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III CHEMICAL SCIENCES

LAWS OF MICELLE FORMATION IN AQUEOUS SOLUTIONS OF AZOMETHINES BASED ON MONOETHANOLAMINE AND ACETALDEHYDE

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Abstract: This paper investigates the micellization behavior of azomethine compounds synthesized from monoethanolamine (MEA) and acetaldehyde (AA) in aqueous solutions at different molar ratios (1:0.5, 1:1, 1:2, 1:4). The critical micelle concentration (CMC) was determined by conductometric and tensiometric methods. Particle size distribution and zeta potential were analyzed using laser diffraction technique (Mastersizer 3000). The results showed that all synthesized compounds exhibit amphiphilic properties and spontaneously form spherical micelles above CMC. The MEA:AA = 1:1 sample demonstrated the lowest CMC value (0.25 g/L) and the highest surface activity with minimum surface tension of 32.1 mN/m. Micelle size increased from 125 nm to 580 nm with increasing AA content, while the zeta potential reached maximum value (+32.2 mV) for the 1:1 ratio, indicating high colloidal stability. These findings suggest that MEA-AA based azomethines, particularly at 1:1 molar ratio, are promising surfactants for applications in gas purification, emulsification, and corrosion inhibition.

Keywords: azomethine, surfactant, micelle, CMC, colloid chemistry, zeta potential, monoethanolamine, acetaldehyde, surface activity, aggregation.

Introduction. Azomethines (Schiff bases) and their derivatives have attracted considerable attention in recent years not only in organic synthesis and coordination chemistry but also from the perspective of colloid chemistry [1]. The presence of both polar (C=N, -OH) and nonpolar (hydrocarbon radicals) fragments in azomethine molecules imparts amphiphilic properties, classifying them as surfactants [2].In aqueous media, amphiphilic molecules spontaneously associate above a certain concentration – the critical micelle concentration (CMC) – forming colloidal-sized aggregates called micelles. The micellization process and the properties of formed micelles (size, shape, charge, stability) play a crucial role in the practical applications of surfactants [3, 4]. Azomethines derived from monoethanolamine (MEA) and acetaldehyde (AA) possess unique amphiphilic characteristics due to the presence of both azomethine bond and hydroxyl group. However, the micellization behavior of these compounds in aqueous solutions and the effect of reactant molar ratios on this process have not been sufficiently studied.

This research aims to comprehensively investigate the micellization properties of condensation products synthesized at different MEA:AA molar ratios and determine their colloid-chemical parameters.

Literature review. Schiff bases, first synthesized by Hugo Schiff in 1864, represent an important class of organic compounds containing the azomethine group (C=N) [5]. The electronic structure of the azomethine group determines its reactivity, with the high electronegativity of the nitrogen atom and the presence of an unshared electron pair leading to strong bond polarization [6]. The fundamental method for synthesizing azomethines involves the condensation reaction of primary amines with carbonyl compounds (aldehydes or ketones). The reaction proceeds via a nucleophilic addition-elimination mechanism with the formation of an intermediate product – carbinolamine [7].From the colloid-chemical perspective, the amphiphilic nature of azomethines is their most important characteristic. The presence of polar and nonpolar fragments gives them surfactant properties [8]. In aqueous solutions above the CMC, these compounds self-associate to form micelles [9]. Several studies have investigated the surface-active properties of Schiff bases and their metal complexes [10, 11]. Malikov et al. [12] studied the adsorption isotherms and thermodynamic parameters of new Schiff base surfactants, demonstrating their potential as effective emulsifiers and corrosion inhibitors.The micellization process involves several stages: initially, dimers and trimers (pre-micellar associates) form through hydrogen bonding; above CMC, spherical micelles appear; at higher concentrations, cylindrical or lamellar structures may form [13]. The surface activity of azomethines manifests in their ability to form dense adsorption layers at phase boundaries, leading to reduced surface tension [14]. Azomethines derived from monoethanolamine are particularly interesting due to their bifunctional structure, retaining both the azomethine bond and free hydroxyl groups, which provide additional donor centers [15]. However, systematic studies on the effect of MEA:AA molar ratios on micellization behavior are lacking in the literature.

