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MASTER

AGGREGATION OF SODIUM ALKYL BENZENESULFONATES IN AQUEOUS SOLUTION

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INTRODUCTION

The origins of the ultralow tensions (less than  $10^{-2}$  dyn/cm) between phases in multicomponent systems containing surfactants are currently being actively investigated. Generation and maintenance of these ultralow tensions are essential for successful mobilization of residual oil in immiscible surfactant-water or microemulsion flooding processes. We are particularly interested in one facet of the problem: whether surfactant aggregation in the aqueous phase has anything to do with the production of ultralow interfacial tensions (IFTs). Since commercially available petroleum sulfonates contain complex mixtures of surfactants (plus other components) which are unsuitable for fundamental physicochemical work, we chose to work with two pure sodium alkylbenzenesulfonates which can serve as models for the commercial material. The surfactants studied were sodium p(1-heptylnonyl)benzenesulfonate,  $8\phi C_{16}SNa$ , also known as Texas #1, and sodium p(1-pentylheptyl)benzenesulfonate,  $6\phi C_{12}SNa$ .

The phase behavior and state of aggregation of multicomponent systems containing Texas #1 have been studied by several groups of workers (1-4).

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The Minnesota group (3) has been particularly interested in "discovering connections between low tensions and the tendency of surfactants to form micelles and liquid crystals in aqueous solutions". Their data lead to the conclusion that micelles are not the cause of low tensions, in direct contrast to the conclusions of the Texas group (2) that "low interfacial tensions are associated intimately with swollen micellar systems". The results obtained at Minnesota on the importance of dispersed surfactant (located in a surfactant-rich third phase at the oil-water interface) in generating ultralow IFTs are supported by Hall's work (5) on commercial systems.

We became interested in the question of whether  $8\phi C_{16}SNa$  forms micelles or a lamellar liquid crystalline mesophase as the first aggregated structure in water when we examined reported critical micelle concentrations (c.m.c.) for two of its homologues (6,7). From the expression  $\log c.m.c. = A - Bn_{eff}$ , where  $n_{eff}$  is calculated after (8), the estimated c.m.c. for  $8\phi C_{16}SNa$  is

Glossy A

obtained. This estimated value is approximately a factor of six below the solubility limit of Texas #1 in water at 60°C (3). The Texas #1 -H<sub>2</sub>O system thus possesses a very restricted isotropic solution region [Figure 1(9)], a characteristic shared with many other surfactants having two alkyl groups

per molecule [for example, the short-chain phosphatidylcholines (10)]. As the alkyl groups get longer, a point will be reached where the solubility limit (effectively the solution - solution +LC boundary) lies at a concentration below the estimated c.m.c. Since the Minnesota group's conductivity measurements produced no evidence for a c.m.c. for Texas #1 in water, they concluded that this point is reached at (or before) Texas #1 in the homologous series of which it is a member. This experimental result is at odds with our c.m.c. estimate described above. We therefore set out to reinvestigate the aggregation behavior of Texas #1 in water, using data collected for  $6\phi C_{12}SNa$ , a known micelle-former (11), as a guide in interpreting the Texas #1 results.

It should be noted that the aggregation behavior of Texas #1 is potentially of interest for reasons other than those related to enhanced oil recovery. The theoretical treatment of Israelachvili, et al. (12) correctly predicts that the first LC mesophase formed by a surfactant such

Figure 1

as Texas #1, which possesses a bulky hydrophobic region, should be lamellar. Furthermore, the micelles formed (if any) in the isotropic solution region prior to crossing the solubility limit should be discs (12,13). This latter prediction fails for the phosphatidylcholines (14), which in fact form rodlike micelles prior to a lamellar mesophase, as surfactant concentration is increased.

#### EXPERIMENTAL

Surfactant Purity. A gift of sodium p(1-pentylheptyl)benzenesulfonate was received in analytically pure form (C: 61.88%, theorect 62.06; H: 8.59%, theorect 8.39) from Henkel. Sodium p(1-heptylnonyl)benzenesulfonate was synthesized at the University of Texas and further purified at Minnesota (3) or at Carnegie-Mellon University (1). We thank these research groups for providing the pure surfactant.

Conductivity measurements were carried out as described previously (15), using either separate surfactant solutions or successive dilutions as a means of changing concentrations.

Density measurements were performed using a Mettler/Par Paar DMA 601 HT vibrating tube densitometer. It has a precision of  $\pm 5 \times 10^{-6}$  g/cm<sup>3</sup> and was calibrated using air and triply distilled water. We thank Professor W. A. Van Hook, University of Tennessee, for permission to use the densitometer.

Viscosity measurements were carried out in ASTM-calibrated Cannon-Fenske viscometers, Size 50.

EMF measurements, for determination of Na<sup>+</sup> binding to the aggregates, employed an Orion 90-02-00 reference electrode (NH<sub>4</sub>Cl outer filling solution) and an Orion 94-11A sodium electrode. All solutions were stirred magnetically, using a flea bar stirring bar which does not create a vortex.

Static and dynamic light scattering measurements were performed at the

University of Michigan. The spectrometer and the data-handling techniques have been described previously (16). Samples for light scattering were filtered through 0.22  $\mu\text{m}$  Millipore filters and then centrifuged for a few hours in the scattering cells to settle any dust present. Intensities were determined at angles of 40°, 60°, 90° and 120°.

All solutions were prepared on a wt/wt basis, with measured densities being used to convert to a wt/vol basis when needed. In the case of Texas #1, the water was always thermostatted first, followed by addition and dissolution (or dispersion) of the surfactant with magnetic stirring. All solutions were thermostatted in constant temperature water or oil baths (minimum precision  $\pm 0.05^\circ\text{C}$ ) before measurements were made.

#### RESULTS AND DISCUSSION

The  $6\phi\text{C}_{12}\text{SNa}$  material is known to be very soluble in water [at least 0.1 M (11)] and to possess an (apparent) c.m.c. at  $(2-3) \times 10^{-3}$  M, depending on temperature. Figure 2 shows the density data for  $6\phi\text{C}_{12}\text{SNa}$  solutions at 25°C which suggest a c.m.c. of  $2.2 \times 10^{-3}$  M, consistent with predictions. From Figure 3 and the application of Equation 1 (17,18), one can determine  $\Delta\bar{V}^m$  ( $\approx \phi_v^m - \phi_v^s$ ) for this surfactant to be 13.6 ml/mole. There is some

$$\phi_v = (\text{cmc}/m)\phi_v^s + [(m-\text{cmc})/m]\phi_v^m; \phi_v^s = 288.7 \text{ ml/mole monomer} \quad 1)$$

uncertainty in the determination of  $\phi_v^s$  from Figure 3, since we are working at surfactant concentrations low enough to produce large error bars on the calculated apparent molal volumes. The  $\phi_v^s$  value of 288.7 ml/mole was determined by using Equation 2 below the c.m.c. ( $\phi_v \approx \text{MW} \times \bar{v}$ ). Despite the

$$\rho = \rho_0 + (1-\bar{v}\rho_0)c, \quad c \text{ in g/ml} \quad 2)$$

problems with precision the value of  $\Delta\bar{V}^m$  obtained for  $6\phi\text{C}_{12}\text{SNa}$  is reasonable,

since sodium dodecylsulfate (a surfactant molecule of similar length) has reported values of  $\Delta\bar{V}^m$  ranging from about 10.8 to 13.5 ml/mole (17,19).

Double tailed surfactants which form micelles often show high ionization degrees ( $\alpha$ ), a result of the low aggregation number of their micelles. To a first approximation,  $\alpha$  may be equated to the ratio  $S_2/S_1$ , where  $S_1$  = slope below and  $S_2$  = slope above the break in a surfactant's specific conductivity vs. concentration plot. Evans' (20) determined an  $\alpha = 0.76$  for sodium 1-pentylundecylsulfate, whose aggregation number equals 24. These double tailed surfactants also often display equivalent conductivity vs.  $\sqrt{c}$  plots which show massive deviations from Onsager limiting law behavior at sub-c.m.c. concentrations. Dialkyldimethylammonium chlorides (21) and sodium dialkylsulfosuccinates (22), in addition to Evans' sodium alkylsulfates (20), show this behavior.

