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Solubilities of Various Alkali Metal and Alkaline Earth Metal Compounds in Methanol

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Solubilities of the halides, nitrates, carbonates, sulfates, and some perchlorates of all the alkali metals and alkaline earth metals in methanol at room temperature have been determined. Data on some, such as cesium and rubidium fluoride, nitrate, carbonate, and sulfate, appear to be reported for the first time. Comparison with earlier results from the literature reveals a number of discrepancies.

A comprehensive study on this subject was published by Harner et al. in 1963 (*18*). They cited several references but made no comparison of their results with the earlier data, which they said showed discrepancies attributable to impurities in the solutes and moisture in the methanol. For their own study they relied on the purity requirements for ACS Reagent Grade materials. Unfortunately, several of the reagents have requirements only for the hydrates, and others such as the alkaline earth fluorides and some sulfates are not covered. Also, ACS requirements allow up to 0.10% water in methanol. An additional difficulty with some of the Harner data is that the solubilities of barium carbonate and sulfate appear to be higher in methanol than in water, which would seem rather unlikely.

Harner et al. (*18*) did not determine the solubilities of the bromides of strontium and barium nor of the iodides of these and lithium. In the present paper, the solubilities of these compounds have been included and measurements have also been made on ammonium, rubidium, cesium, and magnesium compounds. Because of the excellent work of Willard and Smith (*40*) on perchlorates, their results have been included, with newer confirmatory values in a few instances.

Accurate solubilities are of practical interest in developing separation methods for specific pairs or groups of compounds, or for example in the removal of most of a given compound preparatory to testing for certain impurities, such as by ion chromatography. They can also be useful in connection with theoretical studies relating solubility to ionic radii or other possible solvation parameters.

Experimental Section

Chemicals. As far as possible, anhydrous ACS Reagent Grade chemicals were used. In a number of cases material of the highest available purity was obtained from specialty suppliers such as Aldrich, Alfa, or Johnson-Matthey. For several of the hydrates, dehydration was necessary. One method of doing this was by storage over phosphorus pentoxide in a vacuum desiccator, sometimes at elevated temperatures. Cesium fluoride was ignited in a platinum dish at 650 °C and stored in a tightly capped plastic bottle over P_2O_5.

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. To avoid possible effects from moisture contamination, no water bath was used. In this laboratory the temperature is maintained relatively constant at 22−23 °C. Therefore the mixtures of methanol and excess solid in appropriate tight containers (glass or polyethylene) were kept, with frequent shaking, either in a cabinet protected from sunlight or in a nitrogen-filled drybox containing trays of P_2O_5. Whenever a settled mixture was sampled, the temperature was recorded to within 0.1 deg. Samples were usually taken by pipet, transferred to a tared dish or beaker, weighed quickly, evaporated, and weighed again, the mass of methanol being obtained by difference.

Table 1. Precision of Results

g/100 g of solvent	
reported	reproducibility (±)
<0.001	0.0005
0.001−0.01	0.0005−0.001
0.01−0.10	0.001−0.004
0.10−1.0	0.01
1.0−5.0	0.05
5.0−15.0	0.1−0.2
15−30	0.3−0.5
30−75	0.5−1.0
75−125	1.0−2.5
>125	2.5−5.0

Halides other than fluoride were determined by argentimetric titration. Some of the alkaline earth metal salts were determined by EDTA titration. In a few cases ammonium compounds were determined by hypochlorite titration. Some materials were checked by conversion to a different form, cesium fluoride to sulfate, for example. Soluble carbonates were determined by acidimetric titration.

Results and Discussion

The new results together with many by earlier investigators are given in the tables. Values from prior to about 1960 were usually obtained from Seidell and Linke (*35*), though the references cited there have been consulted wherever possible to correct any errors.

No earlier values were found for the iodides of ammonium, barium, and strontium, the fluorides, nitrates, carbonates, and sulfates of rubidium and cesium, nor the fluoride and carbonate of magnesium.

Pure ammonium carbonate is not available commercially since it readily loses ammonia to form the bicarbonate. The commercial material, ordinarily prepared from NH_3 and CO_2 under pressure, is a mixture of the bicarbonate and ammonium carbamate with a trace of urea. The value in the table was calculated as $HNH_4CO_3{\cdot}NH_4CONH_2$ based on the determination of total ammonia by acidimetric titration to bromocresol green. In separate experiments under similar conditions the solubility of 99% ammonium

