Evaluation of Mixed Surfactants for Improved Chemical Flooding

Topical Report

By
Feliciano M. Llave
Troy R. French
Phil B. Lorenz

February 1993

Work Performed Under Cooperative Agreement No. DE-FC22-83FE60149

Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy

Jerry Casteel, Project Manager
Bartlesville Project Office
P. O. Box 1398
Bartlesville, OK 74005

Prepared by
IIT Research Institute
National Institute for Petroleum and Energy Research
P.O. Box 2128
Bartlesville, OK 74005

MASTER

TABLE OF CONTENTS

TABLES

ILLUSTRATIONS

ILLUSTRATIONS - cont...

ILLUSTRATIONS - cont...

ILLUSTRATIONS - cont...

ILLUSTRATIONS - cont...

ILLUSTRATIONS - cont...

EVALUATION OF MIXED SURFACTANTS FOR IMPROVED CHEMICAL FLOODING

by Feliciano M. Llave, Troy R. Frei, and Phil B. Lorenz

ABSTRACT

Phase behavior studies were conducted using combinations of a primary surfactant component and several ethoxylated surfactants. The objective of the study is to evaluate combinations of surfactants, anionic-nonionic and anionic-anionic mixtures, that would yield favorable phase behavior and solubilization capacity. The dependence of the solution behavior on the additive surfactant structure, surfactant type, oil, surfactant proportion, salinity, HLB, and temperature was observed.

The results showed that the ethoxylated surfactants can improve the solution behavior of the overall system. The increase in optimum salinity range of these solutions corresponded to an increase in the degree of ethoxylation of additive surfactant, up to a certain limit. The nonionic surfactant additives yielded much higher salinities compared to the results from the ethoxylated anionics tested. The proportion of surfactant component in solution was critical in achieving a balance between the solubilization capacity and the enhancement in the system's salinity tolerance. Some combinations of these types of surfactants showed improved solution behavior with favorable solubilization capacity.

The phase inversion temperature (PIT) method has been shown to be a relatively fast method for screening candidate surfactant systems. Comparisons were made using both the conventional salinity scan and the PIT method on selected chemical systems. The results showed good agreement between the salinity regions determined using both methods. Several observations were also made during these screening studies. A difference in the dependence of optimal salinity on HLB was observed for the different nonionics tested. The linear alkyl alcohol ethoxylates exhibited a behavior distinct from the dialkyl phenols at similar HLB levels with and without the primary sulfonate component in the solution.

Other experiments performed at NIPER have shown that surfactant-enhanced alkaline flooding has good potential for the recovery of oil from Naval Petroleum Reserve Number 3 (NPR No. 3). Recovery of oil from NPR No. 3 can be increased by application of surfactant-enhanced alkaline flooding, which is also referred to as alkali/surfactant/polymer (ASP) flooding when polymer is added to the formulation in order to achieve better mobility control. Due to the highly fractured nature of NPR No. 3

reservoirs, chemical flooding (and waterflooding) should be more efficient after application of gels that could improve conformance.

INTRODUCTION

The National Energy Strategy-Advanced Oil Recovery Program (NES-AORP) was developed as a means of improving domestic oil production and extending the productive life of United States' resources. The focus of this program is the technical advancement of the best currently defined enhanced oil recovery (EOR) methods and application of these methods to improve recovery from targeted reservoirs. Chemical flooding has been identified by the U.S. Department of Energy (DOE) as an important production technique targeted for Class 1 reservoirs.[1] For many U.S. domestic oil reservoirs, this may be the only viable EOR method. The objective of this research program is to develop improved chemical flooding systems that are both cost-effective and have improved adaptability to different ranges of selected Class 1 reservoir conditions for recovery of light crude oils. The research work conducted under this program for FY92 has been focused primarily on identifying mixed surfactant systems that can be formulated with chemical components that synergistically yield high oil recovery potential and improved solution behavior and adaptability.

