(16) A. P. Brown, C. Koval, and F. C. Anson, *J. Electroanal. Chem.*, **72**, 379 (1976).
(17) M. T. Spitler and M. Calvin, *J. Chem. Phys.*, **66**, 4294 (1977).
(18) P. D. Fleischauer and J. K. Allen, *J. Phys. Chem.*, **82**, 432 (1978).
(19) P. R. Moses, L. M. Wier, J. C. Lennox, H. D. Finklea, J. R. Lenhard, and R. W. Murray, *Anal. Chem.*, **50**, 576 (1978).
(20) P. R. Moses and R. W. Murray, *Anal. Chem.*, **47**, 1882 (1975).
(21) N. R. Armstrong, A. W. C. Lin, M. Fujihara, and T. Kuwana, *Anal. Chem.*, **48**, 741 (1976); A. W. C. Lin, N. R. Armstrong, and T. Kuwana, *Ibid.*, **49**, 1228 (1977).
(22) F. H. Moser and A. L. Thomas, *ACS Monogr.*, **No. 157** (1963).
(23) R. Shepard, C. Linkous, and N. R. Armstrong, unpublished results.
(24) L. D. Rollman and R. T. Iwamot, *J. Am. Chem. Soc.*, **90**, 1455 (1968).

(25) S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, **97**, 7427 (1975), and references therein.
(26) H. Tachikawa and L. Faulkner, *J. Am. Chem. Soc.*, **100**, 4379 (1978).
(27) N. Maki and N. Tanka, "Cobalt", in "Encyclopedia of Electrochemistry of the Elements", A. J. Bard, Ed., Vol. III, Marcel Dekker, New York, 1973, p 43.
(28) N. S. McIntyre and M. G. Cook, *Anal. Chem.*, **7**, 2208 (1975).
(29) G. Schön, *Surf. Sci.*, **35**, 96 (1973).
(30) Y. Hiwa, H. Kobayashi, and T. Tsuchiya, *J. Chem. Phys.*, **60**, 799 (1974).
(31) A. M. Yacynych and T. Kuwana, *Anal. Chem.*, **50**, 640 (1978); A. W. C. Lin, Ph.D. Dissertation, Ohio State University, 1978.
(32) J. H. Scofield, *J. Electron Spectrosc.*, **8**, 129 (1976).

Detergentless Water/Oil Microemulsions Composed of Hexane, Water, and 2-Propanol. 2. Nuclear Magnetic Resonance Studies, Effect of Added NaCl[1]

Bruce A. Keiser,[2] David Varie, Roland E. Barden, and Smith L. Holt*[2]

Department of Chemistry, The University of Wyoming, Laramie, Wyoming 82071 (Received July 26, 1978; Revised Manuscript Received February 15, 1979)

A pseudophase diagram for ternary compositions of *n*-hexane, water and 2-propanol has been published previously. Some of the compositions exhibited the physical characteristics of a water/oil (w/o) microemulsion even though a detergent was not present. We have now determined the effect of ionic materials on the system by replacing water with NaCl solutions. Addition of NaCl caused significant changes in the location of region boundaries. The microemulsion was stabilized while a region of small H-bonded aggregates appeared to be destabilized by the added NaCl. An investigation of these systems by ¹H NMR, with or without added NaCl, showed that "bulk" water was present in the detergentless microemulsion. In addition, ¹H NMR was found to be a useful tool for locating region boundaries and for elucidating the nature of compositions assigned to these regions.

Introduction

Certain compositions of *n*-hexane, water, and 2-propanol display the physical characteristics of microemulsions even in the absence of detergent.[3] The ternary pseudophase diagram for this system, constructed on the basis of conductivity and ultracentrifugation experiments, shows four regions.[3] In an attempt to ascertain the effect of various concentrations of sodium chloride on the ternary diagram of this system, we have undertaken an extensive series of conductivity and ultracentrifugation measurements. In addition, recent studies[4-7] have utilized ¹H NMR to locate region boundaries and obtain structural information about detergent stabilized microemulsions. We wished to ascertain whether ¹H NMR would be equally useful in characterizing detergentless ternary solutions, in the presence and absence of NaCl. The data presented here show that ¹H NMR detects transitions between regions of common structure in these systems and that the boundaries are located in the same place as those constructed from conductivity data.

