



Determination of the solubility of inorganic salts by headspace gas chromatography

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Abstract

This work reports a novel method for determination of salt solubility using headspace gas chromatography. A very small amount of volatile compound (such as methanol) is added in the studied solution. Due to the molecular interaction in the solution, the vapor–liquid equilibrium (VLE) partitioning coefficient of the volatile species will change with different salt contents in the solution. Therefore, the concentration of volatile species in the vapor phase is proportional to the salt concentration in the liquid phase, which can be easily determined by headspace gas chromatography. Until the salt concentration in the solution is saturated, the concentration of volatile compound in the vapor phase will continue to increase further and a breakpoint will appear on the VLE curve. The solubility of the salts can be determined by the identification of the breakpoint. It was found that the measured solubility of sodium carbonate and sodium sulfate in aqueous solutions is slightly higher (about 6–7%) than those reported in the literature method. The present method can be easily applied to industrial solution systems.

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1. Introduction

Solubility of salt in aqueous solution is one important parameter in many chemical engineering processes. In the pulp and paper industry, the solubilities of inorganic salts in spent pulping liquor are directly related to the formation of crystals that lead to the scaling of process equipment during liquor concentration. Solubility of a salt is measured by the determination of its concentration in the solution with the application of an oversaturated

amount of salt, i.e. precipitation of salt exists in the solution. Conventionally, the salt concentration in the saturated solution has been directly determined. The measurement of the salt composition in a solution requires the separation of various salts, which is often a difficult task, especially in industrial solution systems. For example, separation of various salts in spent pulping liquor (especially concentrated liquor) is very difficult because of the significant amounts of other suspended solids and dissolved organic materials in the liquor.

It is well known that the vapor–liquid equilibrium (VLE) partitioning behavior of volatile species is affected by the presence of salt in the solution due to molecular interaction, the so-called “salting in” or

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“salting out” effects. We studied the effect of inorganic salt on VLE behavior of methanol aqueous solutions in a previous work [1]. It was found that the presence of inorganic salt reduced the solubility of methanol in water; i.e. the vapor–liquid partitioning coefficient, or dimensionless Henry’s constant, of methanol in water is proportional to the salt concentration of the solution. It is expected that this proportionality characteristic will cease to exist once the salt is saturated in the solution. Therefore, the breakpoint in the relationship between the Henry’s constant of methanol and salt concentration can be used to determine the solubility of salt in the solution. We have developed an indirect headspace gas chromatographic (HSGC) method for the determination of Henry’s constant of a solute without the quantification of the solute concentration [2] in the solution, important to complex matrix solution systems. The objective of the present study is to demonstrate the measurement of salt solubility in complex solutions using the indirect headspace gas chromatographic technique [2], so that salt solubility can be determined without filtration and direct analysis of the salt concentration in the solution. Because filtration and direct solute measurements in solution are not required, the present method for salt solubility determination can be applied to complex industrial systems.

The precipitation of carbonate in spent pulping liquor is a major cause of equipment scaling during liquor concentration in industrial processes. Equipment scaling reduces heat transfer efficiency and therefore increases energy consumption in pulp mills. The determination of carbonate solubility in spent pulping liquors can help to reduce equipment scaling and energy consumption. Carbonate solubility is strongly dependent on the total solids content in the spent pulping liquor, temperature, and other parameters. Limited data are available due to technical difficulties in filtration of carbonate in black liquor using the conventional method for solubility measurements.

2. Experimental

2.1. Chemicals

Methanol of analytical grade (purity >99.4%)

from Fisher was used as solute and deionized water as solvent to prepare methanol–salt–water solutions. Sodium carbonate and sodium sulfate are from a commercial source.

2.2. Apparatus and operation

All measurements were carried out using an HP-7694 automatic headspace sampler and Model HP-6890 capillary gas chromatograph (Agilent Technologies, Palo Alto, CA, USA).

GC conditions: HP-5 capillary column that has a length of 30 m, inner diameter of 0.35 mm. The film thickness of the column is 0.25 μm . The column operating temperature was 30 $^{\circ}\text{C}$; carrier gas helium flow: 3.8 ml/min. A flame ionization detector (FID) was employed with hydrogen and air flows of 35 and 400 ml/min, respectively. Headspace operating conditions: 25 min gentle shaking for equilibration of the sample at the temperature experimented, vial pressurization time: 0.2 min, and sample loop fill time: 1.0 min, loop equilibration time: 0.05 min.

