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Experimental investigation of the solid – Liquid phase equilibria in the water – Ammonium methanesulfonate and in the water – Sodium methanesulfonate systems

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ABSTRACT

The thermal stability of ammonium and sodium methanesulfonates was investigated under inert atmosphere by thermogravimetry. Temperatures and enthalpies of phase transitions were determined for these salts by means of differential scanning calorimetry (DSC). It was shown that sodium salt melts congruently. Solid – liquid phase equilibria in the binary water – salt systems were studied. It was found that hydrate is formed in the water – sodium methanesulfonate system. Melting parameters and composition of this hydrate ($NaSO_3CH_3 \cdot 8H_2O$) were evaluated with the help of DSC. The data on the density of the methanesulfonates aqueous solutions in a wide range of concentrations at 25.00 °C were obtained.

1. Introduction

Methanesulfonic acid [1,2] is the main product of the photochemical oxidation of dimethyl sulfide in the atmosphere. Dimethyl sulfide is produced by processes involving phytoplankton. As a consequence methanesulfonic acid and methanesulfonates are the units of the biogeochemical cycle of sulfur in the Environment. Recently researchers have found various methanesulfonates and their hydrates in ice cores of Antarctica [3]. The properties of ice and the ice crystal inclusions can be used to reconstruct the climate changes or ocean composition during the ice cores formation. They also allow to reconstruct the history of changes in temperature and atmospheric conditions. Thermodynamic modeling allows to predict the most likely mineral structure of geological objects according to its elemental composition or to determine the conditions of formation of any mineral association observed in nature (geothermobarometry). Such calculations provide especially valuable information for objects that are not available for the direct experimental study, in particular, ice cores. It is desirable to know stability parameters of the individual substances and the data on phase equilibria in the binary systems for correct thermodynamic modeling of the systems of various dimensions.

The present work is focused on studying the properties of sodium and ammonium methanesulfonates ($NaSO_3CH_3$ and $NH_4SO_3CH_3$ respectively) as well as water-salt systems because the information about thermodynamic properties of these compounds in the literature is limited. There is only one work wherein melting point of $NH_4SO_3CH_3$ was determined by visual method [4]. It was found that the substance melts at the temperature range 198–201 °C. As to melting point of $NaSO_3CH_3$, this value is presented in several sources [5–7]. Charbonnier et al. [5] observed thermal behavior of $NaSO_3CH_3$ by differential thermal analysis (DTA). Temperature of $NaSO_3CH_3$ thermal decomposition was about 420 °C, melting temperature was 340 °C. Gramstad et al. [6]. and Parham et al. [7]. showed by visual method that $NaSO_3CH_3$ melts at 345 °C and higher than 230 °C respectively. Solid – liquid phase equilibria in the system H_2O – $NaSO_3CH_3$ were investigated by Sakurai et al. [8]. In that work solubility of ice, solidus temperature and single point corresponding to the solubility of salt were determined by DTA. According to [8] H_2O – $NaSO_3CH_3$ refers to the eutectic type system. Data on the phase equilibria in the H_2O –

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$NH_4SO_3CH_3$ system are lacked in literature. There is some evidence about the high solubility of the $NH_4SO_3CH_3$ in comparison with ammonium sulfate [9].

The aims of this work were (1) estimation of the salts thermal stability; (2) determination of the $NaSO_3CH_3$ and $NH_4SO_3CH_3$ phase transition parameters; (3) investigation of the phase equilibria in the $H_2O - MSO_3CH_3$ ($M = Na^+, NH_4^+$) systems at atmospheric pressure with the help of DSC.

2. Experimental

Provenance and purities of the substances used in the present work are presented in Table 1. $NH_4SO_3CH_3$ and $NaSO_3CH_3$ were obtained by neutralization of the methanesulfonic acid by $(NH_4)_2CO_3$ and NaOH respectively. Obtained salts were recrystallized twice from distilled water. The purity of these substances was confirmed by the comparison with literature [10,11] and experimental data on XRD (X-ray powder diffraction data), DSC and elemental analysis. Results of the elemental analysis of the salts are shown in Table 2. $NaSO_3CH_3$ melts congruently and doesn't decompose (see «Results and Discussion»), so it was possible to determine the total molar content of the impurities in this sample with the help of standard DSC procedure (ASTM E928). The results of calculating the purity of salts are presented in Table 1.