Experimental Section

Reagent grade *n*-hexane and 2-propanol were purified by treatment with silica gel, then distilled, and stored over 4Å molecular sieves. The 2-propanol was subsequently redistilled just prior to use so that the conductivity was less than 0.02 μmho/cm. Water was twice distilled in a Pyrex still. Sodium chloride was purchased from Mallinckrodt Chemicals and rhodamine 6G from Eastman

*Address correspondence to Dr. Smith L. Holt, Department of Chemistry, The University of Georgia, Athens, GA 30602.

Kodak. Both were used without further purification.

The ternary pseudophase diagrams were constructed on the basis of room temperature physical properties of various compositions of *n*-hexane, water, and 2-propanol. Initially, each solution contained 10 mL of *n*-hexane and an aliquot of water which was then titrated with 2-propanol in a manner similar to that reported by Bowcott and Schulman.[8] Visual observations and conductivity measurements were made after each successive addition of 2-propanol. Ultracentrifugation and ¹H NMR studies were carried out on selected compositions of *n*-hexane, water, and 2-propanol.

Conductivity measurements were made with a YSI Model 31 conductivity bridge utilizing a Leeds and Northup insertion-type cell (k = 0.1, series 4905). The ultracentrifugation studies were carried out on a Beckman L5-75 preparative instrument using polyallomer tubes. Rhodamine 6G was used to stain the water-rich phase of the w/o microemulsions, as described by Smith et al.[3] The ¹H NMR spectra were taken on a Varian 100-MHz NMR using benzene (7.2 δ) as an external standard. Diamagnetic susceptibility corrections were made by comparing the major resonance of *n*-hexane in the solutions with that of pure *n*-hexane (1.21 δ).

Results and Discussions

Ternary Pseudo-Phase Diagrams. A ternary pseudophase diagram for the system *n*-hexane–water–2-propanol has been described by Smith, Donelan, and Barden.[3] Recent improvements in technique, data interpretation, and solvent purification have led to slight modifications of this ternary diagram. The corrected diagram appears
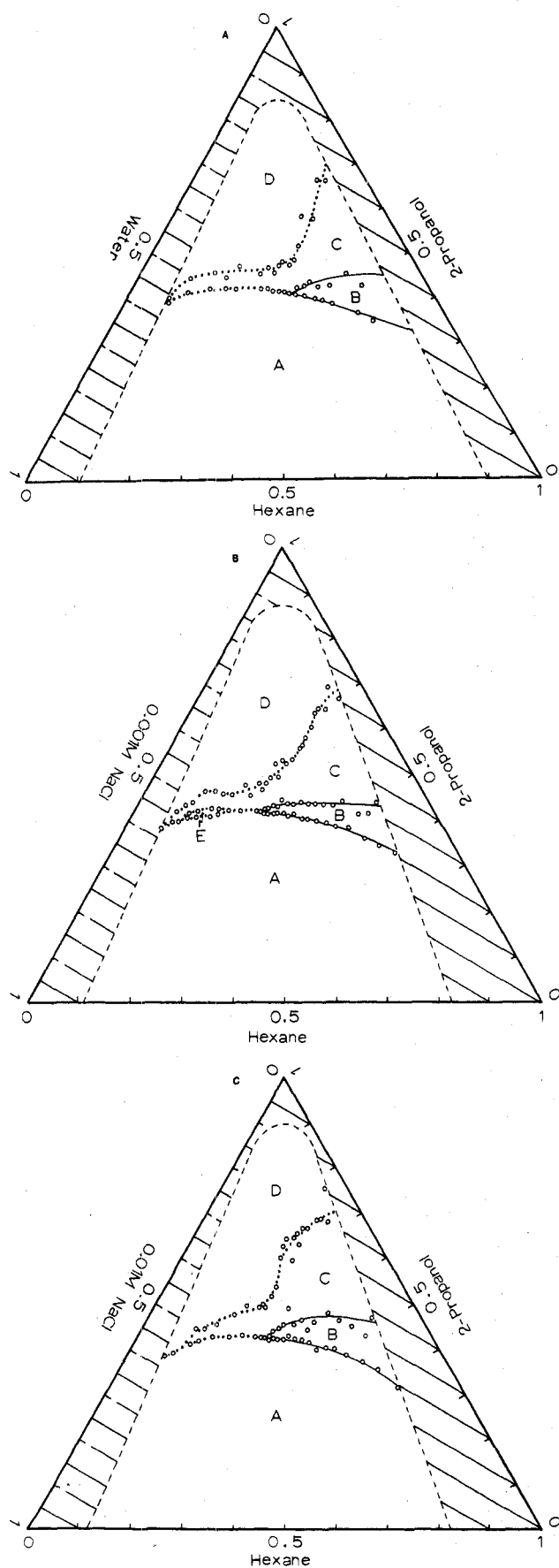
Figure 1. The ternary pseudophase diagrams for the systems containing *n*-hexane, 2-propanol, and (A) water, (B) aqueous 0.001 M sodium chloride, and (C) aqueous 0.01 M sodium chloride.

