Study of the oxidized and non- oxidized bitumen modified with additive «Adgezolin» by using electron paramagnetic resonance

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Abstract. Cationic surfactant (adhesion additive) «Adgezolin» has been developed. It is shown that introduction of «Adgezolin» into the oxidized bitumen increases the relative amount of asphaltenes and monocyclearomatic hydrocarbons. By means of electron paramagnetic resonance (EPR) it is demonstrated that the introduction of additive «Adgezolin» increases the number of paramagnetic «free» carbon radicals (FR) in the oxidized bitumen and decreases that in the unoxidized species. In both types of bitumen shift from the Lorentzian to Gaussian EPR lineshape of FR is obtained that could be connected with as an increase of the samples homogeneity. It is supposed that while in the oxygenated bitumens introduction of additives leads to the disaggregation of asphaltene-resins compounds, in the unoxidized samples the balance is shifted towards formation of di-radicals.

1. Introduction

The strength and durability of road surface depends largely on the quality of bituminous binder, which allows associating different mineral materials and formation of lasting wearproof and weatherproof monolith (asphalt) [1]. In the Russian Federation oil bitumens and mineral fillers used in the preparation of asphalt mixtures don't have a proper adhesion. This is one of the main causes of premature destruction. Ability to maintain properties during prolonged exposure to high and low temperatures is an important feature for bitumen. To advance bitumen adhesion to the surface of mineral materials asphalt mixtures production technology uses additives (surfactants) [2].

The introduction of additives has a significant influence on the structure of oil dispersed systems (ODS) including a change in composition of oil and structure of the complex structural unit (CSU) composed of asphaltenes and solvate shell mostly composed of resins. Solvate shell includes internal and peripheral parts, consisting of alcohol-benzene and benzene pitches respectively [3, 4]. In this report an influence of the nitrogen-containing surfactant «Adgezolin» adding into the oxidized bitumen BND 60/90 produced by OJSC «TAIF-NK» (denoted hereafter as TAIF, Russia) and unoxidized bitumen BNN 80/120 produced by the oil-and-gas production department of «Elhovneft» (denoted hereafter as Elhov, Russia) are studied.

It is known that one gram of ODS contains up to 10^{20} paramagnetic centers (PC) [7-10]. These include organic free radicals (FR) in the structure of a condensed polyaromatic core of molecules of high-molecular ODs components as well as paramagnetic porphyrin complexes (VP). FR (as well as VP) in ODS are mainly concentrated in asphaltenes and resins and arise due to the delocalized π electrons of the aromatic rings and stable organic radicals of the side chains. The content of the high-molecular ODS components could reach the values of up to 73 wt. % in natural asphalts and bitumen

[8]. Assuming that asphaltenes and resins have molecular weight of about 1000 amu [8], they could contain up to one unpaired electron per molecule. One of the most informative methods to study paramagnetic centers is electron paramagnetic resonance (EPR) (see [8-11] and references therein).

It is assumed that the dispersed colloidal particle stability in ODS petroleum systems is tightly connected with the concentration of PC, first of all of FR [7, 8, 10, 12]. There was many attempts to track the correlations between the EPR spectroscopic parameters and ODS status (content, changes with the oxidation, modification, ageing, temperature, etc.). In this work an attempt to track and connect the obtained changes in EPR spectra with the addition of the produced additive «Adgezolin» is done.

2. Materials and Method

To ensure proper bitumen adhesion to mineral materials, mineral additive are used, in which cationic surface-active agents (surfactants) are the most frequently applied. Nowadays imidazolines and their derivatives [13,14] are the most widely used as additives for bitumen. Polyethylenepolyamines were exploited for the synthesis of «Adgezolin» [5].

Composition of bitumen was evaluated by using a technique of VNII NP [15] based on liquid adsorption chromatography. Maltens could be divided into paraffin-naphthenic (PN-), monocycloaromatic (MCA), bicycloaromatic (BCA), polycycloaromatic (PCA) hydrocarbons (HC) while resins onto the the benzol (BR), alcohol-benzene (ABR) resins, or resin-1 and resin -2, respectively.

