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Critical Phenomena in Nonaqueous Microemulsions

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ABSTRACT

The pseudoternary phase diagrams of the four-component system glycerol, sodium dodecyl sulfate, hexanol and decane with the weight ratio of hexanol to decane equal to 100/0, 90/10, 75/25, 50/50, and 25/75 were determined at 30 °C. The systems gave only isotropic solutions and no liquid crystalline phases.

The nonaqueous regions corresponding to the W/O microemulsion region in aqueous systems suggested critical behavior as demonstrated by the convergence of tie lines and by light scattering intensity which gave a pronounced maximum at the point of converging tie lines.

This maximum was transferred to higher glycerol/hexanol ratios with added surfactant and to smaller ratios with added decane. Viscosity measurements were made for the solutions on the demixing line. There was no anomalous viscosity values around the points of converging tie lines.

INTRODUCTION

The knowledge about association structures of aqueous surfactant systems has developed rapidly after Ekwall's pioneering contributions [1] with a great number of investigations reporting on the structure and dynamics of the systems [2–4].

Recently, the analysis of the structure of these systems has turned to the concept of critical phenomena in the microemulsion systems. The following micellar systems have been discussed.

(1) Binary — water and nonionic surfactant — solutions [6,7].

(2) Ternary microemulsions with nonionic surfactants [8] and with AOT as surfactant [9–11].

(3) Four-component systems with ionic surfactants [12–15].

(4) Five-component microemulsions with water, alkaline salt, surfactant, cosurfactant and oil [16,17].

Two paths of approach to the critical point have been used: variation of temperature at a fixed composition [5,6,9,10,16,17] or variation of the composition of a solution at constant temperature [9,12].

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The following experimental methods have been employed: light scattering [11,13], small angle neutron scattering [10,16,18,19], electrical conductivity plus interfacial tension [20] and viscosity [12].

The theoretical concept of renormalization group theories [11] and mode-mode coupling theories [20] have been used to explain the experimental data. All the above studies were concerned with aqueous microemulsion systems.

Recently, the area of colloidal association structures has been extended to nonaqueous systems using a polar organic compound as replacement for water. Evans and collaborators have investigated micellar solutions in ethylammonium nitrate and hydrazine [21,22], Friberg and collaborators have introduced nonaqueous lyotropic liquid crystals [23,24] and nonaqueous microemulsions have recently been discovered by Robinson et al. [25], Friberg and Podzimek [26] and Lattes et al. [27–29].

Combining the knowledge gathered from the investigations of critical phenomena in aqueous microemulsions with the recent discovery of nonaqueous microemulsions, we found an opportunity to investigate the latter systems for critical behavior appealing. The four-component system of glycerol, decane, sodium dodecyl sulfate (SDS) and hexanol was selected for the investigation. This publication shows the phase regions and the variation of the point of converging tie lines in the system with decane content.

EXPERIMENTAL

Materials

Decane (Aldrich Chemical Company, 99+%, Gold Label) was used without further purification. Hexanol (Sigma Chemical Company, approx. 99%) was dried by excess molecular sieves (Davison Chemical, 8–12 mesh beads, 3 Å effective pore size). Sodium dodecyl sulfate (SDS) (BDH Chemicals Ltd., Poole, U.K.) was recrystallized twice from absolute ethanol. Glycerol was dried by successive treatment of molecular sieves to less than 0.05% water content as analyzed by the Karl Fischer method, using an instrument with potentiometric and end-point detection.

Determination of solubility area

The isotropic liquid region formed by the mixtures of glycerol, SDS, hexanol and decane was determined at 30 °C by direct addition of SDS to mixtures with varied ratios of the glycerol to the hexanol/decane solution. The composition was mixed on a Vortex Genie Mixer (Model S8223) and thermostated at 30 °C.

The solubility region was found between compositions which became transparent with increased SDS and the composition which dissolved no more SDS.

