

Solubility of Ba-Acetate in Mixed Alcoholic Solutions and its Bearing on the Synthesis of Multi-Component Gels

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Abstract. The solubility of Ba-acetate in mixtures of alcohol (ethanol, *n*-propanol and iso-propanol) and H₂O or acetic acid (CH₃COOH) have been determined. In the ROH-H₂O-Ba(OOCCH₃)₂ system a small region of miscibility was found. To a saturated solution of 4.8 mol% Ba(OOCCH₃)₂ in H₂O for each additional mol H₂O, 0.9 mol iso-propanol or 1.1 mol ethanol can be added without precipitation of Ba(OOCCH₃)₂. The solubility in alcohol/acetic acid mixtures is higher. For each mol CH₃COOH, 2.2 mol iso-propanol, 3.2 mol *n*-propanol or 4.1 mol ethanol can be added without precipitation of Ba(OOCCH₃)₂. The results were applied to develop a procedure for the synthesis of gels in the system BaO-Al₂O₃-SiO₂ from metal alkoxides and Ba-acetate. Acetic acid reacts with Al-sec-butoxide to give Al(O-sec-C₄H₉)_{3-x}(CH₃COO)_x. Therefore, the solution of Ba-acetate was controlled only over the H₂O/alcohol ratio.

Keywords: Ba-acetate, solubility, acetic acid, system BaO-Al₂O₃-SiO₂

1. Introduction

The synthesis of Ba containing sols and gels has its major difficulty in finding a suitable Ba-precursor. Ba-alkoxides are hardly commercially available and have the disadvantage of a poor solubility in alcohols and other organic solvents. Nevertheless, Ba-alkoxides are relatively easily synthesized through the reaction of Ba metal with alcohol [1, 2]. For the synthesis of celsian (BaAl₂Si₂O₈) ceramics Chen et al. [3] utilized a Ba-Al double alkoxide which was prepared through reaction of Ba metal with iso-propanol and Al-sec-butoxide. Ba-alkoxides are applied for the preparation of superconducting ceramic materials (YBa₂Cu₃O_{7-x}), BaO containing electroceramics and BaAl₂Si₂O₈-ceramics from gels [3–6].

On the other hand, the utilization of Ba-salts in the sol-gel process is limited through the low water solubility of most Ba compounds and the insolubility of all Ba-salts in alcohols and other organic solvents what may cause difficulties when alcohols are used as a mutual

solvent for water and alkoxides in multi component compositions. Nevertheless, Ba-acetate which has a high water solubility of 720 g/l = 4.8 mol% at 20°C [7] has been employed successfully in sol-gel processing of BaTiO₃-ceramics and glasses and glass-ceramics in the systems BaO-Al₂O₃-SiO₂ and BaO-TiO₂-SiO₂ [8–17].

Since Tredway and Risbud [8] observed during the synthesis of glasses in the system BaO-Al₂O₃-SiO₂ an increased solubility of Ba-acetate in mixtures of H₂O and alcohol at low pH especially acetic acid was used to decrease the pH of the Ba-acetate/water-solution which thus could be added to the alkoxide/alcohol mixture without precipitation. However, quantitative data for the acetic acid and H₂O additions have not been reported, nor any explanation for the observed increase in solubility.

In order to make the sol-gel processing of Ba-containing materials reproducible it would be beneficial to identify the processes and reactions and to determine quantitatively the necessary amounts of the

reagents. For this purpose the solubility of Ba-acetate in mixed alcohol/water/acid solutions has been determined. The results have been applied to establish a procedure for the synthesis of gels in the system BaO-Al₂O₃-SiO₂.

2. Experimental Procedure

As reagents for the solution experiments Ba-acetate¹, ethanol², iso-propanol², *n*-propanol², acetic acid² and distilled water were used. The alcohols were added to the solutions of Ba-acetate in water or 1N HCl until Ba-acetate precipitation was observed. The effect of acetic acid was evaluated by addition of acetic acid and alcohol to a saturated aqueous solution of Ba-acetate. Thus, the solubility of Ba-acetate was in the first case examined in the three-component system H₂O-ROH-Ba(OAc)₂ and in the later cases in the four-component systems H₂O-HCl-ROH-Ba(OAc)₂ and H₂O-CH₃COOH-ROH-Ba(OAc)₂. The solubility limits represent the mean value between the last alcohol addition where the solution remains clear and the following addition resulting in precipitation. The dissolution kinetics of Ba-acetate in pure acetic acid are much slower than in water. The solubility of Ba-acetate in acetic acid has been determined from a saturated solution prepared by dissolving Ba-acetate in acetic acid for one day. From this solution, an aliquot part was drawn off, dried at 80°C and the resulting precipitation was weighed.