Conductivity data for  $6\phi C_{12}SNa$  in water and in aqueous 1-butanol are shown in Figures 4,5 and 6. As Figure 4 indicates, there are breaks in the specific conductivity versus concentration plots. The effect of the 1-butanol on the position of the break is unusual, since 1-butanol generally decreases the c.m.c.s of surfactants (23). The slope ratios derived from Figure 4 for  $6\phi C_{12}SNa$  are 0.724 (water), 0.852 (1.5% 1-butanol) and 0.824 (3% 1-butanol); the alcohol is increasing the apparent  $\alpha$  values, as expected.

The equivalent conductivity ( $\Lambda$ ) vs.  $\sqrt{c}$  plots in Figures 5 and 6 show the anomaly (a decrease in  $\Lambda$  at low concentrations) characteristic of double-tailed surfactants. The anomaly is less pronounced at 45°C, where the behavior of  $\Lambda$  is close to that of the Onsager limiting law for 1:1 electrolytes. The theoretical slope,  $S$ , for the equation  $\Lambda = \Lambda_0 - S\sqrt{c}$  was calculated according to Fuoss (24).

The conductivity of a Texas #1 solution depends strongly on age, a phenomenon which has been observed previously (3). We have observed this



Figure 6

with both Minnesota and Carnegie-Mellon samples of Texas #1; the breaks in the specific conductivity vs. concentration plot at 45°C (chosen for solubility considerations) occur from  $6$  to  $9 \times 10^{-4}$  M, depending on sample history. Figures 7 and 8 show data for the Carnegie-Mellon material; aged solution refers to the stock solution being diluted ( $2.1 \times 10^{-3}$  M, well under the solubility limit of  $3.4 \times 10^{-3}$  M), which was 4 weeks old when measurements by successive dilution were initiated. The  $\Lambda$ 's are extremely high for the aged solution; they agree quite well with those reported by the Minnesota group (25).

Although  $S_2/S_1$  values are often quoted as being numerically equal to  $\alpha$ , Evans' complete equation, Equation 3, should in fact be used when the micelles have small aggregation numbers. Assuming for the moment that the  $8\phi C_{16}$  SNa fresh solutions as well as the  $6\phi C_{12}$  SNa solutions contain micelles,

$$1000 S_2 = \frac{(\bar{n}-m)^2}{\bar{n}^{4/3}} (1000 S_1 - \Lambda_{Na^+}) + \frac{\bar{n}-m}{\bar{n}} \Lambda_{Na^+} \quad 3)$$

$\alpha$  values ( $1-m/\bar{n}$  in Evans' terminology, where  $m$  = counterions per micelle) may be calculated. Aggregation numbers used are  $\bar{n} = 21$  for  $6\phi C_{12}$ SNa (vide infra) and  $\bar{n} = 30$  for  $8\phi C_{16}$ SNa. The latter  $\bar{n}$  is purely an estimate based on Texas #1's longer alkyl chains. For  $8\phi C_{16}$ SNa at  $45^\circ\text{C}$ ,  $\alpha = 0.34$  and for  $6\phi C_{12}$ SNa at  $30^\circ\text{C}$ ,  $\alpha = 0.45$ ; it should be noted that  $\alpha$  for  $6\phi C_{12}$ SNa is practically independent of temperature (at  $45^\circ\text{C}$ ,  $\alpha = 0.46$ ). The  $\alpha$  values determined in this way are higher than values for single-tailed surfactants, but they agree quite well with recent determinations by Zana (26) for dodecyldimethylalkylammonium bromides.

EMF measurements may also be used to estimate  $\alpha$ ; results using an Orion sodium electrode are displayed in Figure 9. The data for  $8\phi C_{16}$ SNa are presented simply to note the similarity with  $6\phi C_{12}$ SNa. Because of solubility limitations, too few data points were obtained above the transition region to reliably determine  $\alpha$ . In addition, the slope of the EMF vs.  $\log c$  plot for  $8\phi C_{16}$ SNa below the initial break is +82 mV per decade, much greater than the Nernstian value of +63 mV at  $45^\circ\text{C}$ . Concentrations have not been converted to activities because the concentrations studied are so small.

The EMF vs.  $\log c$  plot for  $6\phi C_{12}$ SNa, Figure 9(a), is very similar to that obtained recently by Evans and coworkers for SDS (27). They identify the second break point as a second c.m.c., above which micelle-micelle repulsion leads to an ordering of the micelles. It is also possible, however, that the concentration region between the two breaks is simply a transitional one, during which micelle size, counterion binding, etc. is changing. The first break does correspond well to the c.m.c.s determined by conductivity and density measurements. EMF measurements for  $6\phi C_{12}$ SNa in aqueous 1-butanol at  $30^\circ\text{C}$  produced a very surprising result: no break in the EMF vs.  $\log c$  plot, with slopes of 42.8 mV per decade in 1.5% 1-butanol and 53.6

mV per decade in 3.0 % 1-butanol. The low slopes are not due to marked nonNernstian behavior caused by the 1-butanol, since the slope for NaCl solutions in 1.5% 1-butanol at 30°C is 56.5 mV per decade. It is not clear why conductivity appears to detect aggregation beyond perhaps dimerization [which could explain the values of 42.8 mV and 53.6 mV, see Evans (27)], while the EMF measurements do not. Since we have no information on aggregate size in aqueous 1-butanol, this question will not be discussed further.

To calculate  $\alpha$  for  $6\phi C_{12}SNa$  in water at 30°C, Zana's method (26) is employed. The behavior of monomeric surfactant below the c.m.c. is used to calculate the monomers' contribution to the measured potential above the c.m.c., using Equation 4. From equations 5 and 6  $\alpha$  is then calculated

$$E_c = E_o + p \log c; p = 58.3; E_o = 130.4 \quad 4)$$

$$f = \exp[(E_o' - E_c)/p] \quad 5)$$

$$\alpha = [(c \times f) - c.m.c.]/(c - c.m.c.) \quad 6)$$

point-by-point, where  $E_c'$  is the actual measured potential at surfactant concentration  $c$ . The c.m.c. is taken to be the appropriate break-point (i.e., the intersection of the relevant straight lines). When one evaluates the region from  $2 \times 10^{-3}$  M to  $4 \times 10^{-3}$  M  $6\phi C_{12}SNa$  in this manner,  $\alpha = 0.52$  is obtained. If the second c.m.c. possibility is ignored and the region above  $5 \times 10^{-3}$  M  $6\phi C_{12}SNa$  is considered (c.m.c. =  $1.3 \times 10^{-3}$  M),  $\alpha = 0.46$ , the same value the conductivity data yield.

Viscosity measurements were performed for  $6\phi C_{12}SNa$  at 30°C in water, 3% 1-butanol and in 0.03m NaCl; the data are plotted in Figure 10 according to Equation 7. Since we were working at low surfactant concentration, there is

$$(\eta_{rel} - 1)/(c - c.m.c.) = [\eta] + A(c - c.m.c.) \quad 7)$$

considerable scatter. Therefore the intercepts were evaluated by making the

Figure 10

simplifying assumption that  $A=0$ . Whether this assumption is made or not, it is clear that two conclusions can be drawn: (1)  $[\eta]$ , the intrinsic viscosity, is 4.55 kg/mol in both water and 3% 1-butanol and (2) a substantial electroviscous effect, consistent with the high value of  $\alpha$  and the low ionic strength of the solutions, is operating in water.