3. Methods

3.1. Thermogravimetry (TGA)

TGA curves were detected by NETZSCH TG 209 F1 in the temperature range 30–450 °C for the estimation of the compounds thermal stability. Heating rate (HR) of experiments was $10\,°C\cdot min^{-1}$. All measurements were conducted in a stream of N_2 at the flow rate 20 ml min^{-1}. Calibration technique of the instrument was the same as described in Ref. [12].

3.2. Differential scanning calorimetry (DSC)

DSC curves were obtained using a NETZSCH DSC 204 F1 in a stream of dry Air (20 ml min^{-1}) with HR and cooling rates (CR) varying from 0.5 to 10 $°C\cdot min^{-1}$. Maximum temperature range of DSC experiments was -150–420°C. Calibration technique of the instrument was the same as described in Ref. [13].

Samples for DSC and TGA experiments were weighed on an analytical balance A&D GH-202 with an accuracy of 10^{-5} g. Sample preparation for DSC and TGA experiments was carried out as it was done in Ref. [13]. DSC and TGA curves were processed in NETZSCH Proteus Analysis. Temperatures of solidus and liquidus were determined according to the recommendations in the [14,15]. Additional temperature corrections on thermal resistance [15] were made for the accurate determination of liquidus temperatures. The sample of fresh distilled water was used as a standard substance. Standard uncertainties of liquidus temperatures were determined for one composition in every system by the triple repetition of the experiment including the sample preparation stage as it was done in Ref. [13]. Standard uncertainties of solidus temperatures were estimated by statistical processing of the data in the whole range of concentrations.

Table 2
Results of the methanesulfonates elemental analysis.[a]

Substance	w, weight %	C	H	N
$NH_4SO_3CH_3$	Theoretical	10.62	6.24	12.38
	Experimental	10.58	6.25	12.42
$NaSO_3CH_3$	Theoretical	10.17	2.56	–
	Experimental	10.23	2.48	–

[a] Standard relative uncertainty u_r is $u_r(w) = 0.3$.

3.3. X-ray diffraction (XRD)

XRD data were obtained on a diffractometer Rigaku Miniflex 600. Angle 2Θ was varied in the range from 5 to 60 with step of 0.02; the exposure time was 10 s per point. Samples of $NaSO_3CH_3$ and $NH_4SO_3CH_3$ were identified by comparing theoretical and experimental diffractograms [10,11].

3.4. Elemental analysis

Elemental analysis was performed by automatic analyzer CE1106. Sample mass was about 0.8–1 mg. Temperature of specimen burning was equal to 1050 °C. Flash temperature reached 1800 °C in a tin capsule with a sample. Transport gas was helium (flow rate is 120 ml min^{-1}). Separation of degradation products (nitrogen, carbon dioxide and water) occurred at the gas chromatography column. Calculation of the C, H, and N content was carried out automatically by the instrument software. Calibration coefficients were determined in experiments with standard substances, results of the bulk experiment and masses of the samples were taken into account in the software.

3.5. Density measurements

Density measurements of $NH_4SO_3CH_3$ and $NaSO_3CH_3$ aqueous solutions in a wide concentration range at 25.00 °C were conducted by means of an oscillating U-tube densitometer «VIP–2MR». Maximum deviation of densitometer temperature did not exceed ±0.02 °C. Instrument was calibrated with fresh distilled water and dry air immediately before each series of experiments. Calibration procedure is particularly described in Ref. [16]. Absolute error of density determination did not exceed 0.3 kg m^{-3}. Solutions for the density measurements were obtained by mixing components on AXIS AG300 balance with an accuracy of 10^{-3} g. Weight of solutions was 10–15 g.

3.6. Solubility measurements

Method of isothermal solution saturation was applied for $NH_4SO_3CH_3$ and $NaSO_3CH_3$ solubility determination in a wide range of temperatures. Salt and distilled water were placed in

Table 1
Purities and sources of chemicals.

Chemical name	CAS number	Source	Initial purity (weight %)	Purification method	Final purity	Analysis method
HSO_3CH_3	75-75-2	«Alfa Aesar»	≥98	–	–	–
$(NH_4)_2CO_3$	506-87-6	«Labtex»	99.0	–	–	–
NaOH	1310-73-2	«Labtex»	99.0	–	–	–
$NH_4SO_3CH_3$	22515-76-0	synthesis	–	recrystallization	99.6 ± 0.4 weight %	elemental analysis
$NaSO_3CH_3$	2386-57-4	synthesis	–	recrystallization	99.989 ± 0.003 mol %	DSC (ASTM E928)