Temperature Studies of Coacervating Cationic Soap Solutions

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Abstract

The micellar molecular weights (MMW) and the critical micelle concentration (CMC) of the homogeneous phase of the cationic coacervating soap system, Hyamine-1622, as a function of NaCl concn and temp were determined from light scattering and refractive index measurements. At constant temp, an overall two-stage growth process is indicated in this system. At low NaCl concn, the micelle grows to a limiting isotropic structure. At higher NaCl concn, the micellar growth is an exponential function of the NaCl concn. Temp studies of the CMC provide the basis for calculating values of the heats of micellization, ΔH_m in a limited range of NaCl concn (0–0.06*M*). The temp dependence of the MMW at fixed NaCl concn in the range of 17–47C is an exponential function and plots of log (MMW) vs. 1/T give straight lines with positive slopes. At low NaCl concn (0–0.8*M*), where there is an effective charge on the micelles, these slopes are small. At high NaCl concn, where the micelles approach zero effective charge (theta conditions), the slopes increase abruptly and remain approx constant over a wide range of NaCl concn (0.08–0.24*M*).

Introduction

THE SEPARATION of aqueous soaps into two solution phases (coacervation) occurs for a number of cationic and anionic soap (1,2) solutions with the addition of simple electrolyte to these solutions. The homogeneous phase of several cationic soaps, which form coacervates, show two pronounced effects prior to two phase formation (3): a) at low electrolyte concn the degree of micellar ionization is critically suppressed, and b) the soap micelles grow to a size which is of the order of 10^2–$2x10^2$ fold larger than the micelles in an electrolyte-free solution. An additional effect has been observed. Intermediate between zero electrolyte concn and the critical electrolyte concn (CEC) a narrow electrolyte transition range (ETR) may be identified (Fig. 1) for each coacervating system at a fixed temperature (3) in which light scattering, viscosity and diffusion studies indicate an apparent transformation of the micellar species from an essentially isotropic to an anisotropic entity.

In the theoretical treatment of micelle formation in soap systems, micellization is assumed to occur in terms of competitive energetic effects. The energy released by the aggregation of the hydrocarbon chains of the soap monomers is sufficient to overcome the electrostatic repulsion of the ionic groups and to balance the decrease in entropy accompanying the aggregation. The following expression for the critical micelle concn has been found to apply to a large number of ionic micellar systems (4,5).

$$\ln(\mathrm{CMC}) = -k_g \ln C_i + \text{const.} \qquad [1]$$

where C_i is the gegen ion concentration and k_g is an experimental constant with a value in the range of 0.4–0.6. For a large number of soaps, the temp coefficient of the CMC in these systems is small indicating that the energies involved in the aggregation process are relatively small.

There are two main directions in which the thermodynamic treatment of micelle formation has been developed: a) the micellar aggregation is treated as a micelle-monomer equilibrium governed by the mass action law (6,7,8,9), and b) the micelle is regarded as a separate phase in equilibrium with the free detergent molecules at constant activity (10,11,12). It has been demonstrated that in principle both treatments may be regarded as identical (5). If the aggregation number is small or if the change in aggregation number affects the thermodynamic functions appreciably the mass action model for micelle formation may be used. If the aggregation number is very large the separate phase model of the micelle may be applied.

The ultrafiltration and solubilization studies of Hutchinson, Inaba and Bailey (12,13) support the two-phase treatment of micellar systems. The ultrafiltration measurements show that the osmotic pressure of detergent solutions above the CMC is relatively constant, indicating that the free detergent molecule concn is nearly constant. If the composition of the solvent is specified, the CMC will be a function of temp and pressure only. For a given solvent, the composition of the micelle will also be fixed by the temp and pressure.

