ABOUT RADIOLITICHESKY NATURE OF ALKANES IN SALT ROCKS

Makarov V.P. (The Russian State Geological Prospecting University)
litolog@msgpa.ru; ph.: (495) 433 - 56 - 77, add:. 11 – 38

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Studying of conditions of migration of hydrocarbonic gases naturally allows to solve questions of their education more reliably. It is promoted by use of the new methods of interpretation of concentration of these gases in rocks and minerals, raising reliability and revealing new, unknown before property and a condition of migration of these gases. With that end in view were investigated the materials published in [5]. In it are described alkanes from inclusions in silvinate KCl, halite NaCl, carnallite $MgCl•KCl•6H_2O$ on a deposit Verhnekamsky and objects of republic Komi (Seregovsky, Kochmes) [5]. On [5] «some part of gases has entered a hydrochloric deposit from containing breeds: oil fluids under the influence of hydrochloric weight, deformation and owing to a geothermal gradient have got on a time and cracks into the migrating buried solutions and together with them or was separately preserved in галите in the form of inclusions.» [5, p. 134]. A hypothesis interesting, but arguments in its advantage it is not resulted.

We study behavior CH_4 (C1), C_2H_6, (C2) and C_3H_8 (C3), using calculated weight and мольные (micromoles - μM, designated through m) concentration of gases. The term «micromoles» is accepted because concentration of gases is expressed in weight units - of mkg. For the analysis of joint behavior CH_4 and C_2H_6 the diagrammes resulted on fig. 1 and 2 are constructed. On fig. 3 distribution of other pair gases-CH_4 and C_3H_8 is shown.

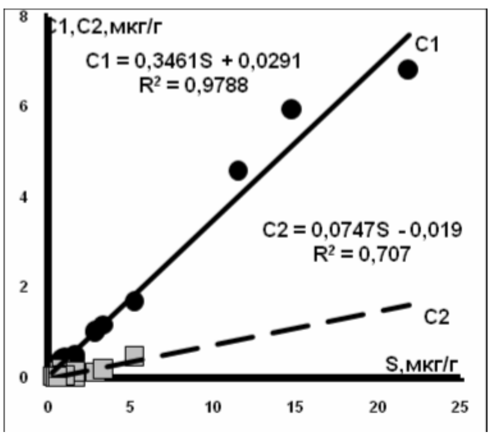

Fig.1. Distribution of weight cconcentrations of gases

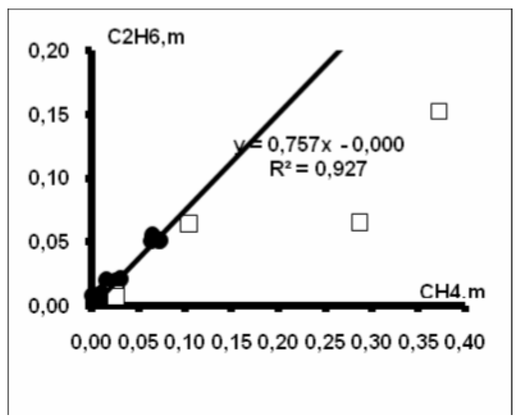

Fig.2. Distribution mole concentrations of gases

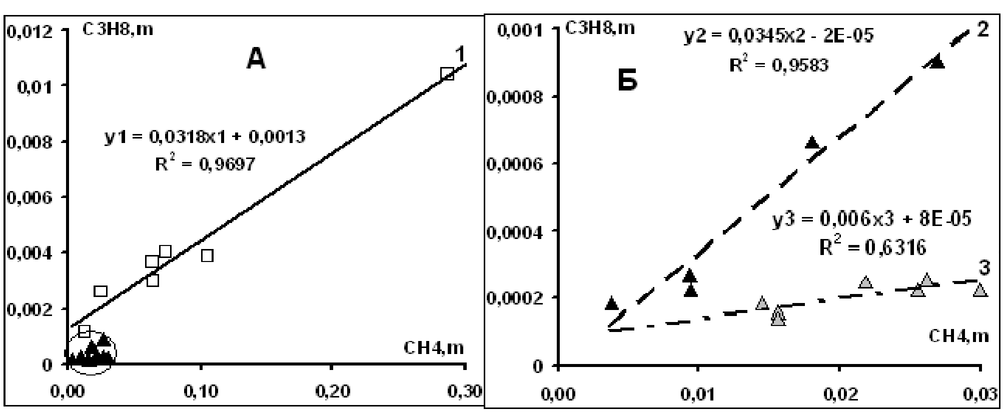

Fig.3. Distribution micromole concentration of methane and the propane. A – total distribution. B- the distribution, allocated with a circle on fig. 3A

Following features of behaviour of gases come to light.