The composition of the demixing line at the lower limit of SDS was determined within the error of 0.05% of SDS according to visual observation.

Density and refractive index measurements

An Anton Parr Digital Density Meter (Model DMA 40) was used to measure densities of solutions along the demixing line. Air and distilled water were used as standards to calculate constant $A = 0.11254$ and constant $B = 10.925$ at 30 °C. The density was calculated in the usual manner using the equation $\rho = A \times (T - B)$ where T is the oscillation period that we measured.

The refractive index measurements were performed at 5893 Å and 30 ± 0.2 °C on an AO Abbe Refractometer (Model Mark II).

Refractive index and density results were used to analyze the compositions of tie lines in the two-phase region and composition of critical point for the systems investigated.

Viscosity measurements

The kinematic viscosity (η/ρ, ρ is the density of solution) of the solutions on the demixing line and near the critical point were measured by using Cannon-Fenske Routine Viscometers (Induchem Lab Glass).

The viscometer was set in a water bath, thermostated at 30 ± 0.2 °C and filled with the sample solution which was already equilibrated at 30 °C. Repeated efflux time was measured for each sample. Portions of the same sample solution was used for density measurement and the absolute viscosity of the solution was obtained by multiplying the kinematic viscosity with the density.

Light scattering measurements

Sample preparation

For ternary systems of glycerol, SDS and hexanol, the phase boundary in the lower surfactant concentration side was carefully determined and 5 series of samples were prepared which contained 1, 2, 5, 11 and 15% excess SDS what was required to give the demixing line and perpendicular to it.

For quaternary systems, only samples with 1% SDS perpendicular to the demixing line were prepared.

Measurement

A Sophica Photo Gonio Diffusometer (Model 42,000) was used for light scattering measurements. A sample cell containing dust-free benzene was used as a reference cell to calibrate and to check the dissymmetry of the instrument. The light scattered at various angles (150–30°) was measured. The average value for the dissymmetry was 0.998. All measurements were done in unpolarized green light ($\lambda = 546$ nm) and the photomultiplier voltage was 800 V. The relative scattering intensities were measured at 90° and the intensity of reference (benzene) was taken as 100.

Sample solutions were made in clean glassware and transferred to sample cells. The filled cells were sealed with teflon film and parafilm, dipped in glycerol and centrifuged at 14,000 rpm (23,500 *g*) for 1–2 h to remove dust particles. A Sorvall Superspeed Automatic Refrigerated Centrifuge (Model RC2-B) was used for centrigufation. The temperature was 30 °C.

Sample cells were first cleaned with distilled water and thoroughly cleaned by chromic acid in the Ultra Sonic Cleaner (Mettler Electronic Corp.) for 1–2 h. The cells were rinsed with distilled water until the glass surfaces were wetted uniformly and dried in a clean oven at 30 °C.

RESULTS

The solubility region, the tie lines and the composition point of converging tie lines for the three-component systems of glycerol, SDS and hexanol are given in Fig. 1.

Hexanol showed only insignificant solubility in glycerol while the latter dissolved in hexanol to 12%. The solubility area extended continuously from pure glycerol to pure hexanol in a crescent with the demixing hexanol/glycerol line going through the critical point 4.3% SDS, 52.6% glycerol and 43.1% hexanol. The maximum solubility of SDS was 22.7%.

Figure 2 shows the light scattering from this solubility region for compositions at a constant and perpendicular distance from the demixing line. The scattering gave a strong maximum for a composition corresponding to the critical point on the demixing line. The maximum intensity of light scattering decreased rapidly for compositions 2 and 5% (SDS) into the solubility region. For 11 and 15% distance from the demixing line, the intensity monotonically increased because the compositions now began to approach the right-hand solubility limit.

The solubility regions in the four-component system with decane are given in Fig. 3 with the region at 0% decane with a two point dashed line. The maximum solubility of glycerol was reduced with addition of decane. The reduction was most severe for the initial additions as shown by Fig. 4, which gives the composition at maximum glycerol content as function of the decane content at that point.

