Work is continuing on the investigation of these phenomena in these laboratories, in particular on the swelling process and the role played by protein configuration in determining the sorption behavior. It begins to appear more and more evident that the technique of gas phase interactions may be expected to yield valuable data on the structure and properties of the native protein molecule.

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# Some Optical Properties of Molten Silver Bromide–Alkali Bromide Solutions

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The refractive indices of molten binary solutions of silver bromide with lithium bromide and rubidium bromide have been determined as a function of temperature and composition. The molar refractivities of these solutions were found to be an additive function of the mole fraction. The temperature dependence of the absorption edge of pure liquid and solid silver bromide has been determined as well as the temperature dependence of the absorption edge of pure molten rubidium bromide and that of an equal molar mixture of silver bromide and rubidium bromide. The concentration dependence of the absorption edge of molten binary solutions of silver bromide with sodium bromide and rubidium bromide also has been determined. No evidence is found for the existence of "complex ions" in these solutions.

## Introduction

In 1932 Hildebrand and Salstrom[2] published a paper which summarized and discussed a previous series of papers on the thermodynamic properties of binary liquid solutions of silver bromide with the bromides of lithium, sodium, potassium and rubidium. The data had been obtained by measuring the e.m.f. of cells which were without transference, consisting of silver and bromine electrodes dipping into fused silver bromide diluted with varying amounts of several alkali bromides. Measurements were made at three temperatures, 500, 550 and 600°, permitting calculation not only of the free energy of dilution but also the enthalpy and entropy, with their dependence upon the mole fraction of alkali bromide. The character of the results is indicated in Fig. 1 where $RT$ ln $\gamma_1$ is plotted against the square of the mole fraction of alkali bromide, $x_2$. Here $\gamma_1$ is the activity coefficient of silver bromide, *i.e.*, its activity referred to pure liquid, $a_1$, divided by its mole fraction, $x_1$.

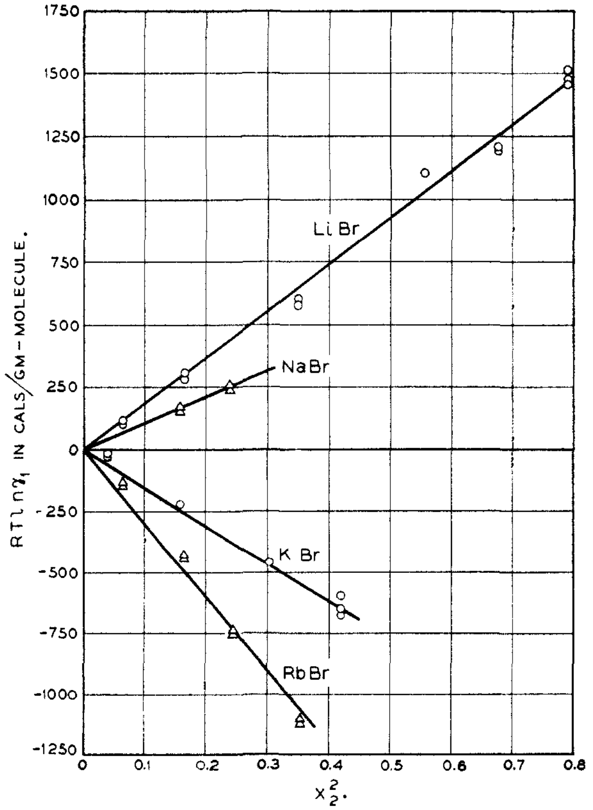

Fig. 1.—The departures from ideality of silver bromide in various molten alkali bromides.

Three highly significant facts are to be noted: first, the lines are all straight, showing that each can be expressed by a simple equation, $\bar{F}_1 - \bar{F}_1^i = kx_2^2$; second, the points for the widely different temperatures all fall on the same line, whence

$$\left[\frac{\partial(\bar{F}_1 - \bar{F}_1^{i})}{\partial T}\right]_x = -(\bar{S}_1 - \bar{S}_1^{i}) = 0$$

*i.e.*, the entropy is ideal and temperature independent and the heat of dilution is $\bar{H}_1 - \bar{H}_1^i = kx_2^2$; and, third, the deviation from the ideal varies from strongly positive when diluted with LiBr, less positive with NaBr, negative with KBr and strongly negative with RbBr.