The addition of 0.03m NaCl greatly screens the electroviscous effect, dropping  $[\eta]$  down to 1.85 kg/mol. Using the effect of added NaCl on  $[\eta]$  for SDS as a model (28), additional NaCl would bring about a further modest decrease in  $[\eta]$ , down to about 1.56 kg/mol, assuming no change in micelle shape. Higher concentrations of added NaCl were not employed experimentally because the surfactant's Krafft point rapidly increases as  $[\text{NaCl}]$  increases (vide infra).

Assuming that the  $6\phi_{12}\text{SNa}$  micelles are spheres (shape factor = 2.5), the micellar hydration may be calculated using  $V_2 = [\eta]/2.5$  and  $V_2 = \bar{v}_{\text{surf}} +$

$\delta/\rho$ , where  $\bar{v}_{\text{surf}} = 0.866$  ml/g (from density measurements),  $\delta$  is grams of water per gram of surfactant and  $\rho$  is the density of water. With  $[\eta] = 4.50$  ml/g,  $\delta$  is therefore 0.93; this corresponds to 18 moles water per mole surfactant. Other sodium alkylbenzenesulfonates show slightly lower extents of hydration: for sodium p-n-octylbenzenesulfonate, the value is nine (29).

The density, conductivity and EMF measurements provide indirect, but physically reasonable, evidence for aggregation of  $6\phi\text{C}_{12}\text{SNa}$  to normal, small, spherical micelles in aqueous solution. The corresponding data for Texas #1 suggest that aggregation occurs in its solutions, but that the nature of the aggregate(s) present depends on solution age and method of preparation. Certainly the conductivity measurements on fresh solutions are suggestive of small, normal micelles here as well. Obviously one needs more direct information on the sizes and shapes of the aggregates present. To this end, we have performed limited, preliminary studies of these systems by static (total intensity) and dynamic light scattering at the University of Michigan. The results are tabulated in Table I.

There was not sufficient time to do measurements at several surfactant concentrations, but the total concentration of aggregated surfactant is only 0.1 to 0.3 wt %. Thus the extrapolation to zero concentration of aggregated surfactant should not greatly change the  $M_w$ 's. Radii of gyration and micellar molecular weights in the  $\theta \rightarrow 0^\circ$  limit were calculated using Equation 8, where  $H = 4\pi^2 n_o^2 (dn/dc)^2 / N_A \lambda_o^4$ ,  $\lambda_o = 5.14 \times 10^{-5}$  cm, and the

$$\frac{H(c-c.m.c.)}{R_{vv,\text{soln}} - R_{vv,c.m.c.}} = \frac{1}{M_w(\text{app})} \left[ 1 + \frac{16\pi^2 n_o^2}{3\lambda_o^2} \langle R_g^2 \rangle_z \sin^2(\theta/2) \right] \quad 8)$$

concentrations are expressed in g/ml. The refractive index increment  $(dn/dc)$  determined for  $6\phi\text{C}_{12}\text{SNa}$ , 0.167 ml/g, was also used for  $8\phi\text{C}_{16}\text{SNa}$ . The reported  $M_w$ 's at  $\theta = 90^\circ$  are simply the  $R_{vv}/H(c-c.m.c.)$  values there. The effective hydrodynamic radii,  $R_H$ , were obtained from the translational

TABLE I. Properties of  $6\phi C_{12}SNa$  and  $8\phi C_{16}SNa$  Aggregates from Light Scattering

Solution	T, °C	Age, hrs <sup>a</sup>	$M_w$ (app) <sup>b</sup>	$R_g$ , Å	$Z^c$	$R_h(\theta)$ , Å
$5.1 \times 10^{-3}$ m $6\phi C_{12}SNa$	30	24	11,600 (at 90°)	-	-	16,920 (40°)
"	55	48	15,700 (at 90°)	-	-	-
"	"	"	29,700	695	1.67	900 (40°)
$8.5 \times 10^{-3}$ m $6\phi C_{12}SNa$	30	8	3,470 (at 90°)	-	-	18 (40°)
"	55	72	8,620 (at 90°)	-	-	-
"	"	"	24,700	705	1.69	1030 (40°)
$8.5 \times 10^{-3}$ m $6\phi C_{12}SNa$ + $6.7 \times 10^{-2}$ m NaCl	55	30	32,900 (at 90°)	-	-	-
"	"	"	46,800	201	1.11	20.3, 1880 (40°)
$3.2 \times 10^{-3}$ m $8\phi C_{16}SNa$	45	30	27,200 (at 90°)	-	-	-
"	"	"	57,000	550	1.51	720 (50°)
"	55	72	-	-	-	"

<sup>a</sup>From time solution was prepared from solid surfactant or by dilution or addition of concentrated aqueous NaCl.

<sup>b</sup>Calculated, except where indicated, by extrapolation to  $\theta = 0^\circ$  using Equation 8. An extrapolation to  $(c - c.m.c.) = 0$  was not done.

<sup>c</sup>Defined as  $I_{soln}(60^\circ) - I_{solv}(60^\circ) / I_{soln}(120^\circ) - I_{solv}(120^\circ)$ .

diffusion coefficients of the aggregates using the Stokes-Einstein relation, Equation 9 (spherical particles assumed). The diffusion coefficients are

$$D = k_B T / 6\pi\eta R_H \quad 9)$$

calculated from the decay constant ( $\Gamma$ ) under homodyne conditions, of the time correlation function of the scattered light's intensity, using Equation 10. An  $8.5 \times 10^{-3}$  m solution of  $6\phi C_{12}SNa$  which was only 8 hours old gave

$$\Gamma = 2Dq^2, \text{ where } q = (4\pi n/\lambda) \sin(\theta/2) \quad 10)$$

the expected simple behavior: evidence for a single, spherical aggregate,  $R_H = 18 \text{ \AA}$ , which is a reasonable value for the length of the  $6\phi C_{12}S$  anion plus a small hydration sheath. A radius of  $15 \text{ \AA}$ , which allows for some gauche conformations along the hydrocarbon chains corresponds to  $\bar{n} = 28$ ; there is some indirect evidence in the literature (30), from data on kinetics of micellization, for  $\bar{n} = 21$ . The latter value is the one we used in applying Evans' treatment to our conductivity data. In this "young" solution, there is no evidence for a second much smaller decay constant in the dynamic measurements.

However, an aging effect is operating, because dilution of the  $8.5 \times 10^{-3}$  m  $6\phi C_{12}SNa$  solution to  $5.1 \times 10^{-3}$  m  $6\phi C_{12}SNa$ , followed by measurements after 24 hours, shows an increase (rather than the expected decrease) in total intensity of the scattered light and the appearance of a second, small decay constant in the dynamic measurements. The sampling times for the two correlation functions are well separated: 2  $\mu\text{sec}$  and 100  $\mu\text{sec}$  at  $\theta = 40^\circ$ ; both are fit nicely to a single exponential function. The appearance of the second decay constant is accompanied by a large dissymmetry in the intensity of the scattered light and of course an increase in  $M_w$ . The same effect is observed in the original stock solution ( $8.5 \times 10^{-3}$  m) as it ages; after 72

hours it is difficult to observe the large (short-time) decay constant correlation function, because the other one continues to increase in importance.

Is the second decay constant really associated with a second aggregate, or is it due to long range correlations (an ordering effect) of the small aggregates (31)? The effect of added salt should distinguish these two possibilities. If an ordering effect is operating, micelle-micelle repulsion will decrease and the second  $\Gamma$  will increase, leading to a decrease in the apparent  $M_w$ . If an aggregate is responsible, the salt should increase its apparent  $M_w$  ( $\Gamma$  decreases). In fact, the latter result is obtained; the small aggregate also increases in size when 0.067 m NaCl is added to 0.0085 m  $6\phi C_{12}SNa$ . (Measurements were done for this system at 55°C, because its Krafft point is roughly 46°C.) However,  $R_g$  and  $Z$  decrease, which is not really consistent with the observed decrease in  $\Gamma$ .

