Electrical conductivity of molten LiCl—NaCl—KCl and LiCl—NaCl—KCl—$AlCl_3$ mixtures

[a]K. MATIAŠOVSKÝ, [b]G. BRÄUTIGAM, [a]M. CHRENKOVÁ-PAUČÍROVÁ, [a]P. FELLNER, and [b]G. SCHULZE

[a]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, 809 34 Bratislava*

[b]*Department of Chemistry, Technical University "Carl Schorlemmer", 42 Merseburg, GDR*

Received 13 November 1979

The specific electrical conductivity was determined experimentally of selected molten ternary LiCl—NaCl—KCl and quaternary LiCl—NaCl—KCl—$AlCl_3$ mixtures which are of interest with respect to new industrial processes for electrolytic aluminium deposition. A method for the calculation of the electrical conductivity of molten ternary and quaternary mixtures on the basis of experimentally determined values of the electrical conductivity and molar volumes of the corresponding binary systems was proposed. The good agreement between the calculated and experimental conductivity values of the ternary and quaternary mixtures confirms the correctness of the proposed method of calculation.

Экспериментально была определена электропроводность некоторых расплавов тройной системы LiCl—NaCl—KCl и четверной системы LiCl—NaCl—KCl—$AlCl_3$, представляющих интерес с точки зрения электролитического выделения алюминия. Был предложен метод, позволяющий рассчитать электропроводность тройных и четверных систем, исходя из данных по соответственным двойным системам. В случае изучаемых систем было найдено очень хорошее согласие рассчитанных и экспериментальных значений электропроводности, подтверждающее пригодность предложенного метода расчета.

The molten systems containing $AlCl_3$ and alkali chlorides are being recently extensively investigated as, besides a purely theoretical interest, they can find technological applications, namely as electrolytes in the electrodeposition of aluminium. The electrowinning of aluminium by the chloride electrolysis is considered to be the most promising alternative to the Hall—Héroult process [1].

It is obvious that the rational control of the electrolytic process requires a profound knowledge of the physicochemical and electrochemical properties of the electrolyte. The experimental investigation of systems containing $AlCl_3$ is rather complicated by its considerable hygroscopicity, high vapour pressure, and corrosiveness of both gaseous and liquid phases. Thus it is not surprising that the experimental data on the electrical conductivity relevant with respect to the systems under study are rather scarce. The only reliable data thus far are those on the electrical conductivity of the binary systems LiCl—KCl, NaCl—KCl [2], and KCl—$AlCl_3$ [3, 4], and of the linear section of the ternary system NaCl—KCl—$AlCl_3$ corresponding to the equimolar ratio (50 : 50 mole %) of NaCl and KCl within the concentration range 0—30 mole % $AlCl_3$ [5]. The data reported for the electrical conductivity of the binary NaCl—$AlCl_3$ and ternary NaCl—KCl—$AlCl_3$ systems [6] render severe doubts as to their reliability. In the system LiCl—NaCl only the electrical conductivity of the melt containing 50 mole % LiCl was determined [7] and in the ternary system LiCl—NaCl—KCl the conductivities of four samples within the concentration region 40.39—41.95 mole % KCl, 55.77—57.93 mole % LiCl, and 0.12—3.84 mole % NaCl were measured in the temperature interval 637—670 K [9].

The rather complicated experimental measurement stimulated the elaboration of a method which makes it possible to calculate the electrical conductivity of ternary and quaternary mixtures based on the known values of the electrical conductivity and molar volumes of the corresponding binary systems [5]. This method has been applied in the present work to the calculation of the electrical conductivities of the investigated systems. The calculated values have been compared with the literature data as well as with the experimentally determined values.

Experimental

The specific electrical conductivities of the ternary LiCl—NaCl—KCl mixtures with equimolar concentrations 50 : 50 mole % NaCl and KCl in the concentration range 0—25 mole % LiCl, and of the quaternary LiCl—NaCl—KCl—$AlCl_3$ mixtures with equimolar concentrations of NaCl and KCl, a constant initial concentration of 5 wt % (appr. 2.4 mole %) $AlCl_3$ and a concentration of LiCl varying from 0 to 20 wt % (appr. 0—30

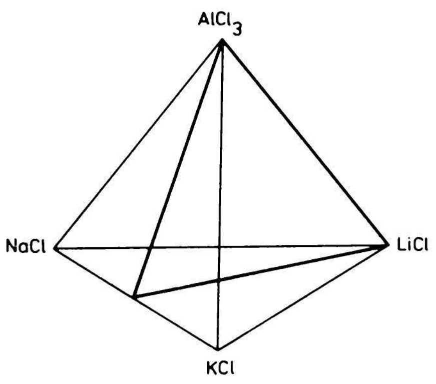

Fig. 1. Concentration tetrahedron of the quaternary system LiCl—NaCl—KCl—$AlCl_3$ indicating the investigated planar section.

mole %) were determined. The above concentration regions were chosen with respect to the utilization of the respective melts in the aluminium electrolysis. The concentration tetrahedron of the system $LiCl—NaCl—KCl—AlCl_3$ with indication of the investigated planar section of the quaternary system is shown in Fig. 1. It should be mentioned that the ternary system $NaCl—KCl—AlCl_3$ has been investigated in a pievious work [5].

