

Concentration Dependence of the Interdiffusion Coefficients in Molten Alkali Nitrate – Silver Nitrate Mixtures

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Dedicated to Professor Rolf Haase on the occasion of his 65th birthday

To measure the composition dependence of the interdiffusion coefficients in molten mixtures of alkali nitrates and silver nitrate, a wave-front-shearing interferometer, together with an initial “plane source” was used.

With this technique, the diffusion coefficients were measured in nearly differential steps in the three mixtures (Na,Ag)NO₃, (K,Ag)NO₃, and (Rb,Ag)NO₃ at 300 °C. The composition dependence of the diffusion coefficients D of all three systems could be described by parabolas of the form

$$D = a + b \cdot x_2 + c \cdot x_2^2,$$

where x_2 denotes the mole fraction of the silver nitrate. The three coefficients a , b , and c all show a clear proportionality to the radii of the alkali ions. Thus an extrapolation to the not measured systems (Li,Ag)NO₃ and (Cs,Ag)NO₃ was possible.

From the theoretical point of view, it is advantageous to measure interdiffusion coefficients in simple binary melts as a function of composition in nearly differential steps. There are two reasons for this:

1. The reference velocity ω in the equation of the diffusion current density J_i of the component i

$$J_i = c_i(v_i - \omega) \quad (1)$$

(c_i = concentration, v_i = mean velocity of component i) is usually the “mean volume velocity”

$$\omega = \sum_i c_i v_i V_i, \quad (2)$$

where V_i denotes the partial molar volume of component i [1].

This reference velocity is equal to zero, if the partial molar volumes are independent of composition. This is also a good approach for the case that the applied concentration difference is small enough.

2. In Fick's second law

$$\delta c_i / \delta t = D (\text{div grad } c_i) \quad (3)$$

the diffusion coefficient is generally not composition independent. The error in assuming a concentration independent diffusion coefficient is the

smaller, the closer the two concentrations are together at the start of the measurement [2].

There is a variety of methods described in literature to measure interdiffusion coefficients in molten salts, but most of them have certain disadvantages. Some of them, e.g. the polarographic and the chronopotentiometric method, work satisfactory only in the region of “dilute solutions”. The others, e.g. the “fritted disc” and the diaphragm cell, need relatively high concentration differences to achieve a sufficient precision.

By modifying an approved interferometric method, we succeeded in measuring interdiffusion coefficients with an applied initial composition difference of 2 mole per cent.

Experimental

Method: The wave-front-shearing interferometer used was described by Bryngdahl [3] and first applied to molten salts by Gustafsson and coworkers [4]. The only principal difference between our and Gustafssons method was the way in which the initial “plane source” was formed. While Gustafsson threw a solid crystal of silver nitrate to the bottom of a cell filled with molten alkali nitrate, this procedure could not be used in our case.

We filled our cell with a nitrate mixture, the mole fraction of silver nitrate being x_2 , and brought a

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second mixture with a slightly higher mole fraction $x_2 + 0.02$ to the bottom of the cell. As the density difference between the two mixtures was not high enough to ensure the fall of the solid crystal to the bottom of the cell, we developed a different technique. A magnesia-rod (diameter 2 mm), fixed to a glass tube as holder, was immersed several times into the melt with the composition $x_2 + 0.02$, until a droplet of about 4 mm diameter was formed. After the droplet became solid, the magnesia-rod was immersed into the cell containing the preheated melt of the composition x_2 . When the projection of the cell in the interferometer showed that all solid material had molten, the magnesia-rod was removed. The disturbances caused by this could be mended by the zero-time correction during the evaluation of the interferograms.

Cell and furnace: The cell was a commercial half-micro-cell of quartz glass, which was surrounded by an aluminum block with slits slightly broader than the inner width of the cell to make possible the optical observation. The cell was placed in a vertical tube furnace with the help of attached "light ports", similar to those used by Gustafsson and coworkers [5]. Both, furnace and aluminum block, had a small central hole to bring in the second mixture. For more detailed information see [6].

