Electrical Conductance in Binary Molten Nitrate Mixtures. 2

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The electrical conductance of molten $(Li,Rb)NO_3$–$Ca(NO_3)_2$ and $(Li,Na,K,Tl)NO_3$–$Cd(NO_3)_2$ mixtures have been measured as a function of temperature and divalent ion content in the mixtures.

In continuation of our studies on electrical conductance measurements in binary molten nitrate mixtures (*2–5*), data for some mixtures of univalent nitrates with calcium and cadmium nitrates over the accessible composition and temperature ranges limited by solubility and thermal stability are presented in this paper.

Experimental Section

LR (BDH) grade thallium nitrate was recrystallized from demineralized water. All other reagents were of AnalaR (BDH) grade. These were pretreated/dehydrated as follows.

Sodium and potassium nitrates were baked at about 200 °C for several days. Anhydrous lithium nitrate was heated at 100–150 °C under vacuum for several days. Calcium and cadmium nitrate tetrahydrates were first dried by *slow* and careful heating under vacuum below 85 °C for 3–4 days and then at 150–200 °C for 12 h. Sample compositions, checked by EDTA titrations, were within the experimental uncertainty, to the intended compositions. Dehydrated samples were stored over anhydrous magnesium perchlorate until used. All manipulations, e.g., preparing the mixtures, loading the conductivity cell, etc., were done in a drybox under a flowing nitrogen atmosphere, the gas having been dried by passing through anhydrous silica gel and magnesium perchlorate columns. The capillary type cells were used. The cell constants (ranging between 120 and 350 cm^{-1}) were determined using 1 N KCl and saturated sodium chloride solutions at 18.0 ± 0.02 °C, employing platinized platinum electrodes of ca. 1 cm^2 area. No significant change in the value of cell constants was observed even after five–six runs; in practice, cells were discarded after this much use. About 50 g of the mixture was taken in one of the limbs of the conductivity cell, held in an electric furnace of high thermal inertia, and fused in situ under a stream of nitrogen.

The melt was *matured* by keeping at a temperature 10–15 °

Table I. Specific Conductance Equations for Some Binary Molten Nitrate Mixtures[a]

$k = a + bt + ct^2 + dt^3$ (ohm^{-1} cm^{-1})

Equiv of divalent ion (x')	No. of data points	Temp range (t, °C)	a	$b \times 10$	$c \times 10^4$	$d \times 10^7$	Std deviation (ohm^{-1} cm^{-1})	Energy of activation E_k (kcal)[b]
$LiNO_3$–$Ca(NO_3)_2$								
0.271	11	233–334	−0.5950	0.3767	0.1016	—	0.0029	6.23–4.06
0.361	13	234–350	0.0734	−0.0931	0.8006	—	0.0027	4.90
0.462	15	231–398	0.1375	−0.1231	0.6982	—	0.0048	4.75
$RbNO_3$–$Ca(NO_3)_2$								
0.561	20	136–335	0.1904	−0.3017	1.3850	−0.1295	0.0013	23.31–5.62
0.657	18	188–354	0.0506	−0.0987	0.4320	—	0.0013	12.96–6.28
0.675	20	192–380	0.1817	−0.2435	0.9450	−0.0616	0.0010	11.85–6.09
0.701	19	166–338	−0.0495	0.0632	−0.3773	0.1184	0.0010	12.12–7.68
$LiNO_3$–$Cd(NO_3)_2$								
0.479	7	200–261	−1.4671	0.1473	−0.4769	0.6509	0.0053	15.24–5.60
0.511	10	197–270	−2.0601	0.2507	−1.032	1.577	0.0018	12.78–6.76
0.698	3	290–315	−3.0162	0.1834	−0.2527	—	0.0021	11.73–8.05
$NaNO_3$–$Cd(NO_3)_2$								
0.462	9	209–273	−0.4607	0.0282	0.0091	—	0.0019	8.61–4.97
0.519	16	190–304	−0.0700	−0.0068	0.0914	−0.0499	0.0010	9.31–5.15
0.639	21	127–248	0.1540	−0.0247	0.0998	—	0.0010	27.68–7.45
0.694	19	138–274	0.1788	−0.0256	0.0931	—	0.0009	26.63–8.22
KNO_3–$Cd(NO_3)_2$								
0.261	12	232–373	−1.5856	0.1052	−0.1263	—	0.0092	12.03–1.55
0.400	20	142–343	−0.0156	−0.0123	0.1328	−0.1735	0.0010	17.97–3.12
0.519	23	119–325	0.1707	−0.0345	0.2020	−0.2368	0.0021	19.79–4.26
0.630	24	128–315	0.2183	−0.0385	0.1957	−0.1999	0.0017	23.48–5.35
0.710	19	144–335	0.4021	−0.0609	0.2756	−0.3083	0.0008	28.68–4.65
0.770	15	187–352	0.6885	−0.0084	0.3458	−0.3603	0.0047	21.50–5.86
$TlNO_3$–$Cd(NO_3)_2$								
0.325	14	133–288	0.2034	−0.0424	0.3304	−0.5421	0.0025	6.39–2.48
0.429	25	76–272	0.0257	−0.0128	0.1452	−0.1903	0.0009	37.62–3.84
0.571	24	85–268	0.1149	−0.0278	0.1944	−0.2506	0.0006	17.02–4.59

[a] Data on some of compositions of the above binary mixtures have been reported by Protsenko *et al.* (*6, 7*) and showed agreement within 2–5% with our results. [b] 1 cal = 4.814 J.

