

SATURATED SOLUTIONS OF $M(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$ ($M = \text{Sr, Ba}$) SYSTEMSMitko D. STOEVA^a and Jose M. A. ROBLEDO^b^a *Institute of General and Inorganic Chemistry,
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The solubility isotherms of the $M(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$ ($M = \text{Sr, Ba}$) systems at 25 °C have been studied. Crystallization fields of the equilibrium existence of the salts $\text{Sr}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ have been found. The structures of the saturated solutions on the basis of statistic calculations and IR spectra have been discussed.

The paper presents a continuation of investigation on the equilibria in systems on the type inorganic salt–water–methanol¹ and on the structures of saturated solutions by spectroscopic methods². The ternary systems $\text{Sr}(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$ and $\text{Ba}(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$ are studied at 25 °C. The purpose is to elucidate the behaviour of $\text{Sr}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$ in a mixed water–methanol solvent and the structures of saturated $\text{Sr}(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$ and $\text{Ba}(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$ solutions.

EXPERIMENTAL

The experimental procedure of the study of equilibria in strontium and barium systems is described in a previous paper³. The infrared spectra were obtained in a digital form with a Philips PU 9500 IR spectrometer having a resolution of 1 cm^{-1} , and were then processed by Philips infrared software. A cell with CaBaF windows was used, the distance between them being 5.153 microns. All samples for IR spectroscopy were prepared with distilled water, anhydrous methanol (a. r., Merck), $\text{Sr}(\text{NO}_3)_2$ (a. r., PANREAC) and $\text{Ba}(\text{NO}_3)_2$ (a. r., PANREAC).

RESULTS AND DISCUSSION*Equilibria in the $\text{Sr}(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$ and $\text{Ba}(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$ Systems at 25 °C*

The results on the equilibria in the systems $\text{Sr}(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$ and $\text{Ba}(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$ are presented in Table I and Fig. 1. The solubility isotherm of the system

Sr(NO₃)₂-H₂O-CH₃OH consists of the equilibrium existence of the salts Sr(NO₃)₂ · 4 H₂O and Sr(NO₃)₂. When 9.7 mass % of CH₃OH is present in the ternary system at 25 °C, the dehydration process Sr(NO₃)₂ · 4 H₂O → Sr(NO₃)₂ takes place in the mixed H₂O-CH₃OH solvent. In binary Sr(NO₃)₂-H₂O systems⁴ this phase transition is observed at 29.3 °C. With rising methanol concentration, the anhydrous Sr(NO₃)₂ is strongly salted out of the saturated solution. Strong salting out is also observed in the Ba(NO₃)₂-H₂O-CH₃OH system. Our previous investigation on the behaviour of strontium and barium salts in a mixed water-methanol (ethanol) solvent^{3,5,6} and studies⁷ on the systems Sr(NO₃)₂-H₂O-C₂H₅OH and Ba(NO₃)₂-H₂O-C₂H₅OH have confirmed that Sr²⁺ and Ba²⁺ are not solvated by methanol (ethanol) molecules in the form of equilibrium solid phases (crystalline solvates).

The Saturated Sr(NO₃)₂-H₂O-CH₃OH and Ba(NO₃)₂-H₂O-CH₃OH Solutions

Figure 2 shows part of the solubility isotherms of the systems Sr(NO₃)₂-H₂O-CH₃OH and Ba(NO₃)₂-H₂O-CH₃OH at 25 °C. The isotherms are decomposed according to the expression:

$$\text{mol MS/mol salt} = \text{mol H}_2\text{O/mol salt} + \text{mol CH}_3\text{OH/mol salt},$$

where MS is the mixed water-methanol solvent. This way of presentation of the solubility isotherms ensures informations on the statistics concerning the saturated solutions, which may help spectroscopic studies aiming at elucidation of the structure of saturated solutions. According to the concentration scale of Emons et al.⁸ classifying

