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Fig. 1. Binary nitrite-nitrate systems. I –liquidus curve; II –isotherms of specific electrical conductivity; III –absolute and relative temperature coefficients; IV –activation energy

Figure 1: Fig. 1. Binary nitrite-nitrate systems. I –liquidus curve; II – isotherms of specific electrical conductivity; III –absolute and relative temperature coefficients; IV –activation energy

## Abstract

## Full Text

## PHYSICAL CHEMISTRY

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# ON THE ELECTRICAL CONDUCTIVITY OF MELTS OF BINARY NITRITE-NITRATE SYSTEMS

(Presented by Academician A. N. Frumkin, October 5, 1963)

The components of binary systems with identical cations of the series  $MNO_2$  – $MNO_3$ , where M is one of the metals Li, Na, K, Rb, or Cs, form continuous series of solid solutions (<sup>1-3</sup>). This gives grounds to suppose that, in the molten state, their mixtures are ionic liquids close to ideal.

The electrical conductivity of melts of individual salts and, in particular, of nitrates is well described by the exponential equation  $\chi = Ae^{-E/RT}$ .

**Fig. 1.** Binary nitrite-nitrate systems. *I* –liquidus curve; *II* –isotherms of specific electrical conductivity; *III* –absolute and relative temperature coefficients; *IV* –activation energy

Its applicability to melts of salts of nitrite-nitrate systems, the components of which form solid solutions, has been demonstrated (<sup>4-7</sup>).

According to Ya. I. Frenkel (<sup>8</sup>), in ideal binary systems with a common metal the conductivity is determined by the migration of cations; therefore his formula for the theoretical calculation of the electrical conductivity of a mixture of two salts with a common cation is applicable to them. The validity of this was illustrated by the author with experimental data only for one system, AgCl–AgBr. However, (<sup>9</sup>) Harrap and Heymann (<sup>10</sup>) indicated that “...the Frenkel criterion for an ideal system (conductivity is due to only one ion) is not applicable to systems of molten electrolytes.”

It is of interest to examine again the applicability of Frenkel' s postulate to

molten mixtures of salts of systems of the type  $\text{MNO}_2\text{—MNO}_3$ . The electrical conductivity of the binary systems  $\text{NaNO}_2\text{—NaNO}_3$ ,  $\text{RbNO}_2\text{—RbNO}_3$ , and  $\text{CsNO}_2\text{—CsNO}_3$  was studied in works <sup>(11–13)</sup>, and  $\text{LiNO}_2\text{—LiNO}_3$ ,  $\text{KNO}_2\text{—KNO}_3$  by the authors of the present article.

## Experimental Part

The electrical conductivity was measured by the method of <sup>(14)</sup>. An INO-3 type oscillograph served as the null indicator. The initial salts, of chemically pure grade, were recrystallized.  $\text{KNO}_2$  was obtained by the exchange reaction of  $\text{Ba}(\text{NO}_2)_2$  with  $\text{K}_2\text{SO}_4$ .