In FY92, research on the use of mixed surfactant systems continues to focus on a specific range of reservoir conditions that have been identified in prior work[2,3] and in accordance with the guidelines from the Federal Oil Program Implementation Plan[1] as suitable for the application of this type of EOR process. With this in mind, experimental investigations were conducted on several mixed surfactant systems containing primary surfactant components with the addition of a series of ethoxylated anionic and nonionic surfactants. These studies were performed to identify trends in the overall surfactant solution behavior of these systems as a function of the amount and type of surfactant component present, and whether they were anionic-nonionic or anionic-anionic mixtures. A systematic identification of different surfactant component parameters was conducted in an effort to develop a chemical system(s) that would yield much improved phase behavior and solubilization capacity, compared to the original anionic formulation. A fairly well-studied base case primary chemical anionic system was selected for this study.[4,5] This chemical system developed relatively low interfacial tensions (IFT) at low optimal salinity and low concentrations of divalent ions. The experimental work conducted was aimed at evaluating combinations of this surfactant with a series of secondary components that may yield much improved salinity tolerance, while maintaining comparable solubilization

2

capacity. Ethoxylated anionic and nonionic surfactants have been selected primarily because of the promising results shown by these types of surfactants in extending the range of primary sulfonate systems to higher salinity levels.[3,6] Combinations of anionic-nonionic surfactants were used in these experiments in order to evaluate the potential of utilizing a hydrophilic-lipophilic balance (HLB) gradient approach in achieving a balance between the hydrophilic and lipophilic tendencies of the overall chemical system for more favorable solution behavior.

NIPER's efforts in developing other cost-effective chemical flooding technologies have also been focused on the use of alkaline-enhanced surfactant flooding technology for the recovery of light, midcontinent crude oils. The Naval Petroleum Reserve Number 3 (NPR No. 3), a U.S. Department of Energy oilfield, is one of the targets for this technology. This particular reservoir is located in Natrona County, Wyoming. Oil production is from several formations that are between 1,000 and 6,000 ft in depth. Several of these oil-containing formations are of sufficient thickness to contain significant amount of oil. Permeability range is from about 10 mD (Frontier formation, north area) up to about 350 mD (Muddy formation). Oil zones are characterized by faults and fractures that can traverse more than one oil zone. Field-wide development began in 1976 with the Shannon formation. Oil production from the Shannon has been low because of the lack of a natural water drive and the heterogeneous lithology. Waterflooding failed due to clay swelling as well as faults and fractures that caused poor sweep efficiency. Improved waterflooding (polymer) has been more successful, which is encouraging.[7] The Frontier formation has been waterflooded during the past 15 years. Oil recovery from this formation has been low due to the heterogeneous, faulted nature of the sandstone. Only about 17% of the original-oil-in-place (OOIP) has been recovered. The primary targets for chemical EOR are believed to be the Shannon and Frontier (or 2nd Wall Creek) formations. Both of these formations still have relatively high oil saturations. Particular emphasis is being placed on the Frontier formation, since production has been so low and is rapidly becoming uneconomical.[8]

The recovery of additional oil from porous media by chemical flooding is relatively easy when there is good conformance control and when permeability is reasonably high, i.e., about 100 mD or greater. Prior results show that oil recovery with chemical flooding is greatly reduced when permeability is low and conformance is poor.[9] In order to improve conformance in NPR No. 3, mobility of the injected fluids in fractures must be decreased, thereby directing injected fluids through the porous medium where oil saturation is high. Conformance can probably be best controlled by injection of polymer gels. When

permeability of the porous medium is low, the polymer used for mobility control must propagate through the porous medium without face plugging and without unacceptable losses due to adsorption. In fact, the transport of both surfactant and polymer is considerably more difficult when permeability is low.[10] Mobility control is best accomplished by using a polymer that will traverse the porous medium, yet maintain sufficient viscosity for good mobility control.