For the gel preparations tetraethylorthosilicate (TEOS) and Al-sec-butoxide³ were used. All syntheses

were carried out in borosilicate glass containers under laboratory atmosphere. Infrared spectroscopy of the CH₃COOH-alcohol solutions has been done in transmission between TlBr/TlI windows (KRS-5) on a Nicolet 510P FTIR spectrometer.

3. Results

The quantitative solubility experiments showed that at room temperature Ba-acetate is soluble to a certain extent in mixtures of H₂O and ethanol or iso-propanol (Fig. 1). The maximum Ba(OOCCH₃)₂ content in pure H₂O is 4.8 mol%. With increasing alcohol content of the solution the solubility decreases and becomes zero at about 50 mol% alcohol. Only minor differences in the solution boundaries are observed when changing ethanol by iso-propanol. When the alcohol and H₂O contents of the solubility limits are normalized to 1 mole Ba(OOCCH₃)₂ the points lie on straight lines which cross the H₂O axis at 19–20 mole H₂O (Fig. 2). This value expresses the minimum molar quantity of H₂O which is necessary to dissolve 1 mole Ba(OOCCH₃)₂ and corresponds obviously to the solubility limit of 4.8 mol% in pure H₂O. The slopes of the straight lines are 1.1 ± 0.1 and 0.9 ± 0.1 for ethanol and iso-propanol, respectively. This means that during alcohol addition to a saturated solution of Ba(OOCCH₃)₂ in H₂O precipitation may be avoided if additional moles of H₂O are added with each 1.1 mole ethanol or 0.9 mole iso-propanol, respectively.

Figure 3 shows the solubility limit of Ba-acetate in mixtures of 1N HCl and ethanol. The data fall again on

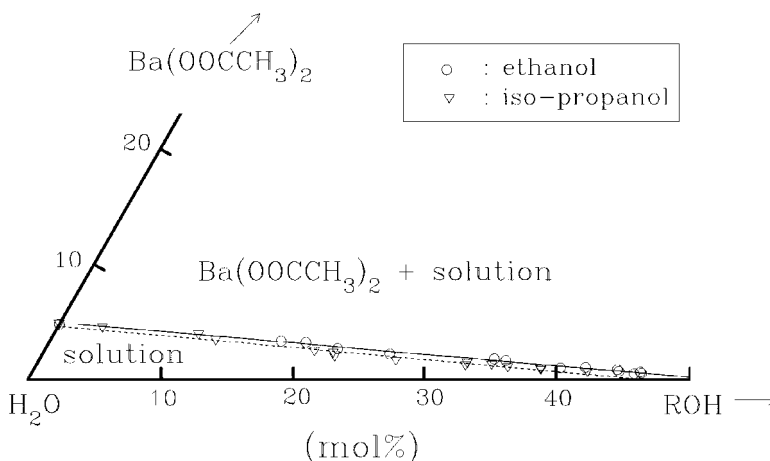


Figure 1. Solubility of Ba-acetate in the system ROH-H₂O-Ba(OOCCH₃)₂.

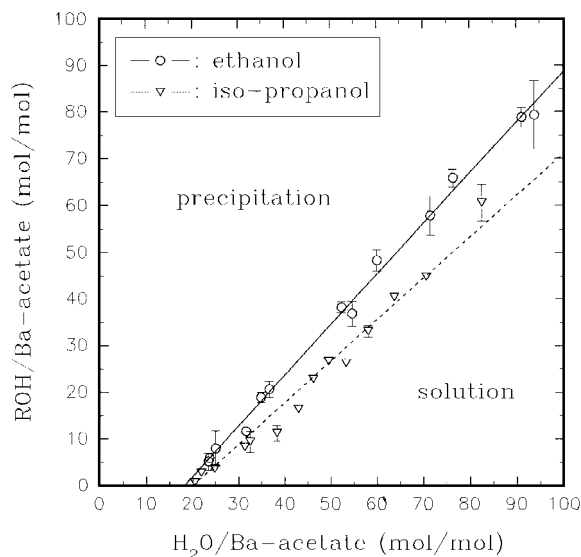


Figure 2. Normalized solubility limits of Ba-acetate in ROH/H₂O mixtures.