EPR spectra were obtained by using ESP 300 spectrometer (Bruker, Germany) operating at 9.4 9.9 GHz (X band) in continuous wave mode with modulation frequency of 100 kHz and amplitude of 0.1 mT. Microwave power level was about 20 µW to avoid saturation effects and to define the EPR parameters correctly. PC concentration was estimated at room temperature in the double cavity ER4105DR by comparing the integrated intensities (I) of the spectra of a test sample and a reference one (Mn(II) in MgO). Heating of the samples in the range of (220-313) K was done in a stream of nitrogen blown through the quartz insert equipped with the VT thermostatic system (Oxford Instruments) with (8 15)°C increment, heating rate of 2°C/min and temperature setting accuracy of not less than ±2°C. To exclude the treatment effect we have measured the PC concentrations at room temperatures before and after heating.

Simulations of the EPR spectra were done by using the functions of the EasySpin module for Matlab software [Stoll et al. 2006] in which the linewidth (Γ) for Gaussian (G) and Lorentzian (L) absorption lineshapes are connected with the full width at half maximum (FWHM) via $\Gamma_G = (2\ln2)^{-1/2} \cdot$FWHM and $\Gamma_L = (3)^{-1/2} \cdot$FWHM.

3. Results and Discussion

Paraffin-naphthenic hydrocarbons are considered to be undesirable because they dramatically reduce the structural-mechanical strength of bitumen [16]. As it follows from the data presented in Table 1, after adding additives one observes a reduction of PN-hydrocarbons in the TAIF bitumen. Because the mixing of «Adgezolin» with bitumen occurs when heated, this decrease possibly connected with the dehydration of naphthenic rings and formation of alkylaromatic compounds. It results in more lyophilic behavior of asphaltenes [16] which are insoluble in paraffin-naphthenic hydrocarbons, but solvate and swell in aromatic hydrocarbons. Therefore, the asphaltenes can form aggregates. The content of the MCA-hydrocarbons increases almost in 2 times from 6.88% for the original bitumen up to 12.65% for bitumen modified with 1 wt. % of «Adgezolin». Transformation of this faction probably occurs at the expense of dehydrogenation of naphthenic rings in naphtene-aromatic compounds, with the formation of resins and asphaltenes. Thus, the additive adding leads to the increase of both asphaltenes and MCA-hydrocarbons from PN-hydrocarbons:

$$\text{MCA-hydrocarbons} \leftarrow \text{-PN-hydrocarbons} \rightarrow \text{asphaltenes.} \tag{1}$$
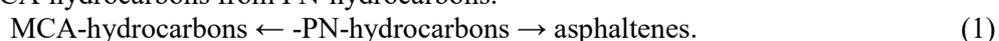
Formation of asphaltenes from PN-hydrocarbons may occur through the resin-1 and resin-2:

$$\text{PN hydrocarbons} \rightarrow \text{resin-1} \rightarrow \text{resin-2} \rightarrow \text{asphaltenes.} \quad (2)$$

There is also a possibility avoid the resin formation stage:

$$\text{PCA HC} \rightarrow \text{MCA HC} \leftarrow \text{PN HC} \rightarrow \text{resin-1} \rightarrow \text{resin-2} \rightarrow \text{asphaltenes.} \quad (3)$$
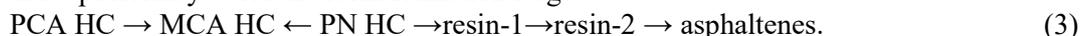
Table 1. Component part of the original and modified TAIF bitumen.