1. In co-ordinates (S, m) (fig. 1) tests of both gases well lay down on straight lines m (C1) = 0.3461S + 0.0291 (R^2 = 0.9414); m (C_2) = 0.017S – 0.0022 (R^2 = 0.9352). Here S - total quantity of hydrocarbons. Thus, with growth of quantity of gas concentration of methane grows. It is clear, as methane is a bearing component. Important that methane tests lay down on a uniform straight line. The same it is possible to tell about этан. As a whole it is possible to speak about a constancy of relations of concentration of gases.

2. On diagrammes мольных concentration (fig. 2) tests on objects are not divided also the overwhelming majority of tests lays down on a straight line m (C_2H_6) = 0.7572 m (CH_4) – 0.0003 (R^2 = 0.9271). It speaks about a generality of properties of the gases selected from different and enough removed from each other objects.

3. On the diagrammes of relative concentration (volume percent) three samples which are not adhered to concrete objects, with return parities between relative concentrations of gas are allocated. A principal cause of similar dependence - isolation of systems from percentage parities. Similar dependence is mentioned in [5], but distributions are put in a basis on objects that has appeared not much informated. These samples are allocated and in coordinates micromoles concentration, but they are in limits fluctuations of concentration of a general totality of tests.

4. Distribution C3 against distributions C1 reveals more difficult picture.

Three samples characterized and various averages are accurately allocated concentration of gases. These samples are not dated for concrete objects.

For an explanation of properties of diagrammes representations about mixture are used. The general theory of mixture is developed and described in job [3], its continuation - [4]. According to it in the elementary case gases are a product of mixture of gases from two sources with a constant of relations of concentration of gases in everyone. In that case for binary system from concentration X and Y some components X and Y and with properties $X_1 < X < X_2$ and $Y_1 < Y < Y_2$ share M_X of component X on this interval is equal $M_X = (X - X_1) / (X_2 - X_1)$, for the second components - $M_Y = (Y - Y_1) / (Y_2 - Y_1)$. Believing $M_X = M_Y$, we come to equation $Y = AX + B$, where $A = (Y_2 - Y_1) / (X_2 - X_1)$, and $B_1 = [(Y_2 - Y_1) / (X_2 - X_1)]\, X_1 + Y_1$.

In system S1-S3 (fig. 3A) the free member of the equation is not equal in sample to zero. Therefore it is possible to speak about mixture of components from two sources. To define their structure it is not obviously possible yet. In samples 2 and 3 (fig. 3Б) free members are close to zero, therefore it is possible to speak about one source for each sample and reflexion of relations of components concentration to their relations in sources, then m (CH_4)$_{12}$/m (C_3H_8)$_{12} \approx$ 0,0345 and m (CH_4)$_{13}$/m (C_3H_8)$_{13} \approx$ 0,006.

In system C_1-C_2 (fig. 1) a free member of the equation ≈ 0; it is possible at m (CH_4)$_1 \approx m$ (C_2H_6)$_1 \approx 0$ and $X_1 \approx Y_1$. Hence m (CH_4)/m (C_2H_6) ≈ m (CH_4)$_1$/m (C_2H_6)$_1$, i.e. the relation micromoles concentration constantly for all tests and to equally initial parity. From here follows, that gases come from one source.

In the elementary case two kinds of sources are possible. In the first case formation of gases occurs on the equation hydrogenization propane $C_3H_8 + H_2 = CH_4 + C_2H_6$. Here on one molecule of methane one molecule ethane is necessary that mismatches the received results.

In the second case initial parities are defined by disintegration of a molecule of methane on reaction $2CH_4 \leftrightarrows C_2H_6 + H_2$, as the most probable; in the course of disintegration CH_4 in the conditions of balance of reaction on two molecules CH_4 one molecule C_2H_6 and theoretically their relation $\alpha = m\,(C_2H_6)/m\,(CH_4) = 0.5$ is necessary. This value to close received relation of concentration of gases m (C_2H_6)/m (CH_4) = 076.