Treating the micelle as a separate phase with constant activity (5), and ignoring small deviations from ideality, Stainsby and Alexander (10) developed the following equation for the heat of micellization:

$$\Delta H_m = -RT^2 \partial \ln(\mathrm{CMC})/\partial T \qquad [2]$$

Matijević and Pethica (14) proposed an expression similar to equation [2] for ionic detergents:

$$\Delta H_m = -nRT^2 \partial \ln(\mathrm{CMC})/\partial T \qquad [3]$$

where n is 1 for complete ion exchange and 2 when

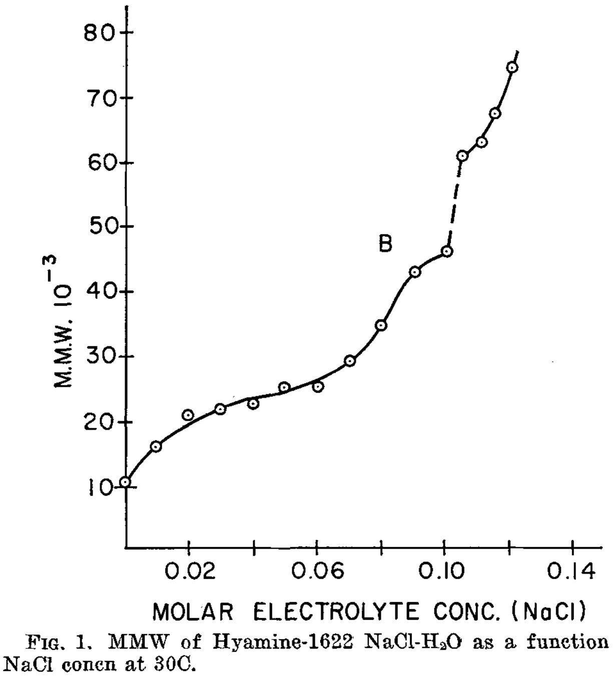

FIG. 1. MMW of Hyamine-1622 NaCl-H_2O as a function of NaCl concn at 30C.

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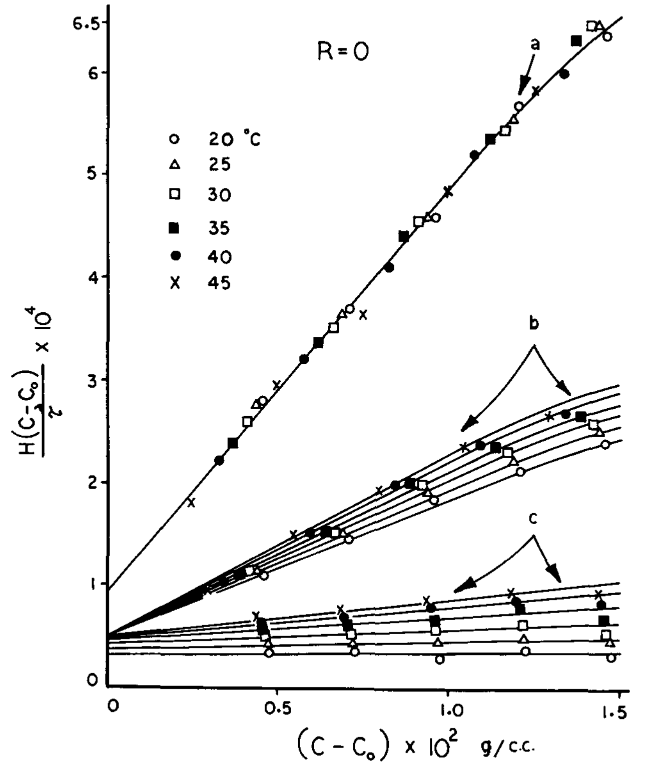

Fig. 2. Light scattering data of hyamine-1622. The effect of temp and NaCl concn.

a) 0*M* NaCl b) 0.01*M* NaCl c) 0.06*M* NaCl

no ion exchange occurs (i.e., the micelle has the same number of gegen ions and paraffin chain ions). When excess salt with an ion in common with the detergent is present the concn of gegen ions does not change with the CMC and the micelle-forming ion will have a constant activity coefficient independent of ion exchange (n = 1). In this latter case, the Matijević and Pethica expression for ionic detergents becomes identical with the Stainsby and Alexander expression. In addition (5), in the presence of an ionic agent the heat of micellization is given by the expression:

$$\Delta H_m = -RT^2(\partial \ln CMC/\partial T)_p - RT^2(\partial \ln C_i/\partial T)_p^{k_g} \quad [4]$$

where k_g is the constant given by Equation [1] and C_i is the gegen ion concn.

