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Efficiency Estimation of the Single- and Multicomponent Anti-hydrate Reagents

Evgeny P. ZAPOROZHETS, Nikita A. SHOSTAK ✉
Kuban State Technological University, Krasnodar, Russia

Different types of technological and technical problems in the oil, gas and chemical industries are connected with the hydrate formation process and with the using of anti-hydrate chemicals. That is why, it is necessary to estimate thermobaric ranges within which reagents does not let hydrate to grow or is their dissociation. Also, to estimate anti-hydrate influence we need to determine the chemicals' anti-hydrate efficiency and chose the best one. They make the reagents consisting of several chemical components depending on the purpose of their application – for prevention of formation and (or) elimination of hydrates. It demands calculations of the optimum concentration and expenses and also the intensity (speed) of hydrates dissociation causing with the reagents.

The analytical method of the anti-hydrate chemical reagents efficiency determination containing one or several components from different classes of chemical compounds – alcohols, salts, acids, compounds of nitrogen and oxygen – is presented in this paper. With its help it is possible to define decrease in temperature of hydrate formation from reagents influence, to count key parameters of reagents anti-hydrate efficiency depending on component compositions of hydrate gas and a phase condition of a hydrate-gas system, to select types of chemical components and their quantity in multicomponent reagents, i.e., to make new compounds. The method can be used for express assessment of anti-hydrate chemical reagents efficiency on criteria sign for practical application in oil, gas and processing industry.

Key words: absorption; anti-hydrate reagent; gas-water system; hydrate; hydrate formation; concentration of reagent; crystallization temperature

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Introduction. The prevention of technogenic hydrates formation and elimination and also gas production from natural hydrates are connected with the use of anti-hydrate chemical reagents (further – reagents). Due to a variety of the reagents differing as on chemicals classes (for example, solutions of alcohols, salts, alkalis and acids) and on their mixes, there is a problem of their choice depending on: efficiency, concentration (in solutions), mutually compatibility, compatibility with the contacting environments (hydrocarbons and the components accompanying them, for example, H_2S, CO_2, the mineralized reservoir waters).

For the solution of this problem calculations are required such as:

- chemicals' anti-hydrate efficiency;
- optimum concentration and expenses of reagents depending on the purpose of their application;
- anti-hydrate influences of the reagents consisting of several chemical components and drawing up their compounds;
- effects of reagents on intensity of hydrates dissociation.

The analytical method of determination of efficiency of the reagents containing one or several components from classes of chemical compounds – alcohols, salts, acids, compounds of nitrogen and oxygen is developed for the solution of these tasks. It can be used for express assessment at use of reagents in oil, gas and processing industry. In the method the following assumptions and restrictions are made: water in an initial hydrate-forming system is in a vaporous, liquid and (or) firm phase; from impact of reagent on a system its equilibrium pressure of hydrate formation remains constant, only equilibrium temperature changes.

Equilibrium thermal conditions of hydrates formation and existence at the reagents influence. The reagent entered into a hydrate-forming system absorbs water component from its vaporous, liquid and (or) firm phases. As a result the new system consisting of a gas-vapor phase with the reduced maintenance of the water component and reagent diluted with water from initial concentration of X to concentration X_r is formed:

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$$X_r = \frac{Xm}{m + m_w}, \quad (1)$$

where m is amount of reagent with initial concentration of X, kg; m_w – total amount of the water absorbed by reagent, kg.

In case of prevention of hydrates formation the amount of the water absorbed by reagent can be found:

$$m_w = m_{w_l} + V(\Omega_1 - \Omega_2), \quad (2)$$

where m_{w_l} – the mass of water in liquid and (or) firm phases in an initial system, kg; V – amount of gas in a system, m^3; Ω_1 and Ω_2 – content (kg/m^3) of water vapors in gas with a pressure of P_h, Pa, and, respectively, at temperatures of T_0 and $T_{h.n}$, K. Quantities Ω_1 and Ω_2 can be determined using the corresponding graphic dependences or the equations of equilibrium moisture content in gases [14].