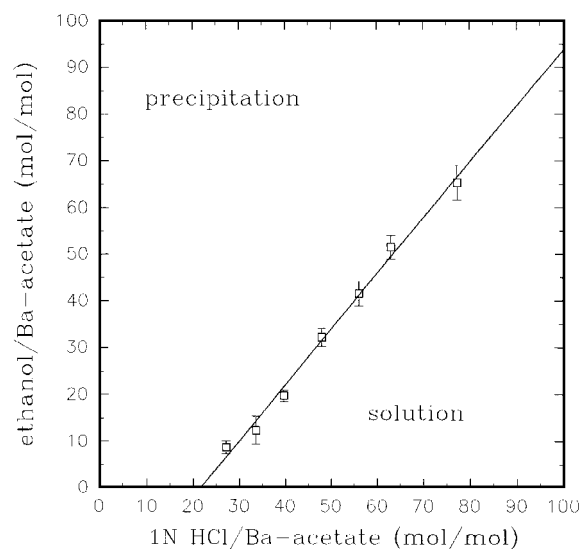


Figure 3. Normalized solubility limits of Ba-acetate in ethanol/1N HCl mixtures.

a straight line with the slope 1.2 ± 0.1 . Obviously, the decrease of the pH through addition of HCl does not increase the solubility of Ba-acetate in H₂O/ethanol solutions since the slope of the solubility limit is unchanged. The precipitation at higher ethanol concentrations may contain also some BaCl₂ beside Ba-acetate as the solubility of the former is lower (3.0 mol% at 20°C).

When other inorganic acids like HNO₃ and H₂SO₄ are added to the Ba-acetate solution other much less or insoluble Ba-salts like Ba(NO₃)₂ or BaSO₄ precipitate.

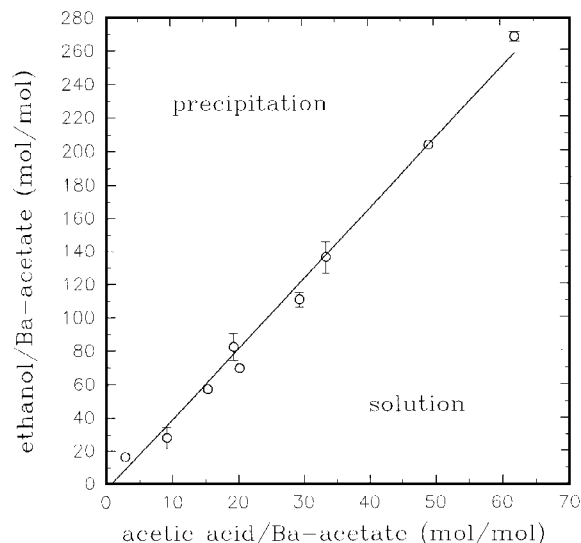


Figure 4. Normalized solubility limits of Ba-acetate in ethanol/acetic acid mixtures.

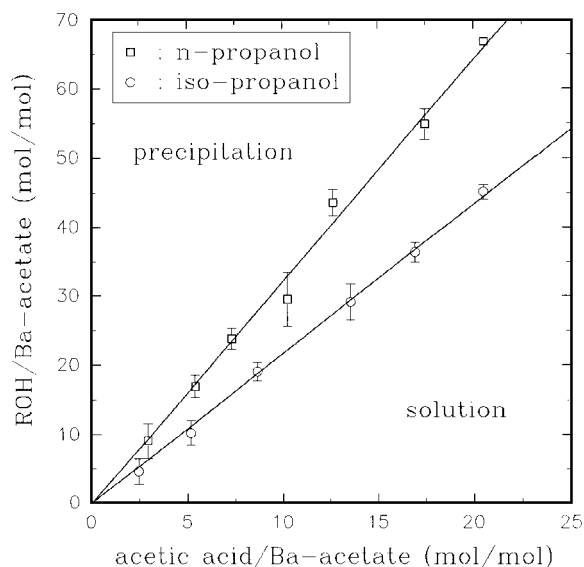


Figure 5. Normalized solubility limits of Ba-acetate in propanol/acetic acid mixtures.