Even in the aged solutions, the small micelles are still the dominant species: the observed total intensities and hence  $M_w$ s are too small for it to be otherwise. However, the large "aggregate" dominates  $R_g$ , as expected (32). We believe that large aggregates are indeed present, since the aging effect is operating. It seems to us unlikely that long range correlations would grow with time. One may then ask what shape these aggregates are; the functional relationship between  $R_g$  and  $R_H$  is known for several particle shapes (32). This allows us to rule out rodlike particles, but either spheres or oblate ellipsoids are consistent with an  $R_g$  modestly smaller than  $R_H$  (for spheres,  $R_g = \sqrt{0.60} R_H$ ). It is not possible to distinguish these two possibilities without a value for the large aggregate's  $M_w$ ; we do not have sufficient data to determine this. The possibility of oblate ellipsoids is of course very attractive, because it agrees with theoretical predictions (12,13) for micelle shapes of lamellar mesophase precursors.

It is unusual, but not unknown, to find two very different micellar



sizes (well separated and quite monodisperse) present in such dilute surfactant solutions. Hoffmann has observed this behavior with certain perfluoro surfactants (33). We do not believe the large aggregate represents a nucleus for phase separation, because of its apparent monodispersity. Hoffmann's model for these large aggregates may be described as a curved surfactant shell enclosing a core containing surfactant-counterion ion-pairs.

The data for  $8\phi C_{16}SNa$  show only the large aggregate in the dynamic measurements; the measured  $R_H$ ,  $Z$  and total  $M_w$  are remarkably similar to what was observed for  $6\phi C_{12}SNa$ . Several facts argue against the large aggregate being a dispersed bit of a liquid crystalline mesophase: (1) the low  $M_w$ , which must imply the small micelle is present but not detected in the dynamic measurements; (2) the apparent monodispersity of the aggregate size distribution (good single exponential fit); (3) the numerical value of  $R_H$ , which is much too small for a mesophase fragment. We did not look for much larger aggregates at much longer sampling times.

The Texas #1 samples do however show aging effects in the conductivity measurements, which  $6\phi C_{12}SNa$  does not show. These take the form of very high  $\Lambda$ s in the aged solutions, which are apparently due to mesophase formation. The reason for this effect is not clear. The large numerical values of  $\alpha$  and the low total intensities of the scattered light argue for the presence of small, spherical normal micelles in these solutions. Unfortunately we are unable to determine an aggregation number for these micelles.

#### CONCLUSIONS

1. The surfactant  $6\phi C_{12}SNa$  forms small spherical micelles in aqueous solution, having an aggregation number of 20-30 and a fractional charge of 0.45. These micelles are hydrated to the extent of approximately 18 moles  $H_2O$  per moles of surfactant.

2. A second larger aggregate is also present in  $6\phi C_{12}$ SNa solutions; its importance increases with solution age. Addition of NaCl causes both aggregates to apparently increase modestly in size.
3. The surfactant  $8\phi C_{16}$ SNa also contains both aggregates in its solutions; the larger one is relatively more important here. The larger aggregate does not correspond to dispersed bits of a liquid crystalline mesophase.

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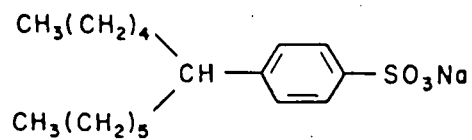
#### LITERATURE CITED

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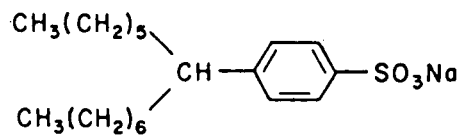
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$$\text{C.M.C.} = 3.12 \times 10^{-3} \text{ M}$$

at  $75^\circ$

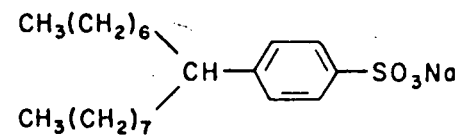
(GRIESS, 1955)



$$\text{C.M.C.} = 1.73 \times 10^{-3} \text{ M}$$

at  $75^\circ$

(ASINGER, et al, 1965)



$$\text{C.M.C.} = 9.6 \times 10^{-4} \text{ M}$$

(est.)

(TEXAS # 1)