in Figure 1A. The regions are identified as follows. Ternary compositions from region A are turbid macroemulsions when freshly prepared or agitated; upon standing

they eventually break into two phases. We have not characterized the equilibrated system for compositions from this region of the diagram. The ternary compositions assigned to region B are stable, transparent microemulsions consisting of water-rich droplets dispersed in a hexane-rich continuous phase. These microemulsions are related to region A in that two distinct phases exist. They differ, however, in that a true microemulsion will spontaneously disperse and is indefinitely stable.[9] As a consequence, we regard microemulsions as a distinct species. Ternary compositions assigned to regions C and D are transparent single-phase solutions. We distinguish between solutions that contain H-bonded aggregates of water and 2-propanol (region C) and ternary solutions having no apparent microheterogeneity, i.e., "true" ternary solutions (region D) (cf. ref 3). Thus, while the C/D boundary is not a phase boundary, it does make a distinction between regions of different characteristics.

The ternary diagrams for the systems *n*-hexane–0.001 M NaCl–2-propanol and *n*-hexane–0.01 M NaCl–2-propanol are shown in Figure 1B and 1C. Each of the diagrams shown in Figure 1 was constructed from visual observations, conductivity, and ultracentrifugation data, as described in ref 3. A comparison of the three diagrams shows that as one replaces pure water with an aqueous solution of increasing concentrations of sodium chloride, the microemulsion region (labeled B in Figure 1A–C) exhibits an increase in area with a concomittal decrease in the area of the small aggregates (labeled C in Figure 1A–C). Thus, sodium chloride is observed to destabilize the small aggregate structure. Since the small aggregate structure depends upon H bonding among the various components, the destabilization would occur through disruption of these H bonds by the added sodium chloride. This is in agreement with the results of Schooley and Alder[10] who, in a study of the effect of electrolytes on the ^{1}H NMR of water, observed that sodium chloride disrupts H bonding in water. However, as the addition of sodium chloride destabilizes the small aggregate structure via this H-bonding disruption, the microemulsion region is observed to increase in area. The increase in area of the microemulsion region suggests that the microemulsion is stabilized. The model proposed by Prince[11-13] can be helpful in understanding the way in which sodium chloride affects this stabilization.

The formation of microemulsions in the absence of surfactant requires that the transient interfacial tension (γ_i) reaches zero at some point consistent with the following:

$$\gamma_i = \gamma_{(w/o)a} - \Pi \qquad (1)$$

In eq 1, $\gamma_{(o/w)a}$ represents the interfacial tension between the oil and water in the presence of an alcohol. The pressure, Π, is the two-dimensional lateral pressure within the duplex film which encompasses the droplet of the dispersed phase. Since 2-propanol does not allow for large values of Π, the interfacial pressure, $\gamma_{(o/w)a}$, must be sufficiently lowered so as to allow γ_i to approach zero. This is accomplished by partitioning of the alcohol between the oil, water, and interface. As the alcohol content is increased two phenomena occur simultaneously. Small amounts of water are gradually transferred from the dispersed water droplets into the continuous phase. Generally, this will be accomplished by H bonding between water and 2-propanol. As a result of the redistribution of the water, the interfacial tension, $\gamma_{(o/w)a}$, changes and the droplet size in turn decreases until a new equilibrium state is reached. The addition of sodium chloride to the system disrupts H bonding in the small aggregate region, therefore,
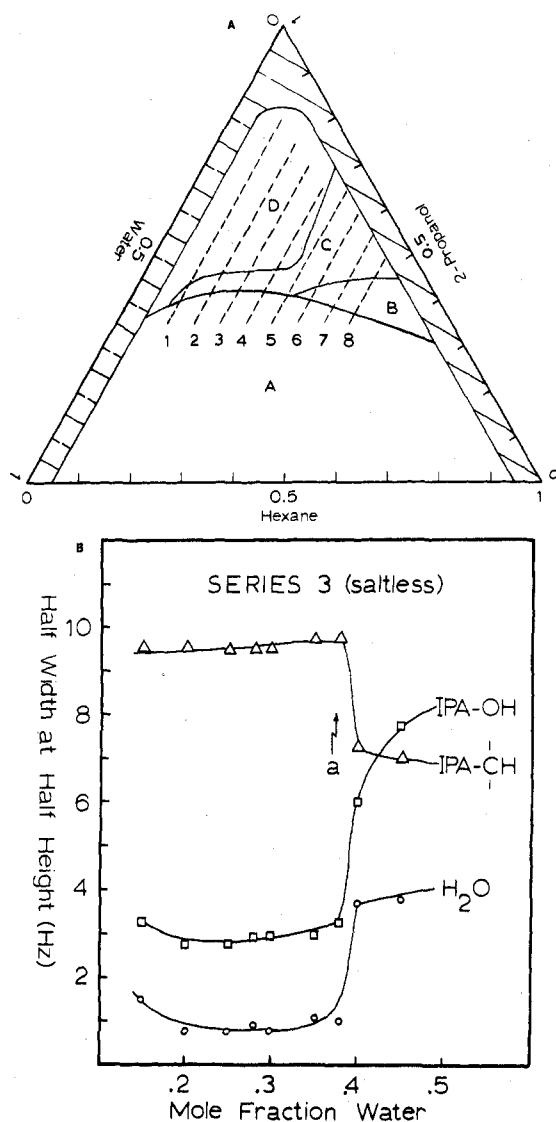
Figure 2. (A) Solutions prepared and studied by ^{1}H NMR at constant mole fraction of n-hexane in the system n-hexane, 2-propanol, and water. (B) Variation of the half peak width at half-height of the hydroxy and methine group proton of 2-propanol and water proton with increasing mole fraction of water at a constant mole fraction of n-hexane of 0.200.

Figure 3. (A) Solutions prepared and studied by ^{1}H NMR at constant aqueous phase mole fraction for the system containing n-hexane, 2-propanol, and aqueous 0.01 M sodium chloride. (B) Half peak width vs. mole fraction of 2-propanol for the hydroxyl and methine group protons of 2-propanol and water proton at a constant mole fraction of aqueous phase of 0.100.

it will disrupt H bonding in the microemulsion region also. This disruption of H bonding will serve to retard the transfer of dispersed water from the droplet into the continuous phase. The retardation of the solubilization process thus caused by sodium chloride serves to stabilize the microemulsion structure.

