THE SOLUBILITIES OF ALKALI CHLORIDES AND SULFATES IN ANHYDROUS ALCOHOLS

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A search of the literature for information on the solubilities of inorganic salts in various anhydrous alcohols will show that comparatively little work has been recorded. Most of the data have been obtained for salts in aqueous alcohols[1] and practically all these data concern only methyl and ethyl alcohols. The solubilities of salts in these alcohols show a wide variation with different investigators. These discrepancies in results may be attributed to varying amounts of water in the alcohols, or the methods for determination may have permitted moisture to reach the solutions.

Most of the data are for one temperature only. No reference was found on the solubilities of sodium and potassium chlorides and sulfates in the lower alcohols over a wider range of temperature. Thus it was thought that such a study might show some relationship between the solubility of a salt in the various alcohols and their increasing molecular weight.

Preparation and Purification of Materials.—The salts used were Baker's C. P. salts. These salts were further purified by two recrystallizations from distilled water. After the final recrystallization, the salts were washed, pulverized and dried in an electric oven at a temperature of 150° until they gave no further loss in weight. They were then transferred to tightly fitting ground-glass stoppered bottles and kept until needed.

The alcohols were first carefully fractionated[2] using the fraction that boiled within 0.5° of the correct boiling point as accepted in the "International Critical Tables." After this fractionation, the alcohols were placed over freshly calcined lime and allowed to stand with frequent shaking, for several days, depending upon the alcohol. Methyl and ethyl alcohols were allowed to stand for a longer time. Then, after refluxing for twelve hours, the alcohols were decanted from the lime and again fractionated, the fraction boiling nearest the accepted boiling point being

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[1] (a) Landolt-Börnstein, "Physikalish-Chemische Tabellen," pp. 730–737; (b) C. A. Lobry de Bruyn, Z. physik. Chem., 10, 783 (1892).

[2] Brunel, Crenshaw and Tobin, THIS JOURNAL, 43, 561–577 (1921).

collected. This fraction was then further dehydrated by the use of aluminum amalgam.

The aluminum amalgam was prepared by refluxing mercury with sandpapered aluminum chips for twelve hours. About 200 g. of this amalgam was used per liter of alcohol.

After standing over the amalgam for several days, the alcohols were carefully decanted to avoid the possibility of the formation of aluminum alcoholates[3] and again fractionated, retaining that fraction which checked the accepted boiling point within 0.2°, pressure and stem corrections being made. To test this method for dehydrating the alcohols, solubility tests on ethyl alcohol were made using potassium chloride as the solute. After its first dehydration with aluminum amalgam, a solubility determination was made and then the alcohol was again treated with aluminum amalgam and a solubility determination repeated at the same temperature. These two determinations checked very closely. In the final fractionation, the alcohols were distilled into double capped ground-glass stoppered bottles. At all times during distillations they were protected from moist air by means of calcium chloride tubes.

Apparatus.—The thermostat was similar to that developed by Goodhue and Dunlap.[4] The thermostat was electrically heated and the temperature controlled to a tenth of a degree. The method of agitation was the same as that used in the above reference.

The method for obtaining samples was similar to that devised by Weber and Dunlap,[5] but a few modifications were made to adapt it to this work It was found more practical to use a 500-cc. Kjeldahl flask provided with a well-rolled cork stopper which had been extracted previously with alcohol. A strip of thin rubber, provided with two small holes for the condenser and the sampling tube, was fastened over the cork and top of the flask to prevent moisture from coming in contact with the cork. The lower end of the sampling tube was fitted with a shortened Soxhlet thimble for filtering out the suspended salts. By forcing dry air into the flask through the driers at the top of the condenser, a sample of any amount could be taken. To prevent the thimble from removing some of the dissolved salt by adsorption, the solution was first forced back and forth through the thimble while the outlet was protected by a drying tube. The thimble was raised out of the solution during the agitation.

Procedure.—The alcohols were carefully transferred to the flasks and an excess of dry pulverized salt was added. The condenser with the filtering apparatus was attached and placed in the thermostat, with the flask submerged. The time of agitation for saturation was determined by

[3] Berger, *Compt. rend.*, **157**, 717–718 (1906).

[4] Goodhue and Dunlap, THIS JOURNAL, **50**, 1916–1922 (1928).

[5] Weber and Dunlap, *Ind. Eng. Chem.*, **19**, 481 (1927).

experimentation.   It was found that an hour and a half was sufficient in most cases, but more time was always allowed.   After equilibrium had been reached, 25 cc. was removed; after one hour and a half, a check sample was also removed.   These were collected in tightly fitting ground-glass stoppered bottles, cooled to room temperature in a desiccator and weighed.