The determination of the solubility of Ba-acetate in pure acetic acid (CH₃COOH) yielded 346 g/l at 23°C. Thus, the molar solubility of Ba-acetate in acetic acid of 7.2% is 1.5 times higher than in water. The stabilizing effect of acetic acid on solutions of Ba-acetate in water and alcohol are depicted in Figs. 4 and 5. The molar acetate and alcohol concentrations are normalized to Ba-acetate. Since acetic acid and alcohol were added to a saturated solution of Ba-acetate in water the

straight lines which confine the solubility limits cross the origin. The slopes are 4.1 ± 0.1 , 3.2 ± 0.1 and 2.2 ± 0.1 for ethanol, *n*-propanol and iso-propanol, respectively. The steeper slopes of the solubility limits compared to those in the Ba-acetate/water/alcohol systems indicate that acetic acid additions are more efficient in keeping Ba-acetate in alcohol containing aqueous solutions than excess water additions: For each mol CH_3COOH 4.1 mol ethanol, 3.2 mol *n*-propanol or 2.2 mol iso-propanol can be added to the solution without precipitation of Ba-acetate.

4. Discussion

Ba-acetate does not dissolve in pure alcohols due to the lower solvent polarity ($\epsilon_{\text{ethanol}} = 24.3$) compared to water ($\epsilon_{\text{H}_2\text{O}} = 78.5$) and the large radius of the Ba^{2+} ion resulting in a relatively high free solution energy in alcohols. The solubility of the alkaline earth acetates in alcohols depends on the radius and electronegativity of the cation, the M-O binding type and the structure. The high difference in electronegativity between oxygen and barium results in a high degree of ionic character of the Ba-O bond. Sr- and Ca-acetate are slightly soluble in methanol while the solubility of Mg-acetate is higher with 52.5 g/l (1.3 mol%). Be-acetate is insoluble in alcohols [18, 19].

The linearity of the solubility data in the alcohol/water systems with a slope of about one in the normalized representation let expect a nearly stoichiometric relationship between H_2O and alcohol. The following hypothesis is proposed to explain the dissolution behavior of Ba-acetate in $\text{H}_2\text{O}/\text{ROH}$ mixtures:

When alcohol and water are mixed, new hydrogen bonds form between H_2O and ROH. It is supposed that this happens also in the aqueous solution of Ba-acetate during addition of alcohol.

The empirical Kohlrausch equation for the molar conductivity Λ of an aqueous solution is

$$\Lambda = \Lambda_{\infty} - k\sqrt{c}$$

where Λ_{∞} is the conductivity at infinite dilution, c is the concentration and k a constant. The degree of dissociation α of the electrolyte is given by $\alpha = \Lambda/\Lambda_{\infty}$. The conductivity Λ_{∞} for a Ba-acetate solution as can be calculated from $\Lambda_{\infty}(\text{Ba}(\text{OAc})_2) = \Lambda_{\infty}(\text{Ba}^{2+}) + 2\Lambda_{\infty}(\text{OAc}^-)$ is $20.9 \text{ mSm}^{-2}\text{mol}^{-1}$. Figure 6 shows the molar conductivity as a function of the square root of the concentration showing that $\text{Ba}(\text{OOCCH}_3)_2$ is at least partly dissociated in an aqueous solution.

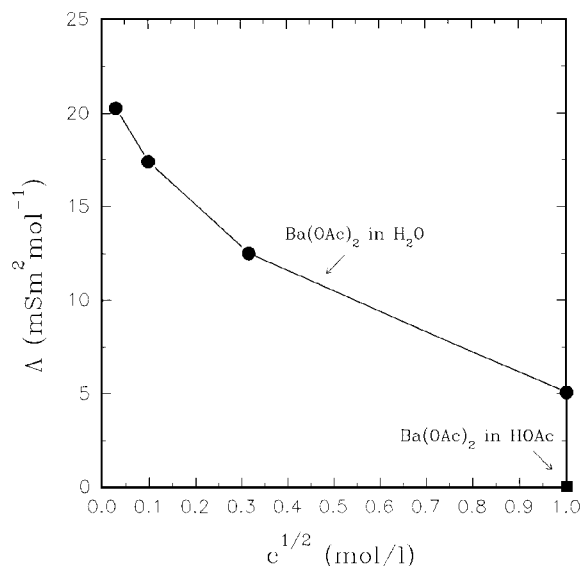
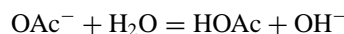


Figure 6. Conductivity of Ba-acetate solutions as a function of the square root of concentration.

