

Effect of third component on separation behavior of water+*t*-butanol+Na₂SO₃/Na₂SO₄ system at 298±2 K

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Received 31 January 2018; revised and accepted 31 May 2018

The liquid-liquid and liquid-liquid-solid equilibria for the ternary *t*-butanol-water-Na₂SO₃/Na₂SO₄ system is reported at ambient pressure and at 298±2 K. The solubility data of solutions of Na₂SO₃/Na₂SO₄ in water, *t*-butanol and solutions of varying compositions of *t*-butanol in water are reported. The phase diagrams for the studied systems are developed and salting-out effect of salt anion has been described. The structural properties of aqueous *t*-butanol solutions and the salting-out effect of SO₃²⁻ and SO₄²⁻ ions to cause phase separation have been explained. The salting-out ability of Na₂SO₃ is higher than that of Na₂SO₄ since the Gibbs free energy of hydration (ΔG_{hyd}) of SO₄²⁻ (-1080 kJ mol⁻¹) is lower than that of SO₃²⁻ (-1295 kJ mol⁻¹) ion.

Keywords: Solution chemistry, Phase diagrams, Butanol, Water, Sulphite, Sulphate, Na₂SO₃, Na₂SO₄, Salting-out

Phase equilibrium investigations of two and three component systems are of considerable practical and theoretical importance¹ to understand the solvent structural changes and salting-in/salting-out effects. Aqueous two phase systems (ATPS) of alcohols are of considerable interest to understand the hydration and hydrophobic interaction by a variety of techniques²⁻⁴. ATPS play an important role in the separation, extraction, purification and fractionation of cells, proteins, enzymes, nucleic acids and metal ions and are now routinely used in the extractive crystallization of inorganic salts⁵⁻¹⁰. The mutual competition between hydrophilic solvent and salt for water molecules leads to the exclusion of hydrophilic solvents and salt crystallization. Alcohol-water mixtures are extensively used as industrial solvents

where the complex concentration dependence of most physical properties affect the behavior of the species dissolved in the aqueous mixtures. Hence, the study on the salting-out and salting-in effects of salts, ions or molecules is important. The selection of phase separation salt with a high salting-out ability is significant in ATPS designing. However, there are no convenient and efficient parameters for the evaluation of these abilities of salts for the exclusion of hydrophilic solvents. In the literature, multicomponent processes in alcohol-water have been studied widely to gain an understanding of the salting-in and salting-out effects, specially involving salts^{11,12}.

The literature survey reveals that in the past, the quaternary systems like water+NaCl+KCl+1-propanol¹³, water+1-butanol+KCl+NaCl¹⁴, water+ethanol+1-butanol+NaCl¹⁵, various ternary systems including but not limited to water+butanol/butanone+NaCl/KCl/KBr¹⁶, K₂CO₃+methanol+water¹⁷, Ammonium sulfate+ethanol/1-propanol/2-propanol+water¹⁸, diazepam+*t*-butanol+water¹⁹, etc., have been studied in detail to understand the salting-out effect of salts and their phase diagrams are available. Recently, we have reported the liquid-liquid-solid equilibrium for ternary systems of Na₂S₂O₃.5H₂O+ethanol+water and Na₂S₂O₃.5H₂O+*t*-butanol+water^{20,21}.

In continuation, of our earlier studies, herein we describe the phase diagrams for the *t*-butanol+water+salt system at 298±2 K. For this study, we selected strong kosmotropic anion and the cation containing salt, viz., sodium sulphite (Na₂SO₃) and sodium sulphate (Na₂SO₄). The reported results will be used to develop the thermodynamic model of ATPS as well as to increase the understanding of the nature of molecular interactions in *t*-butanol+water system. To the best of our knowledge, the complete phase diagram for the *t*-butanol+water+Na₂SO₃/Na₂SO₄ system is not reported. Also, the phase separation ability of Na₂SO₃ and Na₂SO₄ has been compared and described in terms of solubility, Gibbs free energy of hydration and kosmotropic nature of ions.

Experimental

The *t*-butanol (purity of 99.5%) was obtained from Molychem, India. The anhydrous salts of Na₂SO₃ (purity 96%) and Na₂SO₄ (purity 99%) were obtained from SDFCL, India and Lobachemie, India

respectively. All solutions were prepared using distilled deionized water and further care was taken to avoid contact with atmospheric CO_2 . The chemicals were used without any further purification or drying. All solutions were prepared by mass in glass stoppered flat bottom tubes on Shimadzu balance (model AUW220D) with a precision of 0.0001 g.