Mossy A

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BINARY PHASE DIAGRAM FOR SURFACTANT/  
WATER SYSTEMS AFTER LAUGHLIN

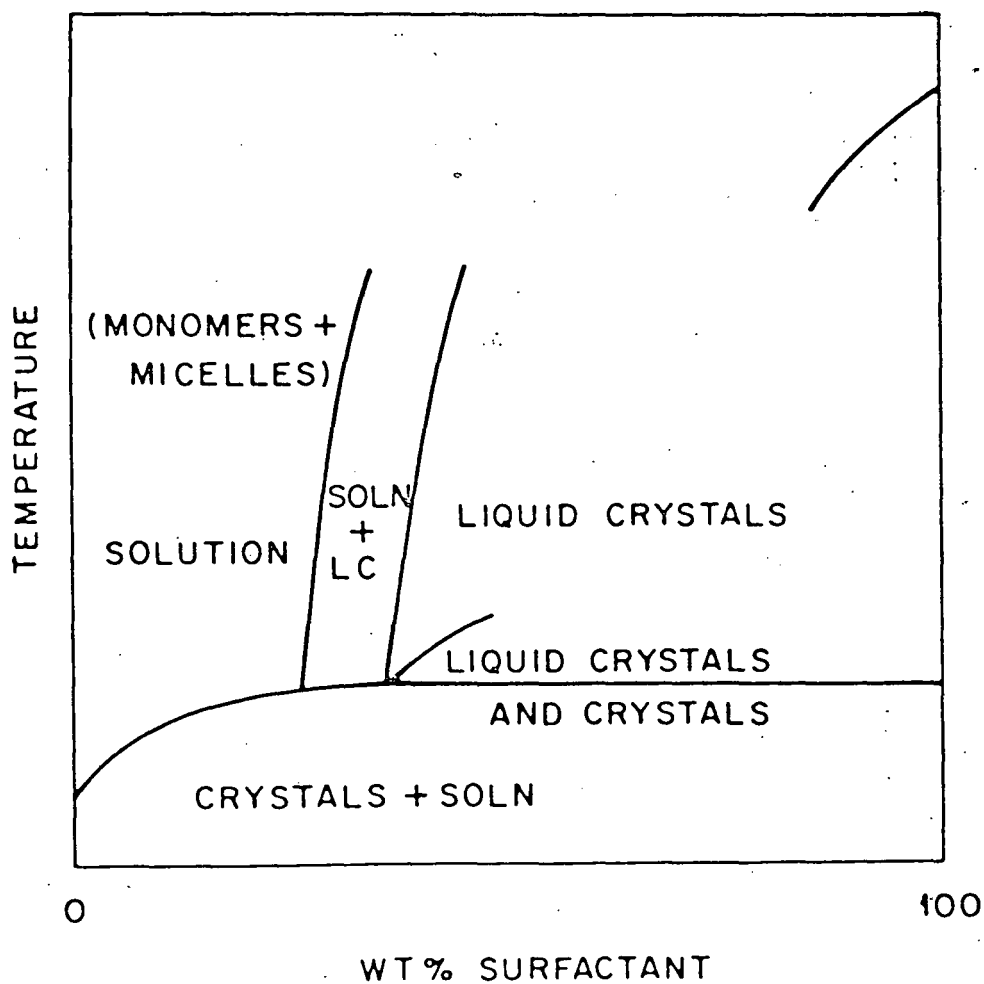
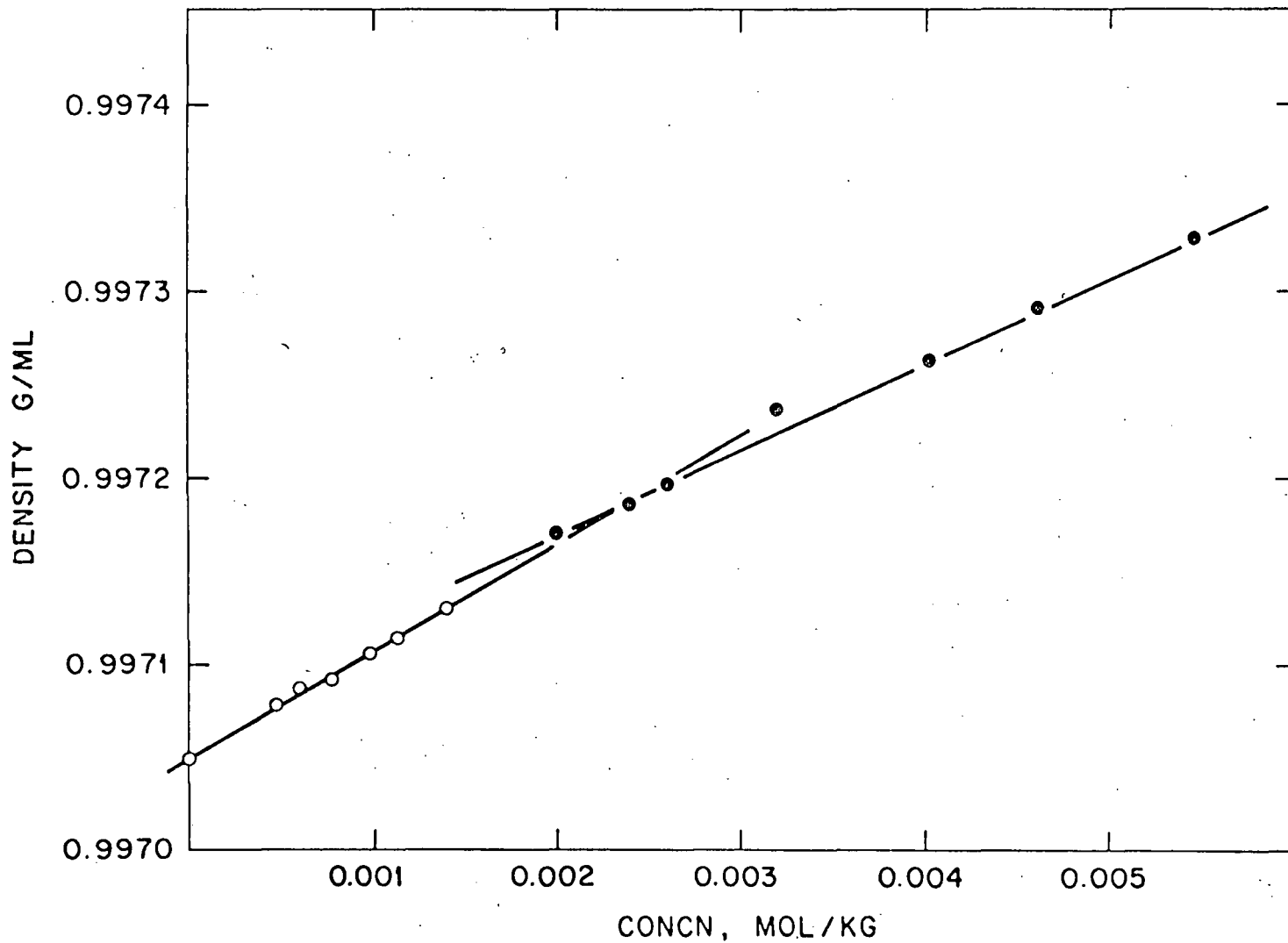


Fig. 2

