

To discuss our findings related to the mechanism of RIEM cleanup, it is beneficial to examine the chemical states of emulsifiers and their adsorption behaviors under various pH conditions. To this end, we refer to Fig. 7 for details. It has been reported that alkylamines primarily take the form of amine ions (RNH_3^+ and $(\text{RNH}_3)_2^{2+}$) in low-pH solutions. As the pH level increases to higher than pH 5–6, the amine molecules start to dissociate, facilitating the formation of the acid soap dimer $(\text{RNH}_2 \text{RNH}_3)^+$. The proportion of acid soap dimers reaches maximum as the pH level increases to about 9–10. When the pH is sufficiently high, all the amine ions are converted to amine molecules (RNH_2) (Liu et al., 1992; Zhang et al., 2012). The chemical states of ethoxylated alkylamines under varying pH are analogous to alkylamines. The cleanup characteristics of RIEM are closely related to the ionization diversity of ethoxylated alkylamine emulsifiers under various pH conditions. Before cleanup using cleaning fluids, ethoxylated alkylamine emulsifiers take the form of amine molecules $(\text{RN}(\text{EO})_2)$. These molecules assume a low hydrophile–lipophile balance (HLB), which facilitates the water–in–oil emulsion state of RIEMs (Fig. 7a). Cleanup at pH 10 cannot change the amine molecular states of emulsifiers, keeping the HLB low and the RIEM in a water–in–oil emulsion state; hence, the RIEM cannot be removed by the solvent effect. This is why RIEM is more difficult to remove at pH 10. However, the amine molecules are uncharged and easily desorbed, allowing the removal of RIEMs to be facilitated by intense and repeated flushes, and the rock surface reverts to a water–wetting condition (Fig. 7b and c). When the pH is near 4 or 6, the emulsifier transforms from a nonionic state $(\text{RN}(\text{EO})_2)$ into an ionic state $((\text{RNH}(\text{EO})_2)^+)$. Emulsifiers in an ionic state assume a higher HLB than those in a nonionic state. The increase in HLB causes the emulsion inversion; a water–in–oil emulsion converts to an oil–in–water emulsion, which enables the efficient removal of RIEMs by the solvent effect. Emulsifiers in an ionic state are positively charged and readily adsorb to the negatively charged quartz surface, causing strong oil–wetting conditions at the quartz surface (Fig. 7d). The isoelectric point (pI) of quartz is approximately 2, and environments in which $\text{pH} > \text{pI}$ enable quartz to acquire negative charges. At pH 8, the emulsifiers take the form of a soap dimer $(\text{RN}(\text{EO})_2 \text{RNH}(\text{EO})_2)^+$. The formation of soap dimers induces the migration of some of the oil phase to the inner phase, creates an O/W/O multiple emulsion. However, it cannot induce emulsion inversion. Hence, the RIEM cannot be removed by the solvent effect. The formation of soap dimers also makes the emulsion drop positively charged, facilitating the stronger adsorption of emulsion drops to the negative surface as well as the positively charged emulsifiers themselves (Fig. 7e). Based on the relationship between pH and the adsorption behaviors of emulsifiers onto both the oil–water interface and the siliceous sample surface, it is sensible to use a combined method to provide a better RIEM cleanup effect. Cleanup at pH 4–6 facilitates the removal of RIEM and can be followed by (cleanup at pH 10 to form a water–wetting condition (Fig. 7f