White and Benson (15) determined the heat of micellization of potassium octanoate by direct calorimetric measurements of heats of dilution. A comparison of these results with heats of micellization estimated from Equation [2] show considerable differences. Although calculations of ΔH_m from calorimetric data are very approximate these workers are of the opinion that Equation [2] leads to erroneous results. Shinoda et al. (5) indicate that the conventional heats of micellization obtained from the CMC temp dependence data require corrections due to 1) the change of activity with the concn of surface active ions, 2) the change in activity with the concn of gegen ions, and 3) the change of aggregation number with temp.

The coacervating system under investigation shows large changes in aggregation number (in the presence of added NaCl in excess of 0.06*M*), as a function of temp. Below 0.06*M* NaCl concn the system is relatively temp insensitive and exhibits negligible changes in the micellar aggregation number with temp over the range of 20–45C. In this range of NaCl concn, heats of micellization were calculated. At higher NaCl concn, where the aggregation number of these micellar systems are strongly temp dependent, the CMC- temp dependence data cannot, without ambiguity, be strictly used to calculate heats of micellization.

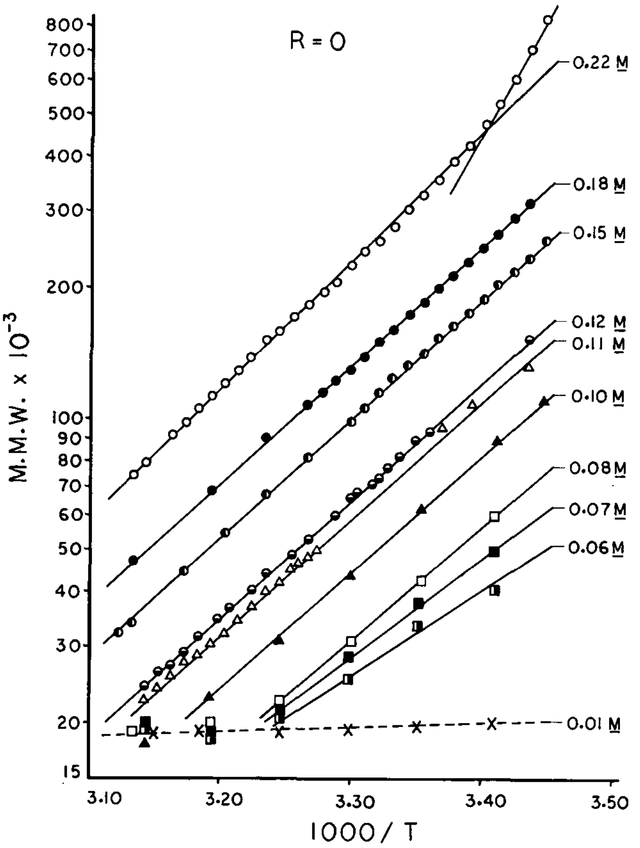

Fig. 3. MMW of Hyamine-1622 as a function of temp and NaCl concn.

Experimental

Materials. The following materials were used in this investigation:

1. Hyamine-1622-di-isobutylphenoxyethoxyethyldimethylbenzylammonium chloride monohydrate. This material (Hy) is a commercial bactericide produced by Rohm and Haas, and it was purified as described elsewhere (16).
2. NaCl was CP grade.