As HOAc is a weak acid dissociated acetate anions react with water to give acetic acid and OH^- :



Thus dissociation is also indicated by the basicity of Ba-acetate solutions. The measured pH of a 1M solution is 8.3 while the theoretical pH assuming complete dissociation is 9.5 according to

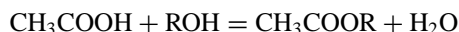
$$\text{pH} \approx -\log \left(\sqrt{\frac{K_{\text{HOAc}} K_{\text{H}_2\text{O}}}{2a_{\text{BaOAc}}}} \right)$$

where K_{HOAc} and $K_{\text{H}_2\text{O}}$ are the dissociation constants of acetic acid and water and a_{BaOAc} is the activity of Ba-acetate).

A minimum of about 20 molecules H_2O are necessary in a saturated solution of Ba-acetate in water to shield the positive charge of a Ba^{2+} cation from the anions and to prevent crystallization of Ba-acetate. The addition of alcohol to a saturated solution may result in the formation of hydrogen bonds between H_2O and ROH which reduces the coordination number of Ba^{2+} and causes crystallization of Ba-acetate. The free enthalpy of a system with solvated Ba-acetate and hydrogen bonded ROH-ROH seems to be higher than that of an assemblage of crystalline Ba-acetate and hydrogen bonded H_2O -ROH. Excess H_2O in the Ba-acetate solution hydrogen binds a nearly equal molar quantity of alcohol.

The reasons for the increased solubility of Ba-acetate in alcohol/acetic acid solutions are not quite clear. To some extent, the higher molar solubility of Ba-acetate in acetic acid compared to water is responsible for this fact. $\text{Ba}(\text{OOCCH}_3)_2$ seems not to be dissociated in acetic acid solutions, in contrast to aqueous solutions [20]. This view is supported by the conductivity measurement of a 1 M Ba-acetate solution in acetic acid giving $0.06 \text{ mSm}^2\text{mol}^{-1}$ which is about 100 times lower than the conductivity of an aqueous solution (Fig. 6). According to Mosset et al. [20] solid Ba-acetate is composed of typical $\text{Ba}_4(\text{OOCCH}_3)_8$ units which are present also in acetic acid solutions. Thus the character of Ba-acetate solutions depends strongly on the solvent and the chemical species present in an aqueous solution may change when acetic acid is added. Beyond that, acetic acid is able to bind more alcohol molecules. Obviously, this is a function of the polarity and the topology of the alcohol molecules: The higher the polarity and the lower the steric hindrance the more alcohol molecules are bound by acetic acid.

One theoretical reaction in solutions of acetic acid and alcohols is the formation of esters according to



This reaction would use one molecule alcohol per molecule CH_3COOH and the by-produced ethylacetate and H_2O could form hydrogen bonds to other alcohol molecules. However, the equilibrium constant is rather low ($K = 3.38$ for ethanol) and the reaction requires a mineral acid as catalyst. The equilibrium constant of secondary alcohols is even lower than that of primary alcohols. The C-O stretching vibrations are different in acetic acid and ethyl acetate, as observed by infrared spectroscopy (Fig. 7). The vibration in the monomer shifts from 1757 to 1744 cm^{-1} , and in the dimer from 1717 to 1727 cm^{-1} . No such shifts were detected in the Ba-acetate solutions (Fig. 7b) indicating that the formation of esters is only of minor importance for the increased solubility of Ba-acetate in alcohol-acetic acid solutions compared to alcohol-water solutions.

