A STUDY OF SORPTION CHARACTERISTICS OF OIL- AND GAS-BEARING SANDSTONES

By

G. SÁNDOR

Department of Applied Chemistry, Technical University, Budapest
Received November 26, 1977

Presented by Prof. Dr. L. Gy. NAGY

Introduction

The knowledge of sorption characteristics of oil- and gas-bearing sandstones is important from the point of view of exact determination of oil and gas reserves, i.e. of the optimization of primary and secondary recovery procedures.

Rim angle measurements usually applied to determine wettability are very difficult to implement in case of porous rocks, while determination of its equilibrium state is difficult, because the θ-angle is time dependent.

The determination of sorption capacity, i.e. specific surface area of sandstone bearers is again a complicated task, because sandstones have a heterogeneous mineral composition, particle size also changes within a wide range [1].

In literature, several specific surface area values, showing deviations by orders of magnitude, are found. Applying the B.E.T. method several authors give a specific surface area value of about 20 m^2/g [2, 3] for clay minerals and shales. Specific surface area values of sandstones determined via the B.E.T. method range from 0.5 to 6 m^2/g, while those calculated by BROOKS and PURCELL according to the KOZENY—CARMAN equation are 0.02 to 0.5 m^2/g [4].

Since surface areas, determined by the KOZENY—CARMAN equation are effective from a hydrodynamic point of view, according to our opinion, specific surface area values determined by binary liquid mixture adsorption — exempt from assumptions in the KOZENY—CARMAN equation — have also to be taken into consideration in discussing the problems of liquid flow in porous systems by liquid-phase adsorption method.

No specific surface area values determined by binary liquid mixture adsorption have been published in the literature on oil mining to now; so application of these data is new in this field. In lack of proper data, elaboration of experimental techniques — such as selection of proper binary liquid mixture, optimization of solid/liquid ratio, application of a suitable method for the determination of concentration — had to be performed as well.

Theory

In order to determine the specific surface area of oil- and gas-bearing sandstones, some authors [4] use the KOZENY—CARMAN equation, in which the Kozeny factor cannot be directly measured:

$$K = \frac{\Phi^3}{k \cdot S^2}$$

where K = hydraulic conductivity; Φ = porosity; S = specific surface area; k = Kozeny factor.

Using geophysical methods, the k factor may be substituted by measurable physical quantities [5].

Applying the binary liquid mixture adsorption method, no such problems arise. In accordance with GIBB's definition, adsorption can be determined from the experimental data without making any assumption, and characterized by the specific surface excess related to the mass unit of the adsorbent [6].

Experimental conditions

For the purpose of the experiment, neogenic sandstones of Pannon age were used. Geological data of some of the studied sandstones are found in Table 1.

Binary liquid mixture adsorption measurements were performed by the method of SCHAY and NAGY [7]. Gas chromatography was used for the purpose of measuring the change in concentration. In order to establish the relationship between the hydrodynamic surface area and the specific surface area determined by adsorption method, it was necessary to know the wetting and swelling characteristics of the rock. For this purpose the following methods were used: immersion microcalorimetry; integral immersion heat and kinetics; X-ray diffraction; IR spectroscopy; electron microscopy.

Evaluation

Using benzene–nitrobenzene mixtures the determined surface areas are of the order of 100 m²/g, and the isotherms are of type IV according to the classification by SCHAY and NAGY (Fig. 1 and Table 1). We have established

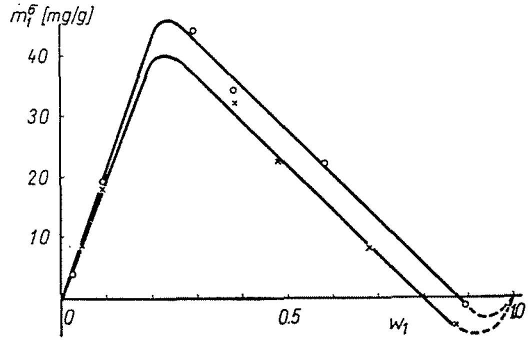

Fig. 1. Surface excess isotherms of benzene (1) — nitrobenzene (2) mixtures on sandstone samples No. 1091 (×) and 1088 (○)

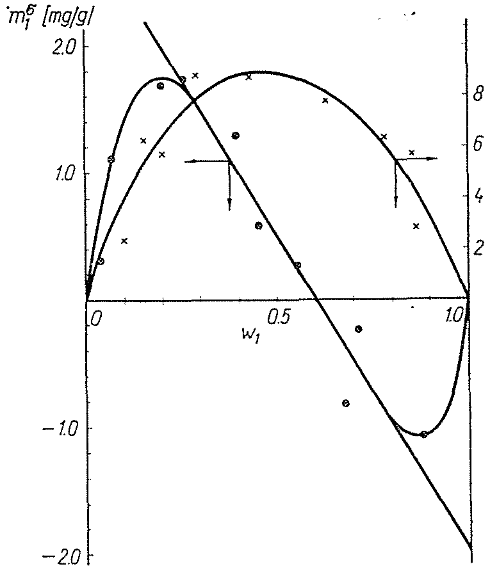

Fig. 2. Surface excess isotherms of *n*-heptane (1) — cyclohexane (2) mixtures on sandstone samples No. 837 (×) and 877 (○)

by immersion microcalorimetric, X-ray diffraction, electron microscopic and IR spectroscopic tests, that the studied sandstone samples contain swelling clay, kaolinite, and that their swelling in benzene–nitrobenzene mixture results in extremely high surface area values.