Chemicals and Preparation of the Mixtures: Silver nitrate (DEGUSSA, special quality) was milled in an agate ball mill and subsequently dried for 36 h in a darkened vacuum drying oven at 60 °C. Sodium nitrate, potassium nitrate and rubidium nitrate (MERCK p. a. quality) were also milled and dried for 36 h at 110 °C under vacuum.

The calculated amounts of salts for a certain mole fraction were weighted in, molten in an auxiliary furnace and transferred to a cold porcelain basin. The solidified molten material was milled again and stored till use in a desiccator over P_2O_5 . The corresponding mixture with the higher mole fraction was weighted in and fused in a porcelain crucible. The magnesia-rod was immersed several times into the liquid until a droplet of the wanted shape was formed.

Results and Discussion

To test the method, the diffusion coefficient of a one molar aqueous KCl solution at 25 °C was measured. The mean value of $(1.879 \pm 0.025) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$

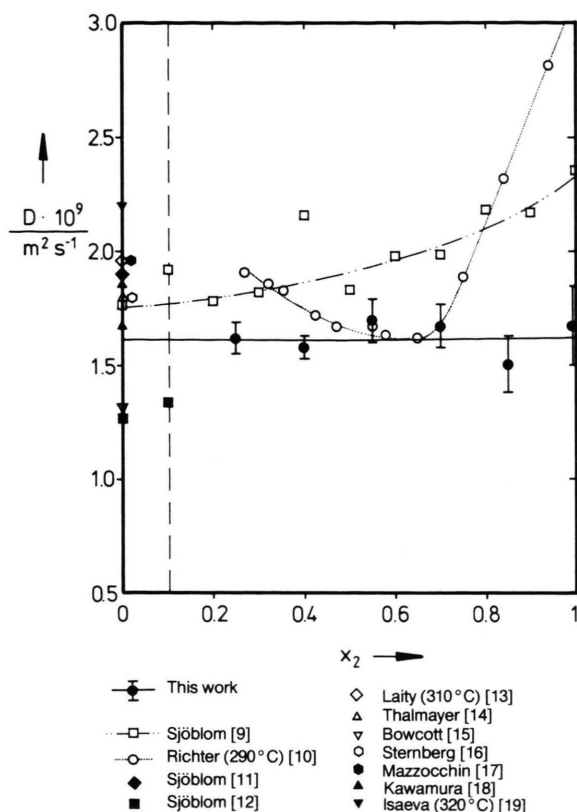


Fig. 1. Interdiffusion coefficients of the system $(\text{Na,Ag})\text{NO}_3$ at 300 °C. Dashed line indicates the liquidus of phase diagram.

obtained in 4 runs is in good accordance with the values of Woolf [7] ($1.858 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$) and Rard & Miller [8] ($1.893 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$).