**Table 1**

### Specific electrical conductivity and temperature coefficients of the systems

$\text{LiNO}_2\text{—LiNO}_3$ ,  $\text{KNO}_2\text{—KNO}_3$

mol. %	$\kappa$ ,	$\kappa$ ,	$\kappa$ ,	$\kappa$ ,	$\kappa$ ,	$\kappa$ ,	$\kappa$ ,	240– 260°	240– 260°
	$\Omega^{-1} \cdot \text{cm}^{-1}$	$\Omega^{-1} \cdot \text{cm}^{-1}$	$\Omega^{-1} \cdot \text{cm}^{-1}$	$\Omega^{-1} \cdot \text{cm}^{-1}$	$\Omega^{-1} \cdot \text{cm}^{-1}$	$\Omega^{-1} \cdot \text{cm}^{-1}$	$\Omega^{-1} \cdot \text{cm}^{-1}$		
	200°	210°	220°	230°	240°	250°	260°	$\alpha \cdot 10^3$	$\beta \cdot 10^3$
0	—	—	0.630	0.690	0.753	0.815	0.865	5.60	6.92
10	—	0.565	0.626	0.687	0.746	0.807	0.865	5.85	7.25
20	0.513	0.570	0.629	0.692	0.749	0.805	0.862	5.65	6.98
30	0.516	0.572	0.629	0.685	0.740	0.798	0.850	5.50	6.92
40	0.509	0.567	0.626	0.684	0.740	0.798	0.854	5.70	7.15
50	0.512	0.569	0.625	0.683	0.742	0.799	0.853	5.55	6.97
60	0.511	0.569	0.622	0.682	0.745	0.790	0.843	5.40	6.84
70	—	—	—	0.690	0.746	0.799	0.854	5.45	6.81
80	—	—	—	—	—	0.797	0.850	5.20	6.51
90	—	—	—	—	—	—	0.845	—	—
100	—	—	—	—	—	—	0.840	—	—

  

mol. %	$\kappa$ ,	$\kappa$ ,	$\kappa$ ,	$\kappa$ ,	$\kappa$ ,	$\kappa$ ,	$\kappa$ ,	420– 460°	420– 460°
	$\Omega^{-1} \cdot \text{cm}^{-1}$	$\Omega^{-1} \cdot \text{cm}^{-1}$	$\Omega^{-1} \cdot \text{cm}^{-1}$	$\Omega^{-1} \cdot \text{cm}^{-1}$	$\Omega^{-1} \cdot \text{cm}^{-1}$	$\Omega^{-1} \cdot \text{cm}^{-1}$	$\Omega^{-1} \cdot \text{cm}^{-1}$		
	360°	380°	400°	420°	440°	460°	480°	$\alpha \cdot 10^3$	$\beta \cdot 10^3$
0	—	—	—	—	1.246	1.315	1.384	—	—
10	—	—	—	1.140	1.209	1.270	1.335	3.25	2.70
20	—	—	1.020	1.098	1.168	1.231	1.295	3.33	2.86
30	—	—	0.985	1.060	1.131	1.190	1.259	3.25	2.80
40	—	0.886	0.951	1.022	1.092	1.156	1.220	3.35	3.07
50	0.799	0.856	0.921	0.991	1.059	1.120	1.183	3.22	3.06
60	0.770	0.830	0.897	0.960	1.030	1.089	1.150	3.22	3.15

mol. %	$\kappa, \Omega^{-1} \cdot \text{cm}^{-1}$ 360°	$\kappa, \Omega^{-1} \cdot \text{cm}^{-1}$ 380°	$\kappa, \Omega^{-1} \cdot \text{cm}^{-1}$ 400°	$\kappa, \Omega^{-1} \cdot \text{cm}^{-1}$ 420°	$\kappa, \Omega^{-1} \cdot \text{cm}^{-1}$ 440°	$\kappa, \Omega^{-1} \cdot \text{cm}^{-1}$ 460°	$\kappa, \Omega^{-1} \cdot \text{cm}^{-1}$ 480°	420– 460° $\alpha \cdot 10^3$	420– 460° $\beta \cdot 10^3$
70	0.748	0.807	0.869	0.934	1.000	1.060	1.122	3.15	3.16
80	0.730	0.788	0.850	0.910	0.978	1.088	1.099	3.20	3.28
90	0.709	0.770	0.830	0.890	0.956	1.012	1.072	3.05	3.21
100	0.694	0.755	0.816	0.876	0.936	0.995	1.053	2.97	3.18

The electrical conductivity was measured polythermally in the temperature range of stability of the salts and their mixtures. The experimental results are given in Table 1. Along with the specific electrical conductivity, the absolute and relative temperature coefficients of conductivity were calculated (Table 1), as well as the activation energy of ionic migration (Table 2).