The sample preparation and measurement procedures were as follows: prepare an aqueous methanol–water solution with methanol concentration of 800 mg/l. Weigh the salt to an exact amount and add it into a set of 20-ml vials. Then add 0.5 ml deionized methanol–water solution to each vial. Close the vials and place them in the headspace sampler tray for measurements.

Because the nondimensional Henry’s law constant of methanol in aqueous solutions is very small at the temperature of interest, the effect of the variation of V_g/V_l due to salt addition on methanol determination in this study is insignificant based on material balance.

3. Results and discussions

3.1. Effect of salt on VLE behavior of methanol and solubility determination

Various inorganic salts were used to study the effect of salt on methanol VLE partitioning in water. It was found that the Henry’s law constants of methanol in salt-containing solutions increase with salt molar concentration at a given temperature. Fig. 1 shows that the logarithm of the methanol dimen-

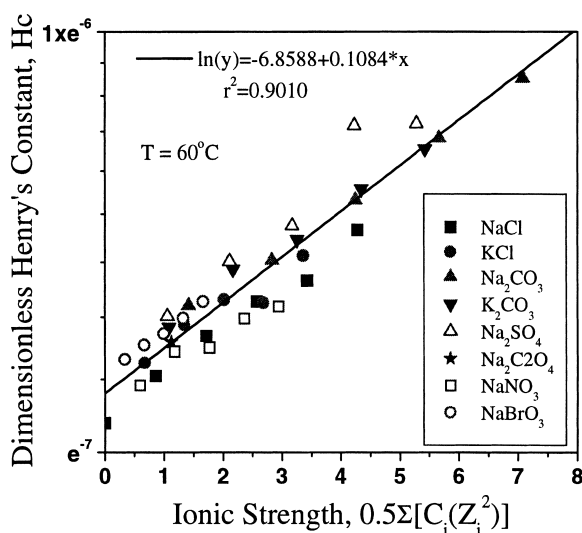


Fig. 1. Effect of ionic strength on the VLE behavior of methanol in salt-containing aqueous solutions at 60 °C.

Dimensionless Henry's constant (the ratio of the solute concentrations in the headspace and in the liquid phase at equilibrium) linearly correlates well with ionic strength as expressed by Eq. (1) for the eight sodium and potassium salts tested. The results shown in Fig. 1 agree with the limited data reported in our previous study [1]. A recent dissertation [3] indicated that this salting effect on methanol VLE behavior holds in a wide temperature range, important to the validity of the present method for salt solubility determination:

$$\ln(H_c) = -6.86 + 0.1084x \quad (1)$$

Because of the solubility limit of the salt in solutions, it is expected that the vapor–liquid partitioning coefficient, or dimensionless Henry's constant, will be a constant once the solubility of the salt is reached. In other words, a breakpoint can be found in the plot of dimensionless Henry's constant and salt concentration. This breakpoint can be used to determine the solubility of the salt. Therefore, the solubility of the salt in a solution can be indirectly determined by measuring the vapor–liquid equilibrium behavior of a volatile species present in the solution. Fig. 2 shows the relationship between GC detector signal from methanol and the weight percentage of sodium carbonate in the sodium carbonate solution that is spiked with methanol at two different

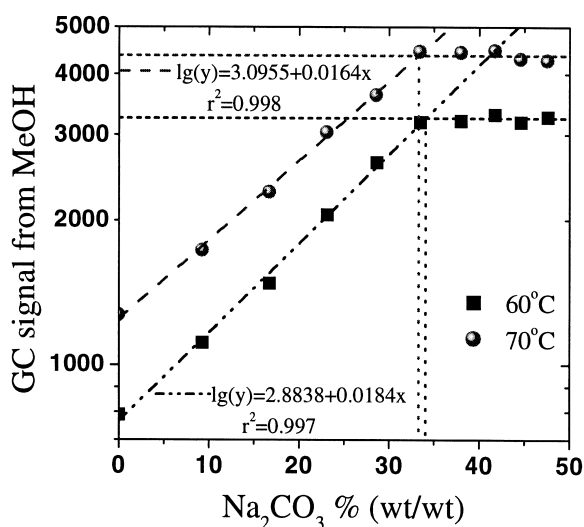


Fig. 2. Effect of sodium carbonate on the VLE behavior of methanol in sodium carbonate aqueous solutions.