Apparatus. Light scattering measurements were performed in a modified Brice-Phoenix photometer, using incident unpolarized monochromatic light of wavelength 5460Å. The instrument was modified in such a way that the temp of the solution could be controlled by an air bath which does not interfere with the measurements. The temp of the air was controlled by a thermistor temp controller (Direct Dialing), and the YSI Thermistemp Model 71 of Yellow Springs Instrument Co., Inc. was used. The main control dial is graduated to 0.5C and the fine adjustment vernier dial is graduated in ten divisions (±0.05C). Probes are sensitive to better than ±0.1C above 60C, and better than ±0.05C below 60C. For the exact temp measurement of the solution in the cell, a surface temp probe was used with a time constant of 0.8 sec. The temp of the circulating air was controlled by using an air temp probe with a time constant of 2 min in free still air. The air was circulated by a pressure and vacuum motor-drive pump which has a free air delivery of 3.2 ft^3/min at 15 psi. The air was filtered continuously with a compressed

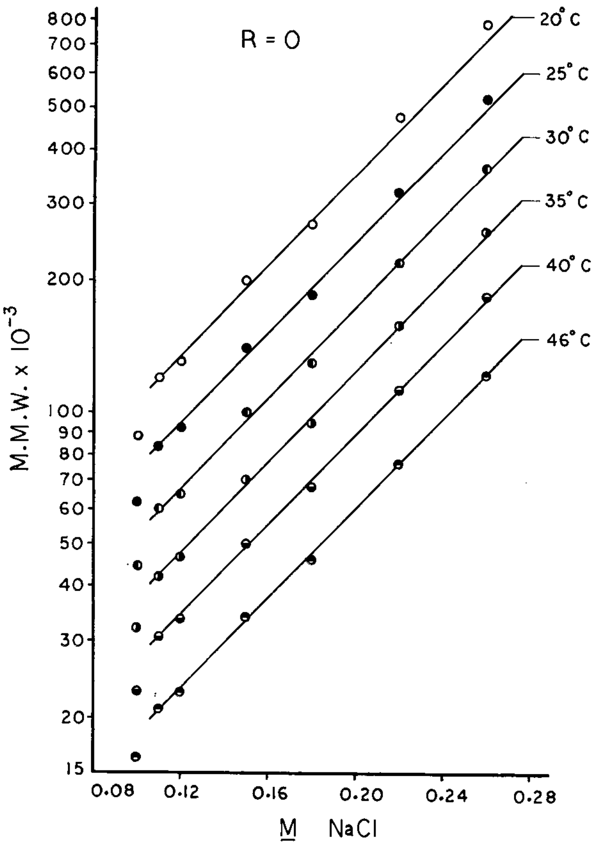

FIG. 4. MMW of Hyamine-1622 as a function of NaCl concn at fixed temp 20-46C.

air constant flow filter (E. H. Sargent & Co.) and also with a millipore filter of 1.2 μ pore size. The upper cyclical part of the special cored cell table of the Brice-Phoenix photometer was cut off and replaced by a fritted stainless steel disc, which allows the air to pass through and cover the cell. Also, the air was dried by passing it through a trap at −60C. The measurements were carried out in a cylindrical cell with solutions which had been filtered several times through millipore filters of 0.45 μ pore size. Refractive index increments (dn/dc) and CMC's were measured with a Zeiss dipping refractometer. For soap concn in excess of the CMC, dn/dc is independent of electrolyte concn, micellar size and shape, and temp. The refractive index increment for Hy-NaCl-H_2O systems is 0.1913 cm^3/g.

Results and Discussion

Figure 2 represents light scattering data over a temp range of 20–45C for 0,0.01 and 0.06*M* NaCl solutions. In the electrolyte free solutions a) none of the properties of the system are temp dependent over the 25C range of temp studied. In the 0.01*M* NaCl solutions b) the micelle mol wt is unaffected by temp changes. However, the slopes of the $H(C-C_0)/\tau$ vs. $(C-C_0)$ curves increase with increasing temp.

