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Solubilities of Alkali Metal Bromates and Iodates in Methanol at Room Temperature

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Solubilities of alkali metal bromates and iodates in methanol at room temperature have been determined. Lithium bromate is quite soluble but reactive. All the other solubilities are low.

Although solubility data for all of these compounds in water at various temperatures have been reported by Seidell and Linke (1958; 1965), very few values for solubility in methanol have been found in that reference or in a search of subsequent *Chemical Abstracts* indices. Of these compounds, those which have solubilities in other solvents listed in handbooks are usually indicated as insoluble in alcohol, though potassium bromate is shown as slightly soluble (probably in 95% ethanol).

Experimental Section

Chemicals. Anhydrous ACS Reagent Grade chemicals were used when available. Sodium bromate was Fisher Certified. Cesium and rubidium bromates, having fairly low solubilities in water, were prepared from the carbonates and sodium bromate by double decomposition reactions. Lithium bromate was prepared from the carbonate and barium bromate with precipitation of barium carbonate and crystallization of lithium bromate after filtration and evaporation. Iodates of these three elements were prepared from the carbonates and iodic acid, with excess carbonate to avoid the formation of acid biiodates. After filtration, evaporation, filtration, and washing, the products were dried in vacuum, usually at 110 °C but up to 130 °C for lithium bromate. All of the salts were assayed for purity by iodometric titration with sodium thiosulfate (Table 1).

The methanol used was Fisher HPLC grade labeled to contain 0.02% water. Solutes of low solubility were leached with methanol to remove any soluble impurities prior to the solubility determination.

Procedure. The general procedure was similar to that previously described by Stenger (1996). Results were obtained both by direct weighing of the evaporated and vacuum-dried residues and by iodometric titrations with 0.1 M thiosulfate solution. In the case of stable mixtures, they were allowed to stand in a cabinet at room temperature with frequent shaking, until the observed solubilities became constant.

Table 1. Assays of Compounds Studied

	bromate, %	iodate, %
lithium	99.60 ± 0.06	99.95 ± 0.15
sodium	99.95 ± 0.10	100.04 ± 0.07
potassium	99.75 ± 0.15	100.00 ± 0.06
rubidium	99.85 ± 0.06	99.84 ± 0.15
cesium	100.05 ± 0.10	99.88 ± 0.13

Table 2. Solubilities in Methanol (g/100 g of Solvent)

	solvent[a]	
	bromate	iodate
lithium	37.5 ± 2.0 (22.6) 37.0 ± 2.0 (7)	0.170 ± 0.005 (22.5)
sodium	0.200 ± 0.005 (22.8)	0.0130 ± 0.0010 (22.6)
potassium	0.030 ± 0.003 (22.7)	0.0083 ± 0.0006 (22.8)
rubidium	0.012 ± 0.002 (22.7)	0.0022 ± 0.0004 (22.6)
cesium	0.015 ± 0.002 (22.8)	0.0027 ± 0.0004 (22.5)

[a] Temperatures are shown in parentheses (degrees Celsius).

Lithium bromate posed a problem in that at room temperature it reacts with methanol, forming lithium bromide, water, and formaldehyde or its oligomers. The bromide, being very soluble, would lower the observed solubility of the bromate. Water, on the other hand, would raise the solubility. The problem was partially solved by saturating the solution first in a refrigerator at 6−8 °C. Then the mixture was allowed to stand longer at room temperature with frequent shaking. A solution which had stood for 48 h at 23 °C showed 0.55% H_2O. The solubility curve in this region is fairly flat, which is also true of the higher solubility in water. Small samples were diluted with water and titrated to avoid the need for evaporation. Formaldehyde was determined by polarography after derivatization with hydrazine sulfate (Lupton and Lynch, 1944). A sample mixture kept for 24 h at 7 °C showed about 0.01% HCOH. After 24 h longer at 23 °C the content had risen to 0.15%.

No such problem was observed with the other salts, which are much less soluble. Sodium bromate reacts slightly with methanol, but so slowly that the solubility was not affected during 2 days at room temperature though 0.016% formaldehyde had formed. A mixture which had stood for 12 days at 23 °C showed 0.12% H_2O. During this time the apparent solubility by gravimetry went up about 0.02%, whereas that by titrimetry went down an equal amount.

Results and Discussion

The data obtained, together with the precisions found, are reported in Table 2. Usually about three determinations each by gravimetry and titrimetry are represented in the value listed. In the case of lithium bromate only titrimetric data were used. Room temperatures reported, read as each

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sample was withdrawn, and averaged are precise within ±0.2 °C. The refrigerator temperature could vary by ±1 °C.

Kolthoff and Chantooni (1973) have reported the solubility of potassium iodate in methanol as 2.70×10^{-4} M at 25.0 °C. With a density of 0.787, this would correspond to 0.0073 g/(100 g of solvent). Our original values were lower. Correspondence with Dr. Chantooni (1998) did not reveal any reason for the difference unless our solutions were not completely saturated. This was found to be the case. The reagent grade KIO_3 which we had used was a very hard crystalline material. Upon recrystallization of the salt from water, drying, and crushing to a powder, methanol solutions of the product became saturated more rapidly. Our final result was slightly higher than theirs (about 1.0 mg/100 g), probably because of the 0.02% moisture content of our methanol. Their solvent had been distilled over magnesium turnings.

Dr. Chantooni also reported the solubility of sodium iodate in methanol at 25.0 °C as 0.0126 g/(100 g of solvent), in excellent agreement with our value.

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