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

	fluoride	chloride	bromide	iodide	nitrate	perchlorate	carbonate	sulfate
ammonium	2.61 (23.3)[b] 2.48 (20) (*12*)	3.52 (23.5)[b] 3.54 (25) (*35*) 3.35 (19) (*7*) 3.61 (24.8) (*30*) cf (*19b*)	12.85 (23.5)[b] 12.33 (20) (*6*) 12.9 (25) (*19b*) 12.5 (19) (*7*,*13*)	59.8 (23.4)[b]	18.4 (23.4)[b] 16.3 (18.5) (*33*) 17.1 (20.5) (*7*) 20.05 (30) (*34*) 20.2 (30) (*3*)	6.67 (22.7)[b] 6.85 (25.0) (*40*)	ca11 (23.2)[b] 11.3 (25.0) (*4*) See text	0.027 (23.2)[b] <0.02 (30) (*3*) See text
lithium	0.0024 (23.2)[b] 0.0176 (25.0) (*18*)	41.8 (23.2)[b] 41.04 (25) (*29*) 42.24 (25) (*36*) 20.98 (25) (*18*) cf (*25*, *27*)	120 (22.9)[b] 139.2 (25) (*27*) 139.8 (25) (*29*) 116.9 (18) (*29*) 24.29 (25) (*18*)	298 (23.2)[b] 171 (25) (*29*) 343 (25) (*36*) See text	61.2 (23.2)[b] 42.95 (25) (*18*)	175.6 (23.4)[b] 182.2 (25) (*40*)	0.035 (21.8)[b] 0.055 (25) (*18*) See text	0.115 (23.3)[b] 0.126 (25) (*18*)
sodium	0.020 (22.7)[b] 0.041 (18) (*29*) 0.030 (25) (*29*) 0.0231 (25) (*18*) cf (*4*)	1.38 (25) (*1*) 1.401 (25) (*24*) 1.40 (25) (*29*) 1.31 (25) (*36*) 1.401 (25) (*18*) cf (*2*, *22*, *31*, *32*)	16.8 (23.0)[b] 17.36 (25) (*5*, *24*) 18.2 (25) (*19b*) 17.4 (25) (*29*) 62.51 (25) (*18*) cf (*7*, *26*, *32*, *39*)	79.4 (23.0)[b] 78.0 (25) (*25*) 80.5 (25) (*24*) 83 (25) (*29*) cf (*7*, *19b*, *32*, *39*)	2.84 (23.1)[b] 2.78 (25) (*1*, *30*) 2.93 (25) (*18*) See text	51.4 (23.4)[b] 51.35 (25) (*40*)	0.22 (21.8)[b] 0.27 (15) (*4*) 0.311 (25) (*18*)	0.0015 (23.3)[b] 0.0076 (15) (*4*) 0.003 (25) (*29*) 0.0113 (25) (*18*) cf (*15*)
potassium	10.3 (23.4)[b] 10.2 (25) (*29*) 2.28 (25) (*18*)	0.54 (25) (*1*) 0.539 (25) (*24*) 0.53 (25) (*29*) 0.533 (25) (*18*) cf (*9*, *19a*)	2.15 (25) (*1*, *19*, *22*) 2.11 (25) (*24*) 2.16 (25) (*25*) 2.08 (25) (*18*) cf (*32*, *41*)	16.0 (25) (*1*) 16.8 (25) (*19b*) 17.04 (25) (*24*) 17.0 (25) (*29*) 17.07 (25) (*18*) cf (*8*, *32*, *37*, *38*, *39*)	0.357 (23.4)[b] 0.3−0.4 (25) (*1*) 0.3795 (25) (*18*) See text	0.105 (25) (*40*) 0.097 (25) (*2*, *28*)	6.0 (25) (*14*) 6.165 (25) (*18*)	0.0012 (23.0)[b] 0.0009 (25) (*10*) 0.0005 (25) (*18*) cf (*15*)
rubidium	69.7 (23.0)[b]	1.36 (23.4)[b] 1.41 (25) (*9*) 1.34 (25) (*29*)	2.48 (23.2)[b] 2.48 (25) (*9*) 2.52 (25) (*29*)	10.8 (23.3)[b] 10.1 (25) (*29*)	0.46 (23.4)[b]	0.054 (22.8)[b] 0.060 (25) (*40*)	24.9 (23.3)[b]	0.003 (23.2)[b]
cesium	152 (22.2)[b]	3.26 (23.4)[b] 3.44 (25) (*9*) 3.62 (25) (*20*) 3.01 (25) (*29*)	2.12 (23.3)[b] 2.13 (25) (*9*) 2.25 (25) (*29*)	3.45 (22.0)[b] 3.37 (20) (*23*) 3.79 (25) (*29*)	0.309 (23.5)[b]	0.086 (23.3)[b] 0.093 (25) (*40*)	56.1 (21.1)[b]	0.019 (23.0)[b]
magnesium	0.001 (22.9)[b]	15.6 (23.0)[b] 16.7 (30) (*25*)	26.1 (23.3)[b] 27.9 (20) (*26*)	42.3 (22.1)[b] 45.1 (20) (*26*)	17.2 (22.0)[b] 17.3 (20) (*25*) 20.9 (30) (*25*)	51.84 (25) (*40*)	0.004 (22.8)[b]	0.26 (21.6)[b] 0.224 (25) (*17*) cf (*7*, *21*)
calcium	<0.001 (23.0)[b] 0.0145 (25) (*18*)	28.7 (21.1)[b] 24.35 (20) (*26*) 23.26 (25) (*18*)	72.8[b] (22.0)[b] 56.2 (20) (*25*) 62.9 (30) (*25*) 55.83 (25) (*18*)	73.5 (22.1)[b] 126.1 (20) (*25*) 131.2 (30) (*25*) 67.37 (25) (*18*)	112.5 (22.0)[b] 190 (25) (*11*) 134 (10) (*25*) 144 (40) (*25*) See text	237.4 (25) (*40*)	0.005 (23.0)[b] 0.0012 (25) (*18*)	<0.0005 (22.8)[b] 0.0046 (25) (*18*)
strontium	0.0015 (22.8)[b] 0.0142 (25) (*18*)	28.7 (22.8)[b] 18.05 (25) (*18*) cf (*7*)	132 (22.5)[b] 119.4 (20) (*25*) 123.4 (30) (*25*)	156 (21.7)[b]	1.08 (23.2)[b] 1.061 (25) (*18*)	212.0 (25) (*40*)	0.001 (22.0)[b] 0.0014 (25) (*18*)	<0.001 (22.0)[b] 0.0074 (25) (*18*)
barium	<0.0005 (23.0)[b] 0.0044 (25) (*18*)	1.59 (23.2)[b] 1.379 (25) (*18*) cf (*7*)	62.3 (21.8)[b] 41.9 (20) (*25*) 40.9 (30) (*25*)	137 (23.2)[b]	0.048 (25) (*18*) 0.057 (20) (*25*) 0.052 (30) (*25*)	182.2 (25) (*40*)	<0.0005 (22.3)[b] 0.0064 (25) (*18*)	<0.001 (22.0)[b] 0.0065 (25) (*18*)