ORNL DWG 80-1436

DENSITIES OF  $6\phi C_{12}SNa$  SOLUTIONS AT 25°C



ORNL DWG 80-1437  
APPARENT MOLAL VOLUME OF  $6\text{C}_{12}\text{SNa}$  AT 25°C

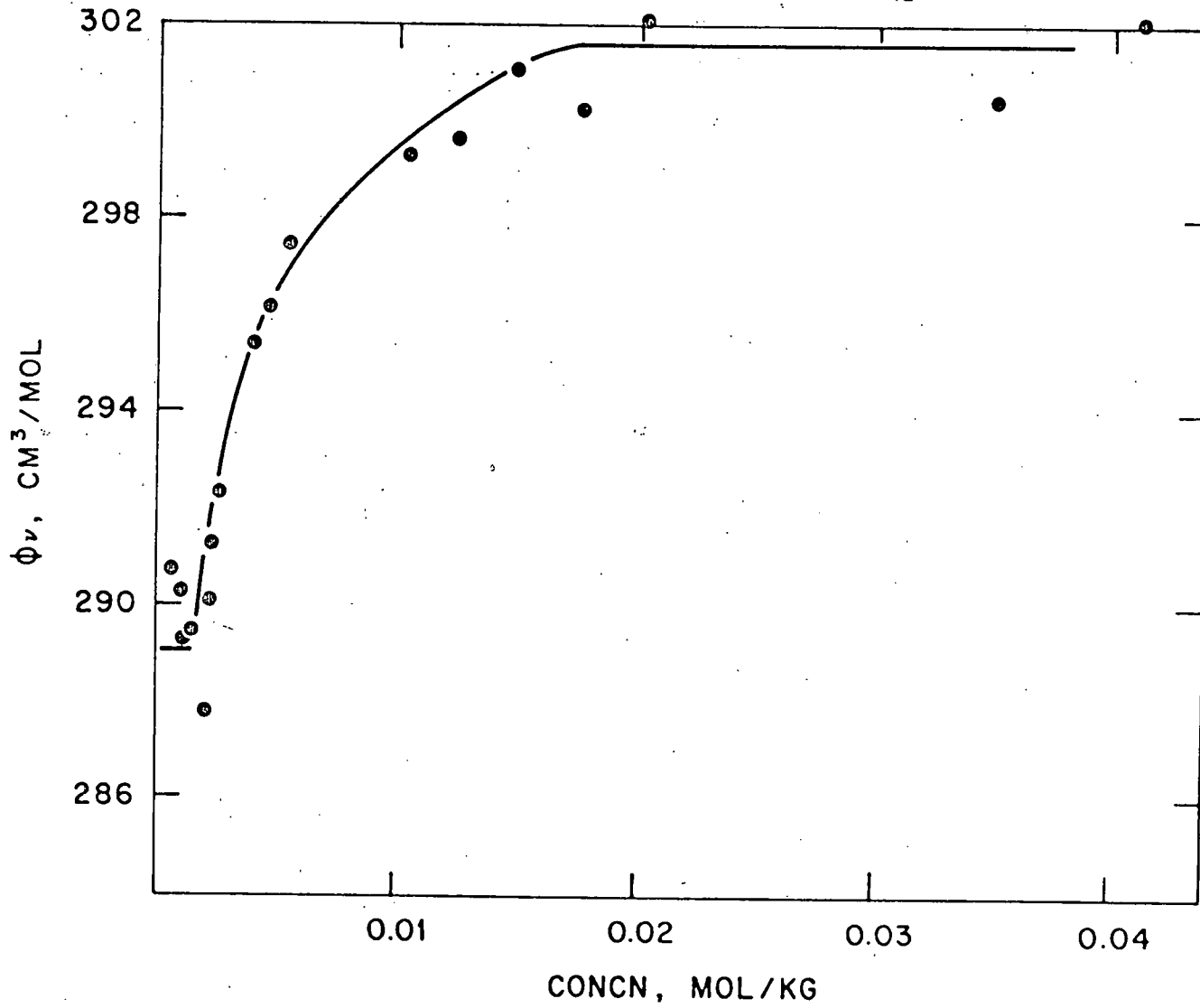
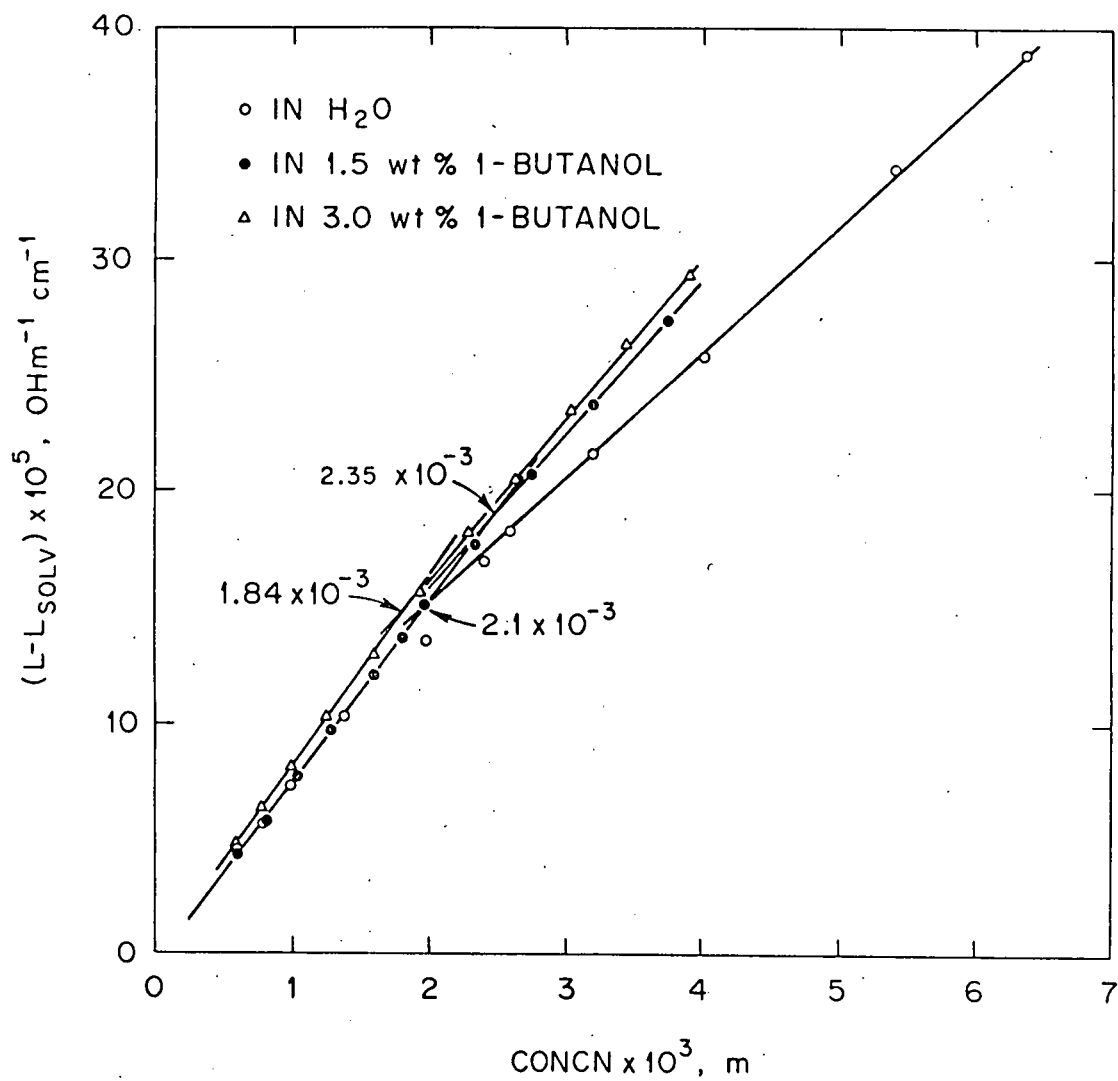


