

UDC 541.123

V.G. Matvienko, Cand. Sci. (Chem.) (Government Higher Educational Institution «Donets National Technical University»)

PHASE DIAGRAM OF THE SODIUM CHLORIDE - WATER - DIETHYLENE GLYCOL - METHANOL SYSTEM AT THE TEMPERATURE OF 25°C

In the process of natural gas dehydration with the help of diethylene glycol the absorbent obtained after drying is a solution of sodium chloride in the ternary solvent diethylene glycol - water - methanol, because methanol is widely used as a gas hydrate inhibitor and droplets of the gas brine mix with the absorbent. For calculation of the technological mode of operation for gas dehydration systems information on the solubility of sodium chloride in the ternary solvent diethylene glycol - water - methanol is necessary. Sodium chloride solubility in two-component solvent diethylene glycol - methanol and three-component solvent diethylene glycol - water - methanol at the temperature 25°C has been studied. In the system investigated, the only liquid phase is formed. The salt solubility increases with the increase in diethylene glycol and methanol content in the three-component solvent. The data obtained can be used in the design of plants for diethylene glycol regeneration from moisture in the conditions of methanol inhibition, as well as in their operation effectiveness analysis.

Key words: solubility, sodium chloride, diethylene glycol, water, methanol

In the process of extraction and transportation of natural gas, especially at low temperatures, the formation of gas hydrates - clathrate compounds of gas components and water (snowlike masses) may take place [1]. Gas hydrates may block the cross-section of pipelines, disturb their normal work and even may damage them. For gas hydrates prevention it is necessary to reduce the partial pressure of water vapor in the compressed gas, which is most often achieved by injecting some substances into gas (hydrate inhibitors). With water these substances form solutions with low partial pressure of water vapor. In practice methanol is widely used as hydrate inhibitor [1]. Gas from the well contains condensed moisture - drops of brine, salt mixture the main component of which is sodium chloride [2]. In case of insufficient condensed moisture separation much of it remains in the gas. Methanol and sodium chloride during the subsequent gas dehydration before feeding it to the pipeline mix with the moisture absorbent. In most cases, gas dehydration is carried out with the help of diethylene glycol (DEG), and therefore the absorbent obtained after drying is a solution of sodium chloride in the ternary solvent DEG - water - methanol. In the process of gas dehydration the sodium chloride concentration in the absorbent used grows and there is a risk of crystallization of the salt from the solution during the regeneration of the absorbent out of moisture. For calculation of the technological mode of operation for such systems information on the solubility of sodium chloride in the ternary solvent DEG - water - methanol is necessary.

In the scientific sources, there are experimental data on the solubility of sodium chloride in water, methanol, and two-component solvent water - methanol [3]. We have previously studied the solubility of sodium chloride at different temperatures in DEG and mixtures DEG - water [4]. There are no data on the solubility of the salt in two-component solvent DEG - methanol and ternary solvent DEG - methanol - water. In this regard, we have investigated the solubility of sodium chloride in two-component solvent DEG - methanol and ternary solvent DEG - water - methanol at 25°C.

The method of determining the solubility is described earlier [4 - 7]. The experiment was conducted as follows. A hermetically closed glass cell (the approximate volume is 7 cm³) charged with the salt and a solvent of known

composition was placed in a thermostated glass of water. Two-and three-component solvents were prepared in advance in disposable medical syringes, masses of loaded components being determined by consecutive weighing the syringe on an analytical balance. At the bottom of the cell there was placed a steel rod, mixing the contents when the external magnetic stirrer was turned on. As established by experience, the state of equilibrium at 25°C was set within 15-20 minutes. Yet in order to ensure in the course of experiment the equilibrium concentrations of sodium chloride in the solution, the mixing time was increased to 1 hour. Then the external magnetic stirrer was turned off, and the cell was kept in the thermostated glass for phase separation. After separation of the cells contents by means of a medical syringe and a flexible capillary the solution samples of 0.5 - 1 cm³ for sodium chloride analysis were taken. The exact sample weight was determined by weighing the empty and filled syringe on an analytical balance. This way of sampling eliminates the evaporation of volatile solution components in the sampling process. The sample was then transferred to a titration flask, and the syringe was washed several times with water, which then was poured into the flask too. The concentration of sodium chloride in the saturated solution was determined by titration with 0,05 N solution of silver nitrate, using potassium chromate as an indicator (the Mohr's method).

Diethylene glycol (qualification "h") was distilled at the pressure of 0.2-0.4 kPa. The medial fraction of the distillate was sealed in glass ampoules and then was used in the experiment. The refractive index of the obtained DEG $n^{20} = 1.4470$, water content - 0.036%.

For the preparation of the solutions used qualification "h" methanol was subjected to fractional distillation. The medial fraction was then sealed in a glass ampoule. The purified methanol had refractive index $n^{20} = 1.3286$, density $d^{20} = 791.4$ kg/m³ and contained 0.026 wt. % of water.

