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Synthesis of Glycol Ethers and Their Use for Intensification of Oil Recovery

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Abstract—Monoalkyl ethers of ethylene and triethylene glycols were prepared and tested for intensification of oil recovery. The features of oil displacement with aqueous solutions of glycol ethers from bulk models of strata and the effect of glycol ethers on acid treatment of oil-saturated samples were examined. A correlation between the structure of ether and its performance was revealed. The interphase tension at the boundary between the aqueous solution of the glycol ether and kerosene was determined.

Glycol ethers are widely used as solvents for water–hydrocarbon systems owing to their good compatibility with the aqueous and organic phases, high hydrolytic stability, and low toxicity. In the oil recovery practice, ethylene glycol monobutyl ether (EGMBE) is used as a component of complex acid formulations for treatment of critical zones of oil strata [1]. It is known that dipropylene glycol ethers, e.g., butyl ether used in paint-and-varnish industry [2] or methyl ether used for dissolving oil components [3], surpass cellosolves in performance owing to the higher washing-out power with respect to aliphatic and aromatic hydrocarbons.

The goal of this study was to prepare a series of glycol monoalkyl ethers differing in length of the hydrocarbon radical and number of oxyalkyl units and to choose the best ethers for intensification of oil recovery.

In industry, glycol ethers are prepared by oxyalkylation of alcohols. For their laboratory synthesis, we chose another procedure involving reaction of alkyl halide with glycol in aqueous dioxane in the presence of solid alkali, followed by isolation of the product by vacuum distillation [4]. We prepared ethylene glycol monoheptyl ether (EGMHE) and triethylene glycol monomethyl, monopentyl, and monoheptyl ethers (TEGMME, TEGMPE, and TEGMHE, respectively). Their structures were proved by refractometry and IR spectroscopy (see table).

The synthesized glycol ethers, EGMBE, and ethylene glycol (EG) were tested as additives to acid solutions used in oil recovery for treatment of critical zones of the strata with the aim to improve their filtration properties and capacity. Glycol ethers decrease the interphase tension between oil and water and facilitate removal of fine particles wetted with oil and restoration of the hydrophilic properties of the surface owing to the washing-out effect. The effect of glycol ethers on acid treatment was studied under laboratory conditions using a model of carbonate rock saturated with oil and water. To a weighed portion of the rock we added a solution of HCl and glycol ether and determined the rate of CO_2 evolution. The rate of breakdown of the carbonate rock with HCl (ml CO_2/s) in the presence of various ethers was as follows: no ether, 0.3; EG, 0.26; EGMBE, 0.50; EGMHE, 0.10; TEGMME, 0.37; TEGMPE, 0.56; and TEGMHE, 0.46 (0.01 g of $CaCO_3$, 0.1–0.2 mm fraction, 5 ml of 3% HCl, 10 wt % of glycol ether).

These results show that, in the presence of glycol ethers, the rate of reaction of the acid with the rock

Selected propereties of glycol ethers*

Glycol ether	Yield, %	Published data [5]		Data of this work	
		bp, °C / P, mm Hg	n_D^{20}	bp, °C / P, mm Hg	n_D^{20}
EGMHE	27	92/3	1.4325	90/3	1.4362
TEGMME	15	122/10	1.4380	95/3	1.4376
TEGMPE	27.5	–	1.4410	200/3	1.4413
TEGMHE	26	–	1.4450	250/3	1.4450

* IR data, cm^{-1}: C–O–C 1360, –OH 3800–3400.

