1.918 (3) Å found in $[Co(en)_2(tga)]^+$ is within the range of those previously determined for cobalt-proline[47,48] complexes of 1.924 (7) and 1.88 (14) Å, although perhaps longer than that for a cobalt-glutamate[49] complex of 1.87 (1) Å. It thus becomes clear that it is not possible to assign a constant radius to "octahedral" cobalt(III) or to chromium(III). However, the internal comparison of cis and trans metal-nitrogen bond lengths avoids these difficulties and shows, at least for the cobalt compound, a significant structural trans effect.

Finally, the cobalt-sulfur bond distance, 2.225 (2) Å, for the cobalt-cysteine dication is somewhat shorter than that found for the cobalt-tga monopositive cation, 2.243 (2) Å. The complex cation which bears a net charge of 2+ might be expected to bind its ligands more tightly than the cation with a net charge of 1+. This shortening might also result from reduction of interligand repulsion on replacement of mercaptoacetate by the more flexible β-mercaptoethylamine ligand.

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Registry No. $[Co(en)_2(tga)]Cl\cdot H_2O$, 41212-23-1; $[Cr(en)_2(tga)]$-ClO_4, 41212-24-2; $[Co(en)_2(cys)](SCN)_2$, 41212-25-3.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $5.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2690.

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Enthalpies of Mixing of the Binary Liquid Mixtures of Copper(I) Chloride and Copper(I) Bromide with the Corresponding Cesium Salts

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The enthalpies of mixing of liquid copper(I) chloride and copper(I) bromide with the corresponding cesium salts have been measured at 810° (both salts) and 663° (CuCl only). The molar enthalpies of mixing at 810° can be represented by the following semiempirical relations: for CuCl–CsCl, $\Delta H^M = -N_{CsCl}N_{CuCl}(7423 + 5053N_{CuCl})$ cal/mol; for CuBr–CsBr, $\Delta H^M = -N_{CsBr}N_{CuBr}(6248 + 4348N_{CuBr})$ cal/mol. N is the mole fraction of the indicated salt. There is no significant change of the mixing enthalpy for CuCl–CsCl with temperature. The new experimental results show clear analogies with the corresponding data for the lithium halide–cesium halide mixtures and are interpreted in terms of the ionic conformal solution theory of Reiss, Katz, and Kleppa.

Introduction

The enthalpies of mixing of the mixed cation-common anion alkali halide mixtures are reasonably well accounted for by the ionic conformal solution theory of Reiss, Katz, and Kleppa (RKK),[1] particularly as further developed by Blander[2] and by Davis and Rice.[3] A discussion of these systems was recently given by Melnichak and Kleppa.[4]

On the other hand, the behavior of the mixtures of the silver, thallium(I), and copper(I) halides with the corresponding alkali halides is less well understood. In these salts one has the highly polarizable cations Ag^+, Tl^+, and Cu^+, which differ in important respects from the less polarizable alkali metal cations. Presumably there are also covalent bonding contributions which are of different magnitude in the different salts and which may contribute significantly to the mixing enthalpies.[5]

Among these systems those which contain silver and thallium salts have been studied in some detail both by the emf method[6-9] and by calorimetry.[10,11] Less is known about the corresponding mixtures of the copper(I) halides, for which only emf and phase diagram information has been reported.[12,13] The present investigation was initiated in order to obtain reliable calorimetric data for the liquid copper halide–alkali halide systems. It covers the mixtures of copper(I) chloride and bromide with the corresponding cesium salts. Work on mixtures with the other alkali halides is in progress.

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Experimental Work and Materials

The calorimetric experiments reported in the present work were carried out in a single-unit microcalorimeter suitable for work up to 1000-1100°. Apart from its single (rather than twin) construction, the calorimeter is similar in design to that previously described by Kleppa.[14] In the course of the present investigation we have determined the enthalpies of mixing for the CuCl-CsCl and CuBr-CsBr systems at 810° and also for CuCl-CsCl at 663°. All experiments were carried out using calorimetric vessels made from fused silica.

The cesium chloride used was purchased from Kawecki Chemical Co. as 99.9% pure and was dried at 300° in dry N_2 for several hours. Cesium bromide was prepared from the corresponding carbonate (Kawecki 99.9%) plus analytical grade HBr. The salt was dried as CsCl. CuCl was purchased from Merck (Analytical reagent, 99.9%) and CuBr from Sochibo Co. (99.9%). The major impurities in the latter salts were traces of Cu(II). These were eliminated by the method of Keller, Wycoff, and Marcki.[15] Further purification of the copper(I) halides was achieved by zone refining (24 passes).

It is well known that the copper(I) salts are very sensitive to traces of oxygen and water vapor above 400°. Also, their vapor pressures are quite high at 810°, ~40 mm. To reduce as far as possible the complications resulting from oxidation and vaporization of the copper salts, we adopted in this work the "double break-off" technique of Papatheodorou and Kleppa.[16] All calorimetric experiments were performed in an atmosphere of argon. This gas was purified by passing it through a heated column (350-400°) containing shavings of metallic copper. Most experiments were initiated within about 1 hr after the fused-silica "liner" was introduced into the calorimeter.

For the mixtures rich in copper(I) halide the possible losses through evaporation or decomposition were checked by weighing the contents of the calorimeter (crucible + break-off + salts) after the experiments. The weight losses were of the order of 0.2 mg or less, *i.e.*, insignificant compared to the amounts of salt used, which were of the order of 0.05 mol (~5-8 g).

Results and Discussion

All the experimental results are tabulated in Table I. The last column of this table gives the experimental values of the interaction parameter $\lambda^M = \Delta H^M/N_1N_2$, where ΔH^M is the molar enthalpy of mixing while N_1 and N_2 are the mole fractions of the two salts. The values of λ^M were subjected to a least-squares treatment to fit them to polynomials of the form

$$\lambda^M = a + bN_2 + c(1 - N_2)N_2 \qquad (1)$$

The values of *a*, *b*, and *c* are listed in Table II along with the standard deviation of the experimental points from the analytical curves. This table also gives values of the corresponding coefficients for the two silver-cesium systems.

The silver and copper(I) cations have the same outer electronic structure; *i.e.*, both contain 10 d electrons. However, there is still considerable uncertainty about the "size" of the Ag^+ and Cu^+ ions. Pauling[17] listed the "ionic" radius of Ag^+ as 1.26 Å and that of Cu^+ as 0.96 Å. These values seem unrealistically high for the solid and liquid salts of these metals in view of the known lattice parameter data for the considered silver and copper halides. From such information it has been argued that the "ionic" radius of the silver ion should be comparable to that of sodium (0.95 Å), while the radius of the copper ion should be comparable to or smaller than that of lithium (0.57 Å). Tessman, Kahn, and Shockley[18] gave the polarizability of Ag^+ as 2.4 Å³ and that of Cu^+ as 1.6 Å³.

Table I. Enthalpies of Mixing in Binary Liquid Mixtures of Copper(I) Halide-Cesium Halide

N_{CuCl}	Total mmol	$-\Delta H^M$, cal/mol	$-\lambda^M$, cal/mol
	CuCl-CsCl at 663°		
0.0993	79.7	706.9	7,907
0.2003	80.1	1352.6	8,443
0.3005	80.2	1842.4	8,765
0.3977	79.5	2277.3	9,509
0.4991	80.2	2463	9,852
0.5993	79.9	2513.8	10,470
0.6967	79.7	2329.3	11,024
0.8023	81.2	1814	11,438
0.9010	80.0	1038.4	11,655
	CuCl-CsCl at 810°		
0.1011	60.0	873.6	8,272
0.1998	60.1	1306.1	8,164
0.3043	60.1	1350.3	8,736
0.3986	59.9	2254.9	9,406
0.5023	60.1	2477.5	9,909
0.6273	61.1	2545.7	10,885
0.7466	60.5	2128.5	11,250
0.8998	60.3	1069.9	11,862
	CuBr-CsBr at 810°		
0.1998	50.0	1125.7	7,048
0.2963	49.9	1514.1	7,262
0.3972	50.2	2004.2	8,372
0.5021	49.8	2149.5	8,598
0.6207	50.0	2100.2	8,921
0.7443	50.7	1760.4	9,251
0.9002	60.3	917.3	10,214