5. Gel Preparation in the System BaO-Al₂O₃-SiO₂ (BAS)

The solubility of Ba-acetate during sol-gel processing is in a first approach a function of the ratio (alcohol + Ba-acetate)/($\text{H}_2\text{O} + \text{CH}_3\text{COOH}$) and the minimum amounts of the later two can be calculated from the

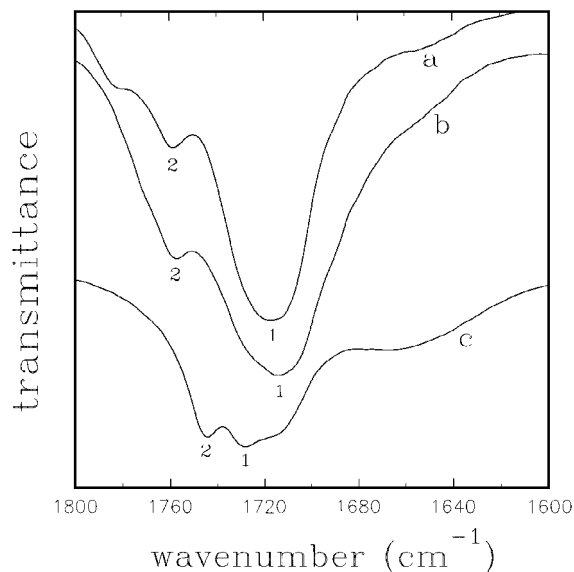
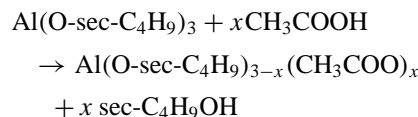


Figure 7. IR spectra of a) CH_3COOH in CCl_4 , b) CH_3COOH + ethanol after 15 h, c) CH_3COOH + ethanol + 1N HCl \rightarrow ethylacetate. 1: $\nu_{\text{C-O}}$ of dimer, 2: $\nu_{\text{C-O}}$ of monomer.

above results concerning the solubilities. However, apart from increasing the solubility of Ba-acetate, acetic acid induces other effects during sol-gel processing:

- Acetic acid acts as a catalyst for the hydrolysis of TEOS, in fact, it is one of the strongest catalysts known. This effect is attributed not only to the decrease of the pH of the sol, but also to a reaction of CH_3COOH with TEOS producing triethoxyacetosilane. This compound reacts with alcohol yielding a silanol group and ethylacetate [21, 22].
- Acetic acid reacts with Al-sec-butoxide according to the reaction:



For $x \leq 2$ this reaction is spontaneous and exothermic [23]. During hydrolysis, the acetic groups react much slower with H_2O than the butoxide groups. In fact, Al-sec-butoxide and other alkoxides sensible to hydrolysis are often modified with acetic acid in order to slow down their hydrolysis and condensation rates and to prevent the precipitation of metal hydroxides [24, 25].

For $x > 1$ Al-diacetate-monohydroxide (Al(OH)(CH₃COO)₂) forms during the hydrolysis whose solubility in alcohols is low. Thus, when a CH₃COOH/Al-sec-butoxide ratio greater than one was applied for the synthesis of BAS gels, Al(OH)(CH₃COO)₂, which was identified by means of x-ray diffractometry, precipitates after a few days when the alcohol evaporates during the drying process. This crystallization creates heterogeneities in the gel and changes the appearance which was formerly transparent to white opaque.

Because CH₃COOH may react with TEOS and Al-sec-butoxide, its amount decreases with time. Thus it is no more available to keep Ba-acetate from precipitation. On the other hand, it is necessary to maintain the acetic acid/Al-s-butoxide ratio lower or equal to 1 in order to obtain a homogeneous gel. A higher ratio induces crystallization of the diacetate-monohydroxide. It seems therefore advantageous to insure the dissolution of Ba-acetate by controlling the (alcohol + Ba-acetate)/H₂O ratio only. Nevertheless, it is necessary to solve the problem of the extremely different reactivity of Al-sec-butoxide and TEOS concerning hydrolysis and condensation. The spontaneous hydrolysis of Al-sec-butoxide and the precipitation of Al-hydroxides during addition of the Ba-acetate/H₂O solution must be avoided. These requirements were satisfied through a pre-hydrolysis of TEOS with 1 mol H₂O/mol TEOS and the modification of Al-sec-butoxide with acetic acid in a molar ratio of 1 : 1 according to the above described reaction. As ethanol and iso-propanol were used as solvents an alcohol exchange on Al-sec-butoxide is likely to take place but is not supposed to change the reaction significantly. During hydrolysis Al-acetate-dihydroxide is formed which is soluble in alcohols.