The amount of the water absorbed by reagent from the dissociating hydrate (at its decomposition) calculates with a following equation:

$$m_w = m_h \omega, \quad (3)$$

where m_h – hydrate mass (its content in a system), kg; ω – water content in hydrate.

Exact values of quantity ω are determined by a technique [2] depending on types of hydrates, component composition of gases-hydrate-forming, hydrate numbers, molar masses and density. As these calculations are difficult, for simplification we accept $\omega \approx 0.9$. It is acceptable for engineering calculations with accuracy of 5 %.

In a new system because of absorption by water reagent the equilibrium temperature of hydrate formation decreases from an initial system T_h towards lower temperature in a new system $T_{h.n}$ by ΔT (Fig.1).

As the baric conditions in the initial and the new system are identical (P_h = const), the amount of decrease in equilibrium temperature of hydrate formation depends only on reagent concentration: $\Delta T = f(X_r)$.

In both systems processes of hydrate formation are identical – crystalline hydrates are formed of molecules of the gases adsorbed by ice alike associates of water molecules [3]. Then processes of formation of such associates in crystalline hydrates of initial and new systems are similar to processes of pure water crystallization at a temperature T_w and waters in reagent solution with lower temperature T_r. Proceeding from this similarity, amounts of decrease in temperatures are equal:

$$T_h - T'_{h.n} \approx T_w - T_r = \Delta T. \quad (4)$$

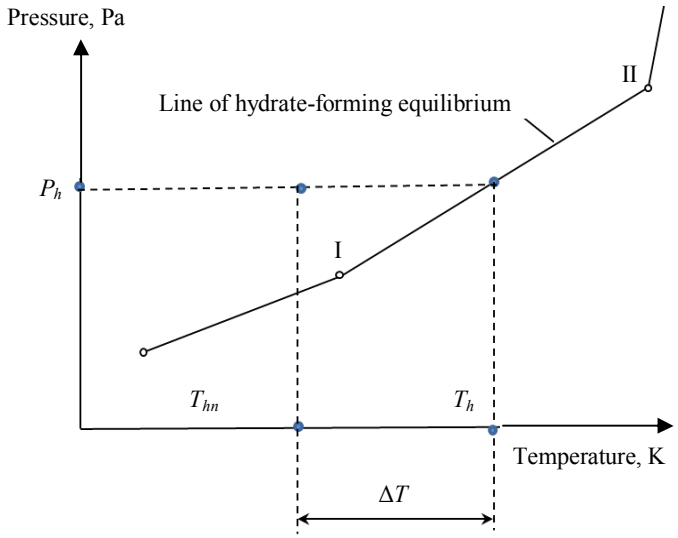


Fig.1. Change of the hydrates formation thermal conditions

Water crystallization temperature T_w is not a constant. It depends on pressure P_h and the type of gas over water:

$$T_w = 273.16 - \frac{M_a}{M_g}\left(0.0731 P_{hw} + 0.0002 P_{hw}^2\right), \quad (5)$$

where M_a и M_g – molar masses of the air and gas-hydrate-former.

Calculation of the amount T_w to within 0.01 K on the equation (5) can be carried out in the range of pressure P_h = = 0.00061173 – 212.9 MPa.

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The crystallization temperature the reagent water solutions consisting of one or several chemical components calculate by a following equation:

$$T_r = \sum_{i=1}^{m} X_{r_i} T_{r_i}, \quad (6)$$

where X_{r_i} – mass concentration of an *i*-component; T_{r_i} – water crystallization temperature in the diluted reagent containing *i*-component.

The exact value of T_{r_i} can be defined by reference books [7-10, 15] or using this equation:

$$T_{r_i} = \alpha X_{r_i}^2 + \beta X_{r_i} + \gamma, \quad (7)$$

where α, β, γ – coefficients for some chemical components with concentration X_{r_i} in the ranges specified in Table 1.