Components, % mass.	Bitumen samples				
	Source	Content of Adgezolin,% of the mass.			
		0.6	0.8	1.0	1.2
P-N HC	17.69	16.17	14.25	12.33	14.20
MCA HC	6.88	8.74	9.77	12.65	12.07
BCA HC	8.26	7.98	7.66	6.85	7.92
PCA HC					
Σ **Saturates+aromatics**	32.83	32.89	31.68	31.83	34.19
Resin-1	22.82	23.16	21.68	21.81	20.60
Resin-2	17.44	16.31	17.39	18.84	19.32
Σ **resins (R)**	40.26	39.47	39.07	40.65	39.92
Asphaltenes (A)	21.98	25.36	24.87	25.67	25.89

The results for the unoxidized bitumen Elhov gained from the heavy superviscous oil of Ashal'chinskoe' basin are shown in table 2. With adding additives up to 0.8 % an increase in the amount of saturates + aromatics occurs from 25.90 % for the original bitumen up to 33.50 %. As the number of additives in the bitumen further increases up to 1.2 wt. %, the amount of saturates + aromatics reduces to 29.43 % by reducing the concentration of resin-2. This change is due to the breaking down of resins-2. Asphaltenes may behave in a similar way.

Comparison of the components with the «Adgezolin» adding demonstrates an advantageous transformation of resin-2:

$$\text{Saturates+aromatics} \leftarrow \text{resins-2} \rightarrow \text{asphaltenes.} \quad (4)$$
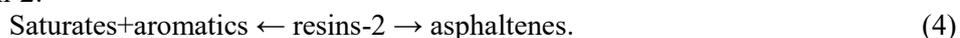
It is possible that the formation of oils (saturates+aromatics) from resins-2 occurs through the resin-1:

$$\text{Saturates+aromatics} \leftarrow \text{resins-1} \leftarrow \text{resins-2} \rightarrow \text{asphaltenes.} \quad (5)$$
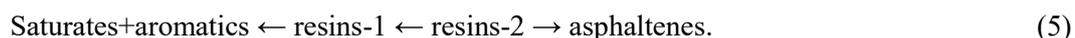
Thus, studies in this part of the work demonstrate the influence of the additive «Adgezolin» on the properties and composition of the modified bitumens.

Table 2. Component part of the original and modified Elhov bitumen.

Components,% of the mass.	Bitumen samples				
	Source	Content of Adgezolin,% of the mass.			
		0.6	0.8	1.0	1.2
Saturates+aromatics	25.90	28.57	33.50	29.67	29.43
Resin-1	31.71	36.07	34.47	33.74	36.63
Resin-2	29.09	17.13	15.57	19.21	17.72
Σ **resins (R)**	60.80	54.20	50.04	52.95	54.35
Asphaltenes (A)	13.31	17.23	16.44	17.38	16.21

EPR patterns in all the studied samples are very similar to each other (Figure 1) and originate from the paramagnetic vanadyl complex VO^{2+} in porphyrins (electronic spin $S = 1/2$, nuclear spin $I = 7/2$; therefore 16 «lines» for the parallel and the perpendicular complex orientations, see [9,17] for details and from FR. Within the accuracy of our experiments, no changes in the spectroscopic parameters of VO^{2+} complexes was obtained with «Adgezolin» addition and temperature dependencies of the integral intensities for VO^{2+} in the investigated samples obeyed Curie law.
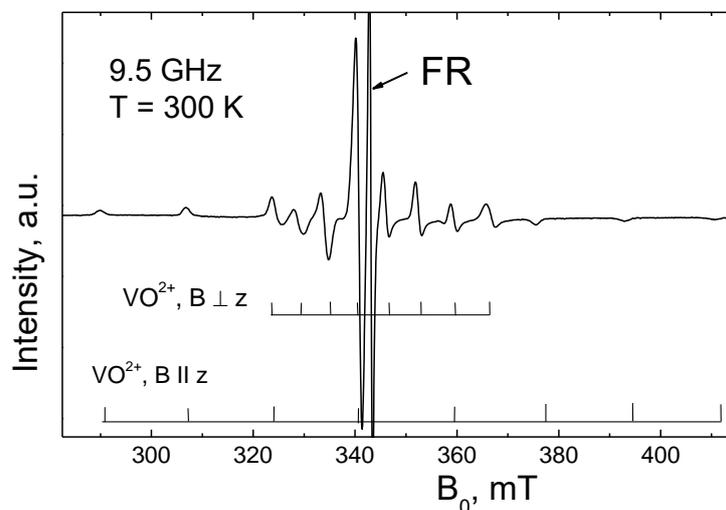
Figure 1. Typical EPR spectrum (TAIF + 0.8 % Adgezolin). Arrow indicates the position of FR; the hyperfine components $A_\parallel$ and $A_\perp$ of VO^{2+} corresponding to the parallel and perpendicular orientations in the external magnetic field are shown. The receiver gain is tuned to present all VO^{2+} lines so the FR signal is out of the analog-digital converter range