Despite some reservoir characteristics that are not especially favorable for chemical flooding, some aspects of NPR No. 3 formations are very favorable to chemical flooding. Reservoir salinities are often very low, and low IFTs can be achieved with certain chemical formulations. The thicknesses of reservoir zones are large enough to contain fairly sizable amounts of oil, but small enough that chemical costs are manageable. Oil viscosities are low such that good mobility control can be achieved with fairly low concentrations of low-molecular-weight polymers. The low-molecular-weight polymers will traverse low-permeability sands without face plugging.

ACKNOWLEDGMENTS

SURFACTANT MIXTURE SCREENING

Materials

A listing of the nonionic and anionic surfactants used in the study is presented in tables 1 and 2. These chemicals were used without further purification, unless otherwise specified. Table 3 is a listing of the different surfactant systems formulated for the study. These systems were formulated primarily with a base anionic surfactant component in combination with nonionic surfactants as secondary additives. These systems were mostly screened using the phase inversion temperature (PIT) measurement. Phase behavior studies and interfacial tension measurements were performed on a number of these systems. The chemical solutions were prepared using reagent grade salts, and the concentrations are reported as weight of chemical to volume of solution (wt/vol).

TABLE 1 - List of nonionic surfactants studied.

Company	Name	Code	Type	Alkane Chain	EO	HLB
Harcros	TDET	TDA-60	Tridecyl alcohol ethoxylate	13	7	12.0
Henkel	Trycol	5949	Tridecyl alcohol ethoxylate	13	7.5	12.5
Hoechst	Genapol	24L-45	alcohol ethoxylate	12-14	6.5	11.8
Hoechst	Genapol	24L-60	alcohol ethoxylate	12-14	7.2	12.2
Hoechst	Genapol	24L-75	alcohol ethoxylate	12-14	8.3	12.9
Hoechst	Genapol	26L-3	alcohol ethoxylate	12-16	3	8.0
Hoechst	Genapol	26L-5	alcohol ethoxylate	12-16	5	10.6
Hoechst	Genapol	26L-60	alcohol ethoxylate	12-16	7.3	12.4
Rhone-Poulenc	Igepal	DM-430	ethoxylated dialkyl phenol	9	7	9.4
Rhone-Poulenc	Igepal	DM-530	ethoxylated dialkyl phenol	9	9	10.6
Rhone-Poulenc	Igepal	DM-730	ethoxylated dialkyl phenol	9	15	15.1
Rhone-Poulenc	Alkasurf	TDA-5	alcohol ethoxylate	13	5	10.6
Rhone-Poulenc	Alkasurf	TDA-6	alcohol ethoxylate	13	6	10.6
Rhone-Poulenc	Alkasurf	TDA-7	alcohol ethoxylate	13	7	12.1
Rhone-Poulenc	Alkasurf	TDA-8.5	alcohol ethoxylate	13	8.5	12.5
Shell	Neodol	91-2.5	alcohol ethoxylate	9-11	2.5	8.5
Shell	Neodol	91-8	alcohol ethoxylate	9-11	8	13.9
Shell	Neodol	25-3	alcohol ethoxylate	12-15	3	7.8
Shell	Neodol	25-7	alcohol ethoxylate	12-15	7	12.3
Shell	Neodol	45-7	alcohol ethoxylate	14-15	7	11.8
Shell	Neodol	45-7T	alcohol ethoxylate	14-15	7.9	12.3

TABLE 2 - List of anionic surfactants studied.

Company	Name	Code	Type	Alkane Chain	EO	HLB
PPG	Avanel	S-30	Ethoxy. alkyl sulfonate	12-15	3	n.a.
PPG	Avanel	S-70	Ethoxy. alkyl sulfonate	12-15	7	n.a.
PPG	Avanel	S-90	Ethoxy. alkyl sulfonate	12-15	9	n.a.
PPG	Avanel	S-150	Ethoxy. alkyl sulfonate	12-15	15	n.a.
Witco	TRS	TRS 10-410	petroleum sulfonate			n.a.