[a] Temperatures are shown in parentheses (degrees Celsius). References are shown by italic numbers. [b] Values from current work.

carbamate was about 8.9 g/100 g of methanol. The solubility of ammonium bicarbonate in methanol saturated with CO_2 was about 10 g/100 g of solvent. Results in these systems are not easily reproducible.

In the case of ammonium sulfate, Aravamudan (*3*), did not determine its solubility in pure methanol. He worked with aqueous mixtures and the lower value in the table was obtained by extrapolation of his values to 0% water.

Measurements on extremely soluble compounds such as lithium iodide and calcium nitrate are very sensitive to moisture and difficult to reproduce. However the low value for lithium bromide reported by Harner et al. (*18*) is likely the result of a mistake in aliquot size or calculation. The same, or failure to reach equilibrium, possibly applies to their low values for lithium and strontium chlorides and potassium fluoride.

Lithium carbonate appears to approach equilibrium very slowly in methanol. This is probably due to absorption of moisture and CO_2. When results from solutions with traces of moisture were extrapolated to 0% water, the solubility found was about 0.020 g/100 g of methanol. Our reported value refers to a solution with 0.018% H_2O.

In the data reported by Äkerlöf and Turck (*1*) the solubility given for sodium nitrate was attributed to International Critical Tables, which had reported an apparently erroneous result from de Bruyn (*7*). When the actual data of Äkerlöf and Turck (*1*) for various mixtures of methanol + water were extrapolated to 100% methanol, the result of 2.78 g of $NaNO_3$/100 g of methanol was obtained, compared with their listed value of 4.12 g. Likewise their solubility for KNO_3 as reported in the table was obtained by extrapolation.

Garcia-Ruiz and Caballero (*15*) studied the formation of K_2SO_4 crystals in mixtures of water and methanol, ethanol, or propanol. They also mention having determined the solubilities in such mixtures but show only those for ethanol.

Two papers offer very confusing values. Kirn and Dunlap (*22*) give numbers expressed in moles of solute per mole of methanol. Calculated as grams per 100 grams, their value of 1.42 for NaCl at 20 °C would be quite acceptable, but results for KCl and Na_2SO_4 are unreasonably high. Germuth (*16*) expressed his data in moles also. His result for KBr in grams per 100 grams, 2.61 at 20 °C, would be rather high, that for NaF is too high, and those for NaBr and KF are far too low. Possibly, the authors miscalculated their original analytical figures.

The high results reported by Harner et al. (*18*) for lithium fluoride and the alkaline earth metal fluorides and sulfates were most likely caused by leachable impurities, or possibly in some cases by traces of suspended solute in the saturated solutions.

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