Condensed Matter Physics 2006, Vol. 9, No 1(45), pp. 109–114

CONDENSED MATTER PHYSICS

Phase transitions in the coal-water-methane system

A.D.Alexeev, E.V.Ulyanova, N.A.Kalugina, S.E.Degtyar

Institute for Physics of Mining Processes,
72 R.Luxemburg Str., 83114 Donetsk, Ukraine

Received July 13, 2005

Low temperature phase transitions in water and methane occurring in fossil coals were studied experimentally using Nuclear Magnetic Resonance (NMR) techniques. Contributions of constituent fluids into narrow line of ^{1}H NMR wide line spectrum were analyzed.

Key words: *fossil coals, water, methane, nuclear magnetic resonance*

PACS: *62.20.Dc, 76.60.-k*

Sudden coal and gas outbursts as well as explosions of methane and air mixtures may be compared to permanent natural disasters taking lives of miners and inflicting tremendous losses. All the aspects of mining safety and methane combustive utilization are therefore very urgent.

Coal is a porous substance. The pressure of overlying rocks and the action of metamorphic gases produce a very specific dispersed porous and fractured structure of fossil coals with multi-level size hierarchy ranging over seven orders of magnitude, from components comparable with molecular sizes of methane or water to cracks with openings up to several millimeters. Coal formation in virgin condition is a complicated natural system existing in the thermodynamic equilibrium and consisting of coal mass, gases (predominantly methane in Donets Basin deposits), and water. Methane and water are here not merely inert components of the system but active agents in a coal seam exerting substantial or even crucial effect on its behavior. One of the main difficulties in studying this system consists in its being a multiphase system constitutive of a solid, a liquid, and a gas. Thermodynamic equilibrium in such systems is quite poorly investigated.

Most attention was focused on solid-water systems [1–7] due to unique properties of water among other liquids (in particular, polymeric nature of molecular structure, cooperative network of hydrogen bonds, etc.). One of the key issues studied was the effect of the solid surface on the behavior of the boundary phase.

A great contribution to understanding the behavior of adsorbed molecules was made by E.K. Rideal [8], J. De Boer [9], and his followers [10]. J. De Boer [9] considered two extreme cases of monomolecular adsorbed layer, local and non-local adsorption. In the case of local adsorption the adsorbed molecules are strongly bonded to adsorption sites, they have no translational degrees of freedom and cannot oscillate either perpendicular or parallel to the surface. Local adsorption does not imply, however, a complete immobility of adsorbed molecules. The mere existence of adsorption equilibrium between the gas and the adsorbed layer indicates the molecular movements in both perpendicular and parallel directions to the solid surface.

Migration of adsorbed molecules along the surface occurs by jumps from one adsorption site to another. A site residence time τ_c is related to the jump movement activation energy V_0 using Frenkel equation [11]

$$\tau_c = \tau_0 e^{V_0/RT}, \tag{1}$$

where τ_0 is a constant proportional to the oscillation period of the adsorbed molecule, V_0 is a difference between adsorption heat values at the active surface site and between two sites. Consequently, V_0 is much less than adsorption heat Q. At physical adsorption on hydrophilic (polar) surfaces, the V_0 value is usually from one third to half of Q value which is about 40 kJ/mol or higher [12]. These values are much higher than the energy of thermal motion $RT \sim 2.4$ kJ/mol at $T = 290$

to 295 K. As a result, the residence time τ_c is higher than the oscillation period $\tau_0 \sim 10^{-13}s$ but certainly less than the adsorption time τ. At a physical adsorption on polar adsorbents, the τ/τ_c ratio is equal to about 5,000 [9,12].

When V_0 becomes less than energy of thermal motion, the adsorbed molecules begin to move freely along the surface in both directions. Adsorption layers consisting of such molecules show the behavior similar to a two-dimensional gas. In this case, adsorption is described by non-local model. According to De Boer, the adsorbed molecules retain all the rotational and two translational degrees of freedom at the perfect non-local adsorption.

Fossil coals are hydrophobic substances. Almost all hydrophobic adsorbents have hydrophilic adsorption sites (as a rule, energetically different) on their surfaces [13,14]. However, definite data on the adsorbed water molecules on hydrophobic adsorbents with various concentrations and polarity of hydrophilic sites are very rare in the literature. This is due to experimental quantitative determination difficulties of hydrophilic species on the surfaces of hydrophobic adsorbents.