Now positive deviations do not surprise us, for that is characteristic of "regular" solutions, where it results from unequal attractive forces, without involving any changes in molecular species. Negative deviations, however, are quite another matter. It requires far greater differences in molar volume than are found in AgBr–RbBr solutions to account for the large deviation in that case by a Flory–Huggins type of entropy. Large negative deviations do accompany the evolution of heat resulting from solvation, but in that case there is ordinarily a diminution in the number of independent molecules, and less than ideal entropy of dilution. Thus,

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[1] Bell Telephone Laboratories, Murray Hill, N. J.

[2] J. H. Hildebrand and E. J. Salstrom, THIS JOURNAL, **54**, 4257 (1932).

the negative departures from ideality observed by Hildebrand and Salstrom argue in favor of complex ion formation but the ideal entropy of dilution argues against it.

Fromherz and Menschick[3] have pointed out the similarity between the near ultraviolet absorption spectra of concentrated aqueous solutions of alkali halide–silver halide mixtures and dilute solid phase mixtures of the silver halides in alkali halides. On the basis of their conclusion that the new absorption peaks in the aqueous solutions were produced by complex ions they were led to suppose that the same chromophors were responsible for the similar absorption peaks in the solid mixtures.

This work suggests that a study of the absorption spectra of the molten silver bromide–alkali bromide solutions might permit a decision to be made pertaining to the existence and concentrations of complex species in these melts. Since a direct measurement of the absorption spectra presents considerable experimental difficulty, primarily because of the very large absorption coefficients in the spectral regions of interest, an indirect attack has been made.

We have measured the refractive indices of silver bromide–rubidium bromide solutions and silver bromide–lithium bromide solutions as a function of wave length of light, temperature and composition. From this information and the known densities of these solutions the molar refractivities at infinite wave length have been calculated and plotted as a function of the silver bromide concentration and the extrapolated values of the molar refractivity of pure silver bromide compared. It is to be expected that new or stronger absorption bands in the silver bromide–rubidium bromide melts would give rise to a higher extrapolated value of the molar refractivity of silver bromide.

We have also determined the temperature dependence of the long wave length absorption edge of pure silver bromide in both the solid and molten state. This has been compared with the temperature dependence of the absorption edge position of an equimolar silver bromide–rubidium bromide melt and of pure molten rubidium bromide.

A photographic method was used to determine the absorption edge dependence on temperature. By measuring the change in position of the absorption edge on a photographic plate as a function of exposure time and silver bromide concentration in the melt, it was also possible to estimate the change in extinction coefficient of AgBr at constant wave length and temperature as a function of silver bromide concentration.

**Molar Refractivities. Theory.**—Meyer and Heck[4] have measured the refractive indices of several molten hydroxides and nitrates up to temperatures as high as 440°. Rather than use their method of forming a liquid prism by using a tipped crucible with a reflecting bottom, we have used a hollow quartz prism.

The refractive index of a liquid contained in a hollow prism of apex angle $A$ is given by

$$n_\lambda = \frac{\sin {}^1/_2(\delta_\lambda + A)}{\sin {}^1/_2 A} \qquad (1)$$

where $\delta_\lambda$ is the angle of minimum deviation of the wave length $\lambda$.[5]

## Experimental

A small hollow prism was made of 1-mm. thick Vycor sheet (Corning ultraviolet filter #791). A 5 × 2.5 cm. strip was heated in the middle and folded over the long way until the two opposite edges touched to form the apex angle of the prism. After sealing these edges a sheet of Vycor was sealed in place to make a top and another to make a bottom to the prism. A tube was attached to the top through which the prism could be loaded. A spectrometer was used in the normal manner to measure the apex angle.

A Gaertner student spectrometer was modified to accommodate an electric furnace into which the prism could be placed. The standard nichrome wound ceramic heating element of the furnace was in two halves each contained separately in a transite insulating box 14 × 12 × 7 cm. in size. These two boxes were hinged in such a manner that when closed the furnace heating elements were brought into position to form a horizontal cylinder 10 cm. long and 3.2 cm. in diameter and to give the furnace the over-all dimensions 14 × 12 × 14 cm.