TABLE 3 - List of surfactant systems studied using PIT method.

System No.	Components and Concentration of Surfactant Systems	HLB*
1	2 wt% DM-530	10.6
2	2 wt% N-25-7	12.3
3	1 wt% DM-530 and 1 wt% TRS 10-410/IBA [50:50]**	10.6
4	1 wt% N-25-7 and 1 wt% TRS 10-410/IBA [50:50]	12.3
5	2 wt% N-25-7/DM-530 [50:50]	11.45
6	1 wt% N-25-7/DM-530 [50:50] and 1 wt% TRS 10-410/IBA [50:50]	11.45
7	2 wt% N-45-7	11.8
8	2 wt% N-91-8	13.9
9	2 wt% N-45-7T/N-25-3 [83:17]	11.45
10a	2 wt% N-45-7T/N-25-3 [50:50]	10.0
10b	2 wt% N-45-7T/N-25-3 [61.4/38.6]	10.5
11	1 wt% N-45-7T/N-25-3[50:50] and 1 wt% TRS 10-410/IBA[50:50]	10.0
12	2 wt% DM-530/N-25-3 [78.5/21.5]	10.0
13	1 wt% N-45-7T/N-25-3[83:17] and 1 wt% TRS 10-410/IBA[50:50]	11.45
14	2 wt% N-25-3	7.8
15	2 wt% N-45-7T	12.2
16	2 wt% N-25-7/N-25-3 [93.3:6.7]	12.0
17	2 wt% N-25-7/N-45-7 [40:60]	12.0
18	2 wt% N-45-7/N-25-3 [80:20]	11.0
19	2 wt% N-25-3/N-25-7 [29:71]	11.0
20	2 wt% Igepal DM-430	9.4
21	2 wt% DM-430/DM-730 [72:28]	11.0
22	2 wt% DM-530/DM-730 [91:9]	11.0
23	2 wt% DM-430/DM-530 [50:50]	10.0
24	2 wt% Genapol 26-L-5	10.6
25	2 wt% Genapol 24-L-60	12.2
26	2 wt% Genapol 26-L-5/26-L-3 [77:23]	10.0
27	2 wt% N-45-7/N-25-3 [55:45]	10.0
28	2 wt% N-25-7/N-25-3 [49:51]	10.0
29	2 wt% N-91-2.5	8.5

* HLB for pure component is based on manufacturer's information; HLB for mixtures or surfactant combinations is based on linear mixing rule and wt% of each component and the manufacturer's stated HLB.

** wt% of component 1 vs. wt% of component 2

TABLE 3 - List of surfactant systems studied using PIT method. - cont.