For the preparation of samples (~40 g) reagent grade alkali chlorides and sublimated aluminium chloride (99.5 wt % $AlCl_3$) were used. The samples were weighed-in in a dry-box and the closed crucible with the sample was transferred into the measuring device. The melting and measurement were carried out in argon atmosphere.

The measurement was carried out by means of a quartz capillary measuring cell at a frequency of 20 kHz. The resistance capacity of the cell was determined by means of molten KNO_3 and NaCl with reference values recommended in [9]. A detailed description of the measuring procedure is given in [5]. The temperature was measured by a PtRh10—Pt thermocouple connected to a digital voltmeter, with an accuracy of ±1°C.

In the preliminary measurements it was found that the composition of samples changed owing to the evaporation of components (namely of LiCl and $AlCl_3$), the major changes occurring on melting while thereupon during the conductivity measurement the composition remained practically stable. Therefore each sample was analyzed after the measurement and the analytically determined composition was considered to be a basis for the subsequent evaluation.

The reproducibility of an individual determination was within ±2%. Considering all the above aspects, the total error in the experimentally determined values of the specific electrical conductivity was estimated to ±3%.

Calculation

As demonstrated in [10], the electrical conductivity of ternary molten salts systems can be calculated with a fair accuracy on the basis of the knowledge of molar conductivities of the boundary binary systems. The calculation is based on the assumption that the excess molar conductivity of a ternary system can be expressed as a sum of contributions of the corresponding binary systems

$$\lambda^E = x_1x_2(A_{12} + B_{12}x_2) + x_2x_3(A_{23} + B_{23}x_3) + x_3x_1(A_{31} + B_{31}x_1) \qquad (1)$$

where λ^E is the calculated excess molar conductivity of the ternary system, x_i is the mole ratio of the component i, A and B are the empirical constants determined on the basis of the experimental data of the boundary binary systems. These constants are functions of the temperature and pressure.

In the calculation of the molar electrical conductivity the molar volumes are to be known. For the system LiCl—NaCl—KCl the values reported in [11] were accepted. The densities of the quaternary mixtures $LiCl—NaCl—KCl—AlCl_3$ are not known thus far, therefore they were calculated by the proceeding used in [10] on the basis of the experimentally determined values for the corresponding binary systems. The constants describing the molar volumes of the corresponding binary mixtures are summarized in Tables 1 and 2.

Table 1

Values of the molar volumes of components in the system $(NaCl + KCl)_{equimol}$—LiCl—$AlCl_3$ applied to the calculation

Compound	V_0 / $cm^3\ mol^{-1}$	Ref.
LiCl	28.98	[12]
$(NaCl + KCl)_{equimol}$	42.06	[3]
$(NaAlCl_4 + KAlCl_4)_{equimol}$	151.39	[6]

Table 2

Values of the constants A and B applied to the calculation of the excess molar volumes in the system $(NaCl + KCl)_{equimol}$—LiCl—$AlCl_3$ at 700°C

System	A / $cm^3\ mol^{-1}$	B / $cm^3\ mol^{-1}$	Ref.
LiCl—$(NaCl + KCl)_{equimol}$	−0.86059	−0.92303	[12]
$(NaCl + KCl)_{equimol}$—$(NaAlCl_4 + KAlCl_4)_{equimol}$	−4.89167	2.10309	[6]
$(NaAlCl_4 + KAlCl_4)_{equimol}$—LiCl	0	0	—

Table 3

Values of molar electrical conductivities of the system $(NaCl + KCl)_{equimol}$—LiCl—$AlCl_3$ at 700°C applied to the calculation

Compound	λ^0 / $S\ cm^2\ mol^{-1}$	Ref.
LiCl	178.95	[3]
NaCl	117.24	[3]
KCl	91.10	[3]
$(NaCl + KCl)_{equimol}$	98.34	[3]
$(NaAlCl_4 + KAlCl_4)_{equimol}$	166.53	[6]

For the binary systems relevant with respect to the ternary systems LiCl—NaCl—KCl the conductivity data presented in [2, 7] were accepted. The values of the empirical constants describing the molar electrical conductivity of those systems are summarized in Tables 3 and 4. In the calculation of the molar electrical conductivity of molten quaternary LiCl—

