO_3$, KNO_3, and $AgNO_3$ have been chosen.

A previously described[1] conventional cryoscopic apparatus has been employed. All salts (C. Erba RP, Merck "pro analysi" or BDH) have been carefully dried before use.

The experimental results are shown in Figs. 1 – 3. A number of numerical data, interpolated from the experimental ones and used in the following discussion, are summarized in Table 1.

Discussion

The possibility of evaluating cryoscopically active species ν and, in general, of applying the cryoscopic method is usually conditioned to the fact that solute and solvent do not form solid solutions. In order to ascertain this point in the systems here involved,

System	$m = 0.04$	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20	0.22	0.24
Ag_2SO_4 in KNO_3	3.43	5.02	6.56	8.09	9.53	10.91					
Ag_2SO_4 in (KNO_3+0.10 m. $AgNO_3$)	3.23	4.78	6.27	7.69	9.04	10.37	11.67				
Ag_2SO_4 in (KNO_3+0.25 m. $AgNO_3$)	3.05	4.49	5.92	7.27	8.54	9.75	10.95				
$ZnSO_4$ in $NaNO_3$			1.92	2.35	2.75	3.13	3.47	3.81	4.12	4.44	4.74
$ZnSO_4$ in ($NaNO_3$+0.049 m. Na_2SO_4)			1.75	2.13	2.49	2.83	3.17	3.51			
$ZnSO_4$ in ($NaNO_3$+0.119 m. Na_2SO_4)			1.47	1.79	2.09	2.39	2.69	2.99	3.27	3.56	3.84
$ZnSO_4$ in KNO_3	1.77	2.42	3.01	3.59	4.14	4.69					
$ZnSO_4$ in $AgNO_3$	1.94	2.78	3.57	4.29	4.95	5.58					

Table 1. ΔT_{exp} (°C) interpolated values for partially ionized sulphates.

* Work carried out with the help of the Consiglio Nazionale delle Ricerche (Rome).

[1] M. ROLLA and P. FRANZOSINI, Ann. Chim. Rome **48**, 723 [1958]. — P. FRANZOSINI and C. SINISTRI, ibid. **49**, 970 [1959]; Ric. Sci. **33** (II, A) 411 [1963].

a preliminary series of cryoscopic measurements have been carried out on diluted solutions of Li, Na, K sulphates in the corresponding nitrates; measurements on solutions of Ag_2SO_4 in $AgNO_3$, of $TlNO_3$ in Li, Na, Ag nitrates and of $AgNO_3$ in Li, K nitrates had already been made in previous works[1]. All the above systems show, for $m=0$, a value $\nu=1$. Cryoscopies of $Zn(NO_3)_2$ in the nitrates chosen as solvents could not be carried out owing to the difficulty of preparing a thoroughly dried sample of the former salt. Therefore we thought it advisable to make X-rays powder spectrograms in order to ascertain whether or not there were mixed crystals in the systems containing $ZnSO_4$. The interference lines characteristic of the Li, Na, K, Ag nitrates and found on previously fused mixtures of $ZnSO_4$ with each of these nitrates have not shown significant variations in comparison with the lines of the pure nitrates used as standards. It cannot be excluded that solid solutions, possibly formed at higher temperatures, demix at the temperature at which the spectrograms have been taken (room temperature): however, the results, though not categoric, allow to consider the immiscibility in the solid state of $ZnSO_4$ with the chosen nitrates (at least in the $ZnSO_4$ concentration field where we have worked) as very probable.

The systems $Ag_2SO_4+NaNO_3$ and $Tl_2SO_4+KNO_3$ will not be taken into account, inasmuch as the mixtures $AgNO_3+NaNO_3$ and $TlNO_3+KNO_3$ form solid solutions.

It is well known[2] that, when a solute thoroughly dissociates in a given melt forming ν cryoscopically active species, the function $\nu(m)$ is not necessarily a constant, but the curve representing it shows a slope either positive or negative, according to the type of interaction between the different ionic species which are present. As a negative slope might also be an indication of partial dissociation, in the cases we have studied the sulphate was considered completely dissociated only if the curve $\nu(m)$ had a positive slope: if the slope was zero or slightly negative further experiments were carried out by introducing common ions, the effect of which allowed to decide between the two possibilities; finally, if the curve, starting with a highly negative slope, assumed a typically "boat shape", the salt was considered as partially ionized.