In coals, adsorption sites can be formed by various π-bonds, single electron pairs, small cations, oxygen-containing groups, radicals such as CH, CH_2, CH_3, etc. Just these sites primarily adsorb water molecules.

As for methane, its sorption in coal can hardly be interpreted as simply condensation from gas phase onto the pore surface. Firstly, pores in coals are bulk filled and hence the pores volume rather than the pore surface is the sorption parameter. Secondly, methane was incorporated into the coal mass due to a joint action of gas pressure and mechanical loads at coalification during metamorphism without forming any chemical bonds [15,16]. Since such incorporated methane molecules are contained in the cavities of the same size, the concept of solid-gas interface, as well as the concept of adsorption layer, are unimportant. Such an incorporated methane was referred to as “methane in solid solution” [17,18]. It accounts for about 80% of all the absorbed methane.

The use of classical models (developed for getters) to estimate the methane amount and behavior in coals is a common error by many researchers. In references [19–21] the authors estimate the methane behavior in coals based on the assumption that the methane sorption occurs on the pore surface. However, a conventional determination of methane amount and condition using sorption isotherms introduces a significant uncertainty into the results obtained. In particular, the applied approaches fail to explain why coking (“K”) and fat (“J”) coals are capable of containing as much methane as up to 35 m^3/ton while possessing smallest (as compared to other coal types) specific porosity.

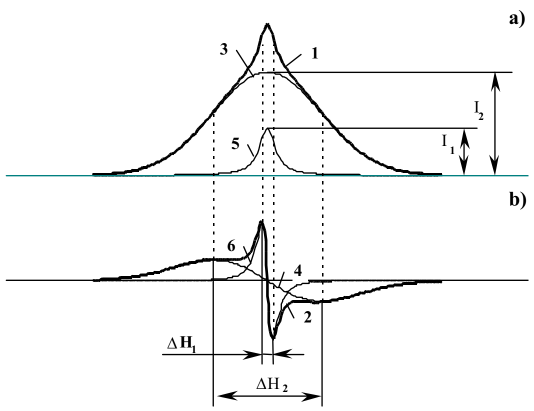

Figure 1. NMR absorption line of a solid-fluid system (a) and derivative of this line (b): I_1 and I_2 are intensities; ΔH_1 and ΔH_2 are linewidths for narrow and wide components of the spectrum line, respectively.

Over a long time, coals were studied using laboratory techniques, which had caused coal destruction, with subsequent extraction of soluble products. The integrity of coal structure was thereby broken at all levels, from micro to macro ones. Such an approach precluded the study of the coal interaction with fluids. A substantial advancement in solving the global coal problems became possible only after the implementation of nondestructive physical techniques.

NMR techniques are among those being most successfully applied to the study of fluids in various heterogeneous systems [22–24]. NMR wide line technique is especially useful in studying the effects of fluids in coals.

We have used ^{1}H NMR wide line spectrometer with the autodyne circuit in order to enhance the sensitivity and measurement accuracy. Raw experimental NMR absorption spectra in the coal-water, coal-methane, or coal-water-methane systems, see figure 1(a), were numerically differentiated into final derivative spectra, see figure 1(b), consisting of two superimposed lines, namely, wide and narrow lines [25]. The wide line originates from the hydrogen incorporated into the coal structure while the narrow line is caused by the hydrogen of water and methane. Linewidth values ΔH are determined by ^{1}H nuclei mobility in the system. Wide and narrow line widths ΔH_1 and ΔH_2 in NMR spectra differ by about an order of magnitude [26,27]. In particular, the resonance line width of the adsorbed water and methane ΔH_1 varies from 0.079 to 119.4 A/m depending on nuclei mobility while the linewidth ΔH_2 of coal organics varies from 437.7 to 517.3 A/m depending on the coal metamorphism extent.

NMR spectrum line intensities I_1 and I_2 depend on both numbers of resonating nuclei and their mobility. The numbers of resonating nuclei being equal, the intensity values I will be different if the mobility values are different [28].