Methodology. Monoethanolamine (MEA, ≥99%, Sigma-Aldrich) and acetaldehyde (AA, ≥99.5%, Merck) were used as starting materials without further purification. Distilled water was used for preparing all solutions. Azomethine compounds were synthesized at four different MEA:AA molar ratios: 1:0.5, 1:1, 1:2, and 1:4. The synthesis was carried out under solvent-free conditions with stepwise temperature increase (10→50°C). The reaction products were purified by vacuum distillation and characterized by FTIR and NMR spectroscopy [16]. Aqueous solutions of the synthesized azomethines were prepared in the concentration range of 0.01 to 10.0 g/L. All solutions were freshly prepared before measurements.CMC values were determined using two independent methods:

Conductometric method: Electrical conductivity measurements were performed using an "Expert-002" conductometer at 25±0.1°C. The CMC was determined from the break point in the conductivity versus concentration plot.

Tensiometric method: Surface tension measurements were carried out using the Du Noüy ring method with a tensiometer at 25±0.1°C. The CMC was determined from

the intersection point of the two linear portions of the surface tension versus log concentration plot. The average hydrodynamic diameter and zeta potential of micelles were determined using a "Mastersizer 3000" laser diffraction analyzer (Malvern Instruments, UK) at 25°C. Measurements were performed at a concentration of 1.0 g/L (above CMC for all samples). Each sample was measured three times, and average values were reported. Viscosity measurements were performed using a rotational viscometer at 25°C with varying shear rates to evaluate the flow behavior of the micellar solutions. The maximum surface excess concentration (Γ_{max}) and minimum area per molecule (A_{min}) at the air-water interface were calculated using the Gibbs adsorption isotherm equations:

$\Gamma_{max} = -(1/RT)(d\gamma/d \ln C)$

$A_{min} = 1/(N_a\Gamma_{max})$

where γ is surface tension, C is concentration, R is gas constant, T is absolute temperature, and N_a is Avogadro's number.

Results. The CMC values for all synthesized MEA-AA azomethines were determined and found to depend significantly on the molar ratio. Table 1 presents the CMC values and surface activity parameters.

The results show that the MEA:AA = 1:1 sample exhibits the lowest CMC value (0.22-0.25 g/L) and the highest surface activity (lowest surface tension at CMC, γ = 32.1 mN/m). This indicates optimal hydrophilic-lipophilic balance (HLB) at this ratio, resulting in the highest tendency for micelle formation in aqueous media.For the 1:4 ratio, a sharp increase in molecular mass and excessive hydrophobicity leads to decreased water solubility and surface activity, reflected in higher CMC values.The minimum area per molecule (A_{min}) values indicate packing density at the interface. The 1:1 sample shows the smallest A_{min} (47.4 Å²), suggesting the most compact arrangement of molecules at the air-water interface.Laser diffraction analysis revealed that all samples form colloidal-sized particles (micelles) at concentrations above CMC (1.0 g/L). Table 2 presents the size distribution and zeta potential data. Micelle size increases progressively with increasing AA content, from 125 nm at 1:0.5 ratio to 580 nm at 1:4 ratio. This correlates with increased molecular mass and higher aggregation numbers. The relatively low polydispersity index (PDI) values (0.12-0.25) indicate monodisperse size distribution of the formed micelles.Zeta potential values reflect the electrokinetic stability of micelles. The highest positive zeta potential (+32.2 mV) was observed for the 1:1 sample. Values above $|\zeta| > 30$ mV indicate high aggregative stability. The lower zeta potential values for other samples, particularly the 1:4 ratio (+15.1 mV), suggest greater tendency for aggregation and potential precipitation over time.Viscosity measurements showed Newtonian behavior for all samples at concentrations up to 5.0 g/L. At higher concentrations (above 10 g/L), the 1:2 and 1:4 samples exhibited slight shear-thinning behavior, indicating possible structural transitions in the micellar system.