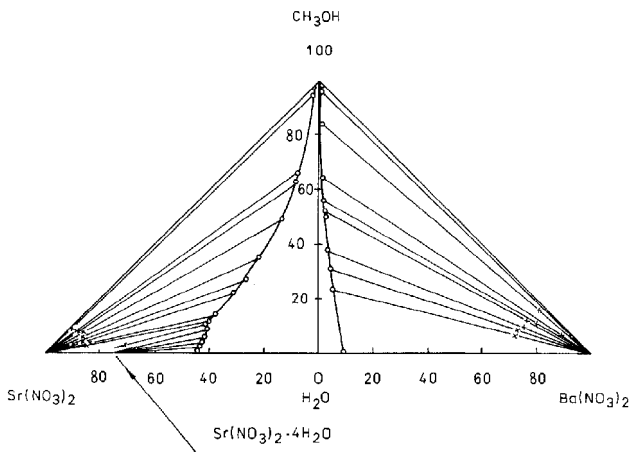


FIG. 1

Solubility diagrams for the M(NO₃)₂-H₂O-CH₃OH (M = Sr, Ba) systems at 25 °C

TABLE I

Solubility isotherms for the $M(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$ ($M = \text{Sr, Ba}$) systems at 25 °C

No.	Liquid phase, mass %			Wet residue, mass %		Equilibrium solid phase
$\text{Sr}(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$						
	CH_3OH	H_2O	$\text{Sr}(\text{NO}_3)_2$	H_2O	$\text{Sr}(\text{NO}_3)_2$	
1	0.00	55.96	44.04	—	—	$\text{Sr}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$
2	2.8	54.3	42.84	31.7	69.53	
3	4.5	53.3	42.20	34.4	66.68	
4	6.3	52.4	41.23	31.0	68.58	
5	9.3	50.0	40.62	31.5	66.26	
6	9.7	49.5	40.80	26.5	70.00	$\text{Sr}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O} +$ $\text{Sr}(\text{NO}_3)_2$
7	11.4	48.5	40.02	9.0	90.15	$\text{Sr}(\text{NO}_3)_2$
8	14.4	48.0	37.52	9.0	88.85	
9	22.4	46.0	31.52	1.5	97.42	
10	27.5	46.0	26.46	9.0	86.05	
11	35.5	41.5	22.93	5.5	89.89	
12	50.8	36.0	13.15	6.5	85.38	
13	63.2	28.5	8.25	3.5	89.72	
14	66.2	25.7	8.04	3.0	88.72	
15	97.3	0.9	1.80	0.3	90.45	
16	98.94	0.00	1.06	—	—	
$\text{Ba}(\text{NO}_3)_2\text{-H}_2\text{O-CH}_3\text{OH}$						
	CH_3OH	H_2O	$\text{Ba}(\text{NO}_3)_2$	H_2O	$\text{Ba}(\text{NO}_3)_2$	
1	0.00	90.69	9.31	—	—	$\text{Ba}(\text{NO}_3)_2$
2	24.0	70.5	5.44	21.9	72.14	
3	31.2	63.5	5.30	17.0	72.82	
4	38.6	58.1	3.24	14.0	76.00	
5	50.6	47.2	2.20	11.3	77.10	
6	52.5	45.6	1.81	8.0	81.77	
7	56.9	41.7	1.36	5.7	88.81	
8	64.8	33.7	1.43	5.7	88.81	
9	83.6	16.1	0.24	5.0	81.21	
10	97.0	2.9	0.09	2.0	92.38	
11	99.95	0.00	0.05	—	—	

salt solutions, diluted solution exist down to 20 mol MS/mol salt, while concentrated solutions exist between 20 and 10 mol MS/mol salt. The system Sr(NO₃)₂-H₂O-CH₃OH is, from 0 to 0.2 molar fractions (m.f.) of CH₃OH in MS, within the region of saturated concentrated solutions. Ions Sr²⁺ are solvated by the molecules of both components of the mixed solvent, and the first coordination sphere is formed in the saturated solution. On the second coordination sphere the mixed solvent molecules are oriented electrostatically under the effect of the molecule from the first coordination sphere. In this case, the pure solvent region is absent. Above 0.2 m.f. CH₃OH in MS, the Sr(NO₃)₂-H₂O-CH₃OH system and the whole solubility isotherm of the system Ba(NO₃)₂-H₂O-CH₃OH belong to saturated diluted solutions. The structure of the mixed water-methanol solvent is predominant in these solutions. The Raman and IR spectra of the saturated solutions of the type inorganic salt-water-methanol have a complex character⁹ due to the simultaneous presence in the solution spectrum of lines of the solvents (water, methanol) and the inorganic salt. Figures 3 and 4 present the results obtained after subtracting the IR spectrum of the mixed water-methanol solvent from the spectra of the saturated Sr(NO₃)₂-H₂O-CH₃OH and Ba(NO₃)₂-H₂O-CH₃OH solutions, respectively. The presence of Sr(NO₃)₂ and Ba(NO₃)₂ salts in the mixed water-methanol solvent is registered in the IR spectrum directly (the line of the ν₃(E') stretching mode of NO₃⁻ at 1 390 cm⁻¹) and indirectly (the intensity charge of the ν_{OH} stretching mode for H₂O and CH₃OH at 3 200 - 3 700 cm⁻¹ and of the ν_{CH} stretching mode of CH₃OH at 2 750 - 2 900 cm⁻¹). With increasing amount of the molar fraction