[2] C. Sinistri, Z. Phys. Chem. Frankfurt **30**, 349 [1961].

Ag_2SO_4 in Li, K Nitrates

The results regarding these two systems are shown in Fig. 1. For Ag_2SO_4 in $LiNO_3$ the number of cryoscopically active species is 3 as $m\to 0$: this, together with the fact that, within the experimental concentration range, the slope of the curve $\nu(m)$ is positive, shows the complete dissociation of the solute.

For Ag_2SO_4 in KNO_3, ν is always between 2 and 3 (see Fig. 1, curve a): this indicates that, presumably, there are no indissociate solute molecules in the melt, while the equilibrium

$$AgSO_4^- \rightleftarrows Ag^+ + SO_4^{--} \qquad (1)$$

takes place. Thus it is possible to calculate the constant K governing the equilibrium, e. g., according to the following procedure. By indicating with φ the quantity (formally similar to an ionization degree):

$$\varphi = (\Delta T_{exp} - \Delta T_{2\nu}) / (\Delta T_{3\nu} - \Delta T_{2\nu}) \qquad (2)$$

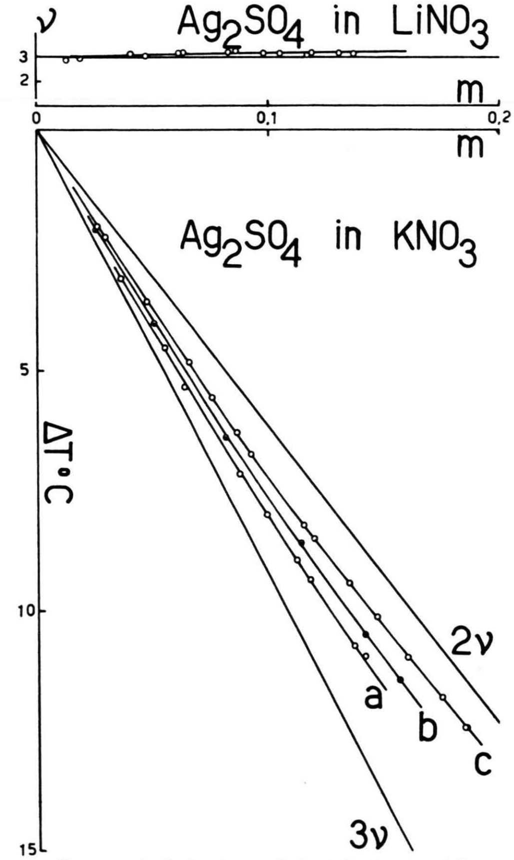

Fig. 1. Cryoscopic behaviour of Ag_2SO_4 in fused Li and K nitrates (the curves a, b and c refer to the solvents: pure KNO_3, KNO_3+0.1 m. $AgNO_3$ and $AgNO_3$+0.25 m. $AgNO_3$, respectively).

where $\Delta T_{2\nu}$, $\Delta T_{3\nu}$ are respectively the cryoscopic depressions corresponding to $\nu = 2$ and $\nu = 3$ (evaluated from the results of previous works [1]) and ΔT_{exp} is the experimental one, it is easy to draw the equation

$$K' = m\,\varphi \cdot (1+\varphi)/(1-\varphi). \tag{3}$$

As Eq. (2) gives a true dissociation degree only when $m \to 0$, it is apparent that K is to be singled out by extrapolating at infinite dilution the values K', previously calculated at finite concentrations by means of Eq. (3). Curve a in Fig. 4 illustrates the results of the calculation.

Measurements have also been taken on solutions of Ag_2SO_4 in the mixed solvents (KNO_3 + 0.1 m. $AgNO_3$) and (KNO_3 + 0.25 m. $AgNO_3$): the curves b and c of Fig. 1 indicate how the ΔT_{exp} values gradually diminish owing to the influence of the common ion. In the elementary assumption that, even in presence of $AgNO_3$, only equilibrium 1 exists, the evaluation of K is possible by extrapolating for $m = 0$ the quantity:

$$K'' = \frac{\varphi}{1-\varphi}(m + m\,\varphi + m(\mathrm{AgNO_3})) \tag{4}$$

where $m(\mathrm{AgNO_3})$ represents the $AgNO_3$ molality in the mixed solvent, the melting point of which is conventionally taken as zero. The results are represented by the curves b and c of Fig. 4: the three curves of the figure converge rather satisfactorily towards a value $K \sim 0.3$. A correction for the extrapolated values not being isothermal is probably smaller than the uncertainty weighing on K.