Proton NMR. Peak Width (Nonsalted System). Figure 2A shows a series of solutions studied by ^{1}H NMR in the n-hexane–water–2-propanol system. The half peak widths of the proton resonances of water and the hydroxyl and methine groups of 2-propanol for series 3 are plotted in Figure 2B. (Similar plots are obtained for the salt containing systems.) In all eight series large changes in half peak widths occur at a mole fraction of water which corresponds to the previously determined AB, AC, or AD region boundaries. The half peak width of the methine group resonance is observed to decrease while the half peak widths of the hydroxyl group resonances of 2-propanol and water are observed to increase. The narrowing of the methine group proton signal is suggestive of more rotational freedom in the 2-propanol molecule. At the same time, the broadening of the hydroxyl group of 2-propanol and water proton signals implies that the rate of proton exchange is increasing. Together, these observations
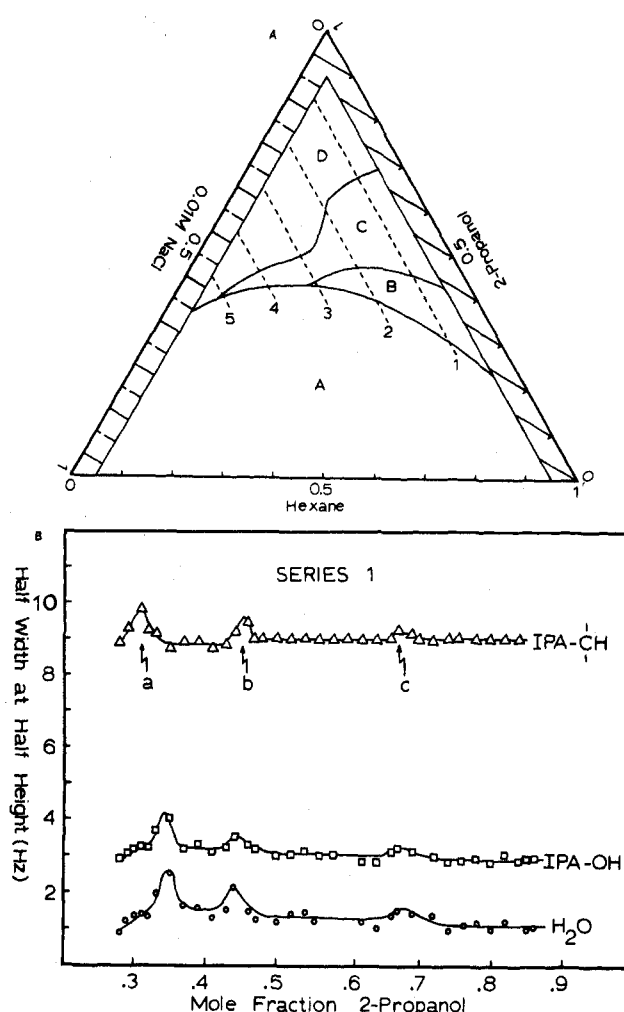
suggest that a transition from an ordered (H-bonding structured aggregates) to a less ordered (macroemulsion) system is occurring.

Peak Width (Salted System). The system n-hexane–0.01 M NaCl–2-propanol and n-hexane–0.001 M NaCl–2-propanol were also studied using ^{1}H NMR. Since the results were similar for both systems, only the n-hexane–0.01 M NaCl–2-propanol system will be discussed in detail.

The solutions studied are illustrated in Figure 3A. The half peak widths of the resonances of the methine and hydroxyl protons of 2-propanol and the water protons are plotted in Figure 3B. Here the half peak widths are seen to pass through a maximum. For series 1, these occur at mole fractions of 2-propanol of 0.310, 0.450, and 0.675. Analogous behavior is seen in all series studied (Figure 3B), under constant water conditions for all three systems (H$_2$O, 0.001 M NaCl, and 0.01 M NaCl). In contrast to the constant hexane conditions, the half peak width of all three groups (i.e., the methine and hydroxyl groups of 2-propanol and water) are observed return to a base value after transiting the region boundary. This result is similar to that reported by Shah and Hamlin.[6] The broadening of the methine proton peak would suggest that in every case the 2-propanol molecule is experiencing a more rotationally restricted environment at the boundaries than within a given phase. In addition, the degree of rotational freedom
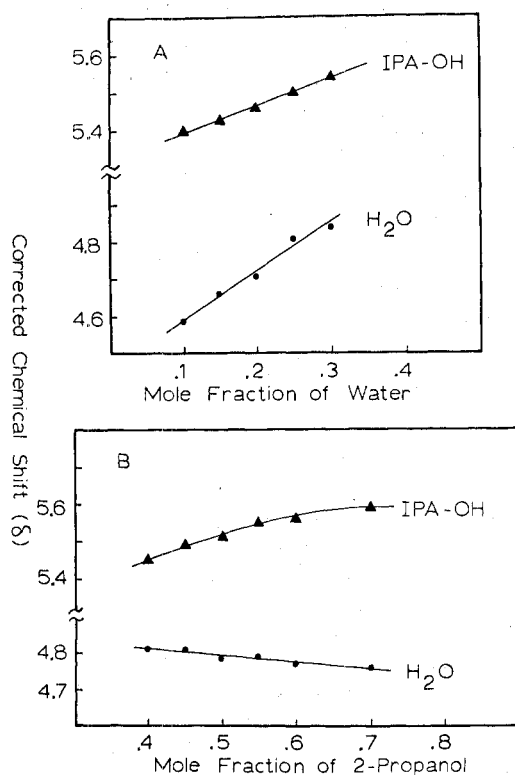
Figure 4. The chemical shift of the hydroxyl group of 2-propanol and water protons as a function of the mole fraction of (A) water at constant 2-propanol mole fraction (0.500) and (B) 2-propanol at constant water mole fraction (0.250) for the system *n*-hexane, 2-propanol, and water.