**Table 2**

**Activation energy of binary nitrite-nitrate systems with a common cation**

mol. %	LiNO <sub>2</sub> —LiNO <sub>3</sub> $\Delta E\kappa, \text{kcal/mol}$	NaNO <sub>2</sub> —NaNO <sub>3</sub> $\Delta E\kappa, \text{kcal/mol}$	KNO <sub>2</sub> —KNO <sub>3</sub> $\Delta E\kappa, \text{kcal/mol}$	RbNO <sub>2</sub> —RbNO <sub>3</sub> $\Delta E\kappa, \text{kcal/mol}$	CsNO <sub>2</sub> —CsNO <sub>3</sub> $\Delta E\kappa, \text{kcal/mol}$
0	3.7	0	2.8	0	2.9
10	4.0	10	2.5	10	2.6
20	3.8	20	2.8	20	2.8
30	3.7	30	2.6	30	2.7
40	3.9	40	2.7	40	3.0
50	3.8	50	2.9	50	3.0
60	3.7	60	2.6	60	3.0
70	3.7	70	2.3	70	3.1
80	3.6	80	2.7	80	3.2
90	—	90	2.9	90	3.0
100	—	100	2.7	100	3.2

**Discussion of Results**

For systems of the type  $MNO_2-MNO_3$ , where  $M$ —Li, Na, K, Rb, Cs, the isotherms of  $\kappa$  are linear or have a very slight deviation from a straight line toward lower conductivity values. They increase monotonically from nitrates to nitrites. The curves of the absolute and relative temperature coefficients are smooth and without extrema (Fig. 1).

The activation energy of ionic migration (Table 2, Fig. 1) in the systems  $\text{LiNO}_2$ – $\text{LiNO}_3$ ,  $\text{NaNO}_2$ – $\text{NaNO}_3$ ,  $\text{KNO}_2$ – $\text{KNO}_3$ ,  $\text{RbNO}_2$ – $\text{RbNO}_3$ ,  $\text{CsNO}_2$ – $\text{CsNO}_3$  changes hardly at all, since the  $\Delta E_\kappa$  values of the components as chemical individuals are close to one another and do not deviate from a straight line. This indicates the identical structure of salt melts of all systems at any component ratios, while the high value of  $\kappa$  confirms their ionic nature.

A somewhat special place in this series of binary systems is occupied by the  $\text{LiNO}_2$ – $\text{LiNO}_3$  system. Here the isotherms of specific electrical conductivity are almost parallel to the abscissa axis, since the conductivities of lithium nitrite and nitrate in the temperature range of our measurements are close to one another. Lithium nitrite has anomalously low electrical conductivity, but a high value of the activation energy of ionic migration and a considerably higher viscosity than other alkali-metal nitrites. This is apparently explained by strong association of ions in the melt, caused by the large specific charges of the lithium ion and the nitrite ion. By the specific charge of ions one should understand the quotient obtained by dividing the ion charge, expressed in electrostatic units, by its mass. This concept was introduced by us for an approximate quantitative electrical characterization of cations and anions. The large specific charges of the ions  $\text{Li}^+$  and  $\text{NO}_2^-$  create powerful force fields, which promotes the formation of stable associates. The latter retard the rate of ionic migration, as a result of which conductivity decreases. It is precisely this that accounts for the fact that, in the series of alkali-metal salts from lithium to cesium, replacement of the nitrate ion by the nitrite ion leads to an increase in electrical conductivity, and only in lithium nitrite does it remain almost unchanged.

The theoretical calculation of the specific electrical conductivity for mixtures of salts of the entire series of binary systems  $MNO_2$ – $MNO_3$  was carried out by Frenkel' s formula, which, for convenience of calculation, was put in the form

$$\ln \kappa_{\text{mix}} = \ln \kappa_1 + \ln \frac{\kappa_2}{\kappa_1} \cdot C_2,$$

**Table 3**

**Specific electrical conductivity of binary nitrite-nitrate systems with a common cation, calculated by Frenkel' s formula**

System	$t$ , °C	Component content, mol.%	$\kappa$ exp.	$\kappa$ theor.	discrepancy, %
$\text{LiNO}_2$ – $\text{LiNO}_3$	260	$\text{LiNO}_3$ , 10	0.865	0.862	0.35
$\text{LiNO}_2$ – $\text{LiNO}_3$	260	$\text{LiNO}_3$ , 20	0.862	0.860	0.23
$\text{LiNO}_2$ – $\text{LiNO}_3$	260	$\text{LiNO}_3$ , 30	0.858	0.857	0.12