The EPR spectrum of FR is a single line with the linewidth of $\Delta H_{1/2} = (0.54\text{-}0.64)$ mT situated at g-factor 2.003 ± 0.001. FR lineshape is a convolution of Gaussian and Lorentzian in a ratio of about G:L $\approx 34{:}66$ for the untreated samples at RT up to 43:57 for the 1% of (Fig. 2, Table 3). No connection between the oxidation state and additive addition with the line position, width and shape was found. The shift of the lineshape towards the Gaussian form can be regarded as the more homogeneous distribution of «free» radicals in the samples with «Adgezolin» [10].

Table 3. Parameters of approximation for FR line.

| Sample	FR concentration, 10^{18} spin/g	VO^{2+} concentration, 10^{18} spin/g	Γ_G, mT	Γ_L, mT	$I_{Gauss}{:}I_{Lorentz}$ (% : %)
TAIF	1.65(10)	3.6 (5)	0.72	0.76	34:66
TAIF+0.8%	1.85 (10)	3.1 (6)	0.72	0.75	39:61
TAIF+1%	1.95 (15)	3.7 (5)	0.74	0.73	43:57
Elhov	1.50(15)	8.7(5)	0.84	0.82	34:66
Elhov+0.8%	1.10(10)	8.9 (5)	0.84	0.80	42:58
Elhov+1%	1.0(1)	9.7 (5)	0.83	0.81	39: 61
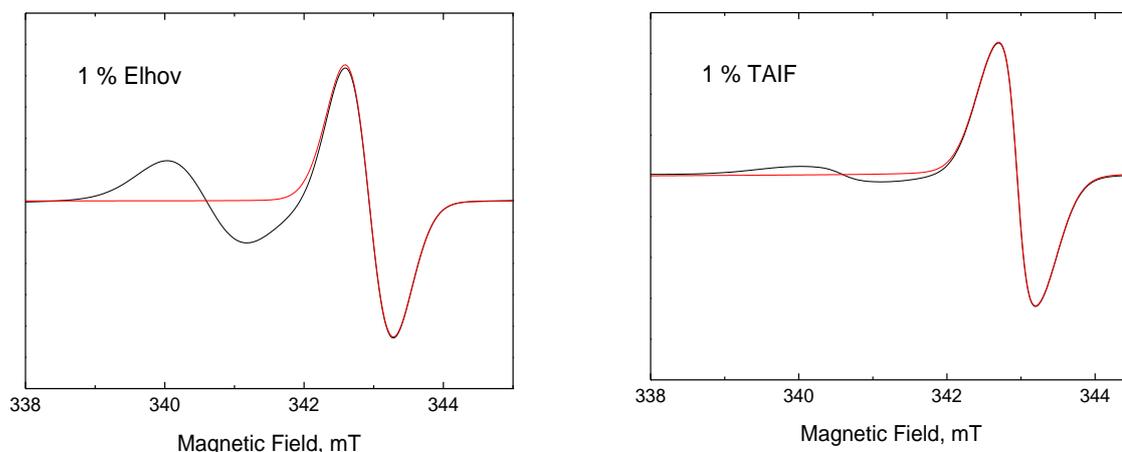
Figure 2. Examples of approximations of FR spectra for 1% Elhov (left panel) and 1% TAIF (right panel). Parts of spectra presenting the most intensive VO^{2+} component and FR line are shown. Details of approximations and their parameters are given in the text

To visualize the $I(T)$ dependencies without Curie contributions, the abscissa and ordinate axis are chosen to be 1000/T and ($I \cdot T$), correspondingly. In the case of pure Curie contribution the ($I \cdot T$) would be parallel to the abscissa [8, 10].