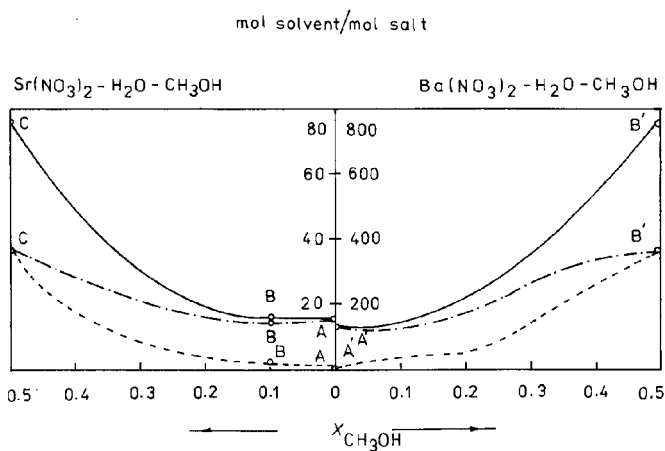


FIG. 2

The solubility isotherms for the M(NO₃)₂-H₂O-CH₃OH (M = Sr, Ba) systems at 25 °C. $X_{\text{CH}_3\text{OH}}$ is molar ratio of methanol in the water-methanol mixed solvent (MS). (—) mol MS/mol salt, (· · · · ·) mol H₂O/mol salt, (----) mol CH₃OH/mol salt, AB = Sr(NO₃)₂ · 4 H₂O, BC =

CH_3OH in the ternary systems, the inorganic salts are salted out. Figure 5 presents comparison of the salting out effects of methanol on $\text{Sr}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ in the $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ mixed solvent. Within the whole concentration range of the mixed solvent, $\text{Ba}(\text{NO}_3)_2$ is salted out more strongly than in the case of $\text{Sr}(\text{NO}_3)_2$.

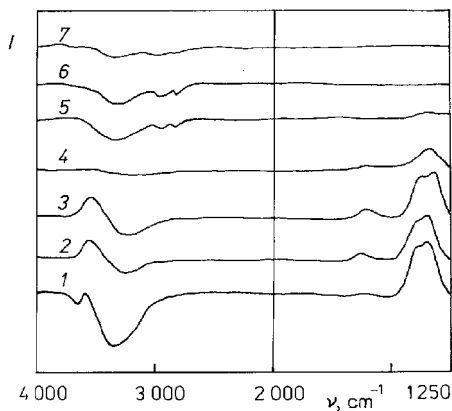


FIG. 3

IR spectra obtained by subtracting the spectrum of the mixed solvent from the spectrum of the saturated $\text{Sr}(\text{NO}_3)_2-\text{H}_2\text{O}-\text{CH}_3\text{OH}$ solution; m.f. CH_3OH in MS: 1 0.0, 2 0.1, 3 0.2, 4 0.5, 5 0.7, 6 0.8, 7 1.0

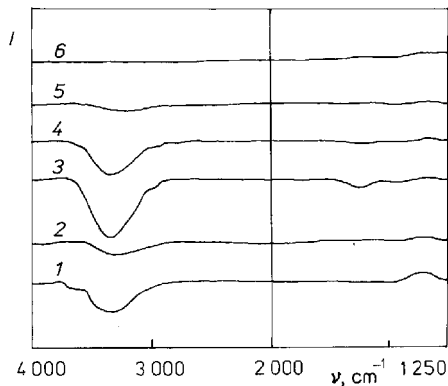


FIG. 4

IR spectra obtained by subtracting the spectrum of the mixed solvent from the spectrum of the saturated $\text{Ba}(\text{NO}_3)_2-\text{H}_2\text{O}-\text{CH}_3\text{OH}$ solution; m.f. CH_3OH in MS: 1 0.0, 2 0.1, 3 0.2, 4 0.3, 5 0.4, 6 0.5

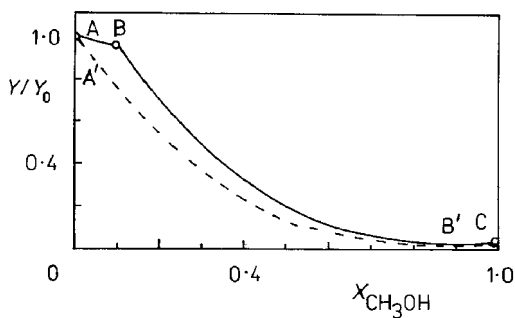


FIG. 5

Salting out process in the $\text{Sr}(\text{NO}_3)_2-\text{H}_2\text{O}-\text{CH}_3\text{OH}$ and $\text{Ba}(\text{NO}_3)_2-\text{H}_2\text{O}-\text{CH}_3\text{OH}$ systems at 25 °C. $X_{\text{CH}_3\text{OH}}$ is molar ratio of alcohol in mixed solvent; Y is amount of substance of salt in 100 mol of mixed solvent (or water (subscript 0)). (—) $\text{Sr}(\text{NO}_3)_2-\text{H}_2\text{O}-\text{CH}_3\text{OH}$, AB = $\text{Sr}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$, BC = $\text{Sr}(\text{NO}_3)_2$. (---) $\text{Ba}(\text{NO}_3)_2-\text{H}_2\text{O}-\text{CH}_3\text{OH}$, A'B' = $\text{Ba}(\text{NO}_3)_2$

4 H₂O and Sr(NO₃)₂. The salting out effect results in $\nu_3(E')$ intensity drop for the NO₃⁻ ion. At 0.8 m.f. CH₃OH in MS for the strontium system and 0.5 m.f. CH₃OH in MS for the barium system the spectra represent a straight line for the $\nu_3(E')$ stretching mode of NO₃⁻. The stretching mode intensity of the nitrate group depends on the salt concentration in the mixed solvent. In the case under consideration the salt concentration in the strontium system is 363 mol MS/mol Sr(NO₃)₂, while in the barium system this concentration amounts to 780 mol MS/mol Ba(NO₃)₂. At these salt concentrations in the mixed solvent, the saturated solutions belong to the strongly diluted solutions in which the mixed solvent structures prevails. The much lower solubility of Ba(NO₃)₂ in the mixed water-methanol solvent in comparison with solubility of Sr(NO₃)₂ leads to a pronounced predomination of the mixed solvent structure, the resulting spectrum representing a straight line. The Sr²⁺, Ba²⁺ and NO₃⁻ ions affect the intermolecular and intramolecular interactions in the mixed water-methanol solvent. As a result of these interactions, the intensities of ν_{OH} and ν_{CH} of the saturated ternary solutions decrease. With 0.5 m.f. CH₃OH in MS in the saturated solutions of the two ternary systems, the intensities of the lines in the 4 000 – 2 000 cm⁻¹ region for the mixed solvent and for the saturated solution become equal, the resulting spectrum being a straight line. Irrespective of the fact that for the strontium system a straight line is observed above 0.8 m.f. CH₃OH in MS of the $\nu_3(E')$ region of NO₃⁻, the minimum Sr(NO₃)₂ concentration in the mixed solvent affects the intermolecular, intramolecular and Fermi resonance interactions in the mixed water-methanol solvent. This procedure changes in the ν_{OH} and ν_{CH} regions of the saturated three-component solution and the resulting spectrum intensity is different from zero. In the region of 0.5 – 1.0 m.f. CH₃OH in MS for the barium system and above 0.8 m.f. CH₃OH in MS for the strontium system, the structure of the mixed water-methanol solvent prevails, the structure of methanol being most pronounced in this solvent. The IR spectroscopy studies on saturated solutions of the systems investigated have confirmed the higher solubility of Sr(NO₃)₂ in the mixed water-methanol solvent than in the case of Ba(NO₃)₂ and have given information on the predominating structures in the saturated three-component solutions.

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