System	$t$ , °C	Component content, mol. %	$\kappa$ exp.	$\kappa$ theor.	discrepancy, %
LiNO <sub>2</sub> — LiNO <sub>3</sub>	260	LiNO <sub>3</sub> , 40	0.854	0.853	0.12
LiNO <sub>2</sub> — LiNO <sub>3</sub>	260	LiNO <sub>3</sub> , 50	0.853	0.852	0.12
LiNO <sub>2</sub> — LiNO <sub>3</sub>	260	LiNO <sub>3</sub> , 60	0.848	0.850	0.23
LiNO <sub>2</sub> — LiNO <sub>3</sub>	260	LiNO <sub>3</sub> , 70	0.854	0.847	0.82
LiNO <sub>2</sub> — LiNO <sub>3</sub>	260	LiNO <sub>3</sub> , 80	0.850	0.845	0.60
LiNO <sub>2</sub> — LiNO <sub>3</sub>	260	LiNO <sub>3</sub> , 90	0.845	0.843	0.24
NaNO <sub>2</sub> — NaNO <sub>3</sub>	320	NaNO <sub>3</sub> , 10	1.449	1.442	0.49
NaNO <sub>2</sub> — NaNO <sub>3</sub>	320	NaNO <sub>3</sub> , 20	1.390	1.390	0.00
NaNO <sub>2</sub> — NaNO <sub>3</sub>	320	NaNO <sub>3</sub> , 30	1.335	1.334	0.07
NaNO <sub>2</sub> — NaNO <sub>3</sub>	320	NaNO <sub>3</sub> , 40	1.280	1.291	0.78
NaNO <sub>2</sub> — NaNO <sub>3</sub>	320	NaNO <sub>3</sub> , 50	1.230	1.246	1.30
NaNO <sub>2</sub> — NaNO <sub>3</sub>	320	NaNO <sub>3</sub> , 60	1.190	1.198	0.67
NaNO <sub>2</sub> — NaNO <sub>3</sub>	320	NaNO <sub>3</sub> , 70	1.150	1.157	0.60
NaNO <sub>2</sub> — NaNO <sub>3</sub>	320	NaNO <sub>3</sub> , 80	1.100	1.115	1.36
NaNO <sub>2</sub> — NaNO <sub>3</sub>	320	NaNO <sub>3</sub> , 90	1.060	1.075	1.40
KNO <sub>2</sub> — KNO <sub>3</sub>	440	KNO <sub>3</sub> , 10	1.209	1.214	0.14

System	$t$ , °C	Component content, mol. %	$\kappa$ exp.	$\kappa$ theor.	discrepancy, %
KNO <sub>2</sub> — KNO <sub>3</sub>	440	KNO <sub>3</sub> , 20	1.168	1.177	0.77
KNO <sub>2</sub> — KNO <sub>3</sub>	440	KNO <sub>3</sub> , 30	1.131	1.144	1.14
KNO <sub>2</sub> — KNO <sub>3</sub>	440	KNO <sub>3</sub> , 40	1.092	1.111	1.74
KNO <sub>2</sub> — KNO <sub>3</sub>	440	KNO <sub>3</sub> , 50	1.050	1.080	1.95
KNO <sub>2</sub> — KNO <sub>3</sub>	440	KNO <sub>3</sub> , 60	1.030	1.050	1.90
KNO <sub>2</sub> — KNO <sub>3</sub>	440	KNO <sub>3</sub> , 70	1.000	1.020	2.00
KNO <sub>2</sub> — KNO <sub>3</sub>	440	KNO <sub>3</sub> , 80	0.978	0.991	1.31
KNO <sub>2</sub> — KNO <sub>3</sub>	440	KNO <sub>3</sub> , 90	0.956	0.963	0.73
RbNO <sub>2</sub> — RbNO <sub>3</sub>	440	RbNO <sub>3</sub> , 10	0.905	0.919	1.54
RbNO <sub>2</sub> — RbNO <sub>3</sub>	440	RbNO <sub>3</sub> , 20	0.882	0.894	1.36
RbNO <sub>2</sub> — RbNO <sub>3</sub>	440	RbNO <sub>3</sub> , 30	0.852	0.869	1.88
RbNO <sub>2</sub> — RbNO <sub>3</sub>	440	RbNO <sub>3</sub> , 40	0.830	0.845	1.80
RbNO <sub>2</sub> — RbNO <sub>3</sub>	440	RbNO <sub>3</sub> , 50	0.803	0.821	2.22
RbNO <sub>2</sub> — RbNO <sub>3</sub>	440	RbNO <sub>3</sub> , 60	0.784	0.799	1.94
RbNO <sub>2</sub> — RbNO <sub>3</sub>	440	RbNO <sub>3</sub> , 70	0.769	0.777	1.04
RbNO <sub>2</sub> — RbNO <sub>3</sub>	440	RbNO <sub>3</sub> , 80	0.745	0.756	1.47