Homogeneous gels were also obtained when the hydrolysis rate of Al-sec-butoxide was controlled by modification with acetylacetone (molar ratio 1 : 0.5) or triethanolamine (molar ratio 1 : 1) [26, 27].

The procedure used to synthesize BaO-Al₂O₃-SiO₂ gels is outlined in Fig. 8. In order to calculate the minimum quantity of water, R_{H₂O}, necessary for the Ba-acetate solution, the above determined Ba-acetate solubility values are rounded and the small differences of solutions of H₂O with ethanol, propanol or butanol neglected. Thus, 1 mol H₂O/mol alcohol and 20 mol H₂O/mol Ba-acetate have to be added, plus the amount of H₂O which is consumed during hydrolysis. The calculation of R_{H₂O} is as follows:

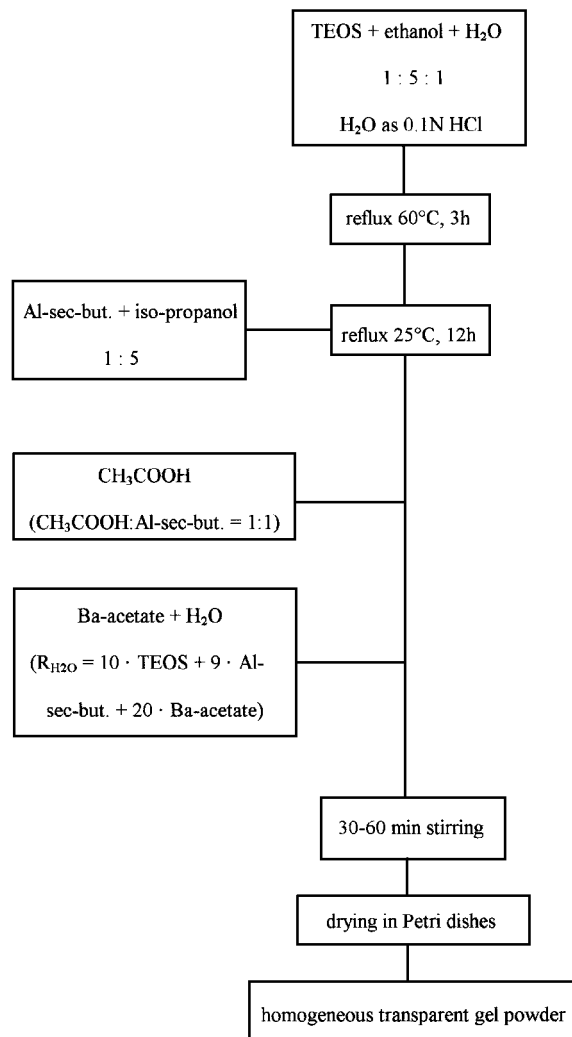


Figure 8. Procedure of gel preparation in the system BaO-Al₂O₃-SiO₂.

The molar quantity of alcohols per mol TEOS is 5 ethanol(solvent) + 4 ethanol(TEOS) = 9. During hydrolysis 4 mol H₂O are consumed yielding a total R_{H₂O}(TEOS) = 13. One mol H₂O has already been added for the pre-hydrolysis (R_{H₂O}(TEOS) - 1 = 12). During the condensation, half of the consumed H₂O is released. Assuming that the condensation rate is high compared to the hydrolysis rate two mol H₂O can be subtracted giving a final R_{H₂O}(TEOS) = 10.

Correspondingly, the molar quantity of alcohols per mol Al-sec-butoxide is 5 iso-propanol(solvent) + 3 butanol(Al-sec-butoxide) = 8. The hydrolysis consumes 2 mol H₂O only since the modification with

