Surface-Active Properties of a Series of 1,1-Dimethyl-1-alkylhydrazinium Chlorides


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Abstract—The surface-active properties of a series of 1,1-dimethyl-1-alkylhydrazinium chlorides with C_{10}–C_{18} in length were studied in comparison with Neonol AF 9-12 and Oksifos B surfactants. The limiting wetting angle, detergent and solubilization power, and foaming kinetics of these surfactants were studied in relation to the concentration of formation of monomolecular layer and type of the resulting micellar structures.

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In contrast to highly toxic 1,1-dimethylhydrazine widely used as a component of liquid propellant, the use of its low-toxic 1-alkyl derivatives in various branches of industry seems promising [1–5].

1,1-Dimethyl-1-alkylhydrazinium chlorides (DMAHCs) are tertiary hydrazinium salts (THSs) and surfactants, which strongly decrease the surface tension at the water–air boundary [6]. However, the data on their surface-active properties are scarce and available only for a few compounds [6, 7]. In this study we examined the surface-active properties throughout the DMAHC homologous series.

EXPERIMENTAL

DMAHCs of the general formula [R(CH_3)_2 NNH_2]Cl (where R = C_{n}H_{2n+1}; n = 10, 12, 14, 16, and 18 and mixture 12 + 14) were prepared by quaternization of 1,1-dimethylhydrazine with primary chloroalkanes using the known procedure [8] and purified by double or triple recrystallization from acetone. The content of the product in the samples, which was no less than 96%, was determined by the modified procedure given elsewhere [9].

The solubilization power was evaluated with respect to Sudan I oleophilic dye, which, being insoluble in water, is soluble in the hydrophobic part of micelles. The dye content was determined from the optical density of the solution recorded on an FEK-56M photocolorimeter (λ = 400 nm). Then, using the calibration curve, the content of the solubilized dye s in unit volume was calculated. The calibration curve was plotted using the solutions of Sudan I in benzene. The solubilization power of surfactants S was calculated as the ratio of s to the surfactant concentration:

\[ S = \frac{s}{c}, \]  

where c is the surfactant concentration in the solution (g l^{-1}) and s is the concentration of the solubilized dye (mg l^{-1}).

The detergent power with respect to M20 industrial oil and Tsiatim-221 lubricant was determined by the gravimetric method using St. 20 steel plates. A drop of the pollutant was deposited onto the plate, spread over its surface with a brush, and dried. Then, after drying, this procedure was repeated. After 1-day storage, the plates were weighed on an analytical balance with an accuracy of ±0.0002 g. The samples were immersed in the washing solution (40 ml) and stored in this solution with shaking for 3 and 30 min for the oil and lubricant, respectively. Then, the plates were carefully removed (holding at the edge), thoroughly washed with distilled water, and dried in air for a day. The dried plates were weighed. The detergent power (DP) (%) of the solutions in question was calculated from the following expression:

\[ WP = \frac{(P_2 - P_3)}{(P_2 - P_1)} \times 100, \]  

where P_1, P_2, and P_3 are the weights of the plates after 1-day storage, 3 min washing, and 30 min washing, respectively.
where \( P_1 \), \( P_2 \), and \( P_3 \) are the weights (g) of the plate before the experiment, with deposited model pollutants, and after treatment with the washing solution and distilled water, respectively.

The limiting wetting angle at the glass–DMAHC solution boundary and the kinetic stability of the foam were determined by the bubbling and shaking procedures, respectively [10].

The results given in this paper were averaged over three or four measurements, and the relative measurement error, as a rule, did not exceed 2–4%. The foam volume was normalized to 1 l of the disperse system. The experiments were performed at 20\(^\circ\)C.

### RESULTS AND DISCUSSION

The limiting wetting angles of DMAHC studied and of some surfactants of the other classes (anionic Oksifos B and nonionic Neonol AF 9-12) are listed in Table 1. All the compounds studied are the penetrating (wetting) agents, i.e., they hydrophilize the glass surface and decrease the limiting wetting angle at the glass–surfactant solution boundary (limiting wetting angle at the glass–water boundary 44°). As seen, Neonol AF 9-12 is the most active agent, except the concentration of 1 g l\(^{-1}\), when the minimal wetting angle is observed for DMAHC with \( R = C_{12} \) and \( C_{14} \) (technical name ChGS-1214).

As seen from Table 1, the dependences of \( \cos \theta \) on the surfactant concentration are nonmonotonic for both individual compounds (DMAHC with \( R = C_{10} \)–\( C_{18} \)) and their mixtures (Neonol AF 9-12, Oksifos B, and DMAHC with \( C_{12} + C_{14} \)), which is probably due to the features of the surface layer structure and micelle formation with increasing surfactant concentration.

The isotherm of the limiting wetting angle of DMAHCS passes through a minimum at low surfactant concentrations (3–4 g l\(^{-1}\)). Similar minima for DMAHCS were found previously in the isotherms of the surface tension at concentrations smaller than the critical micellization concentration (CMC), which was attributed to the presence of impurities with higher surface activity as compared to DMAHCS [6]. The disappearance of this minimum with increasing surfactant concentration is probably due to the solubilization of the impurity with the micelles of the main surfactant, appearing upon attainment of CMC, which slightly increases the limiting wetting angle at high concentrations of the surfactant.

Study of foaming in the aqueous surfactant solu-

### Table 1. Limiting wetting angle \( \theta \) at various concentrations of DMAHC \([R(CH_3)_2NNH_2]Cl]\)

<table>
<thead>
<tr>
<th>( R )</th>
<th>0, deg, at indicated concentration, g l(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{10}H_{21} )</td>
<td>47</td>
</tr>
<tr>
<td>( C_{12}H_{25} )</td>
<td>41</td>
</tr>
<tr>
<td>( C_{16}H_{33} )</td>
<td>40</td>
</tr>
<tr>
<td>( C_{18}H_{37} )</td>
<td>38</td>
</tr>
<tr>
<td>( C_{12-14} )</td>
<td>33</td>
</tr>
<tr>
<td>Oksifos B</td>
<td>36</td>
</tr>
<tr>
<td>Neonol AF 9-12</td>
<td>36</td>
</tr>
</tbody>
</table>

In most cases, foams prepared at high surfactant concentration \((c > 30\ \text{g}\ \text{l}^{-1})\) are unstable (Fig. 2). This is probably due to the fact that, with increasing concentration, the viscosity of the adsorption surfactant layers increases and they become heavier, which causes rapid foam degradation. The maximal lifetimes of the foam are listed in Table 2. The most stable foams are observed in the concentration range corresponding to the formation of the saturated adsorption layers [6].

![Fig. 1. Stability of foam obtained with different surfactants; surfactant concentration 5 g l\(^{-1}\). (V) Foam volume and (t) time. (1) DMAHC with \( R = C_{12} + C_{14} \), (2) Oksifos B, and (3) Neonol AF 9-12.](image-url)