Bidistillate of water was used in the experiment.

The experimentally determined sodium chloride concentrations values in the solvents studied are presented in the tables 1 and 2.

Table 1. Concentration of sodium chloride in the saturated solutions of sodium chloride - DEG – methanol system

Methanol concentration in the solvent, % wt.	0.0	19.2	39.9	60.8	81.2	100.0
Concentration of sodium chloride in the solution, % wt	4.18	4.04	3.58	2.93	2.17	1.29

Table 2. Concentration of sodium chloride in the saturated solutions of sodium chloride - DEG - water – methanol system

Ratio (by weight) DEG: water -74.8: 25.2

Methanol concentration in the solvent, % wt.	0.0	27.7	50.3	73.3	100.0
Concentration of sodium chloride in the solution, % wt	8.30	5.77	4.15	2.79	1.29

Ratio (by weight) DEG: water - 49.1: 50.9

Methanol concentration in the solvent, % wt.	0.0	26.9	48.4	71.4	100.0
Concentration of sodium chloride in the solution, % wt	13.9	8.93	5.81	3.28	1.29

Ratio (by weight) DEG: water - 26.2: 73.8

Methanol concentration in the solvent, % wt.	0.0	26.4	46.9	72.4	100.0
Concentration of sodium chloride in the solution, % wt	19.9	12.8	8.07	3.76	1.29

The figure illustrates the dependence of sodium chloride solubility on the methanol concentration in two-component solvent DEG - methanol and ternary solvent DEG - water – methanol at the temperature 25°C.

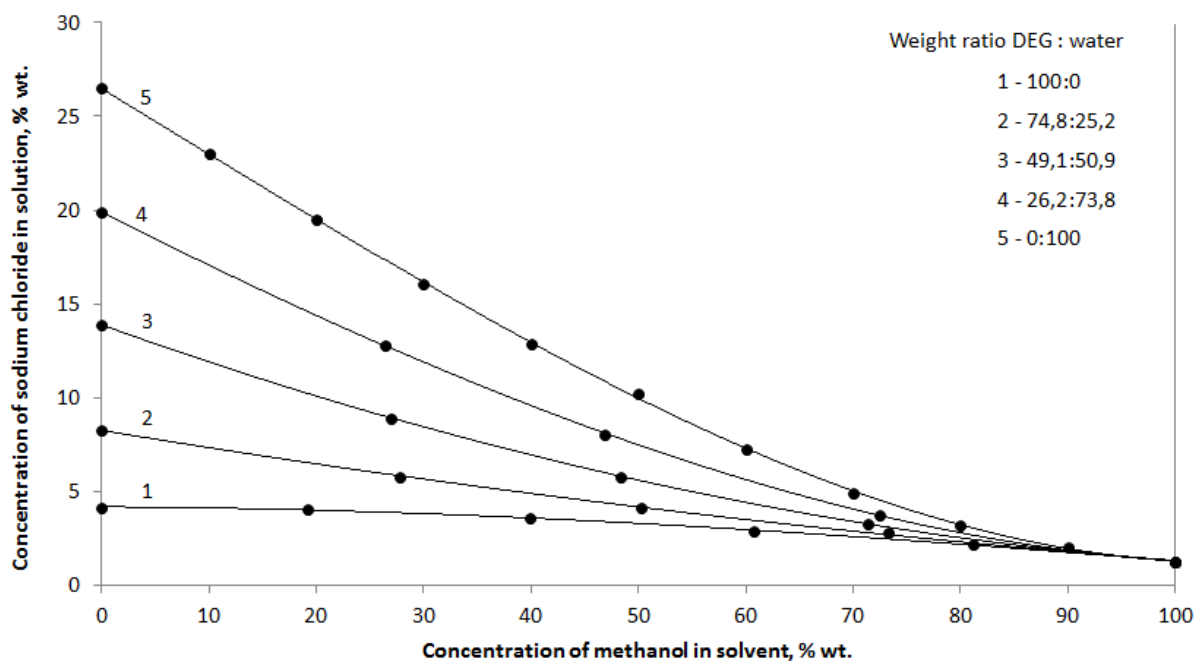


Fig.1. Dependence of sodium chloride solubility on the methanol concentration in binary solvent DEG - methanol and ternary solvent DEG - water – methanol at the temperature 25°C

As it follows from the figure and the tables' data, in the system investigated, the only liquid phase is formed. Increase of methanol concentration in two-component solvent DEG - methanol and ternary solvent DEG - water - methanol reduces the solubility of sodium chloride. In solutions rich with methanol the chloride concentration is close to its concentration in pure methanol.

The data obtained can be used in the design of plants for DEG regeneration from moisture in the conditions of methanol inhibition, as well as in their operation effectiveness analysis.