The tie lines are not drawn in the figure: they are, in general, outside the plane used in the diagram, but the point to which they converge is marked with a filled circle. The converging point was found at lower glycerol content with higher hydrocarbon content (Table 1). The light scattering results, Fig. 5, for compositions 1% perpendicularly into the solubility region from the demixing point gave maxima at the points of tie line conversion.

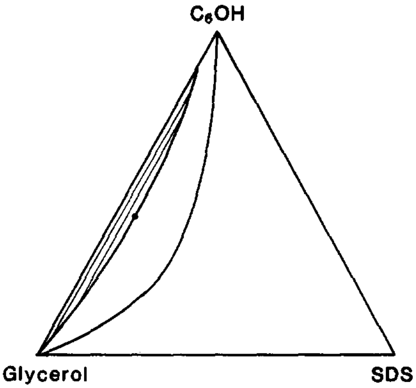

Fig. 1. The solubility region, tie lines at low surfactant content and the critical point in the system of glycerol, sodium dodecyl sulfate (SDS) and hexanol (C_6OH). (•) Indicates a critical point.

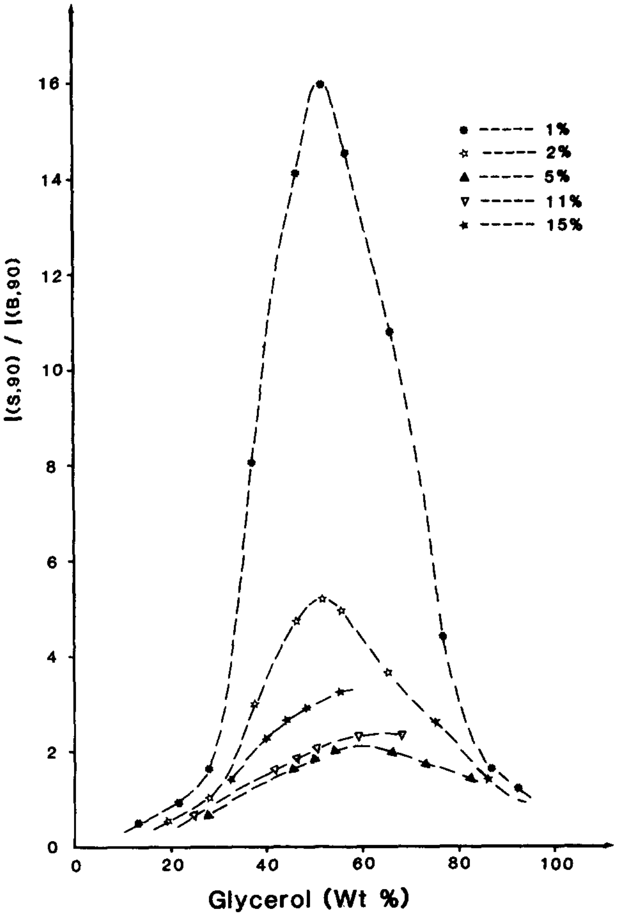

Fig. 2. Light scattering intensity for compositions at constant and perpendicular distance from the left demixing line in Fig. 1. One intensity scale unit is the scattering from pure benzene. Concentrations of glycerol are given in the Fig.