Table 4

Values of the constants A and B applied to the calculation of the excess molar conductivities of the $LiCl—NaCl—KCl$ and $(NaCl + KCl)—LiCl—AlCl_3$ mixtures at 700°C

System	A / $S\ cm^2\ mol^{-1}$	B / $S\ cm^2\ mol^{-1}$	Ref.
LiCl—NaCl	− 42.1149	12.4009	[8]
NaCl—KCl	− 26.6064	4.8387	[3]
KCl—LiCl	− 67.4158	−191.7580	[3]
$LiCl—(NaCl + KCl)_{equimol}$	−144.4818	78.9843	This paper
$(NaCl + KCl)_{equimol}—(NaAlCl_4 + KAlCl_4)_{equimol}$	−221.5300	124.4200	[6]
$(NaAlCl_4 + KAlCl_4)_{equimol}—LiCl$	0	0	—

$—(NaCl + KCl)_{equimol}—AlCl_3$ mixtures, with respect to the very low conductivity value of $AlCl_3$, the calculation was carried out for the subsystem $LiCl—(NaCl + KCl)_{equimol}—$ $—(NaAlCl_4 + KAlCl_4)_{equimol}$. The constants describing the molar electrical conductivity of the binary $(NaCl + KCl)_{equimol}—LiCl$ and $(NaCl + KCl)_{equimol}—(NaAlCl_4 + KAlCl_4)_{equimol}$ mixtures are presented in Tables 3 and 4. In the system $(NaAlCl_4 + KAlCl_4)_{equimol}—LiCl$ the additivity of the molar electrical conductivities was assumed.

Based on the values presented in Tables 3 and 4 the molar electrical conductivities were calculated using the proposed mathematic formalism and the calculated values were transformed into the corresponding values of the specific electrical conductivity.

Results and discussion

The results of the experimental determination of the electrical conductivity of the investigated systems are summarized in Tables 5 and 6. The isotherm of the electrical conductivity of the ternary system LiCl—NaCl—KCl at 700°C based on the calculated values is shown in Fig. 2 (the range of the existence of liquid phase in the system is limited by the isotherms for 700°C according to the phase diagram of the system [12]).

The calculated and experimentally determined values of the specific electrical conductivity of the investigated systems are compared in Tables 7 and 8 (the values $\varkappa_{exp}$ were obtained by interpolation from the temperature dependences presented in Tables 5 and 6). From this comparison it is evident that in all cases the differences between the corresponding values are within ±3%. This fair agreement indicates that the proposed method gives reliable results in the calculation of the electrical conductivity of the ternary and quaternary systems based on the experimentally determined density and conductivity data of the corresponding

Table 5

Specific electrical conductivities of the $(NaCl + KCl)_{equimol}$—LiCl mixtures

Concentration of LiCl/wt %							
—		3.76		9.18		17.84	
$t/°C$	$\varkappa/S\ cm^{-1}$	$t/°C$	$\varkappa/S\ cm^{-1}$	$t/°C$	$\varkappa/S\ cm^{-1}$	$t/°C$	$\varkappa/S\ cm^{-1}$
692	2.32	689	2.35	692	2.46	707	2.70
700	2.34	709	2.42	706	2.52	714	2.71
700	2.34	713	2.44	730	2.59	728	2.77
704	2.35	720	2.46	736	2.62	732	2.77
720	2.40	742	2.53	758	2.69	732	2.78
724	2.41	758	2.58	762	2.70	740	2.79
		772	2.63	770	2.72	758	2.85
		776	2.65	776	2.75	770	2.89
		784	2.67			779	2.92
		814	2.76			786	2.92
						790	2.96

Table 6

Specific electrical conductivities of the $(NaCl + KCl)_{equimol}$—LiCl—$AlCl_3$ mixtures

Concentration of LiCl (c_1) and $AlCl_3$ (c_2)/wt %									
$c_1 = 2.00$ $c_2 = 3.34$		$c_1 = 4.52$ $c_2 = 4.91$		$c_1 = 5.8$ $c_2 = 6.3$		$c_1 = 14.17$ $c_2 = 4.26$		$c_1 = 19.96$ $c_2 = 3.56$	
$t/°C$	$\varkappa/S\ cm^{-1}$	$t/°C$	$\varkappa/S\ cm^{-1}$	$t/°C$	$\varkappa/S\ cm^{-1}$	$t/°C$	$\varkappa/S\ cm^{-1}$	$t/°C$	$\varkappa/S\ cm^{-1}$
688	2.31	701	2.20	695	2.16	688	2.31	688	2.48
696	2.33	707	2.22	700	2.17	696	2.33	705	2.50
700	2.34	716	2.25	700	2.17	700	2.34	714	2.53
708	2.37	723	2.27	715	2.20	708	2.37	727	2.59
740	2.45	732	2.29	728	2.24	740	2.45	731	2.61
757	2.50	748	2.32	742	2.27	757	2.50	738	2.63
765	2.51	779	2.40	745	2.28	765	2.51	742	2.63
770	2.53	794	2.42	761	2.31	770	2.53	753	2.67
		800	2.43	763	2.32			757	2.68