As seen from Figure 3, in the temperature range of interest of (220-313) K the EPR intensities for FR practically obey Curie law and can serve as a good number for evaluating FR concentration. Furthermore, because the linewidthes of VO^{2+} and FR only slightly deviates from their values at RT, the peak-to-peak amplitudes (App) of the corresponding EPR lines can be used for this purpose in the same way. That gives a potential opportunity to use EPR as a rapid test for qualitative and quantitative analysis of the surfactant introduction.

From Table 3 it follows that the «Adgezolin» introduction is connected with the significant decrease of the FR numbers in the unoxidized bitumen (Elhov) and increase of those in the oxidized bitumen (TAIF) so that the EPR intensities can differ up to 2 times from sample to sample. This difference, probably, is determined by the nature of asphaltenes and resins. Indeed, it is known that asphaltenes and resins extracted from the bitumens after the high-temperature processing differ from those derived from the natural bitumen. The latter ones are characterized by the lower molecular masses, lower H / C ratio, etc [18]. Increase of amount of FR in the oxidized bitumen, most likely, indicates that the additive «Adgezolin» promotes the dispersion of polar compounds (asphaltenes and resins) resulting in a larger number of the polar particles. In the unoxidized samples «Adgezolin» could also act as a «bridge» for formation of di-radicals which are non-paramagnetic (EPR silent) at least in the investigated temperature range [8, 10].
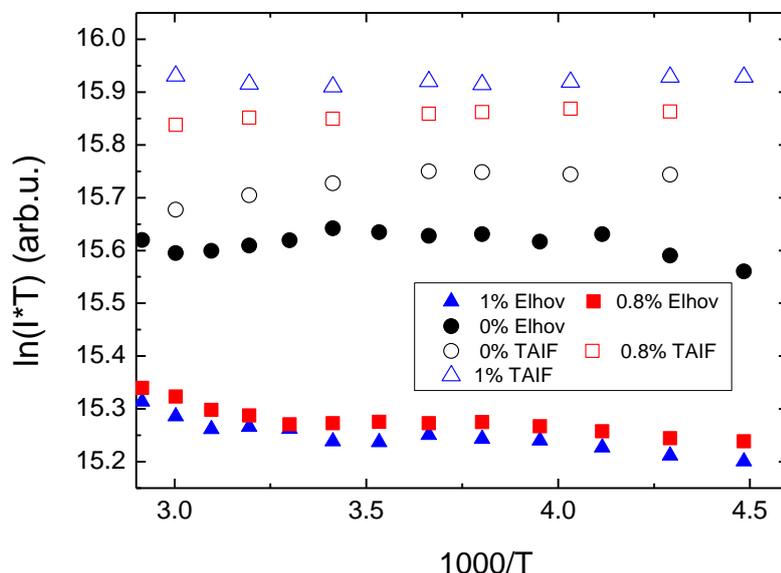
Figure 3. Temperature dependencies of the integral intensities for FR EPR lines for TAIF (open symbols) and Elhov (solid symbols) samples with different content of the adhesion additive «Adgezolin». Horizontal axis is given in a reciprocal temperature (1000/T), the vertical axis is the natural logarithm of product (I·T) to exclude the Curie contribution in determination of FR amount.

4. Conclusion

The establishment of a correlation between the malacometric parameters and a set of parameters determined by using EPR seems to be can help to unravel the mechanism(s) of the modifying action of the «Adgezolin» additive. Namely, the optimal dosage, the way of the additive introduction into the asphalts of various origins, etc., can be derived from these kinds of measurements. This can be used to develop an express method for the rapid control of content and for the qualitative analysis of the modified bitumen.

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