System	$t$ , °C	Component content, mol. %	$\kappa$ exp.	$\kappa$ theor.	discrepancy, %
RbNO <sub>2</sub>	440	RbNO <sub>3</sub> , 90	0.732	0.735	0.40
—					
RbNO <sub>3</sub>					
CsNO <sub>2</sub>	440	CsNO <sub>3</sub> , 10	0.771	0.759	1.55
—					
CsNO <sub>3</sub>					
CsNO <sub>2</sub>	440	CsNO <sub>3</sub> , 20	0.748	0.737	1.46
—					
CsNO <sub>3</sub>					
CsNO <sub>2</sub>	440	CsNO <sub>3</sub> , 30	0.732	0.714	2.45
—					
CsNO <sub>3</sub>					
CsNO <sub>2</sub>	440	CsNO <sub>3</sub> , 40	0.714	0.693	2.94
—					
CsNO <sub>3</sub>					
CsNO <sub>2</sub>	440	CsNO <sub>3</sub> , 50	0.697	0.671	3.71
—					
CsNO <sub>3</sub>					
CsNO <sub>2</sub>	440	CsNO <sub>3</sub> , 60	0.683	0.651	4.68
—					
CsNO <sub>3</sub>					
CsNO <sub>2</sub>	440	CsNO <sub>3</sub> , 70	0.661	0.631	4.58
—					
CsNO <sub>3</sub>					
CsNO <sub>2</sub>	440	CsNO <sub>3</sub> , 80	0.645	0.612	5.11
—					
CsNO <sub>3</sub>					
CsNO <sub>2</sub>	440	CsNO <sub>3</sub> , 90	0.621	0.593	4.51
—					
CsNO <sub>3</sub>					

where  $\chi_{\text{mix}}$ ,  $\chi_1$ , and  $\chi_2$  are the specific electrical conductivities of the mixture and of the first and second components;  $C_2$  is the mole fraction of the second component, and, contrary to the assertions of (10), showed its complete applicability. As follows from the data in Table 3, the values of the calculated electrical conductivity agree quite well with the experimental data. At the same time it should be noted that, on going from binary systems containing lithium to systems in which the components are potassium and cesium, an increase was observed in the deviations of the calculated electrical-conductivity values from the experimental ones. This, apparently, can be explained by the fact that already from  $\text{K}^+$  to  $\text{Cs}^+$ , with commensurability of the radii of the

cations and anions ( $r_{K^+} = 1.33$ ,  $r_{Rb^+} = 1.49$ ,  $r_{Cs^+} = 1.65$ ,  $r_{NO_2^-} = 1.55$  and  $r_{NO_3^-} = 1.89$  Å), the share of anionic conductivity increases. This casts doubt on its anionic character in such systems.