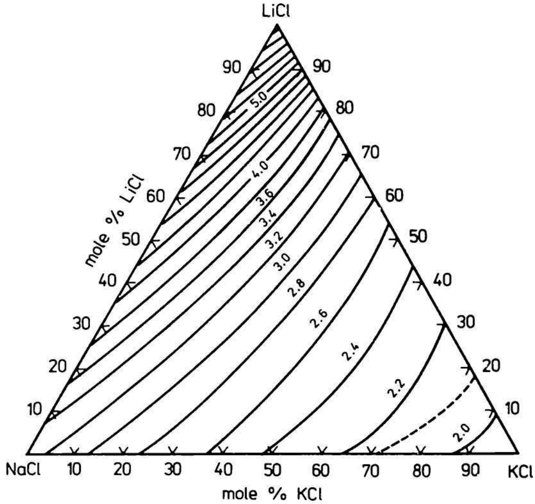

Fig. 2. Isotherm of the specific electrical conductivity of the ternary system LiCl—NaCl—KCl at 700°C calculated according to the proposed method (the dashed lines indicate the range of existence of the liquid phase).

Table 7

Experimentally determined and calculated values of the specific electrical conductivity $\varkappa$/S cm^{-1} of the $(NaCl + KCl)_{equimol}$—LiCl mixtures at 700°C

Concentration of LiCl		$\varkappa_{exp}$	$\varkappa_{calc}$
wt %	mole %		
0	0	2.34	2.34
3.76	5.77	2.39	2.42
9.18	13.69	2.50	2.54
17.84	25.41	2.67	2.72

Table 8

Experimentally determined and calculated values of the specific electrical conductivity $\varkappa$/S cm^{-1} of the LiCl—$(NaCl + KCl)_{equimol}$—$AlCl_3$ mixtures at 700°C

Concentration of LiCl		Concentration of $AlCl_3$		$\varkappa_{exp}$	$\varkappa_{calc}$
wt %	mole %	wt %	mole %		
1.98	3.12	3.34	1.67	2.21	2.20
4.91	7.66	4.52	2.24	2.20	2.20
5.80	9.09	6.30	3.14	2.17	2.18
14.17	20.99	4.26	2.01	2.34	2.35
19.96	28.58	3.56	1.62	2.52	2.53

binary mixtures. The application of this method made it possible to reduce the experimental measurements in ternary and quaternary systems to a limited number of control measurements, this being important especially with systems where the experimental determination of physicochemical properties appears to be rather complicated, as it is in the given case.

References

1. Grjotheim, K., Krohn, C., Malinovský, M., Matiašovský, K., and Thonstad, J., *Aluminium Electrolysis.* Aluminium-Verlag, Düsseldorf, 1977.
2. Artsdalen, van, E. R. and Yaffe, I. S., *J. Phys. Chem. 59,* 118 (1955).
3. Grothe, H., *Z. Elektrochem. 53,* 362 (1949).
4. Boston, C. R., Grantham, L. F., and Yosim, S. J., *J. Electrochem. Soc. 117,* 28 (1970).
5. Matiašovský, K., Fellner, P., Chrenková-Paučírová, M., Bräutigam, G., and Emons, H.-H., *Electrochim. Acta 25,* 195 (1980).
6. Borisoglebskii, Yu. V., Vetyukov, M. M., and Stekolshchikov, M. V., *Zh. Prikl. Khim. 50,* 539 (1977).
7. Olteanu, M. and Zuca, S., *Rev. Roum. Chim. 15,* 1503 (1970).
8. Sax, N. I., *Dangerous Properties of Materials.* Van Nostrand, New York, 1969.
9. *Molten Salts Standards Program* (preliminary results), sponsored by NBS under the supervision of G. J. Janz, Molten Salts Data Center, Rensselaer Polytechnic Institute, Troy, New York, 1977.
10. Fellner, P. and Chrenková-Paučírová, M., *Chem. Zvesti 33,* 705 (1979).
11. Fellner, P., Votava, I., and Chrenková-Paučírová, M., *Chem. Zvesti 34,* 330 (1980).
12. Janz, G. J., Allen, C. B., Bansal, N. P., Murphy, R. M., and Tomkins, R. P. T., *Physical Properties Data Compilations Relevant to Energy Storage. II. Molten Salts: Data on Single and Multi--component Salt Systems.* U. S. Dept. of Commerce, NSRDS-NBS 61, Part II, Washington, 1979.

Translated by K. Matiašovský