within each is similar to that noted for every other phase (i.e., the half peak width for the methine and hydroxyl proton resonances return to approximately the same value on either side of a phase boundary). At the same time the 2-propanol hydroxyl proton and water proton half peak widths are increasing, suggesting that proton exchange is more rapid. Upon referring to the diagram for this system (Figure 3A), the boundaries for series 1 are located by conductivity at mole fractions of 2-propanol of 0.310, 0.450, and 0.670 for the AB, BC, and CD boundaries, respectively. Upon returning to the half peak width graph (Figure 3B), the maxima observed occur at these same points. Thus, these maxima locate the boundaries and suggest that, as the system is transformed from one region to another, the ability of the 2-propanol to move between the oil, water, and interfacial regions is more restricted. However, as the second system begins to predominate, the rotational freedom and also the mobility of the 2-propanol between the various regions returns to a limiting rate. In addition, the more rigid nature of the 2-propanol at the oil–water interface fosters a more rapid proton exchange between the hydroxyl proton of 2-propanol and water.

Chemical Shift. For the three systems discussed above (i.e. *n*-hexane and 2-propanol with water, 0.01 M NaCl, or 0.001 M NaCl), the chemical shift of the 2-propanol hydroxyl group proton resonance and the water proton resonance are similarly affected and therefore the discussion will be restricted to the results for the salt free system.

In Figure 4A, the chemical shift of the hydroxyl group proton of 2-propanol and the water proton signals is graphed as a function of increasing water content for solutions containing a constant mole fraction of 2-propanol. The position of both signals is shifted downfield with increasing water content.

The downfield shift of these resonances implies that both protons are being deshielded as the water content is increased. The deshielding of the water proton may be accomplished by increasing the fraction of water–water H bonds. Similarly, the deshielding of the hydroxyl group proton of 2-propanol may be brought about by increasing the alcohol–water H bonding. Close inspection of Figure 4A suggests that the downfield shift of the water proton occurs at a faster rate than the downfield shift of the hydroxyl group proton of 2-propanol. Thus we may conclude that, at a constant mole fraction of 2-propanol, as the water content increases the "bulk" water character increases resulting in droplet size increases and more water–water interactions. At the same time, 2-propanol is being absorbed from the continuous phase into the interface to stabilize the droplet, bringing more alcohol into proximity with the water of the droplet and increasing the alcohol–water H bonding. A similar conclusion was reached by Hansen[7] in his study of the ^{1}H NMR of surfactant containing microemulsions.

The chemical shift of these same two proton signals, however, behave differently under the condition of constant mole fraction of water with increasing content of 2-propanol. Figure 4B shows the plot of the chemical shift vs. mole fraction of 2-propanol. In this case, the water proton signal shifts upfield while the hydroxyl group resonance of 2-propanol shifts downfield. The upfield shift of the water proton signal is the result of an increase in the shielding of the proton resulting from a decrease in the number of water–water H bonds. The downfield shift of the hydroxyl group proton of 2-propanol implies a decrease in the shielding of the proton resulting from an increase 2-propanol–water H bonding. The chemical shifts of the two signals followed suggest the system is undergoing a transition from a system which contains a large degree of bulk water character (i.e., water–water H bonding) to one of little or no bulk water character (i.e., mainly 2-propanol–water H bonding). As the water content remains constant and the 2-propanol is increased, the chemical shift of the two proton signals suggests that the system gradually loses "bulk" water character while the amount of alcohol–water interaction grows. The implication is that the water droplets decrease in size and the water becomes solvated in alcohol aggregates dispersed in the oil phase. Thus, by referring to Figure 1A, the transition the ^{1}H NMR data support for the increase in 2-propanol content at a constant mole fraction of water is from a macroemulsion (large amount of bulk water) to a "ternary" solution (no bulk water present).