Table 1

Coefficients for chemical components

Reagent name	Reagent concentration in a solution X_{r_i}, kg/kg	Coefficients		
		α	β	γ
Alcohols				
Methanol	0.10-0.60	–138.93	–40.15	271.89
Ethanol	0.025-0.719	–10.40	–70.26	275.93
Propanol	0.08-0.65	28.83	–63.80	274.40
Ethylene glycol	0.02-0.663	–160.62	11.44	270.20
Diethylene glycol	0.02-0.62	–131.77	13.14	271.73
Triethylene glycol	0.02-0.50	–101.47	7.41	272.16
Propylene glycol	0.05-0.59	–153.29	16.51	269.72
Glycerin	0.050-0.667	–116.58	14.74	270.78
Salts				
Lithium chloride	0.05-0.25	–1130.70	19.79	270.55
Magnesium chloride	0.014-0.206	–840.22	16.46	271.84
Sodium chloride	0.015-0.224	–212.97	–45.24	272.86
Calcium chloride	0.059-0.284	–840.90	126.63	263.66
Calcium nitrate	0.02-0.35	–102.86	–16.29	272.86
Calcium permanganate	0.05-0.42	–295.6	48.35	269.16
Acids				
Nitric acid	0.02-0.33	–332.73	–14.39	271.75
Sulfuric acid	0.04-0.38	–618.46	50.86	269.68
Hydrochloric acid	0.012-0.239	–479.60	57.50	269.69
Acetic acid	0.065-0.555	–15.27	–31.92	273.29
Compounds of nitrogen				
Ammonia	0.02-0.33	–937.69	28.37	268.27
Monoethanol amine	0.10-0.50	–480.14	122.40	262.47
Diethanol amine	0.10-0.50	–153.57	30.64	269.65
Trietanolamine	0.10-0.60	–158.93	50.54	268.65
Compounds of oxygen				
Potassium hydroxide	0.02-0.32	–670.91	25.91	270.26
Sodium hydroxide	0.02-0.19	–498.06	–46.32	272.43
Hydrogen peroxide	0.05-0.50	–87.73	–65.31	274.14
Formaldehyde	0.015-0.250	–29.81	–57.01	273.12

The calculated values of decrease in temperatures ΔT (4) from influence of reagents water solutions are presented in the form of graphic dependences (Fig.2, 3).

In some reagents solutions the water crystallization temperature has no strictly fixed values. It is noted [9] temperatures of emergence of the first crystals and full hardening. The equation (7) is intended for calculation of the first crystals emergence temperature.