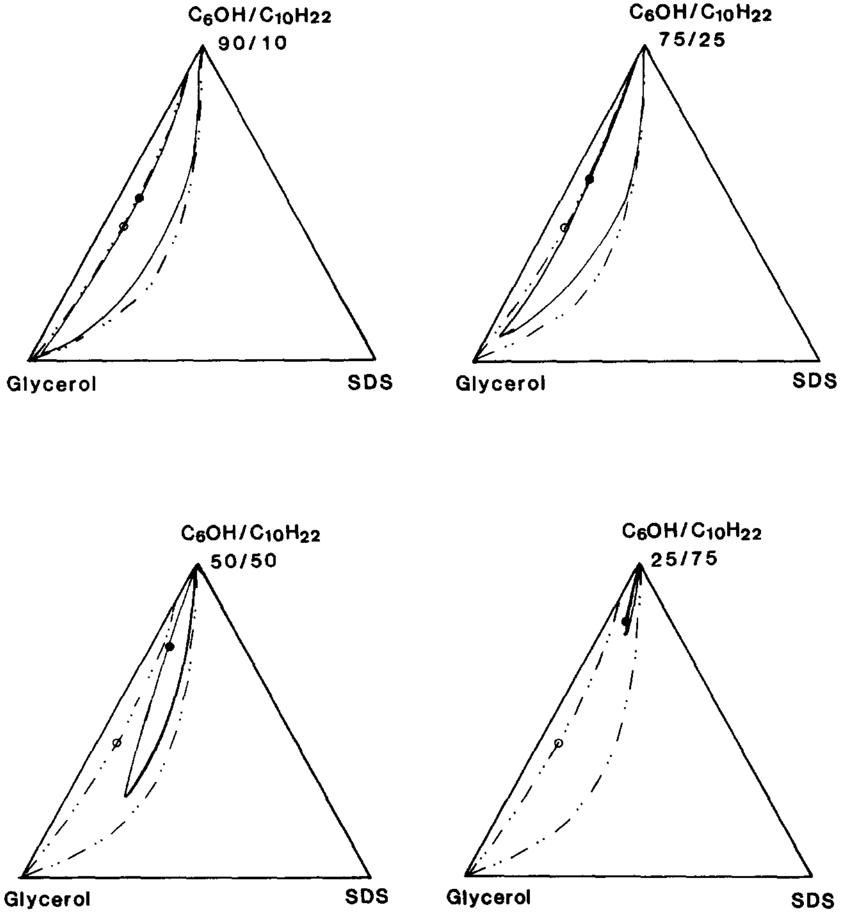

Fig. 3. The solubility regions (——) and corresponding critical points (•) in the system glycerol, sodium dodecyl sulfate (SDS), hexanol (C_6OH) and decane (C_{10}). The area for zero hydrocarbons (—··—) and its critical point (o) are also given.

Viscosities of the solutions along the demixing lines, Fig. 3, were measured and are reported on Fig. 6. The results show that the viscosity increased smoothly as the amount of glycerol increased. There was no extreme of viscosity in the vicinity of the critical point.

DISCUSSION

The results showed similar behavior in the glycerol-in-decane microemulsions from the one with no hydrocarbon to the one with the highest hydrocarbon content. The behavior was characterized by the fact that compositions with the solubility region with small changes in composition spontaneously separated into two solutions with almost identical composition.

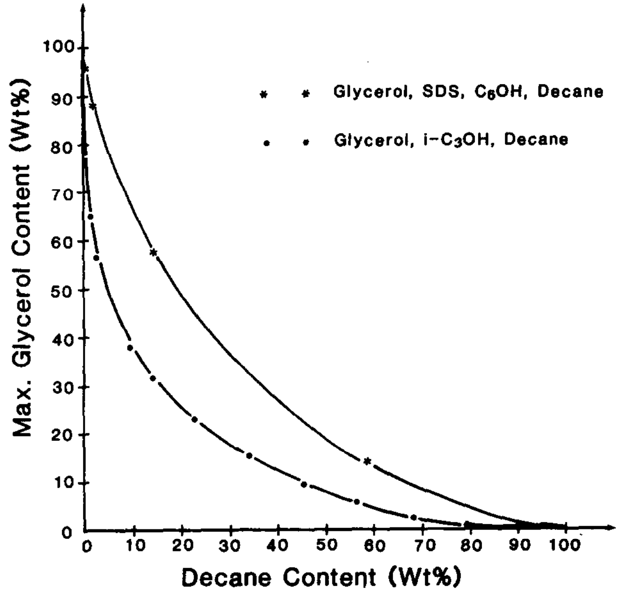

Fig. 4. The maximum solubility of glycerol was rapidly reduced with the hydrocarbon content.