Table II. Summary of Enthalpy of Mixing Data[a] for Copper(I) Halide-Alkali Halide Systems: $\Delta H^M = N_1N_2(a + bN_2 + cN_1N_2)$

Systems	Temp, °C	$4\Delta H^M_{0.5}$	*a*	*b*	*c*	Std dev
CuCl-CsCl	810	−9949	−7423	−5053	0	209
CuCl-CsCl	663	−9897	−7446	−4902	0	115
AgCl-CsCl	810	−5078	−4288	−1170	−822	
CuBr-CsBr	810	−8422	−6248	−4348	0	218
AgBr-CsBr	810	−5266	−4806	−920	0	

[a] N_1 is the mole fraction of CsCl or CsBr. ΔH^M, *a*, *b*, *c*, and the standard deviation are in calories per mole.

The assessment of the relative importance of ionic, polarization, and covalent forces in the individual silver and copper salts is associated with considerable uncertainty. Even so, there seems to be little doubt that dispersion forces and covalency are less important in the copper halides than in the silver salts. Thus, one might expect that the mixtures of the copper(I) halides with the alkali halides should be somewhat better described by the ionic conformal solution theory of Reiss, Katz, and Kleppa than the corresponding mixtures of the silver salts. This seems to be borne out by the enthalpy of mixing data reported in the present work.

In order to illustrate this point we have plotted in Figure 1 the experimentally determined interaction parameters for the copper(I) halide-cesium halide mixtures along with corresponding data for AgX-CsX, LiX-CsX, and NaX-CsX (X = Cl, Br). Among these binaries the lithium halide-cesium halide systems are the most exothermic mixtures of type AX-BX known so far. Figure 1 shows that the copper halide systems are significantly more exothermic than the lithium halide systems and that they also have somewhat greater energetic asymmetry (*i.e.*, larger numerical values of the parameter *b*). Note also that the copper chloride-cesium chloride mixtures are noticeably more exothermic than the bromides. This is also the case for the lithium-cesium systems but not for sodium-cesium or silver-cesium systems. Finally, we see

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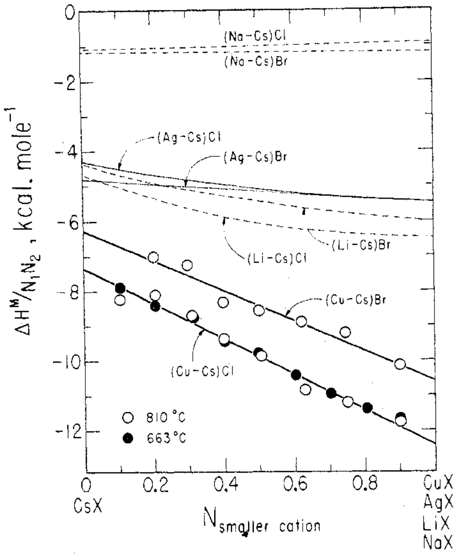

Figure 1. Interaction parameters ($\Delta H^M/N_1N_2$) for indicated systems at the following temperatures: CuX-CsX, 810° (○); CuCl-CsCl, 663° (●); LiX-CsX, 700°; AgX-CsX, 663°; NaCl-CsCl, 810°; NaBr-CsBr, 770°. Data for the lithium systems are from ref 10; those for the silver systems are from ref 11 and 19.

from Figure 1 that the copper chloride-cesium chloride mixtures show little or no dependence of the enthalpy of mixing on temperature. While similar data are not available for lithium chloride-cesium chloride and -cesium bromide, Dantzer and Kleppa[19] recently have found a dependence of the enthalpy of mixing on temperature in silver chloride-cesium chloride.

