The Electric Conductivity of the Molten Salt Systems HgI_2-BiI_3 and BiI_3-CdI_2

S. V. Mentus and M. V. Šušić

Institute of Physical Chemistry, Faculty of Sciences, Belgrade
Department of General and Physical Chemistry, Institute of Chemistry, Technology and Metallurgy, Belgrade, SFR Yugoslavia

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The specific electric conductivity of the molten solt systems HgI_2-BiI_3 and BiI_3-CdI_2 was studied in the temperature range 660—840 K. BiI_3 exhibits a negative temperature coefficient of the conductivity within part of this temperature range and HgI_2 within the entire range. The specific conductivity of the HgI_2-BiI_3 system shows negative deviations from additivity for the HgI_2-rich mixtures and positive ones for the BiI_3-rich mixtures. In the BiI_3-CdI_2 system positive deviations are encountered throughout the whole composition and temperature range investigated. An increase in temperature improves the additivity in both systems.

Introduction

Recent measurements of the temperature dependence of the orthobaric electric conductivity of molten salts (zinc- and cadmium iodides, stannous and cuprous chlorides, mercuric chloride and bromide [1], mercuric and bismuth chlorides [2], bismuth halides [3] and aluminium chloride [4]) along with analogous investigations of lowmelting molecular liquids such as water [5], hydrogen chloride [6], ammonia [7], iodine trichloride and tribromide [8], point out that nonmetallic liquids exhibit a maximum of the orthobaric electric conductivity somewhere in the middle between the melting point and the critical point. The behaviour of mercuric iodide is exceptional as it shows a decrease in conductivity with increasing temperature throughout [9].

Numerous investigations have been reported on the electric conductivity of binary systems of molten salts, viz. ionic [10–13], ionic-molecular [14–19], and molecular [20, 21] salts. However, only a few studies are available on the electric conductivity of binary systems of molten salts over temperature ranges sufficiently wide for at least one of the components to pass to the region of negative temperature coefficients of conductivity. Here we may mention investigations of the systems $HgCl_2$-Hg_2Cl_2 and HgI_2-Hg_2I_2 [18], and of the systems $HgBr_2$-HgI_2 and HgI_2-SbI_3 [21]. In the present work the electric conductivity of the liquid binaries HgI_2-BiI_3 and BiI_3-CdI_2 has been studied under orthobaric conditions over a temperature range in which BiI_3 undergoes a transitions from a positive to a negative temperature coefficient of the conductivity, while the coefficient for CdI_2 and HgI_2 is always positive and negative, respectively.

Experimental

Use was made of Merck analytical reagent grade chemicals previously dried at moderate temperatures in a vacuum of about 1 mm Hg. Because of the volatility of the salts the Pyrex cell with tungsten electrodes (Fig. 1) was filled at room temperature and then sealed under vacuum. The cell constants of the order 50 cm^{-1} were determined with an accuracy

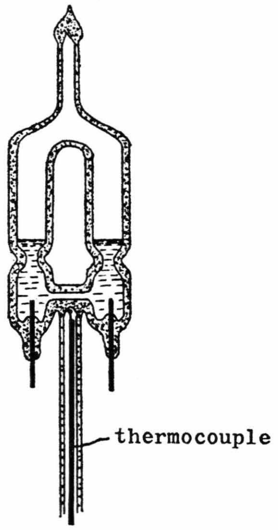

Fig. 1. The pyrex cell with tungsten electrodes.

Reprint requests to Dr. S. Mentus, Institut za fizičku hemiju, Prirodno-matematički fakultet, *1100 Beograd/* Yugoslavia.

Table I. The specific electric conductivity $\varkappa$ (ohnm^{-1} cm^{-1}) of molten HgI_2-BiI_3 at different molar fractions ($\varkappa$) of BiI_3 and temperatures T (K).