A comparison with aqueous systems is interesting and useful. Langevin et al. [12–14] as well as Bellocq et al. [15] found light scattering maxima in quaternary aqueous microemulsion system. It is instructive to compare the above system with the water, pentanol, sodium dodecyl sulfate and cyclohexane system, because the non-hydrocarbon system shows a continuous solubility region reaching from water to pentanol. Such a system must have a critical point and the fact that it was carried into the hydrocarbon containing microemulsion illustrates the similarity between the systems with water and with glycerol.

A comparison with the size of aggregates close to the critical point is also useful. Langevin et al. [12,14] determined the correlation length ζ [30], which may be obtained from the light scattering data using the Ornstein–Zernike relation [31].

$$I(\theta) = A/(1+q^2(\theta)\zeta^2)$$

in which the intensity difference $I(\theta) = (I(\theta)_{\text{sample}} - I(\theta)_{\text{solvent}})/(1+\cos^2\theta)$. A is a constant for each solution; $q(\theta)$ is the scattering wave factor; ζ is the correlation length. A plot of $1/I(\theta)$ versus $q^2(\theta)$ gives a straight line and the correlation length is calculated as the square root of the slope over the intercept [$\zeta = (\text{slope/intercept})^{\frac{1}{2}}$], Fig. 7.

It is not possible to determine the term $I(\theta)_{\text{solvent}}$ because of the highly polydisperse behavior of the solution as the critical point is approached. Chosing

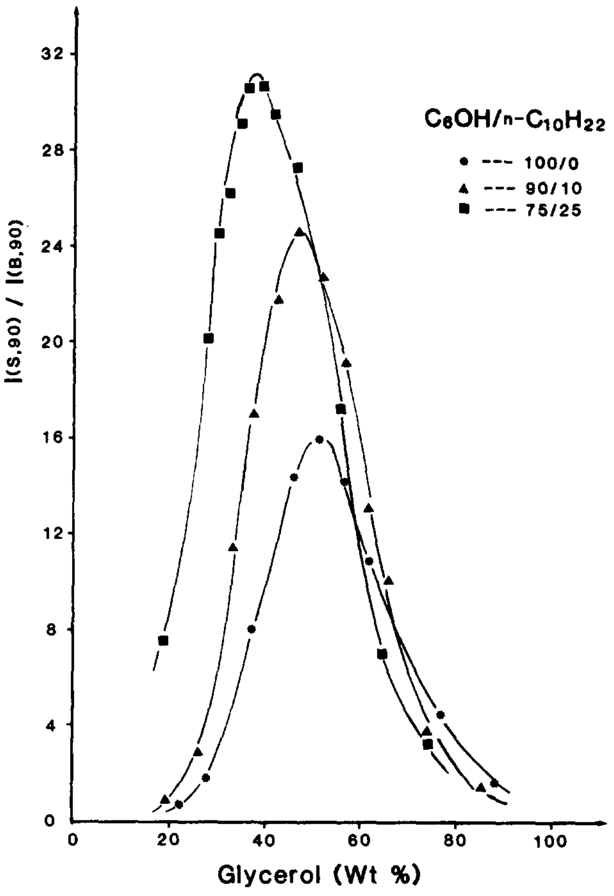

Fig. 5. The light scattering intensity for compositions 1% into the solubility region from the left-hand demixing line in the first two diagrams of Fig. 3.