WATT and BLANDER [3] by means of emf measurements have studied the equilibrium 1 in the same solvent. From the results of these authors it is possible to calculate for K a mean value equal to 0.8 (at the mean temperature of 413 °C). Our value (0.3), which refers to a mean temperature of ~330 °C, is consistent with that of the above mentioned authors.

Tl_2SO_4 in Li, Na, Ag Nitrates

According to the above considerations, it is apparent from Fig. 2 that thallous sulphate is to be considered as completely dissociated in $LiNO_3$ as well as in $AgNO_3$, as in both cases ν is 3 when $m = 0$, and the $\nu(m)$ curve shows a positive slope. On the contrary, in $NaNO_3$ the function $\nu(m)$ has

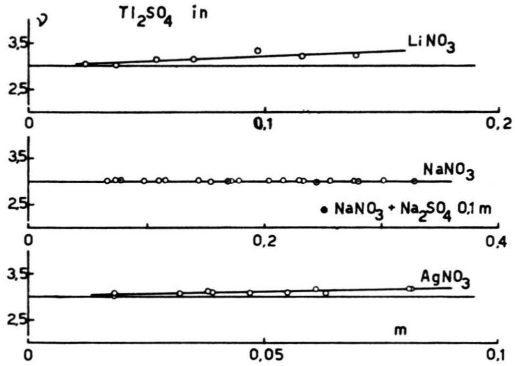

Fig. 2. Cryoscopic behaviour of Tl_2SO_4 in fused Li, Na and Ag nitrates.

an almost constant value: to remove any possible doubt, measurements have been carried out in the mixed solvent ($NaNO_3$ + 0.1 m. Na_2SO_4). As also under these conditions the number of cryoscopically active species remains 3, it may be reasonably concluded that thallous sulphate is completely dissociated in all the three title nitrates.

$ZnSO_4$ in Li, Na, K, Ag Nitrates

The results regarding these four systems are illustrated in Fig. 3. Zinc sulphate, both in pure $LiNO_3$ and in the mixed solvent ($LiNO_3$ + 0.092 m. Li_2SO_4) shows a ν value equal to 2, which allows to consider its dissociation complete.

In the other three nitrates it is $2 < \nu < 3$, which clearly indicates an only partial dissociation. This is also confirmed by the fact that, e. g., measurements carried out in the mixed solvents ($NaNO_3$ + 0.049 m. Na_2SO_4) and ($NaNO_3$ + 0.119 m. Na_2SO_4) show a progressive and considerable displacement towards the simple depression of the $\Delta T(m)$ curves.

The evaluation of the K constants concerning the equilibrium

$$\mathrm{ZnSO_4} \rightleftarrows \mathrm{Zn^{++}} + \mathrm{SO_4^{--}} \tag{5}$$

in the different solvents may be effected by extrapolating for $m = 0$ the quantities

$$K''' = m \cdot \varphi^2/(1-\varphi) \tag{6}$$

calculated at finite concentrations by means of the relation

$$\varphi = (\Delta T_{\text{exp}} - \Delta T_{1\nu})/(\Delta T_{2\nu} - \Delta T_{1\nu}). \tag{7}$$

The results, expressed in terms of $p\,K'''(m)$, are represented in Fig. 4. Extrapolated $p\,K$ values have

[3] W. J. WATT and M. BLANDER, J. Phys. Chem. **64**, 729 [1960].