Discussion. The experimental results demonstrate that the molar ratio of MEA to AA significantly influences the micellization behavior of the synthesized azomethines. The 1:1 ratio appears optimal, showing the lowest CMC, highest surface activity, and most favorable micelle characteristics.The low CMC value for the 1:1 sample (0.22-0.25

g/L) compared to traditional surfactants indicates high efficiency in micelle formation. This can be attributed to the balanced hydrophilic-lipophilic nature of the molecule at this stoichiometric ratio, where the azomethine bond and hydroxyl group provide optimal polarity while the hydrocarbon fragments provide sufficient hydrophobicity. The increase in micelle size with AA content (from 125 to 580 nm) can be explained by two factors: (1) increased molecular mass due to oligomerization at higher aldehyde ratios, and (2) higher aggregation numbers resulting from enhanced hydrophobic interactions. The zeta potential data provide crucial information about colloidal stability. The high positive zeta potential (+32.2 mV) for the 1:1 sample indicates strong electrostatic repulsion between micelles, preventing aggregation and ensuring long-term stability. This is particularly important for practical applications where stable colloidal systems are required. The decrease in zeta potential for the 1:4 sample (+15.1 mV) suggests partial neutralization of surface charge, possibly due to closer packing of molecules or changes in the orientation of polar groups at the micelle surface. Compared to conventional surfactants, MEA-AA azomethines show comparable or superior surface-active properties. The minimum surface tension achieved (32.1 mN/m) is similar to that of many commercial nonionic surfactants, while the CMC values are in the same range as effective anionic surfactants. The bifunctional nature of these compounds, with both azomethine and hydroxyl groups, offers additional advantages for specific applications. The azomethine nitrogen can participate in coordination with metal ions, making these surfactants potentially useful as corrosion inhibitors. The hydroxyl groups provide additional sites for hydrogen bonding, enhancing their emulsifying properties.

Conclusion. Azomethine compounds based on MEA and AA were synthesized and characterized. All synthesized compounds exhibit amphiphilic properties and form micelles in aqueous solutions above CMC.The molar ratio of reactants significantly affects micellization behavior. The MEA:AA = 1:1 sample shows the lowest CMC (0.22-0.25 g/L) and highest surface activity with minimum surface tension of 32.1 mN/m. Micelle size increases with increasing AA content from 125 nm (1:0.5) to 580 nm (1:4). The 1:1 sample forms micelles with mean diameter of 210 nm and narrow size distribution (PDI = 0.12). The 1:1 sample exhibits the highest positive zeta potential (+32.2 mV), indicating superior colloidal stability compared to other ratios. The results demonstrate that MEA-AA azomethines, particularly at 1:1 molar ratio, are promising surfactants for various applications including gas purification, emulsion stabilization, and corrosion inhibition. Further studies should focus on the practical application of these surfactants in specific industrial processes and investigation of their long-term stability under operational conditions.

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Table 1. CMC and surface activity parameters of azomethines at different MEA:AA ratios (25°C)

Sample (MEA:AA)	CMC (conductometric), g/L	CMC (tensiometric), g/L	γ at CMC, mN/m	Γmax·10⁶, mol/m²	Amin, Å²
1:0,5	0,48	0,52	38,5	2,8	59,3
1:1	0,22	0,25	32,1	3,5	47,4
1:2	0,31	0,35	34,8	3,1	53,5
1:4	0,65	0,70	42,3	2,2	75,5

Table 2. Micelle size and zeta potential of azomethine-based systems (C=1.0 g/L, 25°C)

Sample (MEA:AA)	Average particle size (d, nm)	PDI	Zeta potential (ζ, mV)
1:0,5	125	0,15	+18,5
1:1	210	0,12	+32,2
1:2	350	0,18	+25,4
1:4	580	0,25	+15,1

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