TABLE 1

Composition (wt%) of the four-component system glycerol/SDS/hexanol/decane

$C_6OH/C_{10}H_{22}$	Glycerol	SDS	Hexanol	Decane	G/H
100/0	52.63	4.31	43.06	0	1.22
90/10	44.69	4.92	45.35	5.04	0.99
75/25	36.95	5.27	43.34	14.45	0.85
50/50	23.61	5.57	35.41	35.41	0.67
25/75	11.78	5.79	20.61	61.82	0.57

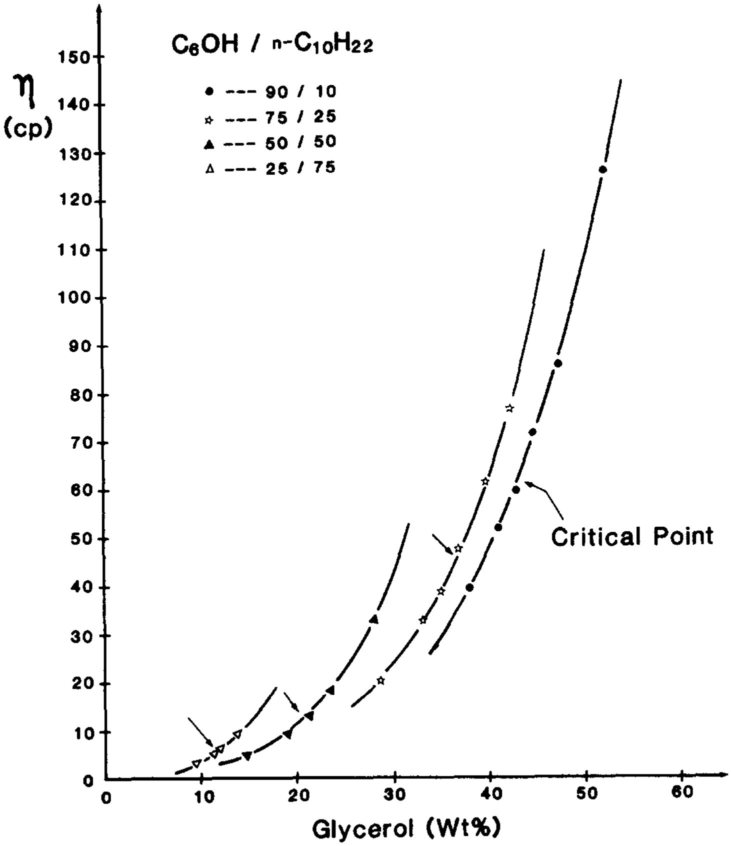

Fig. 6. Viscosities along the left-hand demixing line in Fig. 3 gave no "anomalous" behavior in the critical point range

one of the solvents as the solvent leads to erratic results. In the same manner a sudden change from one solvent to the other at the critical point results in a discontinuity of the correlation length function.

In this investigation we arbitarily chose to use a weighted average of the scattering values for the two solvents in order to provide a continuous variation of $I(\theta)_{\text{solvent}}$ with no claim to this value being the "correct" value. A comparison with the correlation length values using the scattering intensity for one solvent only shows a difference of less than 10%; presumably the correlation length calculated is within a range of less than 10% from the real value.

The results, Fig. 8, gave correlation length with a maximum of 300 Å at the critical point. A comparison with aqueous systems [9–20] is illustrative. Langevin et al. [20] found $\zeta_{\max}$ between 610 and 750 Å in systems of water, sodium dodecyl sulfate, butanol and toluene. Tabony et al. [17] found a corresponding value of 600 Å in systems of cetyltrimethylammonium bromide, butanol, octane