NMR wide-line low-temperature technique made it possible to estimate the effects of porosity and surface active centers on the activation energy V_0 and correlation time τ_c much simpler than, for instance, the measurements of entropy [29], frequency dependence of dielectric losses, or nuclear quadrupole resonance frequency (NQR) [30] in a wide temperature range.

The present studies were carried out, taking into consideration a complicated nature of the coal-water-methane three-phase system, in three steps. First, artificially prepared moistened coals, then methane saturated coals, and finally the complete coal-water-methane system were studied.

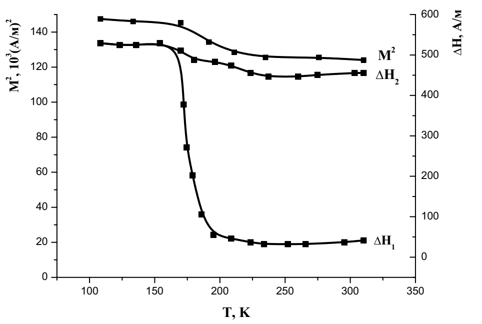

Figure 2. Temperature dependence of NMR line widths (ΔH_1,ΔH_2) and second-order moments (M^2) for coal class A (anthracite coal with $V_\mathrm{G} = 5\%$).

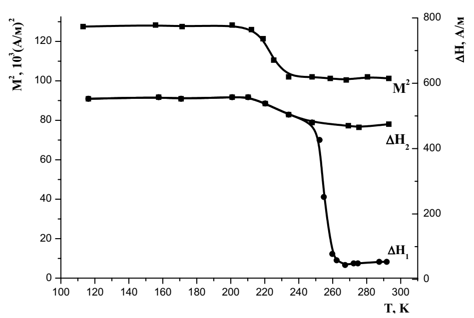

Figure 3. Temperature dependence of NMR line widths (ΔH_1,ΔH_2) and second-order moments (M^2) for coal class K (coking coal with $V_\mathrm{G} = 26\%$).

Experimental data on low temperature NMR line spreading for adsorbed water were processed using approximate theory of Blombergen, Purcell, and Pound [31] to obtain correlation time values τ_c. Correlation time is a characteristic of the mobility of water molecules. According to J. Uo and E. Fedin [32], correlation time τ_c is related to the linewidth ΔH at given temperature and to the linewidth ΔH_0 at the temperature of rigid lattice by the equation

$$(\Delta H)^2 = \frac{2(\Delta H_0)^2}{\pi} \arctan \frac{\alpha\gamma\Delta H}{\omega_c}, \tag{2}$$

where $\alpha = 8\ln 2$; $\gamma = 4258\ \mathrm{s}^{-1}\mathrm{Oe}^{-1}$, and $\omega_\mathrm{c} = 2\pi/\tau_\mathrm{c}$ is a reorientation frequency.

The correlation time τ_c can be derived from equation (2) as:

$$\tau_c = \frac{2\pi}{\alpha\gamma\Delta H} \tan\left[\frac{\pi}{2}\left(\frac{\Delta H}{\Delta H_0}\right)^2\right]. \tag{3}$$

Low temperature behavior of NMR line widths and second-order moments for several coal types is presented in figures 2 and 3.

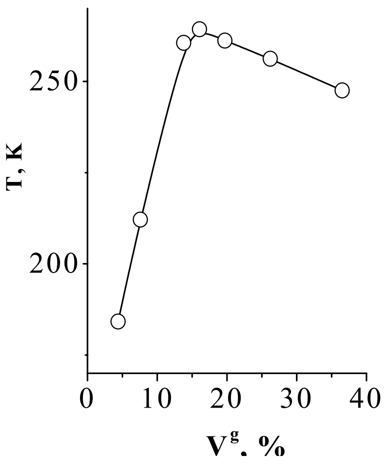

Figure 4. Temperature dependence of adsorbed water liquid-to-solid phase transition for various coal types (volatile content from 5 to 40).

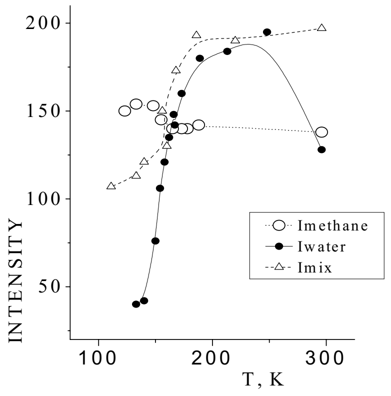

Figure 5. Temperature dependencies of ^{1}H NMR lines for constituent water, methane, and their mixture.