The probable reason of difference - influence of diffusion on migration of gases to a preservation place. Really, methane as easier gas, will faster leave system, enriching system by ethane. The phenomenon is described on the basis of the theory of division of gases at movement of a stream of a mix of gases in a filtrational column [6] by means of diffusion. The comparison standard is «the theoretical plate» [2, 6] (N = 1), i.e. distance at which passage degree division of gases is described by the relation диффузионных factors $\alpha_D = D_i/D_j$; in this case $\alpha_D = D\,(CH_4)/D\,(C_2H_6)$. At movement through N «theoretical plates» division is equal $\alpha_D{}^N$. The general division is equal $\alpha \bullet \alpha_D{}^N = 0.5\, D\,(CH_4) / D\,(C_2H_6)$. In water (V.A. Sokolov, 1971) diffusion is characterised by values: D (CH_4) = 1.49x10^{-5} sm^2/sec, D (C_2H_6) =1.2h10^{-5} sm^2/sec, whence $\alpha_D = D\,(CH_4)/D\,(C_2H_6) = 1.24$. Under the theory of gas diffusion $\alpha_{Dg} \approx \sqrt{}\,(M_{C2H6}/M_{CH4})$ [1, 8], where M_i - molecular weight of components i, ($_g$) - gas; then $\alpha_{Dg} \approx \sqrt{}$ 30/16 =1.34. According to H. Schutze,

M. Mohnke (1981) in free nitrogen (the basic component of air) at 20°C D (CH_4) $_N$ = 0.223 $^{sm2/with}$ and D (C_2H_6) $_N$ = 0.151 sm^2/sec, therefore $\alpha_{DN} = D(CH_4)_N / D(C_2H_6)_N = 1.48$. The best result is received for diffusion in air: $\alpha \bullet \alpha_{DN} = 0.5 \times 1.48 = 0.74$ that is very close to the real relation of concentration of gases.

The analysis of this reaction allows specifying the formation mechanism этана. Gas education by probably three ways: 1. Thermodynamic decomposition. Methane is thermally steady, and under normal conditions its temperature decomposition goes at 500°C [7] and especially at 1000«æ. Decomposition reaction is chain and in the elementary case passes in two stages: $\bullet CH_3 + CH_4 \rightarrow C_2H_6 + H_2$ and¡ + CH_4 $\rightarrow H_2 + {}^{\bullet}CH_3$ (through ($^{\bullet}$) the activated member) is noted. The general reaction looks like $2CH_4 \leftrightarrows C_2H_6 + H_2$ [7]. 2. Biological decomposition; it too is not possible because gases are in conditions, ability to live of organisms in which is limited. 3. All gases are in the breeds essentially enriched калием, so also its radioactive isotope ^{40}K, accompanied radiation β - particles (электронов with energy in 0.54 MeV). Energy of rupture of communication C-H is equal in methane 416.3 *кJ/M* (Novikov G.I., 1988), or 4.31 eV (it is essential less energy of electron). Rupture of communication C-H on methyl – anion and a proton, i.e. on reaction $CH_4 \rightarrow CH_3^+ + H^+$, cannot spontaneously be carried out, as only in a gas phase on it it is required 1305 *kJ/M*. The raised density high-energy radiogene electrons compensates a lack of energy and causes radiolysis CH_4: there is an ionization of a molecule of methane on reaction $CH_4 \rightarrow CH_3^+ + H^+$ because, getting to hydrogen, electrone, breaks off pair With - H, the allocated proton will be neutralized on reaction $H^+ + e^- = H$ (134 кJ/M (1,39 eV)); for the bill of reaction $H + H = H_2$ (217.9 kJ/M (2.26 eV)) hydrogen is deduced from system. Этан it is formed by association methyl groups $CH_3^+ + CH_3^+ = C_2H_6$. As a result of these private processes reaction $2CH_4 \leftrightarrows C_2H_6 + H_2$ also proceed.

Thus, with the account of formation of gases in sources it is had: $m(CH_4)_{11}: m(C_2H_4)_{11}: m(C_3H_8)_{11} \approx 1: 0.5: 0.035$ and $m(CH_4)_{12}: m(C_2H_4)_{12}: m(C_3H_8)_{12} \approx 1: 0.5: 0{,}006$. The nature of these relations is not absolutely clear. By results of studying of oil deposits in gases of a parity of concentration этана and the propane are commensurable at essential prevalence of methane. In the given conditions of the relation of gases it is separated 10 times and more. Similar parities are observed at oil pyrolysis at which considerable distinction of concentration C_2 and C_3 is marked; so on [7] at pyrolysis are formed CH_4 (40-45 %), C_2H_6 (6-10 %), C_3H_8 (1-2 %), but are not enough these parities for the description of the observable phenomena. The resulted material shows, that the studied gases it is impossible to name naphthogened gases.

The carried out researches show, that in small concentration alkanes in salt rocks can be received by radiolysis the methane formed in a wide range of physical and chemical conditions.

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