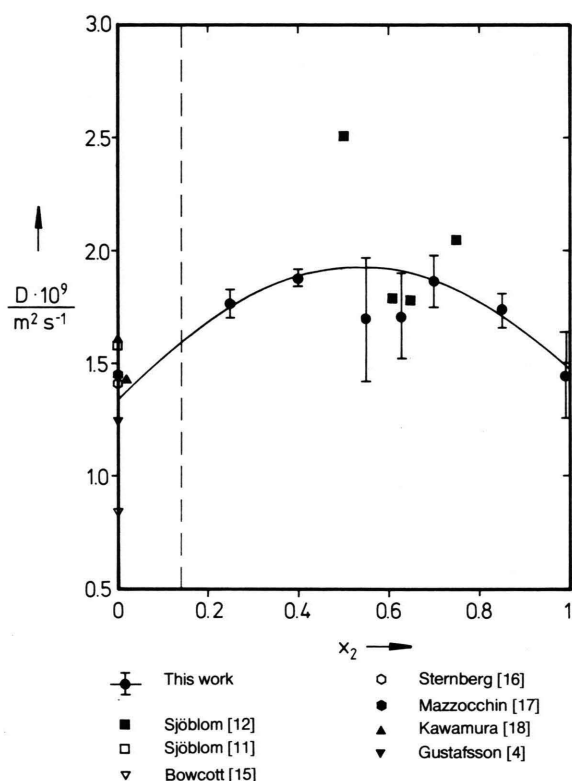
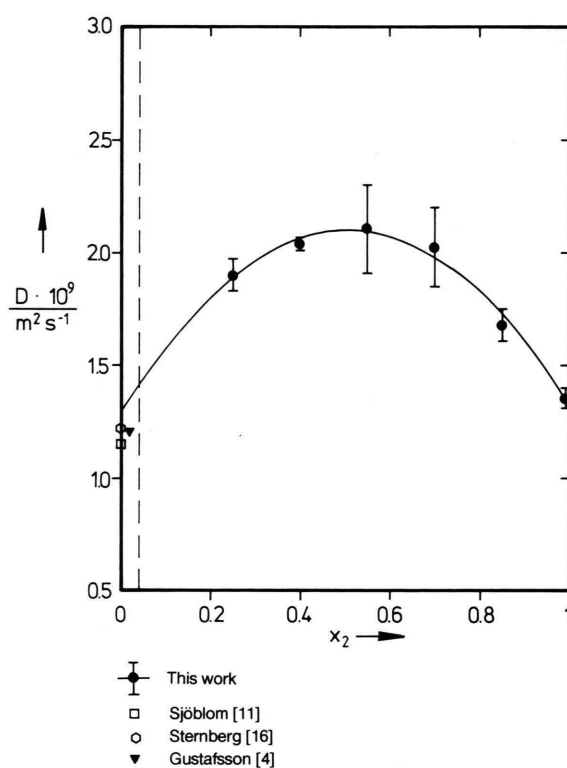
The measured diffusion coefficients of the three systems under examination are presented in Table 1. As the pure alkali nitrates are all still solid at 300 °C, the measurements were only performed down to a mole fraction of $x_2 = 0.25$.

Figures 1–3 show the results together with the literature data. In the $(\text{Na,Ag})\text{NO}_3$ system (Fig. 1), Sjöblom et al. [9] and Richter [10] measured diffusion coefficients at various compositions. Sjöblom varied the temperature, so that his values could be calculated for 300 °C from the given Arrhenius-equations, whereas Richter only measured at 290 °C.

The results of Sjöblom et al. are some 10 per cent higher in the sodium nitrate rich region and show an increase up to $2.35 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for pure silver nitrate. Richter's values are also somewhat higher in the middle composition region, showing a strong

Tab. 1. Measured diffusion coefficients at 300 °C.

x_2^a	(Na, Ag)NO ₃			(K, Ag)NO ₃			(Rb, Ag)NO ₃		
	$\frac{D \cdot 10^9}{\text{m}^2 \text{ s}^{-1}}$	$\frac{s \cdot 10^9}{\text{m}^2 \text{ s}^{-1}}^b$	n^c	$\frac{D \cdot 10^9}{\text{m}^2 \text{ s}^{-1}}$	$\frac{s \cdot 10^9}{\text{m}^2 \text{ s}^{-1}}$	n	$\frac{D \cdot 10^9}{\text{m}^2 \text{ s}^{-1}}$	$\frac{s \cdot 10^9}{\text{m}^2 \text{ s}^{-1}}$	n
0.25	1.624	0.068	5	1.769	0.066	3	1.902	0.071	1
0.40	1.582	0.047	5	1.879	0.036	3	2.042	0.033	1
0.55	1.697	0.094	6	1.696	0.275	3	2.106	0.196	3
0.63 ^d	—	—	—	1.713	0.192	3	—	—	—
0.70	1.670	0.098	8	1.862	0.116	3	2.025	0.175	2
0.85	1.507	0.122	7	1.737	0.075	3	1.680	0.070	3
0.99	1.678	0.174	9	1.453	0.190	3	1.355	0.042	2