In the case of alkali-metal halides, on going from cation to cation the electrical conductivity changes much more than on going from anion to anion (at  $800^\circ$   $\lambda_{NaCl} = 128.8$ ,  $\lambda_{KCl} = 108.0$ ,  $\lambda_{KBr} = 103.0$ ,  $\lambda_{KI} = 101.0$ ). For nitrites we do not have such a regularity (at  $340^\circ$   $\lambda_{NaNO_3} = 49.7$ ,  $\lambda_{NaNO_2} = 62.5$ ; at  $460^\circ$   $\lambda_{KNO_3} = 56.9$ ,  $\lambda_{KNO_2} = 66.7$ ). Replacement of the anion changes the electrical conductivity to the same extent as replacement of the cation. Similar results are obtained if the equivalent electrical conductivities of nitrates and nitrites are compared at temperatures 10% above their melting points:  $\lambda_{NaNO_3} = 49.7$ ,  $\lambda_{KNO_3} = 40.08$ ,  $\lambda_{NaNO_2} = 55.95$ ,  $\lambda_{KNO_2} = 70.6$ .

**Table 4**

Activation energy  $\Delta E_\chi$ , kcal/mol

	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
Cl <sup>-</sup>	1.2	1.5	2.3	2.8	3.3
NO <sub>3</sub> <sup>-</sup>	4.5	2.8	3.5	3.3	2.2
NO <sub>2</sub> <sup>-</sup>	4.2	2.4	2.8	3.7	3.3

The activation energy of ionic migration of alkali-metal nitrites and nitrates, with the exception of cesium salts, is higher than that of the halides (Table 4). This circumstance may be explained either by association of ions in the melts, since it contributes to an increase in  $\Delta E_\chi$ , or by the participation of anions in conduction. In the latter case we have a certain averaged  $\Delta E_\chi$ , owing to bi-ionic conductivity. The possibility is not excluded that, in the presence in the melt of ion associates and bi-ionic conductivity, individual ions are always present alongside the associated ions.

We believe that Frenkel' s formula is widely applicable to ideal systems with a common cation and especially in cases where the cation radius is greater than the anion radius, i.e., if the cationic character of conductivity predominates. A theoretical calculation of the specific electrical conductivity of mixtures of molten salts of the systems AgCl–AgBr and PbCl<sub>2</sub>–PbBr<sub>2</sub>, using Sandonini' s data and carried out by us according to Frenkel' s formula, also convincingly confirms this. In both cases the discrepancies between the theoretical values of the specific electrical conductivity and the experimental ones do not exceed 1%.

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## References Cited

1. P. I. Protsenko, A. Ya. Malakhova, ZhNKh, 2, 2145 (1957).
2. T. A. Andreeva, P. I. Protsenko, Izv. vyssh. ucheb. zav., khim. i khim. tekhnol., 4, 892 (1961).
3. P. I. Protsenko, T. A. Andreeva, ZhNKh, 6, 1875 (1961).
4. H. Bloom, I. W. Knaggs et al., Trans. Farad. Soc., 49, 1453 (1953).
5. B. F. Markov, DAN, 102, 1163 (1955).
6. N. P. Popovskaya, P. I. Protsenko, ZhNKh, 7, 2237 (1962).
7. Yu. K. Delimarskii, B. F. Markov, *Electrochemistry of Molten Salts*, Moscow, 1960.
8. Ya. I. Frenkel, *Kinetic Theory of Liquids*, Publishing House of the USSR Academy of Sciences, 1945.
9. J. Bockris, *Modern Problems of Electrochemistry*, Foreign Literature Publishing House, 1962.
10. B. S. Harrap, E. Heymann, Trans. Farad. Soc., 51, 259 (1955).
11. A. Ya. Malakhova, P. I. Protsenko, *Physicochemical Methods of Analysis and Production Control*, Rostov-on-Don, 1961, p. 203.
12. P. I. Protsenko, T. A. Andreeva, *Physicochemical Analysis of Salt Systems*, Rostov-on-Don, 1962, p. 127.
13. P. I. Protsenko, T. A. Andreeva, ZhNKh, 7, 1648 (1962).
14. P. I. Protsenko, Izv. Sektora fiz.-khim. anal., 26, 173 (1955).

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