CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE JAMES FRANCK INSTITUTE, THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS 60637

The Enthalpies of Mixing of Binary Liquid Mixtures of Cadmium Chloride with Cesium and Lithium Chlorides

BY G. N. PAPATHEODOROU AND O. J. KLEPPA*

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In recent communications we have reported the enthalpies of mixing, ΔH^M, for a series of charge-unsymmetrical fused-salt systems MCl_2–ACl, where A is an alkali metal and M is Pb,[1] Mg,[2] Ni,[3] Mn, Fe, or Co.[4] In the present work our studies of this type of system are extended to the binary mixtures of cadmium chloride with cesium and lithium chlorides. These binaries have already been the subject of a great deal of work and have been explored by a variety of different physicochemical methods.[5-12] Many of these earlier investigations have considered specifically the problem of "complex" formation in the melts, and various authors have postulated the existence in the mixtures of one or more "complexes" of the general formula $CdCl_n^{2-n}$ (with n = 1, 2, or 4). The new data reported in the present work allow a look at this problem in the light of the enthalpy of mixing.

The calorimetric methods adopted were similar to those used in our earlier work.[3,4] The temperature of the measurements was 690° and all the calorimetric vessels were made from fused silica. The cadmium chloride and lithium chloride were Mallinckrodt Analytical reagents and were dried by melting at 700° in an atmosphere of HCl + N_2 (1:1). The cesium chloride was purchased from Kawecki Chemical Co. (99.9% pure) and was dried at 150° for several hours. All calorimetric mixing experiments were performed under an atmoshere of pure argon. The enthalpies of mixing measured in these experiments (in kilocalories per mole of mixture) are given in Table I. In the same table we give also the mole fraction of cadmium chloride (X_{CdCl_2}) and the total number of moles used in each experiment.

In the figure we have plotted the enthalpy interaction parameter, $\lambda^M = \Delta H^M/X_2(1 - X_2)$, *vs.* the mole fraction of cadmium chloride. The curves for λ^M for these two binaries show similarities with λ^M for the corresponding MCl_2–ACl binaries studied previously[1-4] and especially with the $MgCl_2$- and $MnCl_2$-containing systems.[1,4] For $CdCl_2$–CsCl there is strong dependence of λ^M on composition with a pronounced dip (stabilization of the mixture) near 33% $CdCl_2$. This stabilization is not present in the $CdCl_2$–LiCl system.

TABLE I
ENTHALPIES OF MIXING OF BINARY LIQUID MIXTURES OF CADMIUM CHLORIDE WITH CESIUM CHLORIDE AND LITHIUM CHLORIDE AT 690°

X_{CdCl_2}	Total moles	$-\Delta H^M$, kcal/mol	X_{CdCl_2}	Total moles	$-\Delta H^M$, kcal/mol
		$CdCl_2$–CsCl			
0.052	0.1003	0.898	0.549	0.0500	4.526
0.105	0.0505	1.758	0.624	0.0500	4.210
0.174	0.0504	2.818	0.699	0.0500	3.760
0.251	0.0502	3.920	0.775	0.0502	3.113
0.326	0.0503	4.645	0.848	0.0502	2.319
0.400	0.0501	4.897	0.924	0.0500	1.281
0.474	0.0501	4.767			
		$CdCl_2$–LiCl			
0.100	0.1016	0.099	0.599	0.1002	0.162
0.199	0.1005	0.159	0.698	0.1002	0.134
0.299	0.1001	0.200	0.799	0.1002	0.075
0.398	0.1006	0.216	0.897	0.1005	0.027
0.499	0.1006	0.195			

In our study of the MCl_2–ACl (M = Mn, Fe, Co, Ni) systems,[3,4] we argued that the interaction parameter curve will show a pronounced minimum near $X_{MCl_2} \approx 1/3$ only when appreciable tetrahedral "complexing" MCl_4^{2-} is present in the mixture. The existence of such MCl_4^{2-} configurations of tetrahedral geometry is consistent with spectrophotometric investigations of dilute and concentrated solutions of these transition metal chlorides in the alkali chlorides.[3] In particular, it is noteworthy that a tetrahedral configuration for $NiCl_4^{2-}$ is found in quite concentrated mixtures of $NiCl_2$ with cesium chloride, in spite of the well-known preference of Ni^{2+} for an octahedral environment.[12] The behavior of the interaction parameter curve for the $CdCl_2$–CsCl binary suggests that a tetrahedral $CdCl_4^{2-}$ "complex" exists and stabilizes the mixtures. Bredig[13] has argued that this complex is also present in KCl–$CdCl_2$. In the $CdCl_2$–LiCl binary, on the other hand, as in the case of the previously studied MCl_2–LiCl binaries, there is no dip in λ^M near 33% $CdCl_2$ and presumably no significant formation of $CdCl_4^{2-}$ complexes.

In Figure 1 we have also plotted estimated interaction parameter curves for the $CdCl_2$–RbCl and $CdCl_2$–KCl binaries. These were calculated from the experimental values of λ^M for the $CdCl_2$–CsCl binary, as follows.