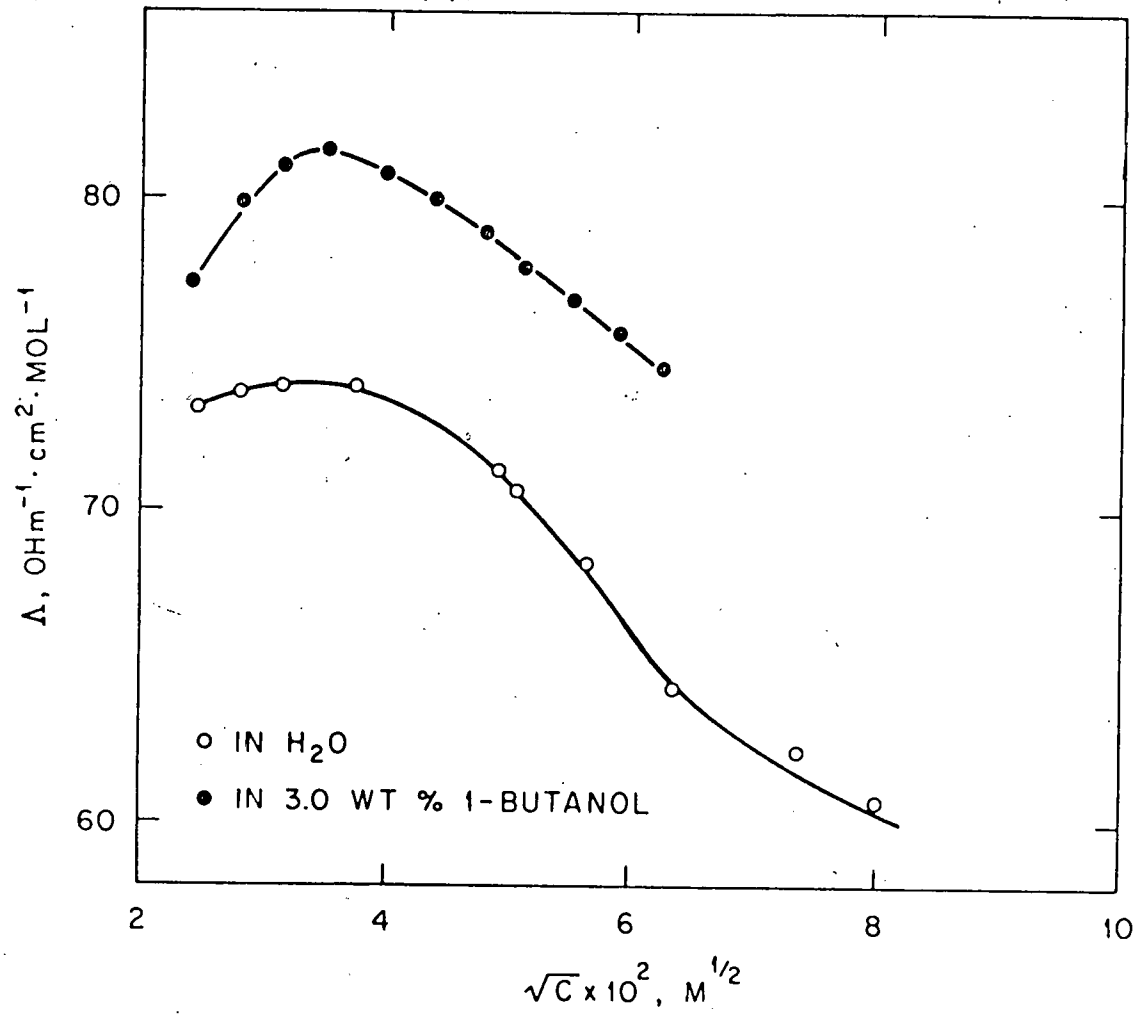
Fig 3



SPECIFIC CONDUCTIVITIES OF  $6\Phi C_{12}SNa$  SOLUTIONS AT 30°C

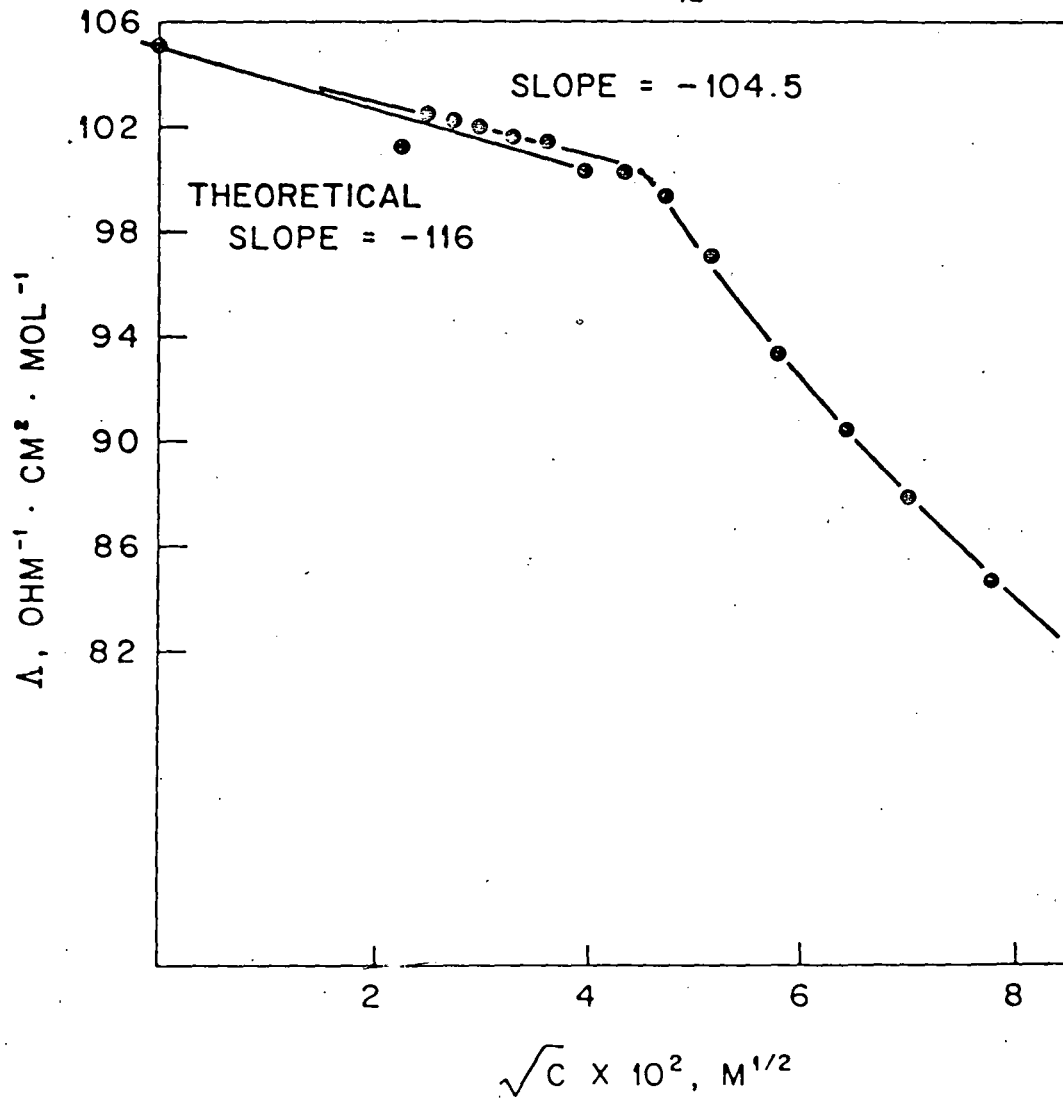
EQUIVALENT CONDUCTIVITIES OF  $6\Phi C_{12}SNa$  SOLUTION AT  $30^\circ C$ 