In order to minimize temperature gradients over the prism, a modified copper cylinder 8 cm. long and 3 cm. in diameter was placed in the furnace cavity. A wedge shaped hole dividing the copper block into two mirror image sections accommodated the prism. A beveled window cut parallel to the long axis of the furnace and in the center of each section of the copper block, permitted light to pass into the furnace, through the prism and out the other side of the furnace. These windows were 1 × 1 cm. next to the prism faces and 1 cm. high by 2.3 cm. wide at the extremities. One side and the top and bottom of each window extended straight through the copper block. The other side was beveled in order to permit the light beam to pass through the prism at the largest angle of minimum deviation used.

The temperature was automatically controlled to ±0.5° during measurements. The temperature recording thermocouple was of Pt–Pt (13%), Rh (87%) elements 0.0085 inch in diameter. The couple was inserted into a small hole in the copper block placing the junction against the face of the prism 8 mm. away from the section through which light was passed.

A mercury arc and a helium discharge tube furnished spectral lines which adequately covered the visible spectrum.

Different melt compositions were made by determining the weight of the empty prism and the weight plus one component then both. The LiBr was always handled in a dry-box. The filled prism was put into place in the furnace on the table of the modified spectrometer, connected to a vacuum system and flushed with purified helium. The heating and measurements were carried out with a pressure of one atmosphere of helium over the sample.

After heating to temperature, the more concentrated mixtures required an hour before the melt was of uniform composition as evidenced by the clarity and stability of the spectrometer slit image.

Differences in position of the slit image could be read on a micrometer screw to 0.1 minute of arc over a 5° range. The temperature dependence of the refractive indices of the solutions studied was in the neighborhood of 0.2 min. of arc per deg. Since the slit images were stable to better than 0.1 min. of arc, the temperature of the melt was believed to be uniform to within 0.5°. At the highest temperature reached, 786°, slit image fluctuations of 0.1 min. of arc were observed.

The refractive indices are believed to be in error by no more than ±0.003 as determined by repeated measurements on water. The differences between two refractive indices of a particular melt are known to ±0.001. The temperature is known to ±3° as determined by visual melting point determinations in the prism. The differences in temperature for a particular melt composition are known to ±1°.

**Reagents.**—Silver bromide was precipitated from an aqueous solution of analytical grade silver nitrate with C.P. grade $NH_4Br$. After washing 12 times over a period of 5 days no further test for ammonium ion was obtained.

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[3] H. Fromherz and W. Menshick, *Z. physik. Chem.*, **B3**, 1 (1929).

[4] G. Meyer and A. Heck, *ibid.*, **100**, 316 (1922).

[5] R. W. Wood, "Physical Optics," The Macmillan Co., New York, N. Y., 1934.

The halide was then put under vacuum and slowly heated to 400°. The moisture was collected in a liquid nitrogen trap and a pressure of $10^{-4}$ mm. finally reached.

LiBr, C.P. grade, was fractionally crystallized from water to give the monohydrate which was partially dehydrated under vacuum by slowly heating to 500°. This material was heated to 560–580° in a Pyrex bulb and HBr bubbled through it for 1 hour. A neutral salt resulted.

C.P. grade RbBr and NaBr were used. Each gave a neutral aqueous solution after vacuum fusion.

## Results

The refractive index as calculated from equation 1 was used to obtain the function $(n^2 + 2)/(n^2 - 1)$. The classical dispersion function

$$\frac{n^2 - 1}{n^2 + 2} = \frac{C}{f_0^2 - f^2} \qquad (2)$$

was used to obtain $(n_\infty^2 - 1)/(n_\infty^2 + 2)$ from which the molar refractivity at infinite wave length may be obtained.[6] It was found that $(n^2 + 2)/(n^2 - 1)$ was linear in $f^2$, the square of the frequency. Small deviations from linearity were observed at short wave lengths for the solutions of highest AgBr concentration, as was to be expected. The data are presented in Table I where the constants of equation 2 are given for the various solutions studied.