temperatures. A logarithmic linear relationship similar to that shown in Fig. 1 can be seen at low salt concentration range; i.e. the relationship follows the form of Eq. (1) when the salt is not saturated in the solution. When sodium carbonate is saturated in the solution, the GC signal from methanol no longer increases with the addition of the salt. Therefore, the solubility of the salt can be easily determined by the breakpoint. For consistency in solubility determination, we conducted semilogarithmic linear regression of the VLE data in the low salt concentration range as shown in Fig. 2. The intercept of the line obtained by regression with a horizontal line with y value equaling the average value of GC signals at high salt concentrations is the breakpoint. The x -coordinate of the breakpoint is the solubility. At a temperature of 70 °C, the slope of the methanol VLE curve at low salt concentration range is about the same as that at a temperature of 60 °C as shown in Fig. 2; however, the breakpoint of the curve is shifted to a slightly lower salt concentration at a temperature of 70 °C. Table 1 shows the comparisons of the solubility of sodium carbonate measured by the present method and those in the literature [4] at two temperatures. The solubility obtained by the present method is consistently higher than that in the literature; however, the relative difference is within 10%. Therefore, the determination of solubility of salt can be realized using an HSGC technique.

Table 1

Comparison of solubility (wt%) of sodium carbonate in aqueous solutions measured by the present method and those from literature [4]

Temperature (°C)	Present method (wt%)	Literature data [4] (wt%)	Relative difference (%)
60	34.0	31.7	7.26
70	33.3	31.3	6.39

We also used this method to determine the solubility of sodium sulfate in an aqueous solution. As shown in Fig. 3, a breakpoint can be clearly seen. The determined solubility of 33.1 is about 7.17% higher than the value of 30.9 reported in the literature [4]. It should be pointed out that the HSGC method gives a relative standard deviation of 2% for water solution and 5% for black liquors, respectively, in the methanol determinations [2,5]. We estimated the maximum possible measurement errors by using the error of the slope obtained from the regression analysis and the measured maximum and minimum terminal values of the GC signal after salt saturation in the solution, i.e. the maximum solubility is calculated using a slope value of slope–slope error and the maximum GC terminal value, while the minimum solubility is calculated using a slope value of slope+ slope error and the minimum GC terminal value. It was found that the solubility of sodium carbonate is in a range of 32.69–35.42, or an error range of about $\pm 4.0\%$. The solubility of sodium

sulfate is in the range of 31.82–34.25, or an error range of about 3.9%.

3.2. Applications

3.2.1. Solubility measurement in a two-salt aqueous solution

The present method can be easily applied to multisalt solution systems without quantitative analysis of the solution composition. For example, to study the solubility of sodium carbonate in a solution containing sodium sulfate, methanol is first spiked in a sodium carbonate aqueous solution with a fixed sulfate concentration. The VLE of methanol in the solution is measured by HSGC with a graduated increase of sodium carbonate concentration. As shown in Fig. 4, a breakpoint in the VLE curve can be clearly identified. The semilogarithmic linear regression technique was again used to identify the breakpoint for solubility determination. It can be seen that the dissolved sodium sulfate has an inverse

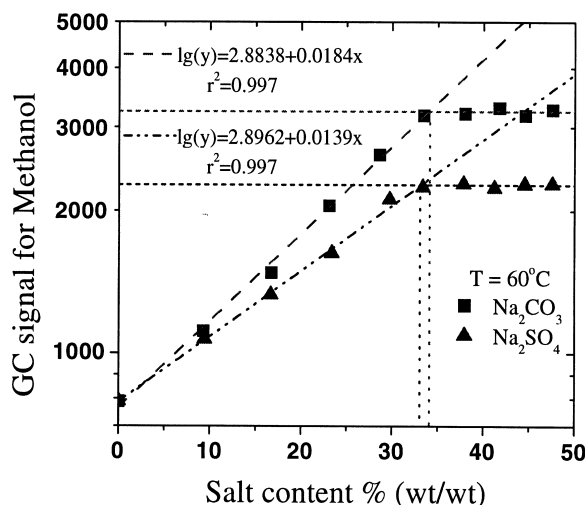


Fig. 3. Effect of sodium sulfate on the VLE behavior of methanol in sodium sulfate aqueous solutions.