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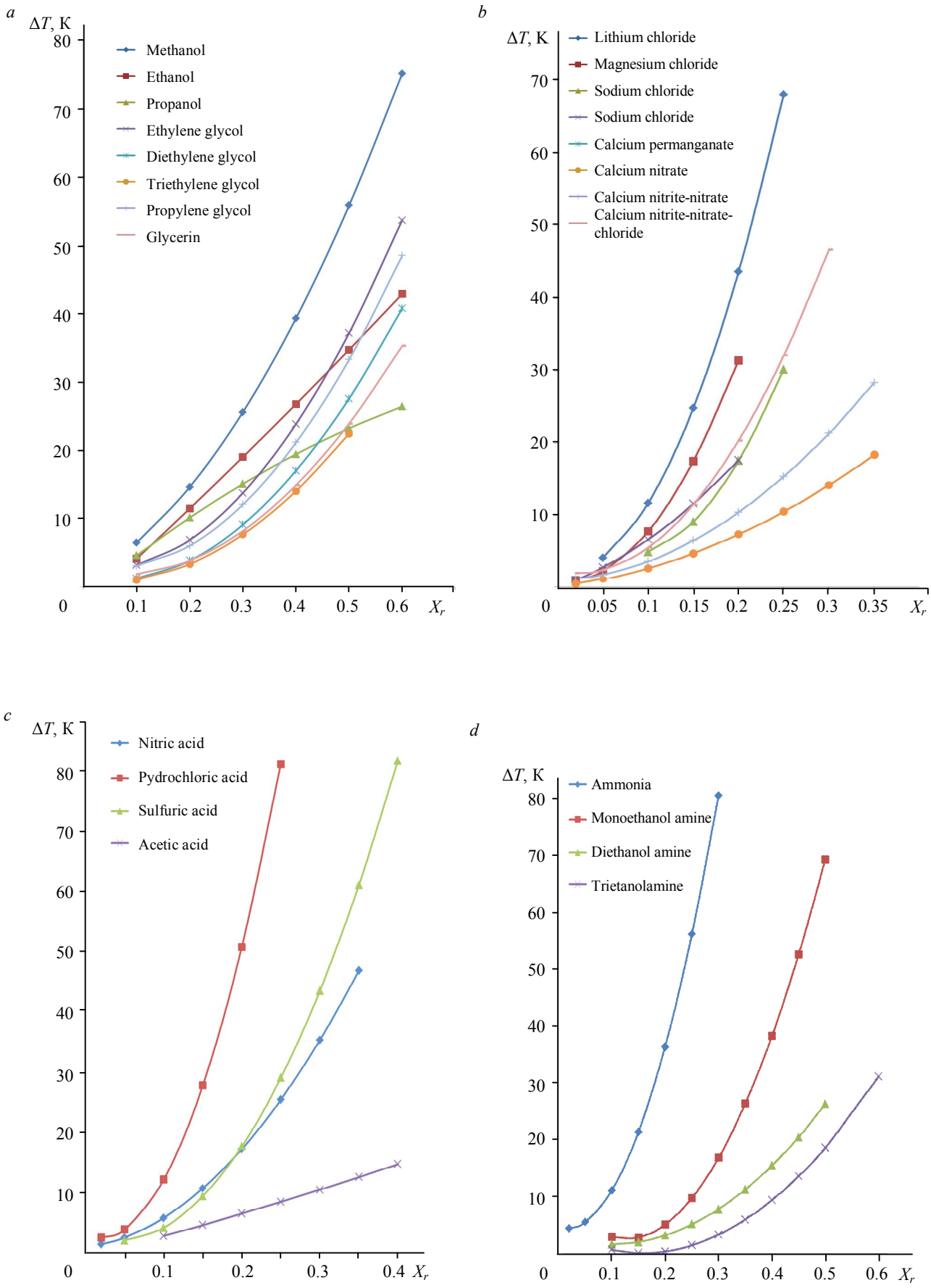


Fig.2. Decrease in temperature of hydrates formation ΔT from the water solutions influence consisting of alcohols (*a*), salts (*b*), acids (*c*), compounds of nitrogen (*d*) with concentration X_r

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The difference between these temperatures increases up to 5-7 °C with increase in reagent concentration X_{r_i} in the solution.

In the equation (4) T_h – the equilibrium temperature of hydrate formation in a system gas – water is determined by a technique [4]. For a system individual gas – water in the first range (from left to right) to a quadrupole point the I (Fig.1) temperature is calculated by a formula:

$$T_{i_1} = \left(\frac{P_1}{a}\right)^{\frac{1}{b}}, \quad (8)$$

where a, b – coefficients (Table 2).

In the second range between quadrupole points of I and II (Fig.1) it is possible to use the equation:

$$T_{i_2} = \frac{\ln\left(\frac{P_2}{c}\right)}{d}, \quad (9)$$

where $e = 2.718$ – basis of a natural logarithm; c, d – coefficients (Table 2).

The nature of a balance line change of a hydrate-former system multicomponent gas – water is identical to balance lines of systems individual gases – water, and its current coordinates submit to the equation:

$$T_h = \sum_{i=1}^{n} Y_i T_{i_1} + \sum_{i=1}^{n} Y_i T_{i_2}, \quad (10)$$

where Y_i – molar share of a hydrate-former component; n – number of a hydrate-former component.