^a Mole fraction of silver nitrate.^b Standard deviation, calculated from the error of each individual run and the scatter of different runs.^c Number of individual runs.^d Eutectic composition of (K, Ag)NO₃.Fig. 2. Interdiffusion coefficients of the system (K, Ag)NO₃ at 300 °C. Dashed line indicates the liquidus of the phase diagram.Fig. 3. Interdiffusion coefficients of the system (Rb, Ag)NO₃ at 300 °C. Dashed line indicates the liquidus of the phase diagram.

increase to the side of pure silver nitrate. As the latter measurements were performed by e.m.f.-measurements in a diaphragm cell, and the e.m.f. strongly decreases to the silver nitrate rich region, this strong increase of the diffusion coefficient

could be due to a great error of measurement in this region.

Many measurements are reported for nearly pure sodium nitrate. To compare them with our value, they had to be extrapolated from the reported tem-

Tab. 2. Parabola coefficients.

System	r_i^a Å	$a \cdot 10^9$ $\text{m}^2 \text{s}^{-1}$	$b \cdot 10^9$ $\text{m}^2 \text{s}^{-1}$	$c \cdot 10^9$ $\text{m}^2 \text{s}^{-1}$
(Li, Ag)NO ₃ ^b	0.60	1.827	-2.162	2.139
(Na, Ag)NO ₃	0.95	1.615	-0.035	0.038
(K, Ag)NO ₃	1.33	1.330	2.249	-2.115
(Rb, Ag)NO ₃	1.48	1.294	3.186	-3.144
(Cs, Ag)NO ₃ ^b	1.69	1.136	4.448	-4.333
R^2 ^c		0.969	0.999	0.998

^a Ionic radius of the alkali ion, after L. Pauling [20].

^b Extrapolated values.

^c Correlation coeff. of linear regression, for measured systems only.

perature dependence, whereas our value is extrapolated from the concentration dependence. For this double extrapolation the difference of some 10 per cent from the average of the literature data is not too bad.

Except for the two points near the eutectic composition, the concentration dependence of the diffusion coefficient in the (K, Ag)NO₃ system shows a parabolic profile (Figure 2). Only four values were

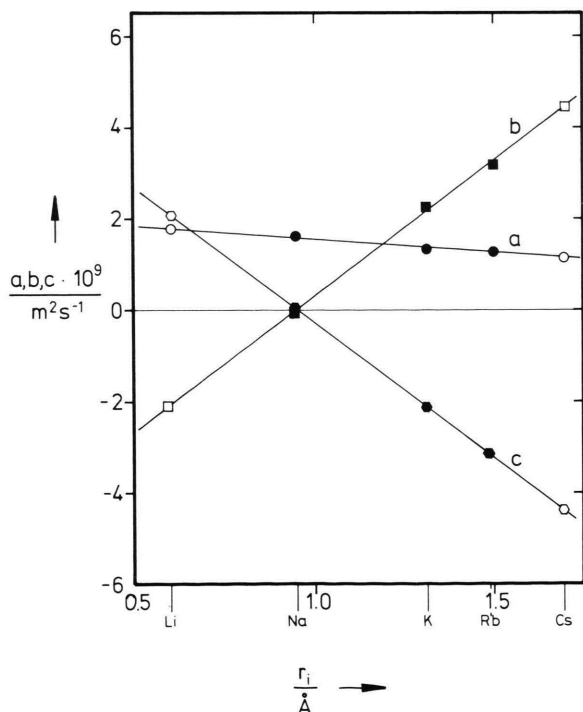


Fig. 4. Plot of parabola-coefficients a , b , and c versus ionic radii of the alkali ions.