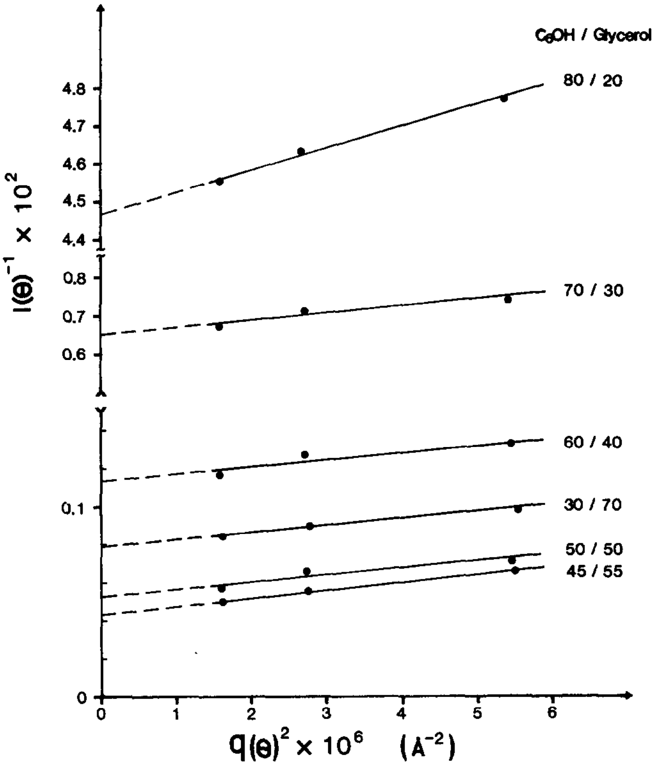

Fig. 7. The plot of $I(\theta)^{-1}$ versus $q^2(\theta)$ gave a straight line for solutions with SDS content 1% in excess of the demixing line.

and water with sodium bromide. Robinson et al. [25] found similar values for Aerosol OT microemulsions using neutron scattering. From these and other data it seems reasonable to predict the glycerol-in-oil microemulsions have correlation lengths comparable to those in aqueous systems.

Our viscosity data showed no "anomalous" behavior at the critical point at variance with the values when the critical point has been approached by change of temperature [32]. Langevin's values for quaternary systems [12] gave anomalous viscosity, when found, is due to the critical fluctuations even if there have been arguments about their extent [33,34].

In summary, it was found that the existence of phenomena reminding those of a critical point in this nonaqueous systems is in no doubt. The spontaneous separation in two phases with infinitesimal difference in composition verifies this statement. In addition, it should be observed that the light scattering maximum close to the point of tie line convergence is the only maximum in the light scattering curve versus composition. It is also supported by the form of the solubility curve in Fig. 4. The curve showing maximum solubility of glyc-

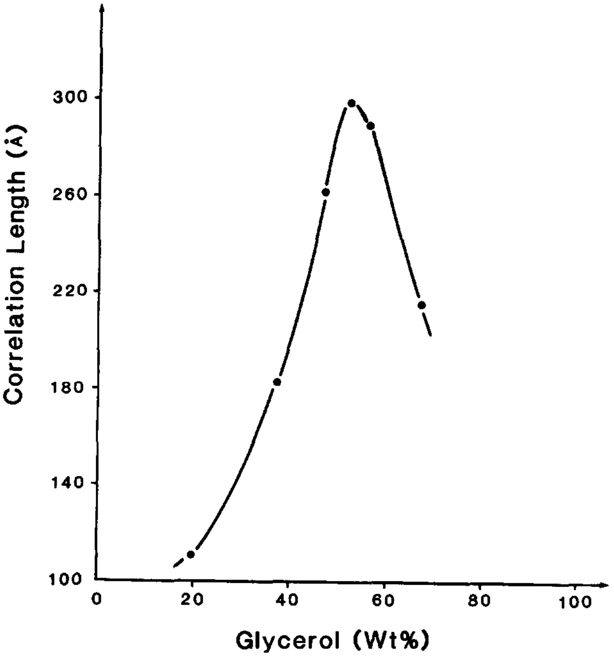

Fig. 8. Correlation length in the system glycerol, sodium dodecyl sulfate (SDS) and hexanol (C_6OH).

erol in the hydrocarbon is similar to the curve with isopropanol as the sole solubilizing agent. On the other hand, the structure of the aggregates as to our investigation gave only limited information; the light scattering results indicates similar phenomena to those in aqueous systems.

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