x=0.02		x=0.06		x=0.22		x=0.12	
T	$\varkappa$	T	$\varkappa$	T	$\varkappa$	T	$\varkappa$
696	1.95	667	3.81	666	1.21	678	6.82
772	1.90	679	3.75	681	1.22	689	6.35
713	1.78	695	3.41	688	1.19	703	5.78
722	1.68	713	3.10	697	1.12	812	5.51
740	1.51	723	2.90	712	1.07	725	5.30
752	1.40	749	2.55	723	1.03	749	4.55
771	1.27	773	2.21	747	0.951	769	4.11
789	1.15	808	1.76	754	0.901	778	3.99
812	1.00	820	1.67	782	0.822	797	3.38
824	0.92	834	1.53	800	0.750	808	3.52
				812	0.698		

x=0.46		x=0.52		x=0.63		x=0.80		x=0.92	
T	$\varkappa$	T	$\varkappa$	T	$\varkappa$	T	$\varkappa$	T	$\varkappa$
663	24.1	679	25.8	672	28.0	680	28.5	678	28.5
696	24.2	693	25.8	708	28.1	702	29.1	688	29.0
728	23.4	723	24.9	730	28.0	723	29.8	698	29.3
734	23.2	756	24.3	749	27.8	743	29.8	713	30.5
743	23.0	783	23.5	772	26.5	769	29.5	730	31.0
763	22.2	798	22.8	801	26.0	783	29.4	742	31.0
782	21.5	827	21.0	826	25.0	800	29.1	763	31.0
798	21.0	833	20.5			812	28.5	783	30.8
823	19.5					822	28.5	796	30.5
830	19.0					832	28.2	823	30.0

Table II. The specific electric conductivity $\varkappa$ (ohm^{-1} cm^{-1}) of molten BiI_3-CdI_2 at different molar fractions ($\varkappa$) of CdI_2 and temperatures T (K).

x=0.11		x=0.20		x=0.32		x=0.44	
T	$\varkappa$	T	$\varkappa$	T	$\varkappa$	T	$\varkappa$
690	0.334	685	0.347	706	0.382	714	0.394
701	0.345	705	0.363	741	0.417	748	0.433
743	0.366	765	0.403	775	0.445	801	0.499
795	0.384	780	0.417	781	0.455	829	0.526
814	0.390	836	0.438	814	0.472		
840	0.400						

x=0.68		x=0.79		x=0.90		x=0.96	
T	$\varkappa$	T	$\varkappa$	T	$\varkappa$	T	$\varkappa$
681	0.350	690	0.334	682	0.295	679	0.269
733	0.432	704	0.368	689	0.312	705	0.322
762	0.479	718	0.388	738	0.399	745	0.400
786	0.512	741	0.432	757	0.436	775	0.461
800	0.536	775	0.491	797	0.511	802	0.515
		797	0.521				
		811	0.550				

of ±0.5 cm^{-1} by measuring the resistance of the cells when filled with HgI_2 and CdI_2, respectively, the counductivities of these salts being taken from the literature ([22] and [1], respectively). The temperature was regulated by a chromel-alumel thermocouple to within ±1 °C in a heater of a size sufficiently large for temperature gradients within the cell to be negligible. The conductivity of the systems was measured with a Wayne-Kerr bridge, model B 224.

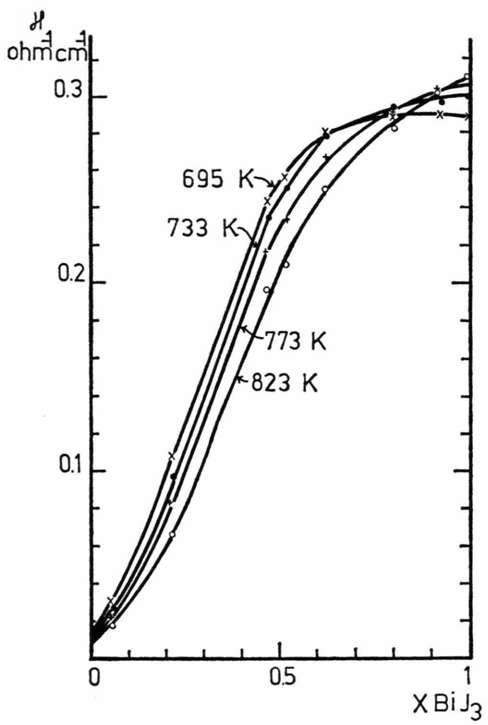

Fig. 2. Isotherms of the specific electric conductivity of molten HgI_2-BiI_3 mixtures.

