Solubilities of Alkaline Earth Metal Bromates and Iodates in Methanol at Room Temperature

Vernon A. Stenger, Richard M. Van Effen,* and Nile N. Frawley

Analytical Sciences Laboratory, 1897 Building, The Dow Chemical Company, Midland, Michigan 48667

Solubilities of alkaline earth metal bromates and iodates in methanol at room temperature have been determined. Magnesium bromate reacts significantly with methanol, so its solubility was also determined at lower temperatures.

Aqueous solubilites of the alkaline earth metal bromates and iodates have been reported at various temperatures by Seidell and Linke.[1−2] Linke[3] studied the system magnesium bromate−water. No data on calcium bromate in water was found in a search of Chemical Abstracts indices since 1947. Handbooks usually report this compound as very soluble in cold or hot water. A rough measurement in this laboratory indicated a value of about 118 g/100 g H_2O at 23 °C.

No data on solubilities of any of these compounds in methanol have been found in the literature. In a few cases, usually for iodates, data on mixtures of organic solvents with water have been reported, but in none of these has the organic concentration been high enough to allow extrapolation to the solubility in pure solvent.

Experimental Section

Chemicals. None of these salts is covered by ACS Reagent requirements. Magnesium iodate tetrahydrate was GFS primary standard grade, recrystallized in the presence of a little magnesium oxide to avoid di-iodate formation. Barium bromate 96% and calcium iodate 98% were obtained from Sigma-Aldrich. Magnesium bromate was prepared from the sulfate and barium bromate as described by Linke.[3] Strontium and calcium bromates were prepared from the carbonates and bromic acid (obtained by treating barium bromate solution with sulfuric acid). Barium and strontium iodates were precipitated from the chlorides and potassium iodate. All of the products were recrystallized and dried in a vacuum, usually at 120 °C to 130 °C. Assay data, by iodometric titration, are given in Table 1. The low results for magnesium and calcium iodates are probably due to water of hydration, which is very difficult to remove completely from these compounds. The magnesium iodate tetrahydrate as originally purchased assayed 99.16%. After two weeks in a vacuum at 130 °C to 145 °C the product was still approximately $Mg(IO_3)_2 \cdot 0.5\ H_2O$. This moisture does not interfere seriously with the solubility because it is likely replaced by methanol during preliminary treatment.

The methanol used was Fisher HPLC grade labeled to contain 0.02% H_2O. Solutes of low solubility were leached with the methanol to remove soluble impurities prior to the determination of solubility.

Procedure. The general procedure was similar to those previously described by Stenger[4] and Stenger and Van Effen.[5] Except in the case of magnesium bromate, results were obtained both by direct weighing of the evaporated and vacuum-dried residues and by iodometric titrations with 0.1 M thiosulfate solution. Because of the reactivity of magnesium bromate with methanol, small samples were

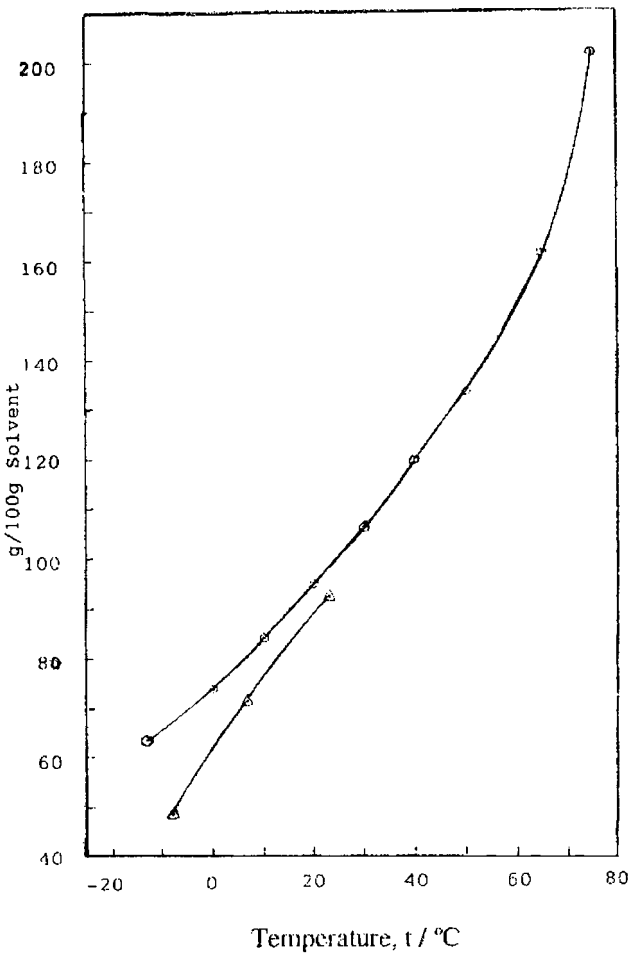

Figure 1. Solubilities of magnesium bromate in water (○) and methanol (△) at various temperatures.