Low temperature NMR spectra of coals have a distinctive feature of the liquid to crystal-like phase transition temperature in adsorbed water, see figure 4. The transition appears extended in a small temperature range rather than abrupt jump, since molecules more loosely bonded to solid surface freeze first. On the contrary, two or three monolayers closest to the surface remain mobile even at very low temperatures where rotational freedom becomes frozen, as it was shown by A. Bloch [33]. This transition begins at 183 K in anthracites, 158 K in coals with $V_G = 26\%$, or 233 K in coals with $V_G = 39\%$.

In accordance with Uo-Fedin equation [32], the magnitude of the potential barrier V_0 hindering the molecular motion can be evaluated using a simple relation

$$V_0 = 155.4T(\mathrm{K})\mathrm{J/mole}, \tag{4}$$

where T is the phase transition temperature.

The highest measured value V_0 was 40.74 kJ/mole for coals with highest volatile content $V_G =$ 39%. Respectively, the lowest measured value V_0 was 28.43 kJ/mole for anthracites with $V_G = 5\%$. It can be concluded that water molecules are most strongly bonded to adsorption centers in coals of intermediate metamorphism degree. It can be derived from equation (3) that the correlation time τ_c of water molecules' in coals with $V_G = 39\%$ is equal to about 28 μs at the temperature 233 K. The same correlation time in coals with $V_G = 26\%$ can be attained at the temperature 253 K while in anthracites with $V_G = 5\%$, correlation time of 31 μs was reached only at the temperature 173 K.

Water and methane in moistened plus methane-saturated coals are irresoluble in NMR spectra at room temperature because they both contribute into a narrow line. Therefore, the intensity and linewidth of the narrow NMR line in the coal-water-methane system give only a total information on the amount and mobility of constituent water and methane species. However, these two fluids would show different behavior at a lowering temperature due to different adsorption mechanisms.

Experimental measurements on methane-saturated coals have proved that the constituent methane does not undergo the phase transitions down to the lowest reached temperatures about 90 K, see figure 5. This fact enables us to separate water and methane contributions using low temperature measurements in water-methane saturated coals.

For example, figure 5 demonstrates the temperature dependence of NMR narrow line intensity for anthracite saturated with water-methane mixture. It can be seen that the constituent water of water/methane mixture converges into crystal-like phase state at the same temperature as the water in the moistened sample. The constituent methane stays thereat in a mobile state (narrow line intensity is equal to 110). Potential barrier hindering molecular motion is about 28.43 kJ/mole for the water adsorbed in anthracite. The same barrier value for constituent methane is as low as 14.1 kJ/mole or lower. It means that the phase transition of the absorbed water in constituent water/methane mixture will take place much earlier during cooling than the transition of constituent methane. This phenomenon makes the separation of water and methane contained in coal possible.

Following to J. De Boer, the adsorption in coals of early or intermediate metamorphism stage should be classified as localized adsorption. As it was shown above, methane adsorption in coals is a rather nonlocalized one. Based on this finding, individual amounts of water and methane in coal can be estimated separately using the low temperature NMR technique.

