Lithium Cationization for Petroleum Analysis by Positive Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Lobodin, V.V. (NHMFL, Chemistry); Juyal, P. (Nalco); McKenna, A.M. (NHMFL, Chemistry); Rodgers, R.P.; Marshall, A.G. (NHMFL, FSU, Chemistry)

Results and Discussion

Lithium cationization can significantly extend the compositional range for analysis of petroleum components by positive electrospray ionization [(+) ESI], by accessing species that lack a basic nitrogen atom and, hence, are not seen by conventional (+) ESI that relies on protonation as the primary ionization mechanism. Here, various solvent compositions and lithium salts enabled us to optimize ionization by formation of lithium adducts ([M + Li]+), and the results are compared to production of [M + H]+ by conventional (+) ESI with formic acid. Lithium cationization (+) ESI Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) of Athabasca bitumen heavy vacuum gas oil (475 − 500 °C) and North and South American crude oils demonstrates considerable improvement over protonation for production of ions from compounds belonging to S_xO_y (SO, SO_2, SO_3, SO_4, S_2O, S_2O_2, etc.) heteroatom classes. Those compounds exhibit much higher affinity for lithium cation than for proton and yield abundant [M + Li]+ ions. Li+ cationization thus opens a pathway for detection and characterization of SxOy class compounds that preferentially concentrate at the interface in oil/water emulsions.

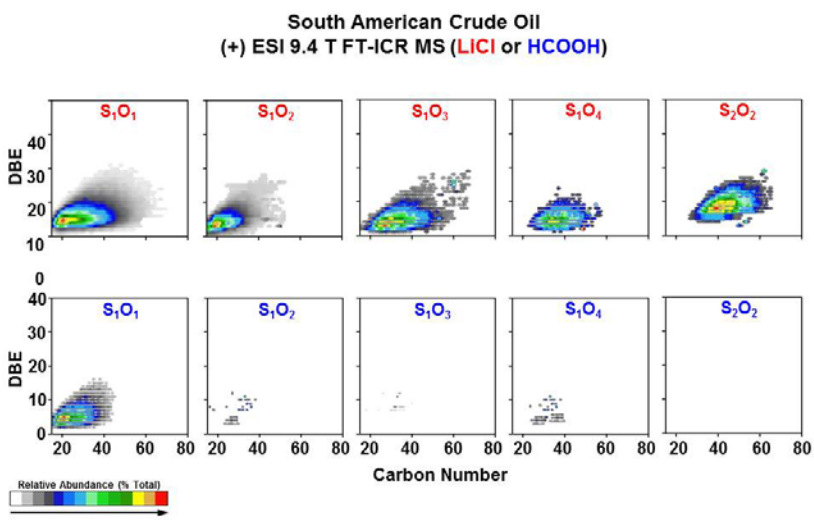

Figure 1. Iisoabundance-contoured plots of DBE versus carbon number for S_1O_1, S_1O_2, S_1O_3, S_1O_4, and S_2O_2 heteroatom classes from South American crude oil with LiCl or HCOOH as a modifier. Litium cationization efficiently ionizes the S_xO_y classes over a wider DBE and carbon number range. S_1O_1 class compounds in the (+) ESI FT-ICR mass spectrum of the crude oil with LiCl as a modifier range from DBE = 1−20 and 15−70 carbons. That class spans narrower ranges of DBE (2−18) and carbon number (15−42) with formic acid as a modifier. S_1O_2, S_1O_3, S_1O_4, and S_2O_2 classes show much greater ionization enhancement by lithium cationization than by protonation. The increase in the number of heteroatoms for the S_xO_y classes ($S_1O_2 < S_1O_3 < S_1O_4$) shifts the distribution to higher carbon numbers. Moreover, the S_2O_2 class also shifts to higher DBE values.

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References

[1] Lobodin, V.V. *et al*., Energy Fuels, **28**, 6841-6847 (2014)