TABLE I

| $x_{AgBr}$ | $t$, °C. | $C \times 10^{-30}$ | $f_0 \times 10^{-15}$ | $\frac{n_\infty^2 - 1}{n_\infty^2 + 2} = \frac{C}{f_0^2}$ |
|---|---|---|---|---|
| | | LiBr–AgBr | | |
| 0 | 557 | 2.159 | 2.513 | 0.3259 |
| | 598 | 2.084 | 2.540 | .3229 |
| | 634 | 2.048 | 2.528 | .3204 |
| 0.135 | 528 | 2.078 | 2.432 | .3513 |
| | 569 | 2.018 | 2.407 | .3484 |
| | 620 | 1.925 | 2.364 | .3446 |
| 0.201 | 544 | 2.012 | 2.371 | .3578 |
| | 596 | 1.950 | 2.346 | .3542 |
| 0.205 | 514 | 2.050 | 2.372 | .3643 |
| | 563 | 2.022 | 2.365 | .3615 |
| | 644 | 1.944 | 2.337 | .3559 |
| | | RbBr–AgBr | | |
| 0 | 695 | 1.549 | 2.424 | .2635 |
| | 729 | 1.476 | 2.381 | .2604 |
| | 753 | 1.449 | 2.369 | .2583 |
| 0.173 | 621 | 1.575 | 2.315 | .2934 |
| | 642 | 1.539 | 2.297 | .2917 |
| | 693 | 1.522 | 2.300 | .2876 |
| | 721 | 1.464 | 2.267 | .2850 |
| | 754 | 1.461 | 2.274 | .2824 |
| 0.301 | 574 | 1.580 | 2.230 | .3178 |
| | 620 | 1.570 | 2.235 | .3142 |
| | 676 | 1.499 | 2.202 | .3090 |
| 0.313 | 555 | 1.636 | 2.263 | .3193 |
| | 619 | 1.571 | 2.237 | .3139 |
| | 667 | 1.541 | 2.230 | .3099 |
| | 732 | 1.508 | 2.225 | .3047 |
| 0.485 | 504 | 1.656 | 2.147 | .3592 |
| | 558 | 1.612 | 2.132 | .3546 |
| | 609 | 1.570 | 2.117 | .3503 |
| | 665 | 1.520 | 2.098 | .3453 |
| | 786 | 1.428 | 2.062 | .3358 |

The molar refractivity at infinite wave length is given by the expression

$$R_\infty = \frac{n_\infty^2 - 1}{n_\infty^2 + 2} V$$

where $V$ is the molar volume of the melt.[6]

Since $R_\infty$ varies somewhat with temperature, a particular temperature was chosen which would enable all solutions to be compared at the same temperature with minimum extrapolation. $(n_\infty^2 - 1)/(n_\infty^2 + 2)$ was a linear function of temperature and a value of this function was obtained at 650° from such plots. These are listed in Table II.

TABLE II

Temperature = 650°

| $x_{AgBr}$ | $\frac{n_\infty^2 - 1}{n_\infty^2 + 2}$ | $V$, cc. | $R_\infty$, cc. |
|---|---|---|---|
| | LiBr–AgBr | | |
| 0 | 0.3193 | 35.09 | 11.20 |
| 0.135 | .3424 | 35.09 | 12.03 |
| .201 | .3504 | 35.09 | 12.30 |
| .205 | .3558 | 35.09 | 12.49 |
| 1.000[a] | .... | ... | 16.8 |
| | RbBr–AgBr | | |
| 0 | 0.2675 | 60.30 | 16.13 |
| 0.173 | .2910 | 55.94 | 16.28 |
| .301 | .3114 | 52.46 | 16.34 |
| .313 | .3114 | 52.23 | 16.26 |
| .485 | .3469 | 47.33 | 16.42 |
| 1.000[a] | .... | ... | 16.8 |

[a] Extrapolated.

The molar volumes of the melts were calculated from the literature values of the densities of the pure melts. These are

LiBr,[7] $d = 2.93 - 7 \times 10^{-4} t$
RbBr,[8] $d = 3.458 - 11 \times 10^{-4} t$
AgBr,[7] $d = 6.023 - 10.3 \times 10^{-4} t$

where $t$ is in degrees centigrade. It is estimated that the densities at 650° are known to ±0.01 g./cc. The small departures from volume additivity exhibited by these solutions were neglected.[2]

Table II includes the molar volumes of the melts and the molar refractivities at infinite wave length calculated for a temperature of 650°. The estimated error in $(R_\infty)_{650}$ is 0.1 cc.