References

1. Byk S.Sh. Gas hydrates / Byk S.Sh., Makogon U.F. and Fomina V.I. — M.: Khimiya, 1980. — 296 p.
2. Bondar A.D. / Bondar A.D., Grybkova V.I., Moiseeva N.F. // Gazovoe Delo. — 1970. — N 2. — P. 43–46.
3. Spravochnik khimika. — M.-L.: Khimiya, 1964. — V. 3. — 1006 p.
4. Yarym-Agaev N.L. Solubility of Sodium Chloride in Diethylene Glycol and Its Aqueous Solutions / Yarym-Agaev N.L., Matvienko V.G. // Russian Journal of Applied Chemistry. — 1978. — V. 51. — N 10. — P. 2344–2345.

5. Matvienko V.G. The Sodium Chloride - Diethylene Glycol – Benzene System / Matvienko V.G., Yarym-Agaev N.L. // Russian Journal of Inorganic Chemistry. — 1979. — V. 24, N 5. — P. 1356–1359.

6. Matvienko V.G. Purification of Diethylene Glycol from Salts Dissolved with Benzene / Matvienko V.G., Yarym-Agaev N.L. // Gazovaya Prom. — 1988. — N 1. — P. 52–53.

7. Matvienko V.G. Solubility of Sodium Chloride in the Three-Component Solvent N-methylpyrrolidone – Diethylene Glycol – Water / Matvienko V.G., Yarym-Agaev N.L. and Cherkasskaya V.V. // Russian Journal of Inorganic Chemistry. — 1980. — V. 25, N 12. — P. 3382–3385.

Надійшла до редколегії 22.01.2013.

В.Г.Матвиенко ФАЗОВАЯ ДИАГРАММА СИСТЕМЫ ХЛОРИД НАТРИЯ - ВОДА - ДИЭТИЛЕНГЛИКОЛЬ - МЕТАНОЛ ПРИ ТЕМПЕРАТУРЕ 25 °С

Изучена растворимость хлорида натрия в двухкомпонентном растворителе диэтиленгликоль – метанол и трехкомпонентном растворителе диэтиленгликоль – вода – метанол при температуре 25 °С. Растворимость соли падает с увеличением концентрации диэтиленгликоля и метанола в трехкомпонентном растворителе.

Ключевые слова: растворимость, хлорид натрия, диэтиленгликоль, вода, метанол

В.Г.Матвиєнко ФАЗОВА ДІАГРАМА СИСТЕМИ ХЛОРИД НАТРІЮ - ВОДА - ДІЕТИЛЕНГЛІКОЛЬ - МЕТАНОЛ ПРИ ТЕМПЕРАТУРІ 25 °С

Вивчена розчинність хлориду натрію в двокомпонентному розчиннику диетилєнглїколь – метанол та трикомпонентному розчиннику диетилєнглїколь – вода – метанол при температурі 25 °С. Розчинність солі зменшується зі зростанням концентрації диетилєнглїколя та метанолу в трикомпонентному розчиннику.

Ключові слова: розчинність, хлорид натрію, діетилєнглїколь, вода, метанол.

Матвиенко Виктор Григорьевич – канд. хим. наук, доцент, профессор кафедры физической и органической химии ГВУЗ «Донецкий национальный технический университет», Донецк, Украина, e-mail: matvienko-1945@mail.ru.

УДК 541.124

М.А. Туровський, канд.хім.наук, доцент, **О.В. Ракша**, канд.хім.наук, доцент, **Ю.В. Берестнева** (Донецький національний університет), **Єресько О.Б.** (Інститут фізико-органічної хімії і вуглехімії ім. Л.М. Литвиненка НАН України м. Донецьк)

КАТАЛИТИЧНИЙ РОЗПАД ГІДРОПЕРОКСИДУ ІЗОПРОПІЛБЕНЗОЛУ В ПРИСУТНОСТІ 1,10-ФЕНАНТРОЛІНАТІВ Cu(II)

Досліджено кінетику каталітичного розпаду гідропероксиду ізопропілбензолу в присутності комплексів солей Cu(II) з 1,10-фенантроліном у суміші розчинників вода – етанол. Показано вплив аніону солі на каталітичну активність комплексу. Константа швидкості каталітичного розпаду гідропероксиду зростає в ряду аніонів: $SO_4^{2-} < Cl^- < CH_3COO^-$, розпад гідропероксиду в присутності нітрату Cu(II) в умовах експерименту не спостерігали.

Ключові слова: гідропероксид ізопропілбензолу, каталіз, 1,10-фенантролінати Cu(II)

Системи на основі гідропероксидів та сполук металів змінної валентності є поширеними ініціюючими системами для радикальних процесів окиснення органічних сполук [1]. Згідно відомої окисно-відновної схеми [2] розпад гідропероксидів під дією іонів металів змінної валентності відбувається в каталітичному циклі з почерговою участю відновленої та окисненої форми іона металу: