

SHORT COMMUNICATIONS

THE MEAN DEBYE-WALLER FACTORS AND DEBYE TEMPERATURES OF $\text{AgCl}_x\text{Br}_{(1-x)}$ MIXED CRYSTALS

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ALTHOUGH considerable information is available regarding the physical properties of AgCl and AgBr, information regarding their mixed crystals is meagre. Recently, the results of an x-ray determination of the Debye-Waller factors and Debye temperatures of AgCl and AgBr were reported from this laboratory¹. Similar results for AgCl-AgBr mixed crystals are now being reported.

Mixed crystals with various compositions were prepared by melting. The lattice constants of the mixed crystals were obtained from x-ray diffractograms and the exact compositions were determined from these lattice constants by assuming Vegard's law. Integrated intensities of Bragg reflections were determined with an x-ray powder diffractometer. The procedures of experimental measurement of intensities and of the analysis of data for the evaluation of the Debye-Waller factor and Debye temperature are the same as given earlier^{1,2}. It may be mentioned that in mixed crystals, the experimentally determined Debye-Waller factor (B_{obs}) includes a static component (B_{static}). This has to be deducted from B_{obs} to obtain the thermal value of the Debye-Waller factor (B_{thermal}). To evaluate Debye temperature, B_{thermal} has to be employed rather than B_{obs} . In the present work, the model of Dernier *et al*³ was employed to estimate the value of B_{static} .

The values of B_{obs} and the x-ray Debye temperature (θ_M) are given in table 1 for several compositions for the mixed crystal system $\text{AgCl}_x\text{Br}_{(1-x)}$. These values are also shown in figure 1 for a visual appreciation of the trends in composition dependence. The Debye-Waller factor shows a highly nonlinear dependence on composition with positive deviations from linearity. The values of the Debye-Waller factor for the mixed crystals, exceed the values for both the end members. On the other hand, the composition dependence of the Debye temperature is almost linear with a very slight negative deviation from linearity.

Debye temperature values determined from the

Table 1 Values of mean Debye-Waller factor (B_{obs}) and the Debye temperature (θ_M) for $\text{AgCl}_x\text{Br}_{(1-x)}$ mixed crystals

Mole fraction of AgCl in AgBr (x)	$B_{\text{obs}}(\text{\AA}^2)$	$\theta_M(^{\circ}\text{K})$	$\theta_E(^{\circ}\text{K})$
0	2.14 ± 0.06	131.4 ± 2	136.7
0.14	2.20 ± 0.06	134.1 ± 3	138
0.32	2.30 ± 0.08	136.2 ± 3	139
0.45	2.33 ± 0.09	137.5 ± 3	140
0.51	2.33 ± 0.08	138.7 ± 3	140
0.76	2.24 ± 0.09	145.5 ± 3	143
1.0	2.19 ± 0.03	148.8 ± 2	146.5

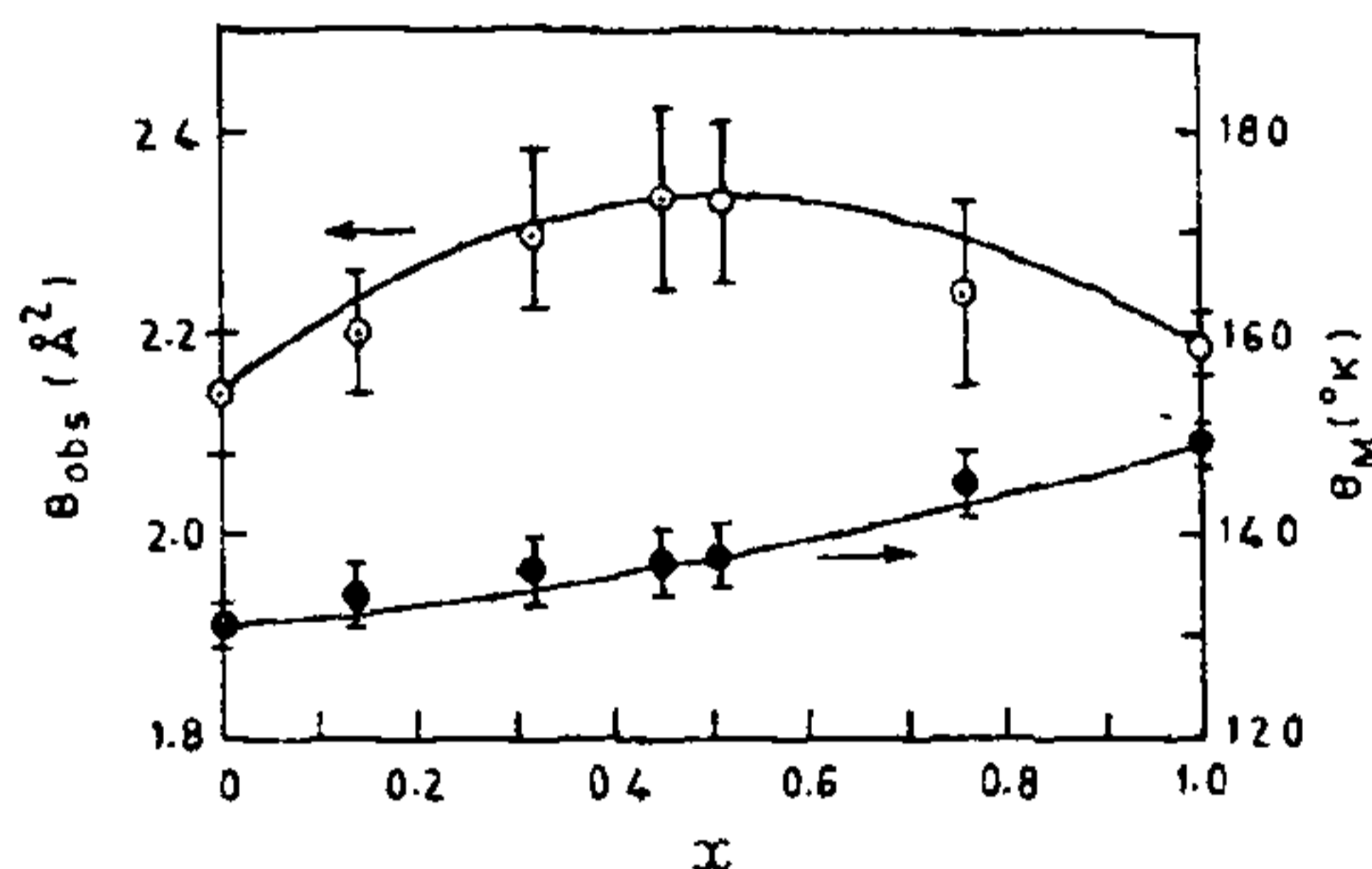


Figure 1. Plot of B_{obs} and θ_M against the molar fraction X of AgCl in AgBr.

specific heats are not available for this system. However, Nagiah and Sirdeshmukh⁴ calculated the Debye temperatures for some compositions from room temperature data on elastic constants. The values of Debye temperatures from elastic constants were plotted against the composition and from a smooth curve connecting the data points, the values were read off corresponding to the composition used in the present x-ray work. These values (θ_E) given in table 1 agree with the x-ray values (θ_M) within limits of experimental error.

25 February 1985

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3. Dernier, P. D., Weber, W. and Longinotti, L. D., *Phys. Rev.*, 1976, **B14**, 3635.
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A NEW METHOD FOR THE STUDY OF DISSOCIATION CONSTANT

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DISSOCIATION of amino acids in general has been studied mainly with electrometric technique using glass electrode which gives reliable results. The ionophoretic technique has been recently introduced to investigate the formation of complexes and determination of stability constants of mononuclear complexes^{1, 2}. The usual procedure is to study the mobility of metal cation spot on a paper strip soaked with background electrolyte buffered at a fixed pH containing progressively increasing concentration of the ligand. This procedure has been drastically modified³⁻⁷. Here the concentration of liganding sample is kept constant but the hydrogen ion concentration of the background electrolyte is progressively decreased by the addition of an alkali solution. Thus the previous technique failed to elucidate the effect of change of relative concentration of the different ionic species of a liganding polybasic acid. Our modified technique has also been used for the study of mixed complexes for the first time⁸⁻¹³.

The electrophoretic technique usually suffers from a number of defects. Temperature during electrophoretic capillary flow on the paper, electroosmosis, adsorption and molecular sieving, affect the mobility of charged moieties. The technique described here is almost free from these vitiating factors. We have extended our modified method to study the nature of dissociation as well as to assess the magnitude of dissociation constants of some amino acids. The technique is very handy and simple. It gives results fairly in agreement with the literature values.

Instrument

Electrophoresis equipment (Systronics model 604 India) has been used. The apparatus consists of a PVC moulded double tank vessel. In order to avoid error due

to heat generated during electrophoresis, two hollow rectangular plates each of one kg weight covered with thin plastic paper have been used through which thermostated water is circulated. The tank is closed with a transparent PVC moulded lid to prevent moisture changes that may upset the equilibrium in paper strip. Each electrolyte tank contains a separate platinum wire electrode. Voltage variation is eliminated with an electrical stabilizer. pH measurements were made with Elico model L₁₋₁₀ pH meter using glass electrode.

Chemicals

A.R. grade perchloric acid, sodium hydroxide and β alanine, 3-amino butanoic acid, 4-amino butanoic acid, 4-amino butanoic acid, 5-amino pentanoic acid and 6-amino hexanoic acid (all BDH) are used. A 0.28% (w/v) solution of ninhydrin in acetone was used for detecting amino acid spots. A saturated solution of silver nitrate (A.R.) in acetone (pure) was sprayed on paper and subsequently fumed with ammonia to detect glucose spot.

Procedure

The level of hollow base plate in the instrument was made horizontal with a spirit level. Perchloric acid (150 ml of 0.1 N) was taken in each tank of the electrophoretic apparatus. The levels of the two tank solutions were equalised. These precautions were taken to check any gravitational and hydrodynamic flow; paper strips (Whatman No. 1) of (30 × 1) cm² size were soaked in the background electrolyte and then excess of electrolyte solution was blotted. The strips in duplicate were then spotted with an aqueous solution (0.01 M) of amino acid and glucose solution (0.01 M) in the centre with a micropipette and were subsequently placed on the base plate and sandwiched under the upper hollow metallic plate and the ends of the strip were allowed 15 min. Then a potential difference of 200V is applied between the tank solutions to initiate electrophoresis. The electrolysis is carried for 60 min. The strips are then taken out and dried horizontally and the spots are detected. This observation was repeated at different pH values of the background electrolyte. The distance recorded in duplicates differed within $\pm 5\%$ and the average distance of the duplicates were noted for calculation. The actual distance of sample spot takes into account the distance travelled by the reference glucose spot. The potential gradient through the strip was found to be 7.57 V/cm.

The plot of overall electrophoretic speed of amino