Peak Shape. The dependence of the chemical shift of the hydroxyl group proton of 2-propanol and water proton signals upon the content of water is also observed in the peak shape of the hydroxyl group proton signal. Figure 5 illustrates this change as a function of increasing water content.

At very low mole fractions of water, the hydroxyl group proton signal appears as a distinct, well-resolved doublet. As the mole fraction of water is increased, the doublet is gradually replaced by a broad singlet. In each system studied (water, 0.001 or 0.01 M NaCl with *n*-hexane and 2-propanol), the transition is essentially complete at a mole fraction of the aqueous phase of 0.300.

Conclusion

Microemulsions are defined as follows: ". . . spherical aggregates of oil or water dispersed in the other liquid and stabilized by an interfacial film of one or more surfactants such that the droplets range in size from 10 to 200 nm."[13] Generally, microemulsions appear as transparent solutions (when white light is passed through them) which exhibit foaming upon agitation. While these physical charac-
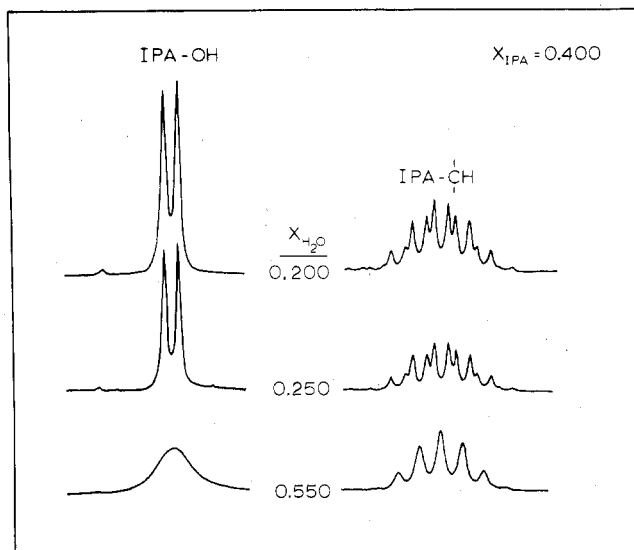
Figure 5. Spectral changes in the hydroxyl group and methine group proton signals of 2-propanol with increasing water content for the system *n*-hexane, 2-propanol, and water.

teristics are present in both detergent-stabilized and detergentless systems found in the literature, other mixed solvent systems (e.g., binary and ternary systems, micelles, etc.) also exhibit these same physical characteristics. Ross and Nishioka[14,15] have demonstrated that binary and ternary systems of various miscible solvents exhibit foaming under suitable conditions, and this phenomenon is commonplace during extractive distillations. These systems are also transparent to white light. Thus, while foaming and transparency are necessary for a system to be a microemulsion, it is not a sufficient condition.

The studies described here show that region boundaries shift upon the addition of sodium chloride (Figure 1). Therefore, if a detergentless microemulsion is to be used as a solvent for a reaction involving inorganic salts, the nature of the total system in the presence of reactants

needs to be carefully examined. While the system may be a microemulsion before the addition of the reactants, afterward it need not be.

The existence of detergentless microemulsions has been established previously by a combination of conductivity and ultracentrifugation data.[3] The boundaries of the ternary diagram were constructed from conductivity data but ultracentrifugation data were required to identify the microemulsion phase. In other words, only ultracentrifugation experiments detected the dispersed water-rich microdroplets. The studies with ^{1}H NMR reported here establish that NMR measurements not only detect the same region boundaries as conductivity data but they also detect the presence of bulk water dispersed in the microemulsion phase. Thus, ^{1}H NMR is a powerful tool for detecting ternary solutions that are detergentless microemulsions.