The phase diagrams were constructed from solubility data by following our previously published experimental procedure^{21,22}. Initially some preliminary studies were carried out for ternary systems with Na_2SO_3 and Na_2SO_4 with aqueous solutions of *t*-butanol. Then, further experiments were designed for the ternary *t*-butanol+water+ $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ system. Briefly, the phase separation data for the phase diagram were obtained using *t*-butanol–water mixture (50 wt%) to which successive additions of salt in small increments were made. The point of alcohol phase separation (salting-out) was detected by appearance of turbidity in the solution. The solution was allowed to stand for an hour to confirm the phase separation and further addition of salt was continued until the solid started separating. Similarly, *t*-butanol-water mixtures of different compositions were used and phase separation data were generated by adding salt in these mixtures. The phase diagram has been constructed from the concentrations of the constituents in terms of percentage mass fraction plotting on triangular graph. The data of composition regarding the two (liquid-liquid) and three (liquid-liquid-solid) phase separation in terms of mass fractions of *t*-butanol (w_1), water (w_2) and respective salt of $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ (w_3) were calculated (Supplementary data, Table S1) and used to construct the triangular phase diagrams.

Results and discussion

The phase diagram has been constructed for *t*-butanol+water+ Na_2SO_4 (Fig. 1) and *t*-butanol+water+ Na_2SO_3 (Fig. 2) system from the concentrations of the constituents in terms of percentage mass fraction plotting on triangular graph. The various areas in both the phase diagrams can be described as follows. The area 'AabcdA' represents one liquid layer (L) consisting of all three components, i.e., *t*-butanol, water and $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$, where point 'a' represents the solubility/saturation point of salt in water. The area 'BabB' (L_A+S) represents solid $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ in equilibrium with water-rich saturated solution. The area 'BdCB' (L_O+S) represents solid $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$

in equilibrium with alcohol-rich saturated solution. The area 'dcdb' represents the two conjugated solutions of salt in water-alcohol mixtures (L_A+L_O), where, L_A denotes water-rich layer, while L_O is *t*-butanol-rich layer which may be separated from L_A . The area 'BbdB' (L_A+L_O+S) represents an invariant system where solid $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ is in equilibrium with the two conjugate liquid layers ' L_A ' and ' L_O '.

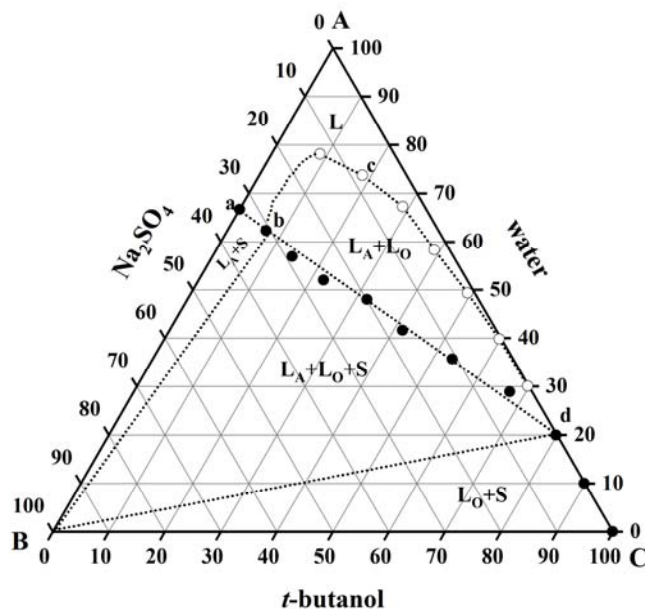


Fig. 1 – Phase diagram of ternary system of *t*-butanol+ water+ Na_2SO_4 . [curve 'bcd' represents liquid-liquid (○) and line 'bd' represents liquid-liquid-solid (●) phase separation].

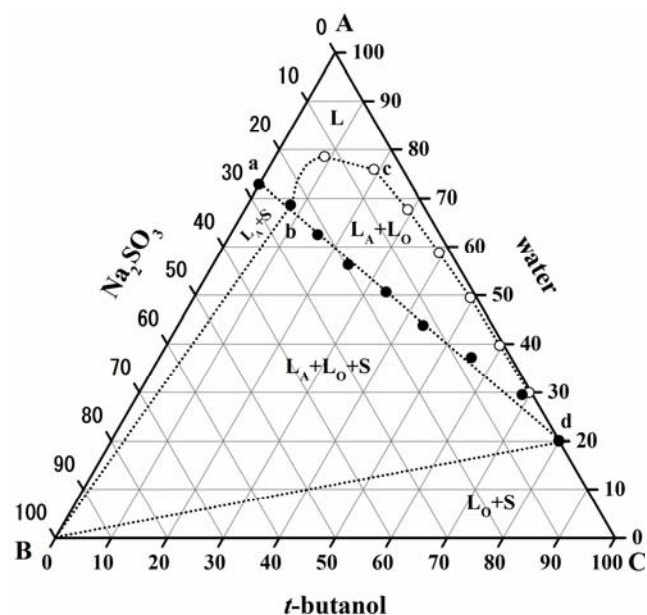


Fig. 2 — Phase diagram of ternary system of *t*-butanol+ water+ Na_2SO_3 . [curve 'bcd' represents liquid-liquid (○) and line 'bd' represents liquid-liquid-solid (●) phase separation].

The curve 'bcd' represents the liquid-liquid phase separation curve which was observed by formation of turbid solution. The line 'abd' represents solid separation point where the solubility of salts ceases so that solid $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ and liquids L_A and L_O coexist in equilibrium. Further addition of salt could not generate any change in the composition of these liquid layers hence, the system is isothermally invariant in the region 'BbdB' (L_A+L_O+S).

The phase diagrams reveal that the point 'a' represents the saturation solubility of $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ in water. The composition at 'a' is 33.33% Na_2SO_4 and 66.67% H_2O for t -butanol-water- Na_2SO_4 system (Fig. 1), while for system t -butanol-water- Na_2SO_3 (Fig. 2) it is 27.21% Na_2SO_3 and 72.79% water. Thus, from 'A' to 'a' we have an unsaturated solution of $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ in water, whereas that from 'a' to 'B', solid $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ is in equilibrium with the saturated solution 'a'.

Similarly, the point 'd' represents the composition of t -butanol and water where solubility of $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ is possible. This also means that Na_2SO_3 and Na_2SO_4 are insoluble (solubility almost nil) in pure t -butanol. We desist to comment on the solubility of $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ in pure t -butanol as no measurements were carried out. The curve 'Bba' is the saturation solubility curve of $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ in water in presence of t -butanol. This region of concentration (t -butanol+water) is known for hydrophobic hydration of t -butanol molecules in water and for binary solution shows extrema for the properties like temperature of maximum density (T_M), partial molar volume of t -butanol and compressibility of solutions. Along the curve 'dcb' we have the formation of two liquid layers (turbidity observed). From Figs 1 and 2 it has been observed that the separation of two liquid layers for both the salts starts from 70% to 10% t -butanol solution in water (taken as a binary system). The concentration corresponding to a plait point on the ternary phase diagram, i.e., point 'c' (for each composition) is a magic concentration where most of the thermodynamic properties like excess free energy change, enthalpy change, viscosity, etc., exhibit extrema. Thus, in this region of t -butanol-water system, the hydrophobic interactions of t -butanol in water are more prominent. Further addition of the salt causes separation of the two liquid phases to the maximum extent and continues up to line 'abd' (with respect to corresponding liquid-liquid separation point) where the solubility of salt ceases and the two liquid layers are in equilibrium with the solid salt.

Also, it has been observed that the addition of $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ up to 2 mol% of t -butanol does not cause separation of the t -butanol-rich layer. However, it starts separating above this concentration of t -butanol. Thus, the salting-out of t -butanol-rich layer depends upon the hydrophobic interactions present in the original mixture and the effect is structural in origin. Our results of phase separation of t -butanol by addition of $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ are thus in agreement with such an interpretation. The experimentation and our previous work also reveal that the anions of the salts, viz., of K_2CO_3 , Na_2SO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ play an important role in determining the phase diagram. It has been observed that K_2CO_3 separates methanol, ethanol as well as t -butanol from water. On the other hand, $\text{Na}_2\text{S}_2\text{O}_3$ is inefficient for the separation of methanol while it separates ethanol and t -butanol efficiently. Na_2SO_4 shows no such separation for both methanol and ethanol at room temperature^{21,22}. In the present work it is observed that the mixture of t -butanol and water can be separated with 2 mol% $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$.

Figures 3 and 4 show the effect of salt anions (SO_3^{2-} and SO_4^{2-}) on the binodal curves of liquid-liquid and liquid-liquid-solid equilibria. From the results it is observed that the salting out ability of Na_2SO_4 is relatively less than that of Na_2SO_3 which may be due to the ion with higher salting out ability having a more negative Gibbs free energy of hydration (ΔG_{hyd}) value²². Our results support this statement as ΔG_{hyd} SO_4^{2-} ($-1080 \text{ kJ mol}^{-1}$) is lower than ΔG_{hyd} value of SO_3^{2-} ($-1295 \text{ kJ mol}^{-1}$) hence the salting-out ability of SO_3^{2-} is higher than that of SO_4^{2-} . The slope of the linear plot of salt concentration

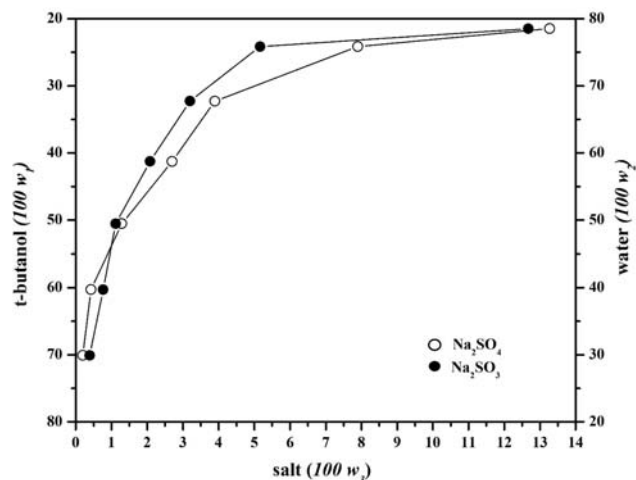


Fig. 3 — Effect of anions (SO_4^{2-} and SO_3^{2-}) on binodal curve of liquid-liquid phase equilibrium.

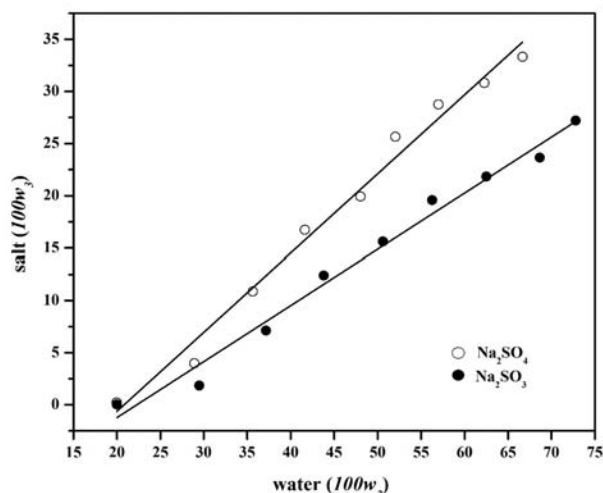


Fig. 4 — Effect of anions (SO_4^{2-} and SO_3^{2-}) on binodal curve of liquid-liquid-solid phase equilibrium.

against concentration of water (Fig. 4) i.e., binodal points of liquid-liquid-solid was fitted using the linear regression method. The correlation coefficient values were found to be 0.9859 and 0.9849 with slopes of 0.5371 and 0.7576 for Na_2SO_3 and Na_2SO_4 respectively from which it can be concluded that Na_2SO_3 has higher ability for the salting-out of *t*-butanol from water. Further studies related to thermo-acoustic properties of these constituents for the system of *t*-butanol+water+ $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ at constant and different temperatures are needed to understand the structure making and breaking abilities and to determine the intermolecular interactions in these systems.

In summary, the phase diagrams for the system *t*-butanol+water+ $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ are constructed from the solubility data. It is observed that above 2 mol% *t*-butanol in water, addition of salt causes separation of *t*-butanol layer from the mixture. These effects are attributed to structural interactions present in *t*-butanol–water mixtures, i.e., below 2 mol%, *t*-butanol is hydrophobically solvated while above 2 mol% hydrophobic interactions are predominant causing salting-out of *t*-butanol. The preference of salts in inducing the phase separation in aqueous two phase system was found in order of $\text{Na}_2\text{SO}_3 > \text{Na}_2\text{SO}_4$, which is attributed to the ΔG_{hyd} value of SO_4^{2-} ($-1080 \text{ kJ mol}^{-1}$) being lower than that of ΔG_{hyd} value of SO_3^{2-} ($-1295 \text{ kJ mol}^{-1}$). Further studies related to thermo-acoustic properties of these constituents for the *t*-butanol+ water+ $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$ system are required to understand the structure making and breaking abilities and to determine the intermolecular interactions in these systems.

Supplementary data

Supplementary data associated with this article are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_57A\(06\)791-794_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_57A(06)791-794_SupplData.pdf).

Acknowledgement

Authors are thankful to the University Grants Commission, New Delhi, India, for grants under Major Research Project [File No: 43-219/2014 (SR) Dt. 18.08.2015], and, the Department of Science and Technology, New Delhi, India, for grant under DST-FIST program (No/SR/FST/College-151/2013(C)) to Jaysingpur College, Jaysingpur.

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