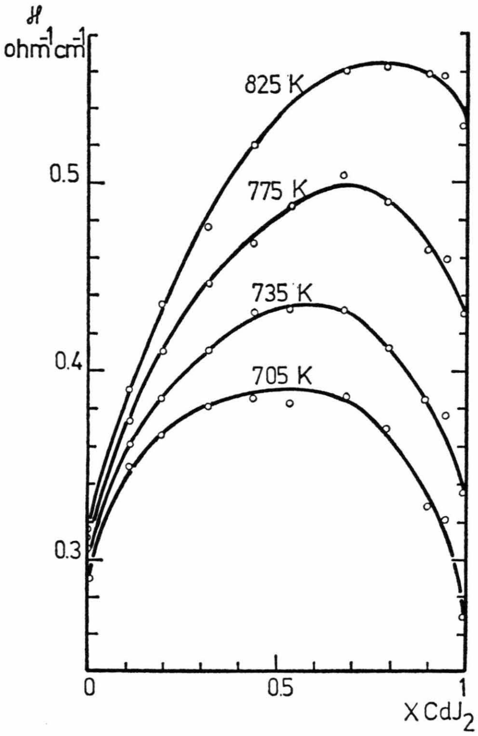

Fig. 3. Isotherms of the specific electric conductivity of molten BiI_3-CdI_2 mixtures.

Results

The results of the measurements are presented in Tables I and II. Figures 2 and 3 show several specific conductivity isotherms. In the case of HgI_2-BiI_3 it is seen (Fig. 2) that there are slight negative deviations from additivity in the HgI_2-rich composition range, whereas pronounced positive deviations appear in the BiI_3-rich composition range. As the temperature rises the negative deviations become more pronounced whereas the positive ones diminish and, on the average, the additivity is improved. In the case of BiI_3-CdI_2 (Fig. 3) positive deviations govern over the entire composition range. As the temperature increases there is a tendency towards negative deviations from additivity in the BiI_3-rich composition region while the conductivity peak shifts to the CdI_2-rich side. Also in this case an increase in temperature somewhat improves the additivity.

Discussion

It is usually assumed that the electric current carriers in molten HgI_2 are mostly the HgI^+ and HgI_3^- ions [21, 23, 24], whereas in molten BiI_3 the carriers are mostly the BiI_2^+ and BiI_4^- ions [17, 25]. In the vicinity of the melting point liquid CdJ_2 has nearly the same conductivity as BiJ_3 (Figure 3). As the temperature increases, however, its conductivity abruptly approaches that of ionic compounds. If the charge carriers in molten CdI_2 are supposed to be the CdI^+ and CdI_3^- ions, this means that the degree of dissociation of CdI_2 into these ionic species sharply increases with rising temperature. The Grotthus mechanism might be confirmed in these melts if it were demonstrated, e. g. by NMR measurements, that a fast ion exchange $A^- + AB\dot{A} = ABA + \dot{A}$ occurres.

The results presented in Figs. 2 and 3 may be interpreted qualitatively in terms of these concepts. In the composition region rich in HgI_2, a salt which is little dissociated compared to BiI_3, addition of BiI_3 would cause an increase in the dissociation of HgI_2 due to the possibility of occurrence of the ion exchange processes $BiI_4^- + HgI_2 = BiI_3 + HgI_3^-$ and $BiI_2^+ + HgI_2 = BiI_3 + HgI^+$. Because of the predominance of the properties of HgI_2, ions in excess are removed by the reaction $HgI^+ + HgI_3^- = 2\,HgI_2$. Therefore a negative deviation of conductivity from additivity appears. In the composition region rich in BiI_3, which allows for the existence of a relatively large number of ions, an increase occurs in the degree of dissociation of HgI_2 in analogy to that occurring in a weak electrolyte on dilution, which leads to a positive deviation of conductivity from additivity. The increase of temperature does not alter the type of deviation from additivity, since the molecular character of both components becomes more and more pronounced, but the additivity is somewhat improved (Figure 2).

In the BiI_3-CdI_2 system at temperatures close to the melting points the pure components have similar values of specific conductivity, and on their mixing an increase occurs in the degree of dissociation of one of the components in the other, hence the conductivity deviation from additivity is positive over the entire composition range (Figure 3). The increase of temperature affects the components differently; namely, it increases the degree of dissociation of CdI_2, and decreases that of BiI_3. Therefore the behaviour of this system approaches that of the HgI_2-BiI_3 system. Namely, it is noticed in Fig. 3 that in the BiI_3-rich composition region at higher temperatures there is a tendency of the appearance of negative deviations from additivity. This tendency might be explained by a disappearance of CdI^+ and CdI_3^- ions in the composition region rich in BiI_3, the molecular character becoming more and more pronounced, just as in the HgI_2-BiI_3 system. On the CdI_2-side the existence of a large number of ions is allowed, hence the degree of dissociation of dissolved BiI_3 proceeds with increasing temperature.

These conclusions, drawn from the results of our conductometric measurements, call for a further verification by other methods.

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