With the chlorides, the contents of the weighing bottles were transferred to casseroles, diluted with water to about 50 cc. and then titrated with standard silver nitrate solution, using potassium chromate as an indicator. This method was checked by running blank determinations with c. p. sodium chloride having present 25 cc. of the alcohol.   The two butyl alcohols, however, are immiscible with water so they were first evaporated to dryness, taken up in water, and then titrated as above.

The solutions containing the sulfates were transferred to weighed casseroles and carefully evaporated to dryness, and then reweighed.   Checks were made on all determinations and only those which gave reasonably close checks were averaged for the final data.   The average deviation of these check determinations was about 0.5% in the methanol, 2% in the ethanol and propanol, and 4% in the isopropanol, butanol and isobutanol solutions. These data calculated to moles of solute per mole of solvent are recorded in Table I.

TABLE I

MOLES OF SALT PER MOLE OF ALCOHOL

	Methanol				Isopropanol		
Temp., °C.	NaCl	KCl	Na₂SO₄	Temp., °C.	NaCl	KCl	Na₂SO₄
20	0.00778	0.00833	0.00555	20	0.00096	0.001235	0.000886
30	.00758	.00729	.00544	30	.00100	.001300	.000939
35	.00744	.00691	.....	35	.00108	.001340	.....
40	.00734	.00642	.00523	40	.00102	.001390	.000928
45	.00720	.00528	.....	45	.00102	.001295	.....
50	.00711	.00415	.00415	50	.00093	.001060	.000739

	Ethanol				Butanol		
20	0.001147	0.001270	0.00143	20	0.0000695	0.0000822	Insoluble
30	.001197	.001378	.00154	30	.0000710	.0000852	Insoluble
35	.001242	.001443	.....	40	.0000762	.0000904	Insoluble
40	.001258	.001454	.00156	50	.0000774	.0000925	Insoluble
45	.001293	.001277	.....				
50	.001142	.000845	.00114		Isobutanol		

	Propanol			20	0.0000280	0.0000326	Insoluble
				30	.0000292	.0000356	Insoluble
20	0.0000446	0.0000700	Insoluble	40	.0000341	.0000400	Insoluble
30	.0000434	.0000796	Insoluble	50	.0000356	.0000407	Insoluble
35	.0000421	.0000793	Insoluble				
40	.0000417	.0000773	Insoluble				
45	.0000384	.0000683	Insoluble				
50	.0000337	.0000473	Insoluble				

Summary

Anhydrous potassium sulfate was found to be insoluble in all the alcohols used, and sodium sulfate is soluble in only three of the alcohols. The solubility of sodium sulfate in methyl alcohol increases with a rise in temperature. In ethyl and isopropyl alcohols, the solubility of sodium sulfate reaches a maximum and then decreases. The solubilities of the sulfates in alcohols follow the general trend of their solubilities in water, that is, the sodium being more soluble than the potassium sulfate.

The chlorides of both sodium and potassium in methyl alcohol show a slight decrease in solubility with temperature. In ethyl, *n*-propyl and isopropyl alcohols both salts pass through a maximum solubility and then decrease, the potassium decreasing more rapidly than the sodium chloride. In the butyl alcohols there is a slight increase in solubility with rise of temperature for both salts.

The solubility of all the salts decreases as the molecular weight of the alcohol increases.

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THE COMPRESSIBILITY ISOTHERMS OF METHANE AT PRESSURES TO 1000 ATMOSPHERES AND AT TEMPERATURES FROM −70 TO 200°

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The formation of methane as a side reaction in high pressure syntheses involving hydrogen and carbon monoxide and its use as a reactant have emphasized the need of compressibility data for the gas over a wide pressure and temperature range. Previously existing data on the compressibility of methane are for the temperature range 0 to 200° at pressures to 300 atmospheres. Amagat[1] determined the compressibility of methane for temperatures between 14.7 and 100.1° at pressures from 40 to 300 atmospheres. The absolute volumes are not given but only PV relative to the volume of a certain manometric tube. Burrell and Robertson[2] measured an isotherm at 15° to a pressure of forty atmospheres. Keyes, Smith and Joubert[3] determined five isotherms for the temperatures 0, 50, 100, 150 and 200° at pressures to about 300 atmospheres. Later Keyes and Burks[4] improved the apparatus used by Keyes, Smith and Joubert, and redetermined the data for the same temperatures and approxi-

[1] Amagat, *Ann. Chim. Phys.*, **22**, 367 (1881).
[2] Burrell and Robertson, Bureau of Mines Technical Paper No. 158 (1917).
[3] Keyes, Smith and Joubert, *J. Math. Phys. Mass. Inst. Tech.*, **1**, 191 (1922).
[4] Keyes and Burks, THIS JOURNAL, **49**, 1403 (1927).