Currently, the conventional BET equation, DR and BJH models are widely used to characterize the pore structures of gas shales. These models, however, were originally constructed on the basis of homogenous materials of micropores or meso-/macro-pores, and therefore they cannot be directly used to characterize the heterogeneous pores in shales.

In this study, nitrogen adsorption was conducted on some Lower Silurian and Lower Cambrian shales from the eastern Sichuan Basin and the Qiannan Depression of Guizhou province, respectively. Using the adsorption isotherms, we investigated how the modified BET equation could be conveniently used to characterize the micropore volume and meso-/macro-pore surface areas of shales. The results show that (1) The modified BET equation can successfully fit the experimental data in the classic BET relative pressure range (0.05–0.3), whereas the conventional BET equation significantly overestimates the adsorption amount at relative pressures higher than 0.15 (Fig. 1); (2) The micropore volumes determined by the modified BET equation are quite consistent with the results from other independent methods (e.g., t-plot) (Fig. 2). Compared with BJH model, the modified BET equation can provide the surface areas of meso-/macro-pores more accurately because it does not need to assume the pore shapes as the BJH model does; (3) Dubinin-Radushkevich (DR) equation overestimates the micropore volumes, and this overestimation is closely related to the non-micropore surface area of shales (i.e. the surface area of meso-/macro-pores) (Fig. 3).

Characterization of pore structures of gas shales using modified BET equation

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Fig. 2 A comparison of micropore volume calculated by modified BET equation and t-plot method. The C value obtained by modified BET equation is not affected by micropores and only reflects the surface characterization of meso-/macro-pores.

\[ y = 0.0362x - 0.0529 \]
\[ R^2 = 0.9971 \]

Fig. 3 Plots showing the relationship between the overestimation of micropore volume by DR equation and the non-micropore surface area calculated by modified BET equation.

\[ y = 0.0322x - 0.0147 \]
\[ R^2 = 0.9841 \]