Determination of the reagents efficiency. The anti-hydrate efficiency of reagents is estimated by criterion for:

• single-component reagent

$$\eta_{r_i} = \frac{T_w - T_{r_i}}{T_h}; \quad (11)$$

• multicomponent reagent

$$\eta_r = \frac{T_w - T_r}{T_h}. \quad (12)$$

If $\eta_r = 0$ – there is no reagent in a system; $\eta_r > 0$ – there is reagent in a system, and the higher quantity corresponds to higher efficiency.

For example, the criterion of the chemical reagent efficiency consisting of water solution of one anti-hydrate reagent – the methanol having mass concentration of $X_1 = 0.6$ in a hydrate-forming system water – methane:

• in the 1st range of a phase state (Fig.1) at $P_h = 2.3 \cdot 10^6$ Pa equal to

$$\eta_r = \frac{T_w - T_{r_i}}{T_h} = \frac{273 - 198}{272} = 0.28;$$

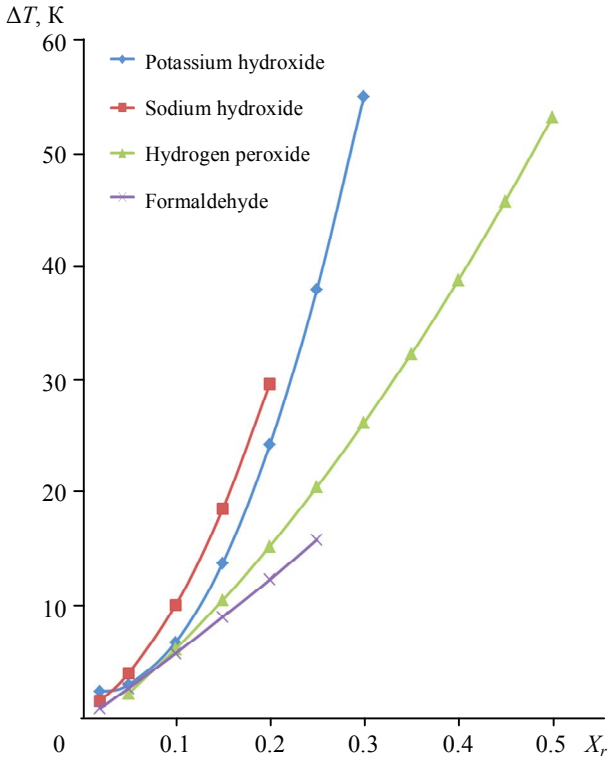


Рис.3. Decrease in temperature of hydrates formation ΔT from the water solutions influence consisting of compounds of oxygen with concentration X_r

Table 2

Numerical values of the coefficients *a*, *b*, *c* и *d*

Gas	*a*	*b*	*c*	*d*
Methane	$4 \cdot 10^{-17}$	9.3415	10^{-7}	0.1128
Ethane	$3 \cdot 10^{-26}$	12.8130	$6 \cdot 10^{-10}$	0.1256
Propane	$2 \cdot 10^{-28}$	13.4980	$8 \cdot 10^{-10}$	0.1281
i-butane	$2 \cdot 10^{-32}$	15.0760	$8 \cdot 10^{-20}$	0.2052
Carbon dioxide	10^{-21}	11.0890	$3 \cdot 10^{-20}$	0.2078
Hydrogen sulfide	10^{-23}	11.4690	$2 \cdot 10^{-8}$	0.1064
Nitrogen	$2 \cdot 10^{-12}$	7.7171	10^{-5}	0.1015
Argon	$8 \cdot 10^{-12}$	7.4047	10^{-7}	0.1168
Krypton	$5 \cdot 10^{-26}$	12.8900	$2 \cdot 10^{-6}$	0.0990
Xenon	$2 \cdot 10^{-24}$	11.8380	$3 \cdot 10^{-7}$	0.0993