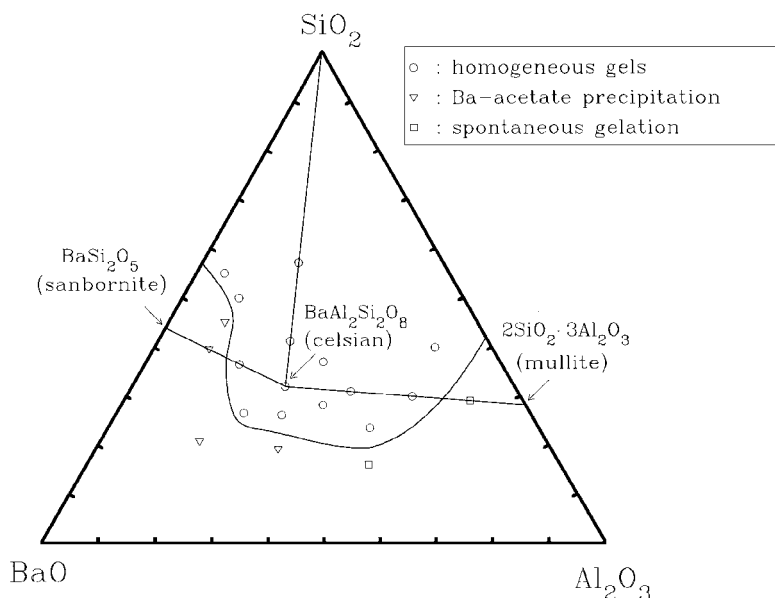


Figure 9. Region of gel formation in the system BaO-Al₂O₃-SiO₂.

acetic acid exchanges one alcohol by an acetate group giving $R_{H_2O}(\text{Al-sec-butoxide}) = 10$. Assuming again a high condensation rate one mol H₂O is released yielding the final $R_{H_2O}(\text{Al-sec-butoxide}) = 9$. This calculation implies that the acetate group is not hydrolyzed. TGA and DTA investigations agree well with the assumption that most of the acetate groups remain in the gel texture as long as the temperature does not exceed 300–400°C [28]. In case of a partly hydrolysis and release of acetate, R_{H_2O} can be further reduced due to the higher effect of CH₃COOH on the Ba-acetate solubility.

The procedure described in Fig. 8 yields homogeneous and transparent gels without precipitations. The calculated R_{H_2O} proved to be sufficient to prevent the precipitation of Ba-acetate for all synthesized gels, indicating that hydrolysis and condensation are nearly simultaneous processes in these compositions and half of the consumed water is released quickly.

Using a smaller R_{H_2O} results in the precipitation of Ba-acetate. This was verified by the synthesis of a BaAl₂Si₂O₈ gel under equal conditions except with $R_{H_2O} = 7$ TEOS + 7Al-sec-butoxide + 20Ba-acetate: During addition of the first drops of the Ba-acetate/water solution to the sol a small amount of Ba-acetate precipitates. This was always observed, even with a higher R_{H_2O} , and is due to the high alcohol/H₂O ratio at the beginning of the Ba-acetate/water solution addition.

When the addition of the solution is completed the precipitates are redissolved immediately. With proceeding hydrolysis the consumption of H₂O and the release of alcohol results in a renewed permanent precipitation of Ba-acetate after about 3 min.

Figure 9 outlines the composition region in which homogeneous and transparent gels could be prepared according to the scheme described in Fig. 8. In BaO-rich compositions Ba-acetate precipitates during condensation after 1–2 days. Obviously, the ability of the (Si, Al)₄O network to incorporate Ba has reached its limit. At higher Al₂O₃ concentrations the sol gelled immediately when the Ba-acetate solution was added, thus preventing a reasonable homogenization.

6. Conclusion

The systems ROH-H₂O-Ba(CH₃COO)₂ with ROH being ethanol or iso-propanol show a limited region of ternary miscibility. Acetic acid tends to increase the solubility of Ba-acetate in mixed H₂O/alcohol solutions. The knowledge of the solubility limits allows to calculate the necessary amount of H₂O and acetic acid relative to the alcohol and Ba-acetate contents in order to keep Ba-acetate in solution. This was demonstrated during the preparation of gels in the system BaO-Al₂O₃-SiO₂ from TEOS, Al-sec-butoxide and

Ba-acetate. As acetic acid reacts immediately with TEOS and Al-sec-butoxide, only H₂O can be used to control the Ba-acetate dissolution. For this purpose a minimum quantity of 20 mol H₂O/mol Ba-acetate and 1 mol H₂O/mol alcohol is sufficient to prevent the precipitation of Ba-acetate during the gelling and drying process.

Notes

1. Johnson Matthey GmbH, D-76185 Karlsruhe.
2. Prolabo, F-69102 Vaulx en Velin.
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