In Fig. 2, the molar refractivity has been plotted as a function of the mole fraction of silver bromide in the melt. It can be seen that within the precision of the data, the extrapolated molar refractivity of pure silver bromide from the lithium bromide solutions is the same as from rubidium bromide solutions.

**Absorption Edge Position as a Function of Temperature and Composition. Theory.**—If $I_0$ is the intensity of light in the wave length region $\lambda + d\lambda$ incident on the melt, and $I$ the transmitted intensity, the absorption coefficient $k_\lambda$ at wave length $\lambda$ is defined by

$$\log I_0/I = k_\lambda l$$

where $l$ is the light path length through the melt.

Let $i_0$ be the intensity of light in the region $\lambda + d\lambda$ incident on the photographic plate when the

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[6] A. Weissberger, "Techniques of Organic Chemistry: Physical Methods," Vol. 1, Chapt. XVI by N. Bauer and F. Fajans, "Refractometry," Interscience Publishers, Inc., 1945.

[7] E. Brunner, *Z. anorg. allgem. Chem.*, **38**, 350 (1904).

[8] R. Lorenz and A. Hochberg, *ibid.*, **94**, 288 (1916).

quartz cell is empty, and $i$ the intensity when the quartz cell is filled. Let $t_0$ be the exposure time for light through the empty cell and $t$ the exposure time for light through the filled cell. If there is no failure of the reciprocity law[9]

$$i_0/i = t/t_0$$

when the density of the developed silver deposit on the photographic plate is the same for both exposures at the position on the plate corresponding to λ. Since

$$i_0/i = I_0/I$$

we have

$$k_\lambda = (1/l) \log (t/t_0)$$

(Over a limited range of low intensities, Schwarzchild's law is a better approximation than the simple reciprocity law.[9] This may be written as

$$(i_0/i) = (t/t_0)^p$$

which leads to

$$k_\lambda = (p/l) \log (t/t_0)$$

where $p$ is usually around 0.8.)

## Experimental

A three meter Baird Spectrograph (5.5 Å./mm. dispersion) was used with type 103-F and I-O Eastman spectrographic plates, 4″ × 10″.

Light from a tungsten ribbon or hydrogen arc was passed through a quartz cell heated in the furnace described previously, and focused on the spectrograph slit. Two cell sizes were used: $l = 0.59 \pm 0.01$ cm. and $l = 0.009 \pm 0.001$ cm. Exposure times ranged from 1 to 64 seconds. An iron arc was used for calibration.

Exposures were first made through the empty cell. Weighed quantities of the various bromides were then added to the cell to make up the desired compositions.

The thin cell was made of one millimeter thick Vycor plates sealed at one end to a quartz rod. A thin copper sheet was used to separate the two plates. After removing the copper spacer, the plates were dipped into a small pool of molten AgBr contained in the larger cell ($l = 0.59$ cm.). The space between the quartz plates was filled by capillary action. When cooled below the melting point of AgBr, a thin, uniform film of solid remained between the plates.

## Results

The results are summarized in Table III. The absorption coefficient was calculated by using the equation

$$k_\lambda = (1/l) \log (t/t_0)$$

A straight line was drawn through the three or four points and the constants of the equation $k_\lambda = a \cdot (\lambda_0 - \lambda)$ evaluated.

The thin cell ($l = 0.009 \pm 0.001$) was used only with pure AgBr. The values of $k_\lambda$ ranged from 70 to 170 cm.$^{-1}$. $k_\lambda$ ranged from 1 to 3 cm.$^{-1}$ for all other melts.

The dependence of $k_\lambda$ on λ for pure AgBr in the thin cell when compared with the results obtained with the large cell shows that $k_\lambda$ is not linear with λ over a large region of the spectrum but curves steeply upward as λ decreases. Consequently, the values of $\lambda_0$ given in Table III result from an extrapolation of the dependence of $k_\lambda$ on λ over a very narrow region of the absorption spectrum.

It has been found that the absorption edge position of these melts, $E_0$, expressed in electron volts, is a linear function of temperature. The constants of the equation $E_0 = A - Bt$, with $t$ in degrees centigrade, are given in Table IV.