References and Notes

(1) Supported by NSF Grant CHE76-00183. R.E.B. is the recipient of an NIH Research Career Development Award (GM 00246). A portion of this material was presented at the 52nd Colloid and Surface Science Symposium, Knoxville, TN, 1978.
(2) Department of Chemistry, University of Georgia, Athens, GA 30602.
(3) G. D. Smith, C. E. Donelan, and R. E. Barden, *J. Colloid Interface Sci.*, **60**, 488 (1977).
(4) I. A. Zlochower and J. H. Schulman, *J. Colloid Interface Sci.*, **24**, 115 (1967).
(5) G. Gillberg, H. Lehtinen, and S. Friberg, *J. Colloid Interface Sci.*, **33**, 40 (1970).
(6) D. O. Shah and R. M. Hamlin, Jr., *Science*, **171**, 483 (1971).
(7) J. R. Hansen, *J. Phys. Chem.*, **78**, 256 (1974).
(8) J. E. Bowcott and J. H. Schulman, *Z. Electrochem.*, **59**, 283 (1955).
(9) L. M. Prince, *J. Colloid Interface Sci.*, **52**, 182 (1975). Not all surfactant chemists agree that microemulsions should be identified as a distinct phase. See D. G. Rance and S. Friberg, *J. Colloid Interface Sci.*, **60**, 207 (1977).
(10) J. N. Schooley and B. J. Alder, *J. Chem. Phys.*, **23**, 805 (1955).
(11) L. M. Prince in "Emulsions and Emulsion Technology", part I, K. J. Lissant, Ed., Marcel Dekker, New York, 1974.
(12) L. M. Prince, *J. Colloid Interface Sci.*, **52**, 182 (1965).
(13) L. M. Prince in "Micellization, Solubilization, and Microemulsion", Vol. 1, K. L. Mittal, Ed., Plenum Press, New York, 1977, p 45.
(14) S. Ross and G. Nishioka, *J. Phys. Chem.*, **79**, 1561 (1975).
(15) S. Ross and G. Nishioka in "Foams", R. J. Akers, Ed, Academic Press, New York, 1976, p 17.

Adsorption of Alcohols and Water on Alumina. 3. dc Conductivity and Dielectric Loss Measurements[†]

G. Clement, H. Knözinger,* W. Stählin, and B. Stübner

Institut für Physikalische Chemie der Universität München, München 2, West Germany (Received October 2, 1978)

dc conductivities of isobutyl alcohol, H_2O, and D_2O adsorbed on γ- and η-Al_2O_3 and dielectric absorptions of isobutyl alcohol adsorbed on η-Al_2O_3 have been measured. The degree of dissociation is strongly enhanced for the adsorbed molecules as compared to the liquid, due to strong coordinative interactions between adsorbent and adsorbed molecule. A degree of dissociation of 10^{-1} is estimated for H_2O adsorbed at 400 K. The resulting surface conductivity is protonic in nature as demonstrated by a large deuterium isotope effect. Dielectric absorption occurs for isobutyl alcohol adsorbed on η-Al_2O_3 at a frequency of 5×10^4 s^{-1} at 189 K, which corresponds to a relaxation time of 3.2×10^{-6} s. An activation energy for this relaxation process between 24 and 31 kJ/mol is estimated. A model for the relaxation mechanism is developed on the basis of a previously reported adsorption structure and the results are compared with nuclear magnetic resonance data reported recently.

Introduction

A detailed understanding of the behavior of alcohols and water adsorbed on alumina surfaces regarding the structure of adsorbed species as well as their dynamics is needed

[†] Dedicated to Professor Dr. G. M. Schwab on his 80th birthday.

since aluminas are active catalysts for alcohol conversions.[1,2] As shown recently by gravimetric and infrared spectroscopic studies of the adsorption of ethyl[3] and isobutyl alcohol,[4] a monolayer is built up on the surface of η-Al_2O_3, at temperatures between 300 and 400 K and in a pressure range up to 10^3 N m^{-2}. Depending on the