

Asphaltene adsorption on metal surfaces: kinetics and thermodynamics

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Asphaltene deposition is responsible for many problem situations during oil production and processing. Stability of the oil asphaltenes may be lost due to a number of factors including pressure, temperature, and composition of the fluid. Adsorption of asphaltenes on metal surfaces plays a key role in such phenomena as asphaltene deposition on oil-production equipment and catalyst deactivation during hydroprocessing. Mechanism of asphaltene adsorption on metal surfaces is a question under investigation. The limited knowledge about asphaltene-metal interactions hinders a development of mitigation techniques. A fundamental investigation of the asphaltene adsorption on metal helps to find out effective treatment procedures. The knowledge of kinetic and thermodynamic parameters of adsorption in perspective opens a way for physical and chemical engineering of liquid-solid interfaces in the oil industry.

In the present study, cast steel shot was used as an adsorbent for the adsorption of asphaltenes dissolved in different model oils at standard conditions. The adsorption parameters of native and visbroken residue asphaltenes were estimated using near-infrared (NIR) spectroscopy. Quantity of adsorbed asphaltenes was determined by measuring the transmittance spectra of the bulk phase above the adsorbent. Employed experimental scheme is described in our work [1]. The maximal adsorbed mass density, the adsorption equilibrium constant, the adsorption/desorption rate constants were calculated under controlled process parameters such as initial asphaltene concentration in the range of 0.01-3 g/L, adsorbent particle size (0.5, 1.4, and 3.6 mm), the source of the petroleum system from which asphaltenes were obtained (West-Siberian crude oils and visbroken products), model oil system composition, asphaltene extraction procedure. The results of the adsorption isotherms show that the adsorption process in a chosen concentration range can be well described in most cases with the Langmuir model. The parameters obtained from Langmuir model should be considered as effective ones.

Kinetic studies show that desorption rate appeared to be much lower than the adsorption rate in all examined systems. Adsorption of asphaltenes on metal was found to be almost irreversible.

During adsorption process asphaltene concentration in the solution decreased and the adsorbed amount of the asphaltenes thus increased at a faster rate as the size of adsorbent grains decreased. Resistance to mass transfer of asphaltenes to inner volume of adsorbent appeared to be significant as the adsorbent grains decrease. Adsorption capacity values for systems with high-grained adsorbent (0.5 mm) were still higher than for systems with middle-grained adsorbent (1.4 mm), however these values are unexpectedly close. Possible explanation is the presence of areas in adsorbent structure that were not involved in adsorption process. "Dead" zones may occur due to capillary aggregation effect reported earlier [1]. The conclusion about primarily role of the pore volume and diameter of the adsorbent in governing the adsorption [2] is confirmed. Surface area of adsorbent appeared not to be a key parameter.

Gibbs energy values correspond to the physical process. Energy of asphaltene adsorption on metal surface (Gibbs potential) was higher, in the same order of magnitude as the adsorption of asphaltenes on mineral [1]. Metal surface has oxide layer which may enhance asphaltene aggregates attraction to the surface by Van-der-Waals interactions.

Visbroken asphaltene adsorption rate values were higher in comparison with native asphaltenes. Phase behavior, hence adsorption behavior of asphaltenes in model oils were influenced by the quality of solvent. Asphaltene extraction procedure is significant: different compositions of extracted material influence the kinetic and thermodynamic parameters of adsorption.

References

- [1] Syunyaev, R.Z. et al. *Energy&Fuels* 2009 23 (3), pp 1230-1236.
- [2] Lopez-Linares F. et al. *Energy&Fuels* 2009 23 (4), pp. 1901-1908.