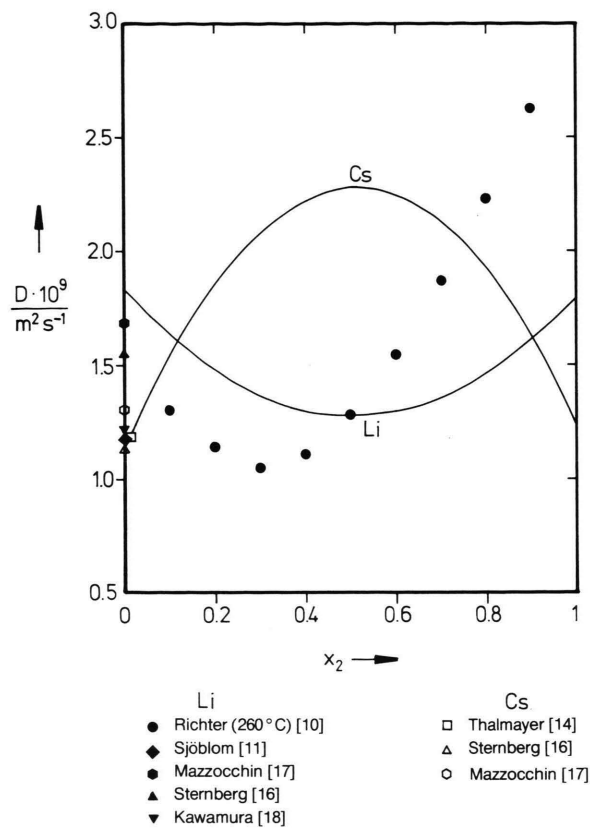


Fig. 5. Predicted concentration dependence of the interdiffusion coefficients in the systems (Li, Ag)NO₃ and (Cs, Ag)NO₃ at 300 °C using the obtained relation between the coefficients a , b , c and the ionic radii.

measured at various compositions by Sjöblom [12]. Two of them fit rather well with our measurements, the two others are significantly higher. One has to remark that they are extrapolated by about 60 °C from the measured region.

For pure potassium nitrate most values from literature stand around $1.46 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$, whereas the extrapolation from the concentration dependence gives $1.33 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

The parabolic profile of the diffusion coefficients is still more obvious in (Rb, Ag)NO₃ (Figure 3). Literature data with variation of the composition were not available. The quoted measurements in pure rubidium nitrate agree rather well with the parabolic extrapolation of our measurements.

To all three measured alkali nitrate + silver nitrate systems, parabolas of the form

$$D = a + b x_2 + c x_2^2 \quad (4)$$

could be fitted. In the (K,Ag)NO₃ system, the two points at $x_2 = 0.55$ and $x_2 = 0.63$ were not regarded. In the (Na,Ag)NO₃ system, the coefficients b and c are close to zero, thus yielding a nearly composition independent diffusion coefficient.

The coefficients a , b , and c of the fitted parabolas are shown in Table 2. When plotting the three coefficients versus the ionic radii of the alkali ions, a linearity of all three coefficients shows up (Figure 4). Thus it is possible to extrapolate for the not measured (Li,Ag)NO₃ and (Cs,Ag)NO₃ systems (open signs). The extrapolated coefficients are also shown in Table 2. They yield the curves in Figure 5. The comparison with literature data in the CsNO₃ rich limiting region shows a good agreement for the (Cs,Ag)NO₃ system, regardless the far-way extrapolation from the measured region (melting-point of pure CsNO₃: 417 °C). For the (Li,Ag)NO₃ system a statement is difficult: On the one hand it is

not unusual that lithium shows a deviating behaviour from the other alkali metals. On the other hand the experimental values show a great scatter, which might be due to the difficult handling of LiNO₃. It is very hygroscopic; a water contents, which can not be neglected, however, might strongly influence the transport properties. Thus it is still possible that the predicted behaviour is right. The composition dependent measurements done by Richter [10] at 260 °C, are in the lithium nitrate rich region parallel to the predicted curve, whereas at higher silver nitrate concentrations the same objections are valid as made for the (Na,Ag)NO₃ system.

Acknowledgement

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