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• in the 2nd range of a phase state (Fig.1) at $P_h = 4.0 \cdot 10^6$ Pa equal to

$$\eta_r = \frac{T_w - T_{r_i}}{T_h} = \frac{272 - 198}{278} = 0.27 .$$

The criterion of inhibitor water solution efficiency with mass concentration of $X = 0.6$, consisting of two anti-hydrate reagents – methanol ($X_1 = 0.4$) and ammonia ($X_2 = 0.2$):

• in the 1st range of a phase state (Fig.1) at $P_h = 2.3 \cdot 10^6$ Pa equal to

$$\eta_r = \frac{T_w - T_{r_i}}{T_h} = \frac{273 - 140}{272} = 0.49;$$

• in the 2nd range of a phase state (Fig.1) at $P_h = 4.0 \cdot 10^6$ Pa equal to

$$\eta_r = \frac{T_w - T_{r_i}}{T_h} = \frac{272 - 140}{278} = 0.47 .$$

As a result, the efficiency of single-component reagent – 60 % of methanol water solution – is approximately identical in both ranges of a phase condition to system water – methane. The efficiency of the two-component reagent consisting of methanol (40 %) and ammonia (20 %) water solution exceeds by 1.75 times the efficiency of a single-component in both ranges phase condition of system water – methane.

It is possible to use the schedules in Fig.2, 3 for determination of individual reagents efficiency. Also it is possible to make effective multicomponent reagents selecting individual reagents and using (6) and (12). However it is necessary to consider chemical interference of reagents of various classes, for example, a negative combination of salts and acids.

Verification. A compliance of the developed method of reagents efficiency determination was established from comparison of ΔT with the one known experimental. The results of comparison are presented in Table 3.

Table 3

Theoretical and experimental values of ΔT

Anti-hydrate reagent	Water solution concentration, mas %	ΔT, K		Reference	Divergence, %
		Theoretical	Experimental		
Methanol (CH_3OH)	0.10	5.7	5.5	[11]	3.6
	0.27	22.0	21.0	[11]	4.7
	0.60	57.9	60.0	[6]	3.6
Ethylene glycol [$C_2H_4(OH)_2$]	0.10	2.9	3.0	[12]	3.4
	0.40	19.7	19.0	[6]	3.6
	0.60	43.7	42.0	[1]	4.0
Triethylene glycol [$C_6H_{12}O_2(OH)_2$]	0.20	3.6	3.5	[12]	2.8
	0.60	37.3	36.0	[1]	3.5
Lithium chloride (LiCl)	0.15	23.3	23.0	[1]	1.3
Magnesium chloride ($MgCl_2$)	0.11	8.7	8.5	[13]	2.3
	0.15	20.1	21.0	[1]	5.0
Calcium chloride ($CaCl_2$)	0.10	5.3	5.5	[5]	4.1
	0.20	17.4	17.0	[1]	2.3

Let's compare different ΔT from reagents influence at various concentrations. It is obvious that the divergence of ΔT values does not exceed 5 % that is acceptable for engineering purposes.

Conclusion. By means of the developed method of anti-hydrate chemical reagents efficiency determination it is possible:

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• to define decrease in temperature of hydrate formation from reagents influence;

• to calculate key parameters of reagents anti-hydrate efficiency depending on component compositions of gas-hydrate-former and a phase condition of a hydrate-forming system;

• to select types of chemical components and their quantity in multicomponent reagents, i.e. to make their new compounds.

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***Authors*: Evgeny P. Zaporozhets,** *Doctor of Engineering Sciences*, *Professor*, *zep1945@inbox.ru* (*Kuban State Technological University, Krasnodar, Russia*), **Nikita A. Shostak,** *Candidate of Engineering Sciences*, *Associate Professor*, *nikeith@mail.ru* (*Kuban State Technological University, Krasnodar, Russia*).

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