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below thermal decomposition temperature for 10–12 h during which the conductivity fell to a constant value. Measurements were made at 5–10 ° intervals in cooling and heating cycles with a Beckmann conductivity bridge (Model RC-18A) at a frequency of 1 kHz. Melt temperatures were controlled and known with a precision better than ±0.5 °C.

Results and Discussion

The impedance of a cell is generally considered as a series combination of a resistance (R_s) and the double layer capacitance (C_s). In measuring bridge, as employed, the resistances in the ratio arms were matched and the balancing arm had a parallel combination of resistance (R_s) and capacitance (C_p). From ac theory (*1*) one has,

$$R_s = R_p/[1 + (R_p C_p w)^2]$$

where $w = 2\pi f$ and f is the ac frequency in hertz.

Specific conductance (k) data at different compositions and over the accessible range of temperature (t, °C) were obtained. At a given composition k–t data could be expressed into various mathematical expressions; those in the form $k = a + bt + ct^2 + dt^3$ are presented in Table I. (Supportive data are available in supplementary material. See paragraph at end of paper.) No significance is attached to these different forms of the expressions, except that they permitted alternate evaluation of Arrhenius coefficients, E_k, at different temperatures through the derivative $\partial \ln k/\partial(1/T)$. The Arrhenius coefficient (apparent activation energies) given by

$$E_k = -R\left[\frac{\partial \ln k}{\partial(1/T)}\right]$$

was found to be temperature dependent. The range of variation of E_k (average of the values obtained from different fits) for different compositions is also included in Table I.

Conductance–composition isotherms (not shown) were smooth curves in all cases, indicating absence of structural transformations (complexation, etc.) on addition of the divalent ion. A gradual decrease in conductivity with the increase in divalent ion content, as observed, may result from increased Coulombic interactions and a shrinkage of the ionic lattice, resulting in hindered ionic migration.

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Supplementary Material Available: Supportive data for Table I (4 pages). Ordering information is given on any current masthead page.

Binary Azeotropes Containing Butyric Acids

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The formation of binary azeotropes by *n*- and isobutyric acids with 11 substances at atmospheric pressure is investigated. The choice of substances is based on consideration of polarity, association, the reduced value in the acid partial pressure, and the formation of compounds. Dimethylaniline, diethylaniline, and toluene form no azeotropes, though slight deviations from normal behavior are noticed. Other substances form positive azeotropes which may be attributed to the acid association at high acid concentration. The characteristics of each two corresponding azeotropes are very close.

Eleven substances have been selected for the investigation of the formation, at atmospheric pressure, of binary azeotropes by *n*- and isobutyric acids. The substances selected are *n*-octane, *p*-xylene, anisole, dimethylaniline, diethylaniline, acetic anhydride, toluene, and four petroleum fractions of boiling points 148.1, 143.3, 140.8, and 129.9 °C, the main constituent of the last fraction being an octane isomer, while those of the other three fractions being nonane isomers. The selection of these substances has been made according to the following.

The dielectric constant values of *n*- and isobutyric acids increase linearly with rise of temperature, due to their dissociation which favors azeotropic formation. The dielectric constant values of the *n*-acid are larger than those of the isoisomer (*6, 7*).

Quite large positive deviations from Raoult's law are obtained if one of the components is nonpolar or slightly polar, as *n*-octane, *p*-xylene, and the four petroleum fractions, while the other component is highly polar.

Negative deviations from Raoult's law may be produced when the added substance has a slightly basic character, such as dimethyl- and diethylaniline, so as to favor the formation of a compound.

To separate an azetrope of two acids, it is necessary to add a substance that reduces the partial pressure of one acid component more than that of the other. It is also desirable that the added substance can be easily removed from the distillate. According to these two basic requirements, *n*-octane, *p*-xylene, anisole, acetic anhydride, and the four petroleum fractions have been selected.

Toluene is reported to have been used in the azeotropic separation of butyric acid isomers (*9*). For this reason it was included among the chosen substances.

Experimental Section

Substances to be used in the experiments were labeled A.R. (analytical reagent). However, each substance, before use, was purified by distillation several times through a packing column. Dimethyl- and diethylaniline were distilled under reduced pres-

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