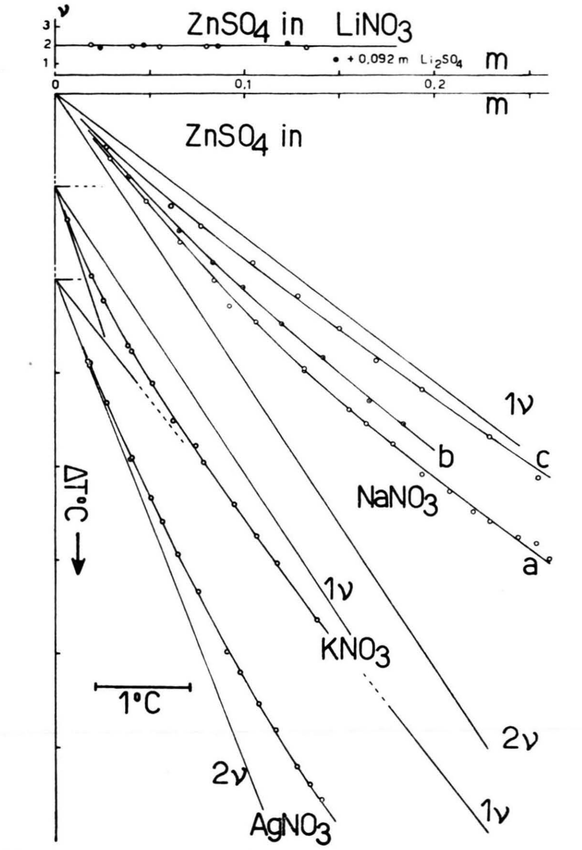

Fig. 3. Cryoscopic behaviour of $ZnSO_4$ in fused Li, Na, K, and Ag nitrates (the curves a, b and c refer to the solvents: pure $NaNO_3$, $NaNO_3$+0.049 m. Na_2SO_4, and $NaNO_3$+0.119 m. Na_2SO_4, respectively).

been: ~1.2 in $NaNO_3$; ~1.5 in KNO_3, and ~0.5 in $AgNO_3$.

It seems most likely that Zn^{++}, in the presence of high concentrations of SO_4^{--}, has a tendency to form complexes of the type $Zn(SO_4)_2^{--}$: in fact, qualitative measurements carried out in the mixed solvents ($NaNO_3$ + 0.20 m. Na_2SO_4) and ($NaNO_3$ + 0.32 m. Na_2SO_4) point out a ν value between 0 and 1.

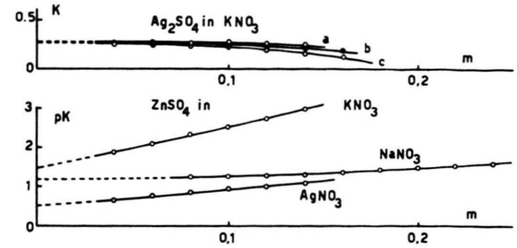

Fig. 4. Ionization constants of Ag_2SO_4 in KNO_3, and of $ZnSO_4$ in Na, K, and Ag nitrates.

Final Remarks

The results obtained are summarized in Table 2. A comparison between the ionizing powers of the three alkali nitrates may be drawn from the behaviour of $ZnSO_4$: the ionization of this salt progressively increases when passing from KNO_3 to $NaNO_3$ and finally to $LiNO_3$ as solvents. It is likely that the progressively decreasing radii of the alkali cations play an essential role, inasmuch as the smaller the size and the higher the charge density of the cation, the greater is the ionizing power of the solvent.

This view is supported also by some results concerning lead sulphate in the three alkali nitrates. In fact also this salt appears thoroughly dissociated in $LiNO_3$, and only partially dissociated in $NaNO_3$ and KNO_3.

Acknowledgment

The spectrograms mentioned in the present paper have been taken partially by Dr. M. Cola (Institute of General Chemistry) and partially by Dr. G. Giuseppetti (Institute of Mineralogy, University of Pavia), to whom we are deeply indebted.

Solute \ Solvent	$LiNO_3$	$NaNO_3$	KNO_3	$AgNO_3$
Ag_2SO_4	complete ionization	—	$pK \sim 0.5$	—
Tl_2SO_4	complete ionization	complete ionization	—	complete ionization
$ZnSO_4$	complete ionization	$pK \sim 1.2$	$pK \sim 1.5$	$pK \sim 0.5$

Table 2. Summarized results [in order to calculate the ionization constants, concentrations expressed as (mole of solute) / (Kg of solvent) have been used].