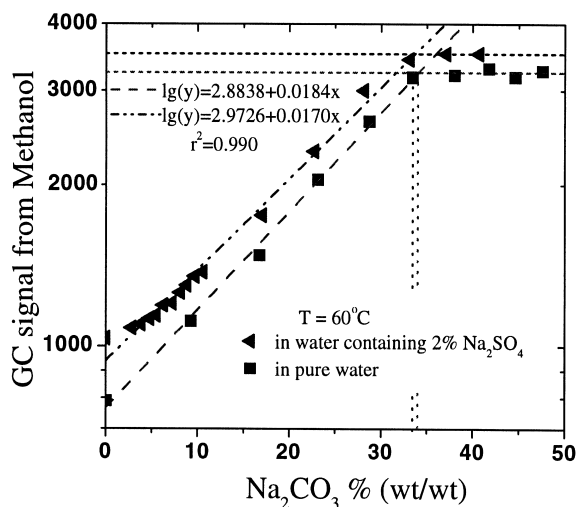


Fig. 4. Effect of sodium sulfate on the solubility of sodium carbonate in salt-containing aqueous solution.

effect on the solubility of sodium carbonate in aqueous solutions. For a solution containing 2% of sodium sulfate, the solubility of sodium carbonate is reduced to 33.7 from 34.0.

3.2.2. Solubility of sodium carbonate in an industrial solution (black liquor)

Black liquor is the spent liquor from wood pulping. Black liquor contains not only inorganic salts such as sodium carbonate and sulfate but also organic compounds such as dissolved lignin. The total dissolved solids content in weak black liquor from pulping (before concentration) is about 15%. Black liquor is concentrated to about 70% of solids through evaporation of water to recover most pulping chemicals by burning the concentrated liquor in a recovery boiler. The inorganic salts in black liquor can significantly affect the efficiency of black liquor concentration in evaporators. This is because the inorganic salts contained in the liquor can be precipitated and form crystals on the heat transfer surface of the evaporator, which reduces the heat transfer coefficient. Therefore determination of the solubility of salt, especially sodium carbonate (the major salt component), in black liquor is important.

It has been found that the solubility of carbonate is much smaller if it contains a large amount of dissolved solids. Since the difficulty in the sample filtration when the content of the dissolved solids is higher, the conventional method failed to determine the carbonate solubility in black liquor. Because the methanol is naturally present in black liquor, we can simply measure the methanol content in the black liquor to determine carbonate solubility in the sample using the present HSGC method. The concentration of sodium carbonate in the original black liquor was first determined to be 2.1% (w/w) by the HSGC method that we developed [6]. Fig. 5 shows the VLE behavior of methanol in black liquor as a function of the total amount of sodium carbonate in black liquor after adding sodium carbonate solid. The solubility of sodium carbonate was determined to be 24.4%, much lower than the solubility of carbonate in an aqueous solution.

3.3. Conclusion

We have demonstrated an HSGC technique for the

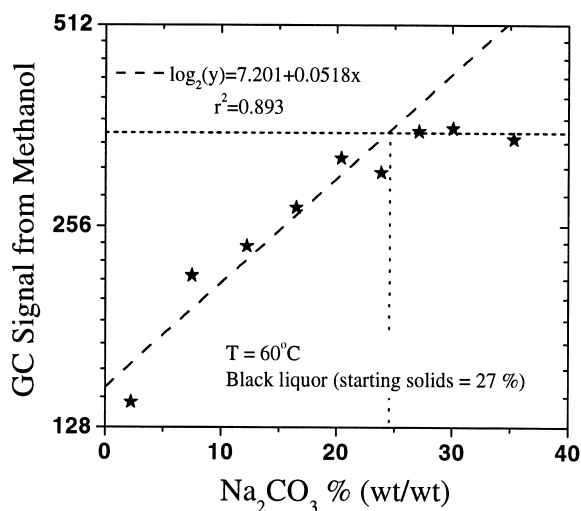


Fig. 5. Measurement of the solubility of sodium carbonate in a slightly concentrated spent pulping liquor at 60 °C.

determination of salt solubility. The measured solubilities of sodium carbonate and sodium sulfate in aqueous solutions agree with the data reported in literature [4], but are consistently higher than those literature values of about 6–7%. The present method was successfully applied to measure solubility in an industrial solution.

Acknowledgements

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