For the 0.06*M* NaCl solutions c) the situation is somewhat more complicated. At the higher temp, 35–45C, the MMW remain fairly constant although the slopes of the light scattering curves were considerably reduced compared to the 0.01*M* NaCl solution curves. For temp below 35C, two new effects become apparent; a) the MMW increase as the temp of the system is decreased, and b) the systems showed θ conditions, i.e., the slopes of light scattering curves are close to zero. Essentially what is described by the 0.06*M* NaCl set of curves is the transition of the micellar systems from one that is relatively insensitive to small temp changes to one that is temp sensitive.

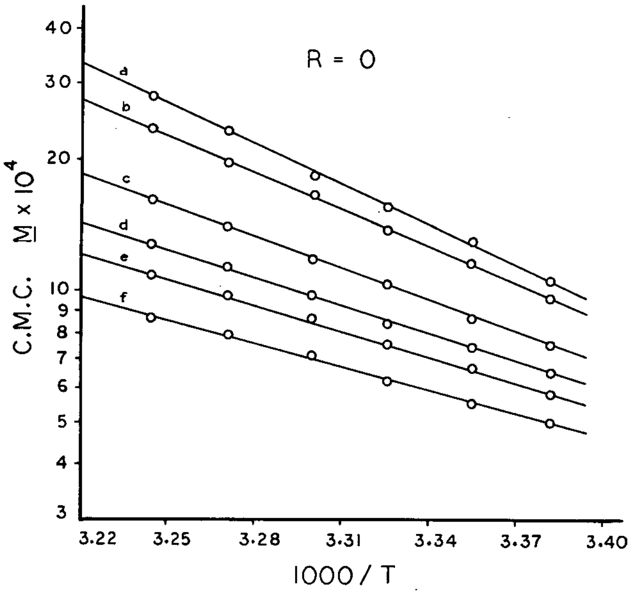

FIG. 5. CMC of Hyamine-1622 as a function of temp at fixed NaCl concn.

a) 0*M* NaCl
b) 0.01*M* NaCl
c) 0.02*M* NaCl
d) 0.03*M* NaCl
e) 0.04*M* NaCl
f) 0.06*M* NaCl

The nature of the transition described above shows in Figure 3. The logarithm of MMW as a function of 1/T at fixed NaCl concn is plotted for electrolyte concn of 0.06–0.22*M* NaCl. The broken line curve represents the MMW of 0.01*M* NaCl solution, and shows no significant micellar growth as a function of decreasing temp. The 0.06*M* NaCl solution shows no micellar growth as the temp is decreased from 45C to 35C. Between 35C and 20C the micelles grow appreciably and this growth is an exponential function of the reciprocal of the temp. The rate of micellar growth as a function of 1/T increases as the NaCl concn is increased to 0.10*M* NaCl. For NaCl concn in excess of 0.10*M* the rate of micellar growth as a function of 1/T remains approx constant.

Figure 4 represents the logarithm of MMW as a function of NaCl concn in the range of 0.10–0.22*M* at fixed temp. For each of these curves, except for the 0.10*M* NaCl solution, micellar growth is indicated to be an exponential function of the NaCl concn. The significance of the deviation in 0.10*M* NaCl solutions of MMW from the logarithmic plots shows in Figure 1. At this NaCl concn the system is in the electrolyte transition region. The data presented in Figure 4 would indicate that the electrolyte transition region is not temp dependent. In a previous paper (16), it was shown that this transition is related to the depression to the micellar ionization induced by the addition of electrolyte to the micellar solution. The transition occurs when the micellar ionization is reduced to approx 4.4%. The deviation from linearity of the upper points of 0.22*M* NaCl curve may be attributed to the

TABLE I

Conventional Heats of Micellization of Hyamine-1622 as a Function of NaCl Concn (0–0.06M NaCl)

$-H_m/RT^2 = (\ln(CMC)/T)_p$

M NaCl	$-H_m$ Kcal/mole
0.00	14.19
0.01	13.05
0.02	11.12
0.03	9.57
0.04	8.97
0.05	8.30

contribution to the light scattering intensity of critical opalescence. At the lower temp the system is close to the critical point.