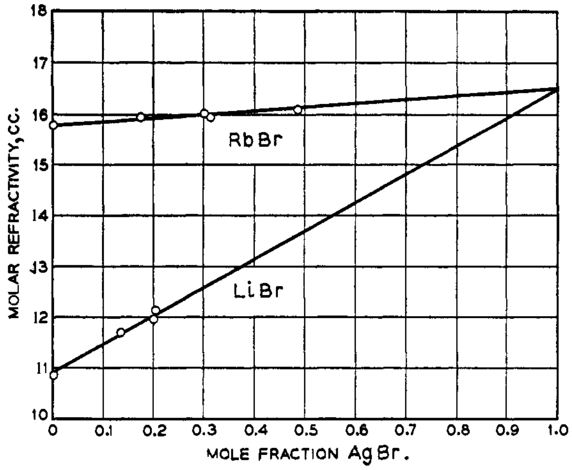

Fig. 2.—The molar refractivity of molten rubidium bromide and lithium bromide solutions of silver bromide at 650°.

TABLE III

$k_\lambda = a(\lambda_0 - \lambda)$

| $x_{AgBr}$ | $t$, °C. | $\lambda_0$, Å. | $a$, Å.$^{-1}$ cm.$^{-1}$ |
|---|---|---|---|
| | AgBr–RbBr | | |
| 1.000[a] | 309 | 4930 | 0.88 |
| 1.000[a] | 379 | 5085 | .76 |
| 1.000[a] | 425 | 5210 | .68 |
| 1.000[a] | 455 | 5590 | .66 |
| 1.000[a] | 556 | 5840 | .54 |
| 1.000[a] | 654 | 6040 | .50 |
| 1.000 | 507 | 6710 | .0113 |
| 0.994 | 507 | 6705 | .0068 |
| .940 | 507 | 6335 | .0093 |
| .900 | 507 | 6095 | .0098 |
| .873 | 507 | 5935 | .0107 |
| .50 | 410 | 4235 | .033 |
| .50 | 549 | 4500 | .026 |
| .50 | 685 | 4850 | .021 |
| .50 | 779 | 5120 | .015 |
| .264 | 686 | 4225 | .020 |
| .180 | 686 | 3965 | .013 |
| .013 | 686 | 3555 | .016 |
| .000 | 686 | 3460 | .017 |
| .000 | 727 | 3560 | .013 |
| .000 | 770 | 3700 | .0099 |
| | AgBr–NaBr | | |
| 0.969 | 507 | 6705 | 0.0061 |
| .915 | 507 | 6310 | .0086 |
| .867 | 507 | 6045 | .0118 |

[a] $l = 0.009$ cm.; all others $l = 0.59$ cm.

TABLE IV

$E_0 = A - Bt$, e.v.

| Solution | $A$ | $B \times 10^3$ |
|---|---|---|
| AgBr, solid | 2.87 | 1.17 |
| AgBr, liquid | 2.58 | 0.82 |
| AgBr–RbBr, $x = 0.5$ | 3.50 | 1.38 |
| RbBr, liquid | 5.46 | 2.73 |

$E_0$ is also a linear function of mole fraction over the concentration ranges studied as long as the end points, $x_{AgBr} = 1.0$ and 0 are not included. In each case the end-points lie at shorter wave lengths than

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[9] C. E. K. Mees, "The Theory of the Photographic Process," The Macmillan Co., New York, N. Y., 1945, p. 236.

would be obtained from an extrapolation of the concentration dependence of $\lambda_0$. The constants of the equation $E_0 = \alpha - \beta x_{\text{AgBr}}$ are given in Table V.

TABLE V

$E_0 = \alpha - \beta x_{\text{AgBr}}$, e.v.

| Solution | $\alpha$ | $\beta$ |
|---|---|---|
| AgBr–RbBr ($t$ = 507, AgBr rich) | 3.817 | 1.98 |
| AgBr–RbBr ($t$ = 686, RbBr rich) | 3.512 | 2.18 |
| AgBr–NaBr ($t$ = 507, AgBr rich) | 3.771 | 1.98 |

The dependence of the absorption coefficient $k_\lambda$ on concentration at constant temperature and wave length shows that wide departures from Beer's law occur when AgBr is assumed to be the chromophor. This conclusion is reached in the following manner. From the measurements made with AgBr in the thin cell and the large cell it can be estimated by roughly sketching in a curve which will fit both sets of data that $k_\lambda$ in the region 5800–5900 Å. is around 30 cm.$^{-1}$. If Beer's law were obeyed, a dilution of AgBr by 13 mole per cent. would be expected to lower the absorption coefficient by 13% at constant $\lambda$. However, from the results tabulated in Table III it is found that the absorption coefficient at 5850 Å. is 1 cm.$^{-1}$ in 13% RbBr–AgBr and about 2 cm.$^{-1}$ in 13% NaBr, AgBr. Thus, $k_\lambda$ is about 15- to 25-fold smaller than if Beer's law were obeyed.