Using cyclohexane–*n*-heptane mixtures, specific surface area values of the order of 10 m^2/g were found (Table 1 and Fig. 2).

According to these data there is some swelling even in the case of cyclohexane–*n*-heptane mixtures. The less the specific surface area, the higher the hydraulic conductivity and the lower the clay content, and vice versa.

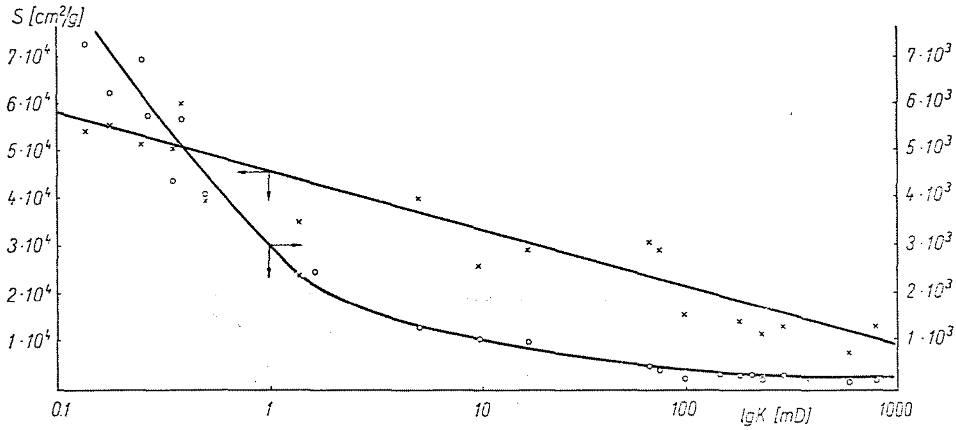

Fig. 3. Relationship between surface area and permeability. Surface area measured by B.E.T. (×), and Kozeny—Carman (○) method

Each of the sandstones was wetted by water. The specific surface area is seen in Fig. 3 as a function of log hydraulic conductivity. Specific surface area values determined by gas adsorption can be stated to show a linear relationship to permeability, while the Kozeny—Carman equation does not

Table I

Geological data and experimental results of investigated sandstone samples

Sample No.	Geological area	Porosity (%)	Permeability (mD)	Specific surface area determined by the adsorption of binary mixtures benzene (1)-nitrobenzene (2) (m^2/g)	Specific surface area determined by the adsorption of binary mixtures *n*-heptane (1)-cyclohexane (2) (m^2/g)
1088	Battonya-K-19	31.36	1007.26	161.35±10%	—
1091	Battonya-K-19	30.39	487.00	177.00±12%	—
877	Ferencszállás-K	17.30	150.50	—	13.06±1.23%
837	Ferencszállás-K	18.30	32.90	—	31.25±17.20%

differentiate in case of higher values of permeability. The reason of deviation is the following: beside external surfaces touching fluid flow, gas adsorption methods measure a part of internal surfaces as well, provided they are in connection with the "dead end" pores, which retain fluid and do not allow it to flow. Besides, a significant part of the deviation is due to the fact that Carman [8] assumed a uniform pore size together with some other factors, considered to help expressing the specific surface of consolidated media.

Specific surface area values determined by binary liquid mixture adsorption method fit well the gas adsorption results in Fig. 3, provided mineral composition and swelling characteristics of the rock are taken into consideration in selecting the liquid mixture to be used.

The binary liquid mixture adsorption method has been found to suit determination of the specific surface area of bearing rocks. Naturally, geological application requires statistical processing of great many measurements.

Acknowledgements

I should like to express my gratitude to Professor and Head of Department, Dr. L. G. NAGY for his comprehensive and extensive help in the solution of theoretical and practical problems; to Dr. Z. BARLAI for his help given to geophysical application; to Mr. and Mrs. BODNÁR, to dr. G. FÓTI, to dr. I. PÁSZLI and to Mrs. KUTY for their technical assistance and valuable suggestions.

Summary

Sorption characteristics of oil- and gas-bearing sandstones have been studied by methods of binary liquid mixture adsorption and immersion microcalorimetry. The effect of the quality of liquid mixture upon the extent of specific surface area has been studied. Mineral quality and swelling properties of the sandstones have to be taken into consideration in selecting the appropriate liquid mixture. Specific surface area values determined by binary liquid mixture adsorption method are suitable for geological application as well as for oil mining engineering.

References

1. BÉRCZI, I.: Acta Geol. Acad. Sci. Hung. **14**, 287—300 (1970)
2. KULIEV, A. M.–ALIEV, A. Y.–GRIGORYAN, E. V.: Gazovaja Promüslennoszt, **16**, No. 2., 8—10 (1971)
3. DÉKÁNY, I.–SZÁNTÓ, F.–NAGY, L. GY.–FÓTI, GY.: Magy. Kém. Foly. **80**, 231—237 (1974)
4. BROOKS, C. S.–PURCELL, W. R.: Petroleum Transactions, AIME, **195**, 289—296 (1952)
5. BARLAI, Z.: Third European Symposium Transactions, SPWLA, October 14—15, London, Paper I. (1974)
6. SCHAY, G.–NAGY, L. GY.: Mixture Adsorption on Liquid/Solid and Liquid/Vapour Interfaces, (In Hungarian) Akadémiai Kiadó, Budapest 1974
7. SCHAY, G.–NAGY, L. GY.: Colloid Interface Sci. **38**, No. 2., 302 (1972)
8. CARMAN, P. C.: Discussion of the Faraday Society, No. 3., 72 (1948)

Gábor SÁNDOR, H-1521 Budapest