Conventional heats of micellization were calculated from Equation [2] for solutions containing 0–0.06*M* NaCl. These results show in Table I.

Conclusion

Hyamine-1622 NaCl solutions at zero and low NaCl concn have low CMC values which are close to those observed in non-ionic detergent systems. Flockhart (17) has shown, in comparative studies of soaps of different hydrocarbon chain lengths, that the lower the CMC the more negative will be the heat of micellization.

The low CMC values and the large negative values of the heats of micellization of the long chain quaternary ammonium salts, which form coacervates, suggest that these micellar systems show some of the properties of simpler monomeric quaternary ammonium salts. The major property of interest in this respect is the hydrophobic character of the quaternary ammonium cation. Hyamine-1622 NaCl micellar solutions exhibit a high degree of sensitivity to small changes in NaCl concn (16) and temp. In addition, these systems show a marked electrolyte specificity (18). These are properties observed in hydrophobic colloidal systems.

In an opposite sense, Matijević and Pethica (14) explain the small negative values of ΔH_m for sodium dodecyl sulfate in terms of the large positive contribution to ΔH_m due to the desolvation of the highly solvated anion of this salt. Both the Matijević and Pethica study and Hyamine-1622-NaCl study indicate that the solvation properties of micellar systems play a significant role in the energetics of micelle formation.

ACKNOWLEDGMENT

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Catalysts for Selective Hydrogenation of Soybean Oil[1] III. Hydrogenation Catalysts Prepared on Molecular Sieves and Other Supports

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Abstract

A survey of nickel, platinum and palladium catalysts prepared on silicas, aluminas and molecular sieves indicated that the nature of such supports contributed importantly to selective hydrogenation of soybean oil. Nickel-molecular sieve catalysts provided both high hydrogenation selectivity and low *trans*-isomer formation. Some kind of spatial hindrance may be postulated in explanation of the results.

Introduction

PRIOR PAPERS in this series were concerned with the development of an experimental evaluation for determining hydrogenation selectivity (1) and application of this method to a variety of commercial catalysts (2). In a kinetic study, Bailey (3) had indicated that under conditions producing selective hydrogenation of soybean oil, the ratio of linolenic to linoleic components reacted was 100/50. With linseed oil, a condition producing a k_{Ln}/k_{Lo} ratio of 2.5 was obtained under selective conditions whereas 1.7 was found under non-selective conditions. This orientation is of particular value in reviewing the survey on selective hydrogenation of soybean oil with various commercial catalysts (2), where the selectivity index ($S_L = k_{Ln}/k_{Lo}$) was 2.4 or better for several platinum, palladium and rhodium catalysts but where many nickel preparations did not demonstrate an S_L value of 2.0. It was felt that development of nickel catalysts would have the greatest import both from a practical as well as technical viewpoint.

The preparation and properties of catalysts for glyceride oil hydrogenation has been reviewed by Feuge (4). While variations in selectivity between different types of nickel catalysts preparations are known, factors producing such selectivity are not presently recognized. Further, it is indicated that platinum and palladium, although producing the most active catalysts, are not selective.

Catalyst Preparation

Impregnation. Most of the catalysts were prepared by impregnation on various supports. The procedure comprised admixture of the support with a metal salt dissolved in sufficient distilled water to form a paste. This mixture was heated with stirring at low heat to drive off excess water and to form a uniform product which was then dried at 110C. This material was placed in a cold muffle and brought slowly to a max temp of ca. 500C. In several cases, the synthetic zeolites were first exchanged with nickel cation, and then impregnated as indicated in Table I. Before

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