## Discussion

The experimental results which have been reported here give indirect evidence that strong new absorption bands do not appear in molten mixtures of alkali bromides with silver bromide. The absorption spectra of aqueous solutions of alkali bromide–silver bromide mixtures show strong new absorption bands which can be attributed to complex ions.[3] Consequently, the experimental results suggest that complex ions are not a major constituent of these molten solutions.

Pauling[10] has suggested that the amount of covalent character in the crystal bonds of AgBr is 26% on the basis of his computation of the per cent. covalent character of the molecule in the vapor state. Mayer[11] has computed the lattice energy of AgBr at 0°K. on the basis of similar assumptions to those used in the calculation of the lattice energies of the alkali halides. The agreement between the theoretical and experimental lattice energies which he took as evidence that AgBr was an ionic crystal no longer holds since recent experimental work has revised some of the thermodynamic properties of AgBr, particularly the heat of sublimation of silver. Using the compilations of Brewer and co-workers[12] the experimental lattice energies of the silver halides at 0°K. have been reevaluated. In Table VI these new values are compared with the theoretical lattice energies of Mayer. The discrepancy of 18 kcal. in the case of AgBr would suggest that covalent interactions make a significant contribution to its stability.

TABLE VI

Lattice energies at 0°K., in kcal. per g. molecule.

| Halide | Exptl.[12] | Theoretical[11] |
|---|---|---|
| AgF | 230 | 219 |
| AgCl | 218 | 203 |
| AgBr | 215 | 197 |
| AgI | 213 | 190 |

Since AgBr crystallizes in the NaCl type lattice, the near neighbor positions about a particular ion are equivalent. The covalent contribution to the lattice energy would be expected to result from an equal contribution by all AgBr pairs. Pauling[10] has described this in terms of a resonating covalent bond.

Following Hildebrand and Salstrom, it is suggested that a similar state exists in molten silver bromide. Thus, the positions of the bromide ions about each silver ion are to be described by a radial distribution function the first peak of which gives the average number and position of the near neighbor bromides which are all equivalent. The positions of the silver ions about each silver ion and the bromide ions about each bromide ion are to be described similarly.

In molten solutions of silver bromide and rubidium bromide, the silver and rubidium ions are thought to be randomly arranged about the bromide ions but since the rubidium ion is larger than the silver ion ($Rb^+$, 1.48 Å.; $Ag^+$, 1.26 Å.[10]) the bromide ions will be in an unsymmetric electric field. The resultant distortion of a bromide ion would bring its electron cloud nearer to the silver ions about it and an increase in covalent character of the $Ag^+$–$Br^-$ interaction would be expected which would lead to negative departures from ideality.

The addition of lithium bromide to molten silver bromide, on the other hand, would be expected to distort the bromide ion in the opposite sense since the lithium ion is smaller than the silver ion (0.60 Å.[10]). This would decrease the covalent character of the $Ag^+$–$Br^-$ interaction and lead to positive deviations from ideality.

On the basis of this model, the departures from ideality arise from energy changes. The entropy of mixing is ideal since the energy changes are too small to produce appreciable ordering.

Changes in electronic polarizability leading to departures from additivity of the molar refractivity would be expected but it is not surprising that such an effect, if it occurred, would be undetectable within the precision of the measurements reported here.

I am indebted to Professor Joel H. Hildebrand for his advice and encouragement.

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(10) L. Pauling, "The Nature of the Chemical Bond," Second Ed., Cornell Univ. Press, Ithaca, N. Y., 1945, p. 73.

(11) J. E. Mayer, *J. Chem. Phys.*, 1, 327 (1933).

(12) "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," National Nuclear Energy Series, L. L. Quill, Editor, 1950. L. Brewer, paper 3, p. 13 and paper 5, p. 60. L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, paper 6, p. 76.