If we are justified in neglecting the possible covalent contributions to the enthalpy of mixing in the copper(I) halide-alkali halides, it should be possible to explain the observed enthalpy data in terms of the RKK theory,[1-3] suitably modified to take into account the London-van der Waals interaction between next nearest neighbor cations. Melnichak and Kleppa[4] have recently shown that the enthalpies of mixing for all the lithium chloride-alkali chloride and lithium bromide-alkali bromide systems can be represented by the semiempirical relations

$$\Delta H^M \cong N_1N_2(U_0^{++} - 410\delta_{12}^2) \quad \text{(chlorides)} \tag{2a}$$

$$\Delta H^M \cong N_1N_2(U_0^{++} - 430\delta_{12}^2) \quad \text{(bromides)} \tag{2b}$$

In these expressions the terms U_0^{++} represent numerical estimates of the (positive) London-van der Waals contributions which arise from next nearest neighbors. The terms $-410\delta_{12}^2$ and $-430\delta_{12}^2$ are of the form suggested by the RKK theory; $\delta_{12} = (d_{AX} - d_{BX})/d_{AX}d_{BX}$, where d_{AX} is the characteristic interionic distance in the pure salt AX. These semiempirical relations neglect energetic asymmetry. For pure copper halide and pure cesium halide the contributions of the London-van der Waals interactions between next nearest neighbor cations to the cohesive energies of the salts are of significant magnitude. However, they are roughly comparable numerically. For this reason the values of U_0^{++} for the CuX-CsX systems, calculated by the method of Hersh and Kleppa,[10] are quite small (less than 1%) compared to the experimental interaction parameters and have been neglected in the present work.

In the absence of unambiguous information on the ionic radius of Cu^+ or on the interionic separation between Cu^+ and X^- (d_{CuX}) in the copper halides, we are unable to calculate ΔH^M for the copper halide-cesium halide mixtures directly from RKK theory. However, we may at this point turn the problem around and use our new enthalpy data to calculate d_{CuX} under the assumption that eq 2a and 2b hold. The experimental values of λ^M at $N_1 = N_2 = 0.5$ are -9949 and -8422 cal/mol for CuCl-CsCl and CuBr-CsBr, respectively. In making these calculations we average eq 2a and 2b, set

$$\lambda^M = \Delta H^M/N_1N_2 = U_0^{++} - 420\delta_{12}^2 \cong -420\delta_{12}^2$$

and obtain $d_{CuCl} = 2.26$ Å and $d_{CuBr} = 2.40$ Å. These values seem quite plausible in view of the available structural information for the two solid copper salts, which both crystallize in the ZnS structure and have the lattice parameters 5.40 and 5.69 Å, respectively.[20] From these values we obtain $d_{CuCl} = 2.34$ Å and $d_{CuBr} = 2.46$ Å. While X-ray structural information is not available for the liquid copper salts, data for the alkali halides indicate a slight shortening of cation-anion distances when the solid salts melt. For example, in solid lithium chloride $d_{LiCl} = 2.56$ Å while the corresponding distance in the liquid at the melting point is 2.46 Å. For lithium bromide the values are 2.75 and 2.68 Å, respectively. If we adopt the ionic radii for Cl^- and Br^- (1.81 and 1.95 Å), this yields an "ionic" radius of copper in these fused salts of about 0.45 Å. These data were all taken from Melnichak and Kleppa.[21]

It is apparent that these values of d_{CuCl}, d_{CuBr}, and r_{Cu^+} must be considered as tentative only and are associated with very considerable uncertainty. First of all, they are, of course, based on the assumed validity of the modified RKK theory. Second, they are sensitive to the procedures adopted in calculating U_0^{++} for the previously studied LiCl-CsCl and LiBr-CsBr systems. If our earlier work *underestimated* U_0^{++} for these systems, the calculated values would be *smaller*; if it *overestimated* U_0^{++}, the values would be *larger*. However, it is of interest to note that the quoted interionic distances also seem quite reasonable if we compare the molar volume of liquid CuCl (26.4 ml) with that of liquid LiCl (28.36 ml).[22] These values also suggest that $d_{CuX} \gtrsim d_{LiX}$, as we have actually found.

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Registry No. CuCl, 7758-89-6; CsCl, 7647-17-8; CuBr, 7787-70-4; CsBr, 7787-69-1.

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