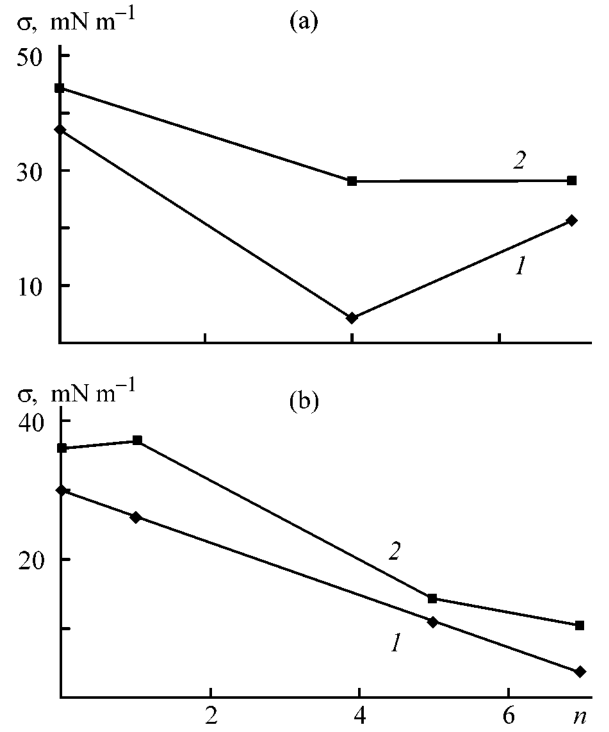

Fig. 1. Influence of the structure of (a) ethylene glycol and (b) triethylene glycol ethers on the interphase tension σ at the water–kerosene boundary. (*n*) Number of atoms in the alkyl group of glycol ether. Concentration of glycol ether, wt %: (*1*) 1 and (*2*) 10.

increases. The performance of an acid formulation depends on the structure of ether, namely, on the length of the hydrocarbon radical and the number of oxyethyl units. The breakdown of the carbonate rock was the fastest with ethers containing 4–5 carbon atoms in the alkyl group. Apparently, glycol ethers with short alkyl group dissolve oil to a lesser extent, and ethers with long alkyl group are worse miscible with the aqueous phase. Owing to their better compatibility with water and oil, triethylene glycol ethers accelerate breakdown of the oil-saturated model rock at any length of the alkyl radical.

Similar trends were obtained in studying the oil-displacing power of ether. A special column modeling an oil stratum was charged with crushed rock and brought to required temperature, after which water, oil, and again water were successively fed until the oil displacement stopped (at a constant rate of filtration of the liquids). From the volume of displaced oil we calculated the oil displacement factor K_0 equal to the fraction of oil displaced from the column with water. After that, an aqueous solution of glycol ether was fed. Below are given the values ΔK_0 by which the oil displacement factor increased on adding glycol (concentration of glycol ether 10 wt %; reagent volume 15% of the pore volume):

Glycol ether	EGMBE	EGMHE	TEGMME	TEGMPE	TEGMHE
ΔK_0, %	18.0	11.8	2.2	24.8	7.0

It is seen that TEGMPE and EGMBE show the best performance. Apparently, 4–5 carbon atoms in the alkyl group are sufficient to ensure the maximal compatibility of a solution being pumped-in and residual oil in the stratum model and its efficient displacement. With longer alkyl radicals, the solubility of an ether in oil becomes the prevailing factor, which results in retention of oil in the stratum model. On the whole, triethylene glycol ethers show a higher oil-displacing power owing to higher hydrophilicity.

The performance of formulations used for oil recovery is usually associated with a decrease in the interphase tension at the aqueous phase–oil boundary. Using a stalagmometer, we determined the interphase tension at the boundary between aqueous solution of glycol and kerosene. As seen from Figs. 1a and 1b, the interphase tension decreases on adding glycol ethers to water (1 or 10%). However, there is no unambiguous correlation between the interphase tension and performance of ethers in intensification of oil recovery. For example, TEGMHE considerably decreases the interphase tension but shows poor performance in oil displacement. In acid treatment, it is adsorbed on the particle surface and makes it more hydrophobic, decreasing the efficiency of reaction of acid with the rock; in oil displacement, it readily mixes with residual oil, is adsorbed on the rock, and is not displaced by liquid. The minimal interphase tension is observed with a 10% solution of EGMBE, though it is not the best oil-displacing agent. Thus, along with interphase tension, some other factors may be significant, e.g., compatibility of ethers with the aqueous and organic phases.

CONCLUSIONS

(1) Ethylene glycol monoheptyl ether and triethylene glycol monomethyl, monopentyl, and monoheptyl ethers were prepared and tested for intensification of oil recovery.

(2) Glycol ethers accelerate breakdown of oil-saturated calcium carbonate with acid formulations owing to washing-out of oil. The breakdown rate depends on the structure of an ether. The highest performance is shown by glycols containing 4–5 carbon atoms in the alkyl group.

(3) Aqueous solutions of glycol ethers make considerably higher the oil displacement factor and can be used for secondary recovery of oil. Ethylene glycol monobutyl ether and triethylene glycol monopentyl ether raise the oil displacement factor to the greatest extent.

(4) High performance of these ethers in acid treatments and oil displacement is due not only to a decrease in the interphase tension at the water–oil boundary but also to compatibility with the aqueous and oil phases.

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