Table 1. Assays of Compounds Studied

	bromate % (w/w)	iodate % (w/w)
magnesium	99.84 ± 0.08	98.1 ± 0.10
calcium	99.48 ± 0.05	99.0 ± 0.30
strontium	99.58 ± 0.21	99.65 ± 0.12
barium	99.62 ± 0.12	99.78 ± 0.30

10.1021/je000152+ CCC: $19.00
Published on Web 10/03/2000

Table 2. Solubilities in Methanol, *s* in g/100 g Solvent[a]

	bromate	iodate
magnesium	92.5 ± 2.0 (23.6 °C)	0.027 ± 0.002 (22.5 °C)
	72.0 ± 2.0 (7.0 °C)	
	49.0 ± 1.5 (−8.0 °C)	
calcium	0.220 ± 0.010 (22.0 °C)	0.0012 ± 0.0006 (22.5 °C)
	0.208 ± 0.010 (6.0 °C)	
strontium	0.0122 ± 0.001 (22.8 °C)	0.0006 ± 0.0002 (22.8 °C)
barium	0.0035 ± 0.001 (22.5 °C)	0.0004 ± 0.0002 (22.8 °C)

[a] Temperatures are shown in parentheses.

weighed and diluted with water; aliquots of the solutions were titrated iodometrically. To minimize the effects of the reaction, the solutions of magnesium bromate were first saturated at −8 °C, then at +7 °C, and finally at room temperature. The reaction of this compound with methanol is similar to that of lithium bromate (Stenger and Van Effen)[5] but somewhat more rapid, probably because of the higher solubility. Accurate results were also more difficult to obtain, since the solutions can easily become supersaturated and because of the effect of moisture. After 24 h at 7 °C, samples showed 0.8% (w/w) water and 0.20% (w/w) formaldehyde. A solution which had stood for two weeks at 7 °C was found to contain 2.6% (w/w) H_2O.

Calcium bromate also reacts with methanol, but much more slowly because of the low solubility. A solution kept at 23 °C for 24 h was found to contain 0.002% (w/w) formaldehyde.

Results and Discussion

The data obtained, together with the precisions found, are reported in Table 2. Usually three or four determinations each by gravimetry and titrimetry are represented. In the case of magnesium bromate, only the titrimetric method was used, but many more analyses were made. Room temperatures (precise within ±0.2 °C) were read as each sample was taken. The refrigerator temperatures could vary by ±1 °C. All the solubilities are of low magnitude except those of magnesium bromate. The latter seemed rather surprising. Figure 1 shows a comparison of our data for methanol with those of Linke[3] for water, the latter recalculated to grams per 100 of solvent. The curves are remarkably close together and could probably serve for extrapolation of our data to higher temperatures, for solutions to be used before much reaction takes place.

Acknowledgment

Thanks are due to Connie March for typing this manuscript.

Literature Cited

(1) Seidell, A.; Linke, W. F. *Solubilities of Inorganic and Metal Organic Compounds*; Van Nostrand Co.: Princeton, NJ, 1958; Vol. I.
(2) Seidell, A.; Linke, W. F. *Solubilities of Inorganic and Metal Organic Compounds*; American Chemical Society: Washington, DC, 1965; Vol. II.
(3) Linke, W. F. The System Magnesium Bromate-Water. *J. Am. Chem. Soc.* **1955**, *77*, 866−867.
(4) Stenger, V. A. Solubilities of Various Alkali Metal and Alkaline Earth Metal Compounds in Methanol. *J. Chem. Eng. Data* **1996**, *41*, 1111−1113.
(5) Stenger, V. A.; Van Effen, R. M. Solubilities of Alkali Metal Bromates and Iodates in Methanol at Room Temperature. *J. Chem. Eng. Data* **1999**, *44*, 173−174.

Received for review May 22, 2000. Accepted August 28, 2000.

JE000152+