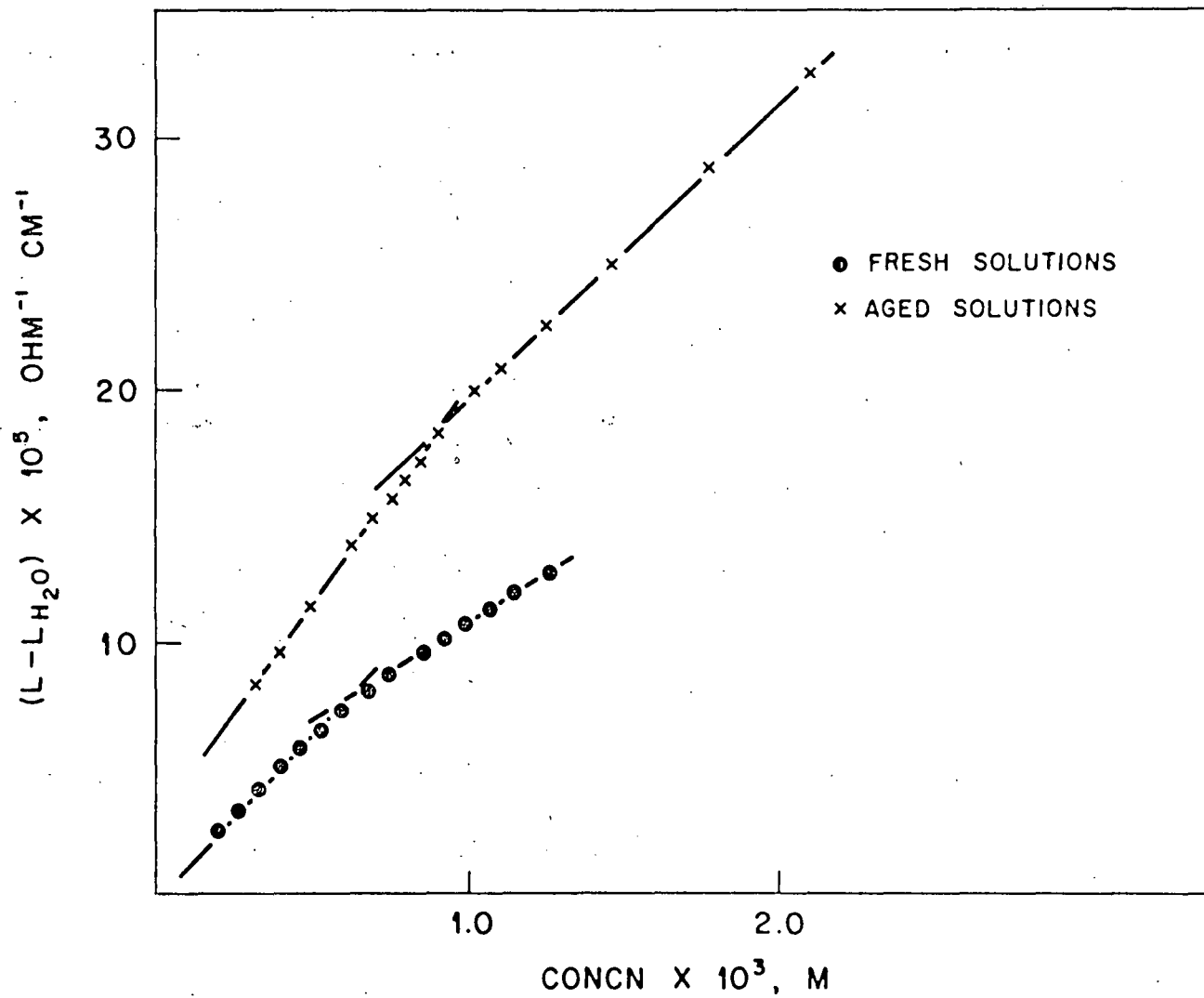
Fig. 5

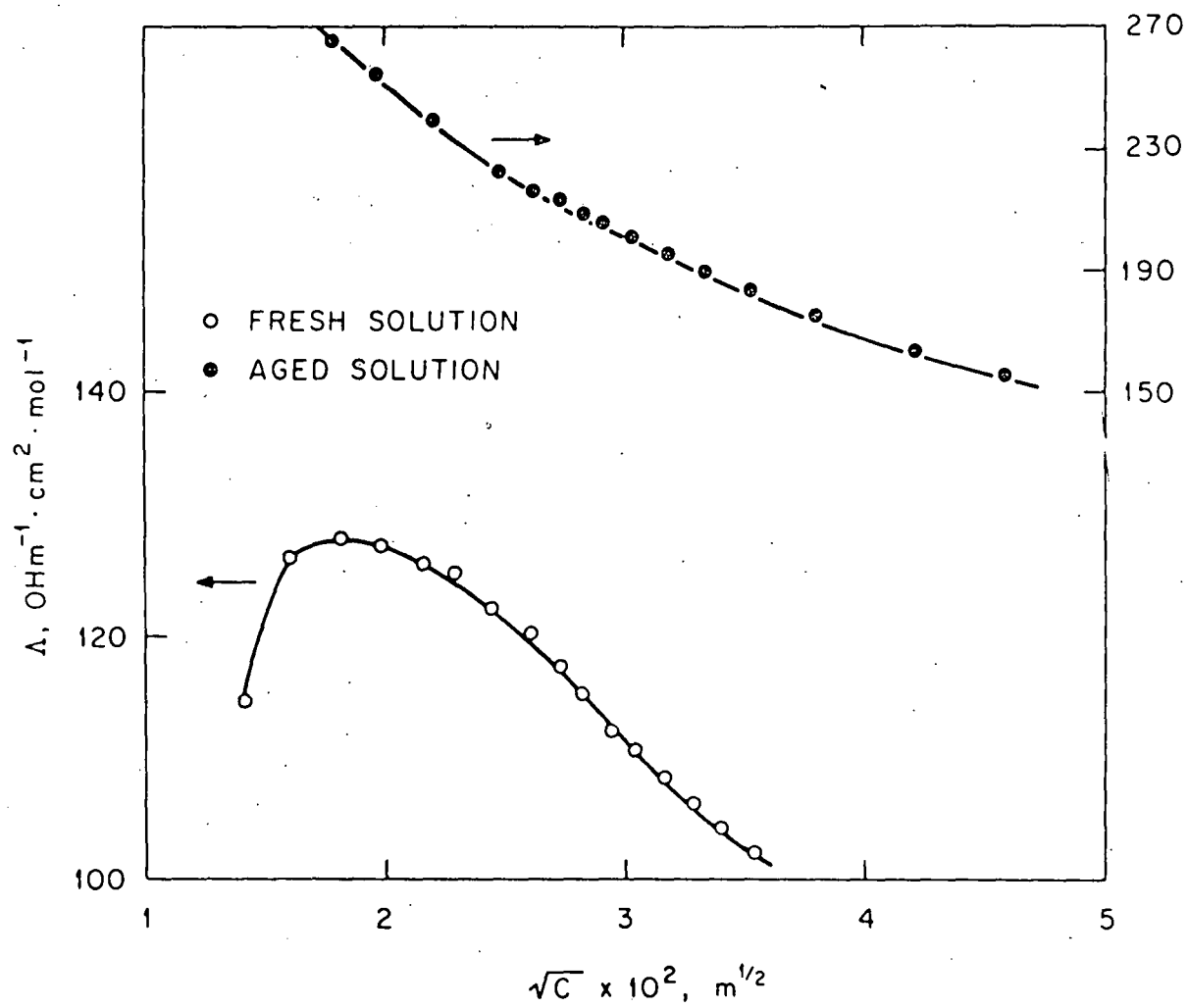


ORNL DWG 80-1438

EQUIVALENT CONDUCTIVITIES OF  $6\phi C_{12}SN\alpha$  SOLUTIONS AT 45°C

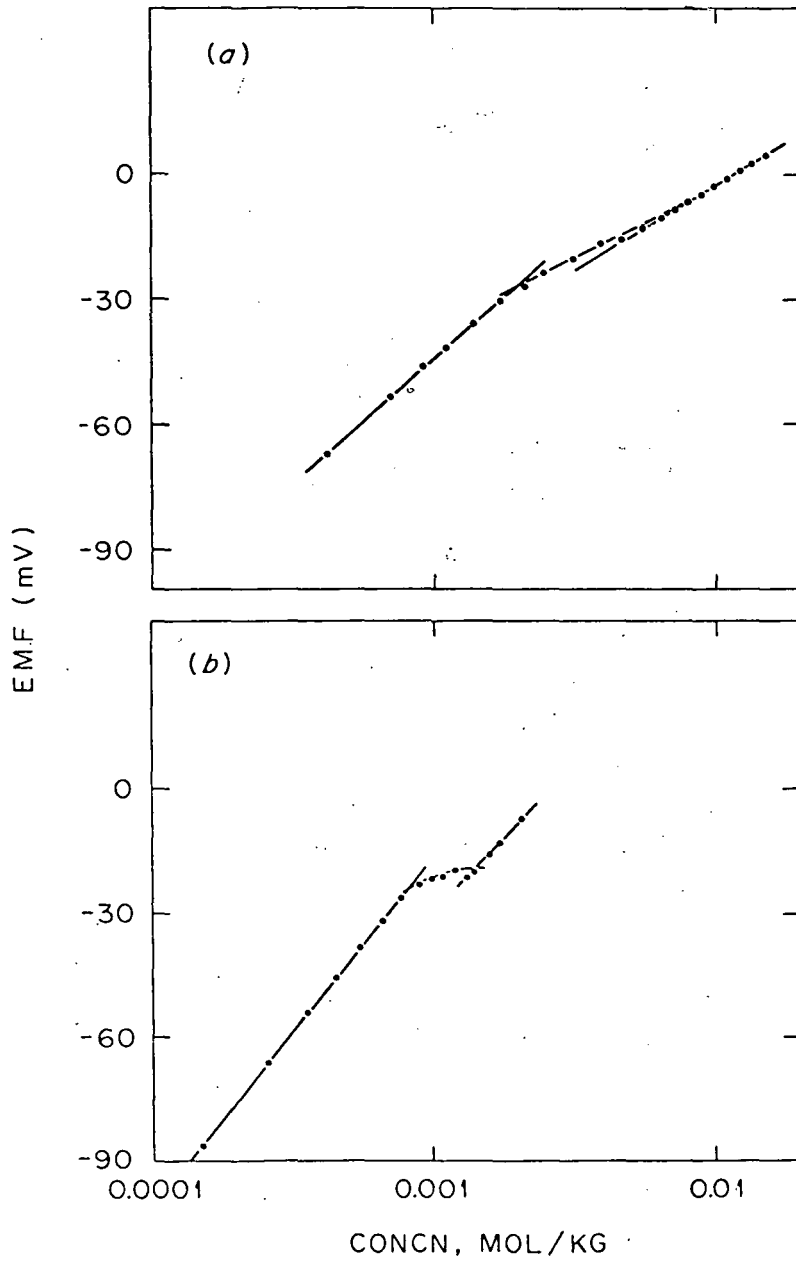


SPECIFIC CONDUCTIVITIES OF  $8\Phi C_{16}SN_0$  SOLUTIONS AT 45°C

EQUIVALENT CONDUCTIVITIES OF  $8\Phi C_{16}SNa$  SOLUTIONS  
AT 45 °C

ORNL-DWG 80-1441

SODIUM EMFs FOR (a)  $6\Phi C_{12}SNa$  AT  $30^{\circ}C$ ;  
(b)  $8\Phi C_{16}SNa$  AT  $45^{\circ}C$



REDUCED SPECIFIC VISCOSITIES OF  $6\phi C_{12}SN_0$  SOLUTIONS AT 30°C