In reviewing our earlier data for the charge-unsymmetrical binaries we noted that for a given mole fraction of transition metal chloride the ratio of the interaction parameter of the MCl_2–ACl binary to the interaction parameter of the MCl_2–A′Cl binary (*i.e.*, the ratio $\lambda^M(A–M)/\lambda^M(A'–M)$), is essentially constant for all the different MCl_2 salts studied (M = Mn, Fe, Co, Ni,

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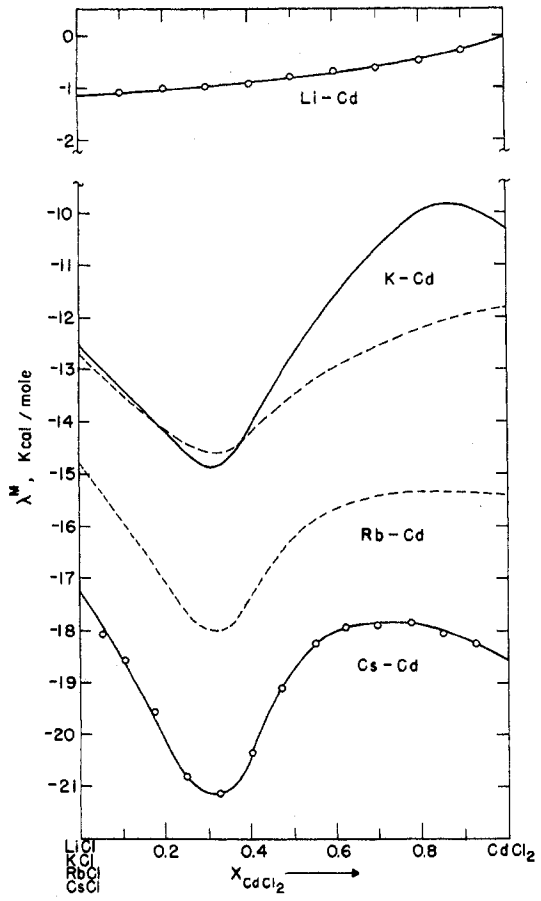

Figure 1.—Experimental enthalpy interaction parameters $\lambda^M = \Delta H^M/X_1(1 - X_2)$ *vs.* X_{CdCl_2} at 690° for the mixtures of $CdCl_2$ with LiCl and CsCl. Dotted curves give calculated values of λ^M for $CdCl_2$–RbCl and for $CdCl_2$–KCl. Solid curve for the latter system was calculated by Bredig[12] from the partial enthalpy data at 780° of Metzger, Brenner, and Salmon.[10]

Mg; A, A′ = K, Rb, Cs). For example, for the binaries of $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, and $MgCl_2$, with CsCl and RbCl, the ratios λ^M(Cs–M)/λ^M(Rb–M) at $X_{MCl_2} = 1/3$ are 1.17, 1.15, 1.18, 1.17, and 1.19, respectively. In Table II we list some average values of the

TABLE II

	X_{MCl_2} = 0	1/3	1/2	1
λ^M(Cs–M)/λ^M(Rb–M)	1.16 ± 0.04	1.17 ± 0.02	1.17 ± 0.02	1.25 ± 0.05
λ^M(Cs–M)/λ^M(K–M)	1.37 ± 0.07	1.44 ± 0.03	1.42 ± 0.06	1.58 ± 0.09

ratios λ^M(Cs–M)/λ^M(Rb–M) and λ^M(Cs–M)/λ^M(K–M), evaluated at different compositions of the mixture. If we assume that these ratios hold also for the $CdCl_2$–ACl binaries, we can use them to calculate the interaction parameters λ^M(Cd–Rb) and λ^M(Cd–K), from the curve for the $CdCl_2$–CsCl system. The calculated curves for λ(Cd–Rb) and λ(Cd–K) are given as dotted lines in Figure 1.[14] In this figure we give also the "experimental" interaction parameter curve for the $CdCl_2$–KCl system at 780°, calculated by Bredig[13] from the partial enthalpy data of Metzger, Brenner, and Salmon.[10] We see that there is quite good agreement between the two interaction parameter curves at mole fraction of $CdCl_2$ below about 0.5. However, the agreement is less satisfactory at higher contents of $CdCl_2$, where the difference between the two curves is as large as about 2.5 kcal/mol at $X_{CdCl_2} \approx 0.85$.

Due to the "intermediate" character of the NaCl–MCl_2[4] binaries the λ^M(Cs–M)/λ^M(Na–M) ratios (and the λ^M(Cs–M)/λ^M(Li–M) ratios) vary as much as 50% for the different MCl_2–ACl systems. Thus a reliable estimate of λ^M for the $CdCl_2$–NaCl mixtures is not possible.

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(14) The dotted curves drawn in Figure 1 are the result of a somewhat more laborious calculation of the λ^M(Cs–M)/λ^M(A–M) ratios, including compositions other than those listed in Table II.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF IOWA, IOWA CITY, IOWA 52240

Mechanistic Implications of the Role of Phenol in the Uranium (IV)–Chlorine(III)–Phenol Reaction

BY EUGENE B. GRIMLEY, ROBERT BUCHACEK, AND GILBERT GORDON*[1]

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Evidence has been reported for the presence of a reactive chlorine intermediate in the reaction of uranium(IV) with chlorine(III) in acidic aqueous solution.[2] When phenol is added to this system as an initial reactant, the resultant kinetics, stoichiometry, and product identification indicate that an intermediate chlorine species has been scavenged by phenol. The purpose of this note is to discuss the results of the present study which was aimed at the determination of the scavenged intermediate chlorine species in the above reaction.

The stoichiometry of the uranium(IV)–chlorine(III) reaction was reported to be variable in the absence of phenol. The criterion for monitoring reactant stoichiometry was the $([Cl(III)]/[U(IV)])_{consumed}$ ratio. In the absence of phenol, this ratio was found to vary from 1.5 to 2.5, depending upon reaction conditions. The reaction was accompanied by the production of chlorate ion as one of the products. The formation of chlorate ion under the strongly reducing conditions imposed by uranium(IV) and a greater than expected consumption of chlorine(III) are two unusual features of the reaction

(1) To whom correspondence should be addressed.
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