References

1. Randles J.E., Phys. Chem. Liquids, 1977, **7**, No. 1–2, 107.
2. Clifford J. Water: A Comprehensive Treatise. Vol. 5, ed. by F.Franks. Plenum, New York, 1975.
3. Dubinin M.M., Izv. AN SSSR Ser. Khimiya, 1974, **5**, 996 (in Russian).
4. Croxton C. Statistical Mechanics of the Liquid Surface. Wiley, Chichester, 1980.
5. Henniker J.C., Rev. Modern Phys., 1949, **21**, 332.
6. Etzler F.M., Drost-Hansen W. Colloid and Interfase Science. Vol.8, ed. by M.Kerker. Acad. Press, New York, 1976, 517.
7. Mank V.V., Lebovka N.I. Physico-Chemical Mechanics and Lyophilic Behavior of Dispersions. Vol. 16, ed. by F.D.Ovcharenko. Naukova dumka, Kiev, 1984, 38 (in Russian).
8. Rideal E. Conceptual Evolution in the Field of Catalysis. Mir, Moscow, 1971 (in Russian).
9. De Boer J.H., Dynamic Nature of Adsorption. Izd. Inostr. Lit., Moscow, 1962 (in Russian).
10. Sholten J.J., Kreyer S. Structure and Behavior of Adsorbents and Catalysts. Mir, Moscow, 1973 (in Russian).
11. Frenkel J.I. Kinetic Theory of Liquids. Nauka, Leningrad, 1975 (in Russian).
12. De Boer J.H. Catalysis: Problems of Theory and Practice of Organic Reactions. Izd. Inostr. Lit., Moscow, 1959 (in Russian).
13. Tarasevich Y.I. Physico-Chemical Mechanics and Lyophilic Behavior of Dispersions. Vol. 16, ed. by F.D.Ovcharenko. Naukova dumka, Kiev, 1984, 28 (in Russian).
14. Mank V.V., Ukr. Chim. Zhurnal, 1978, **43**, 911 (in Russian).
15. Alexeev A.D., Ayruni A.T., Zverev I.V., Physico-technical problems of mining, 1994, **3**, 65 (in Russian).
16. Malyshev Y.N., Trubetskoy A.N., Ayruni A.G. Fundamental and Applied Methods in Solving the Problem of Coalbed Methane. Izd. Akad. Gorn. Nauk, Moscow, 2000 (in Russian).
17. Alexeev A.D. et al. Discovery A-016, Diploma No. 9. Ukraine, 1994.
18. Alexeev A.D, Vasilenko T.A, Ulyanova E.V, Solid State Comm., 2004, **130**, No. 10, 669.
19. Milewska-Duda J., Fuel, 1987, **66**, 1570.
20. Bobin V.A. Abstract of Dr. Tech. Sci. Thesis. IPKON, Moscow, 1992 (in Russian).
21. Harpalani S., Schraufnagel R., Fuel, 1990, **69**, 551.
22. Gabuda S.P., Rzhavin A.F. Nuclear Magnetic Resonance in Crystalline Hydrates and Hydrated Proteins. Nauka, Moscow, 1978 (in Russian).
23. Gabuda S.P., Dokl. AN SSSR, 1962, **143**, 840 (in Russian).
24. Lundin A.G., Fedin E.I. NMR Spectroscopy. Nauka, Moscow, 1986 (in Russian).
25. Alexeev A.D., Morozenko E.V., Serebrova N.N. Dokl. AN USSR, 1979, **8**, 630 (in Russian).
26. Alexeev A.D., Ulyanova E.V., Starikov G.P., Fuel, 2004, **83**, No. 10, 1407.

27. Alexeev A.D., Zaidenvarg V.E., Sinolitskii V.V., Ulyanova E.V. Radiophysics in Coal Industry. Nedra, Moscow, 1992 (in Russian).
28. Pool C. Technology of NMR Spectroscopy. Mir, Moscow, 1970 (in Russian).
29. Valkenstein S. Structure and Physical Properties of Molecules. Izd. Inostr. Lit., Moscow, 1955 (in Russian).
30. Grechishkin V.S., Skripov F.I. Paramagnetic Resonance. Kazan Univ., Kazan, 1959 (in Russian).
31. Bloemberqen N., Purcell E.M., Pound R., Phys. Rev., 1948, **73**, 679.
32. Uo J.S., Fedin E.I., Fiz. Tverd. Tela, 1962, **4**, 2233 (in Russian).
33. Bloch A.M. Structure of Water and Geological Processes. Nedra, Moscow, 1969 (in Russian).

Фазові переходи в системі кам'яне вугілля-вода-метан

А.Д.Алексєєв, Е.В.Ульянова, Н.А.Калугіна, С.Е.Дегтяр

Інститут фізики гірничих процесів,
вул. Р.Люксембург 72, Донецьк 83114, Україна

Отримано 13 липня 2005 р.

Методом НМР досліджені фазові переходи сорбованих викопним вугіллям води і метану при низьких температурах. По спектрах 1Н НМР широких ліній отриманий поділ внесків сорбованих флюїдів у вузьку лінію.

Ключові слова: *викопне вугілля, вода, метан, ядерний магнітний резонанс*

PACS: *62.20.Dc, 76.60.-k*