System No.	Components and Concentration of Surfactant Systems	HLB
30	2 wt% DM-530/DM-730 [80:20]	11.5
31	2 wt% DM-530/DM-730 [69:31]	12.0
32	2 wt% DM-530/DM-730 [58:42]	12.5
33	2 wt% DM-530/N-25-7 [77:23]	11.0
34	2 wt% DM-530/N-25-7 [18:82]	12.0
35	2 wt% Genapol 24-L-45	11.8
36	2 wt% Genapol 26-L-60	12.4
37	2 wt% Genapol 24-L-75	12.9
38a	2 wt% Genapol 26-L-3/26-L-5 [13.5:86.5]	10.25
38b	2 wt% Genapol 26-L-3/26-L-5 [42:58]	9.5
38c	2 wt% Genapol 26-L-3/26-L-5 [61.5:38.5]	9.0
38d	2 wt% Genapol 26-L-3/26-L-5 [81:19]	8.5
38e	2 wt% Genapol 26-L-3/26-L-5 [52:48]	9.25
39a	2 wt% Genapol 26-L-5/26-L-60 [78:22]	11.0
39b	2 wt% Genapol 26-L-5/26-L-60 [47:53]	11.55
39c	2 wt% Genapol 26-L-5/26-L-60 [22:78]	12.0
40a	2 wt% DM-430/DM-530 [29:71]	10.25
40b	2 wt% DM-430/DM-530 [67:33]	9.8
40c	2 wt% DM-430/DM-530 [83:17]	9.6
41	2 wt% DM-530/DM-730 [85.6:14.4]	11.25
42	1 wt% DM-430 and 1 wt% TRS 10-410/IBA [50:50]	9.4
43	1 wt% DM-430/DM-530 [83:17] and 1 wt% TRS 10-410/IBA [50:50]	9.6
44	1 wt% DM-430/DM-530 [50:50] and 1 wt% TRS 10-410/IBA [50:50]	10.0
45	1 wt% DM-530/DM-730 [91:9] and 1 wt% TRS 10-410/IBA [50:50]	11.0
46	1 wt% DM-530/DM-730 [80:20] and 1 wt% TRS 10-410/IBA [50:50]	11.5
47	1 wt% DM-530/DM-730 [69:31] and 1 wt% TRS 10-410/IBA [50:50]	12.0
48	1 wt% DM-530/DM-730 [58:42] and 1 wt% TRS 10-410/IBA [50:50]	12.5
49	1 wt% Genapol 26-L-3/26-L-5 [52:48] and 1 wt% TRS 10-410/IBA [50:50]	9.25
50	1 wt% Genapol 26-L-3/26-L-5 [42:58] and 1 wt% TRS 10-410/IBA [50:50]	9.5
51	1 wt% Genapol 26-L-5/26-L-3 [77:23] and 1 wt% TRS 10-410/IBA [50:50]	10.0
52	1 wt% Genapol 26-L-5 and 1 wt% TRS 10-410/IBA [50:50]	10.6
53	1 wt% Genapol 26-L-5/26-L-60 [78:22] and 1 wt% TRS 10-410/IBA [50:50]	11.0
54	1 wt% Genapol 26-L-5/26-L-60 [47:53] and 1 wt% TRS 10-410/IBA [50:50]	11.55

TABLE 3 - List of surfactant systems studied using PIT method. - cont.

System No.	Components and Concentration of Surfactant Systems	HLB
55	1 wt% Genapol 26-L-5/26-L-60 [22:78] and 1 wt% TRS 10-410/IBA [50:50]	12.0
56	1 wt% Genapol 24-L-60 and 1 wt% TRS 10-410/IBA [1:1]	12.2
57o	2 wt% Genapol 26-L-3/26-L-5 [42:58] with n-Octane	9.5
58o	2 wt% DM-430/DM 530 [83:17] with n-Octane	9.6
59o	2 wt% Igepal DM-430/DM-530 [50:50] with n-Octane	10.0
60o	2 wt% Genapol 26-L-5/26-L-3 [77:23] with n-Octane	10.0
61o	2 wt% DM-530/DM-730 [91:9] with n-Octane	11.0
62o	2 wt% Genapol 26-L-5/26-L-60 [78:22] with n-Octane	11.0
63o	2 wt% DM-530/DM-730 [69:31] with n-Octane	12.0
64o	2 wt% Genapol 26-L-5/26-L-60 [22:78] with n-Octane	12.0
65o	2 wt% Genapol 26-L-5/26-L-60 [47:53] with n-Octane	11.55
66o	2 wt% DM-530/DM-730 [80:20] with n-Octane	11.5
67o	2 wt% Genapol 26-L-5 with n-Octane	10.6
68o	2 wt% DM-530 with n-Octane	10.6

EXPERIMENTAL PROCEDURES

Phase Behavior Measurements

Phase behavior measurements were conducted on selected chemical systems to evaluate the effects of several experimental factors such as: total surfactant concentration, salinity, crude oil type, proportion of different combinations of anionic and nonionic surfactant types, and mixing of nonionic surfactant of different HLBs on the phase behavior of the overall chemical/hydrocarbon systems. Solubilization parameter is an important indicator of interfacial tension than can be obtained from these studies. These tests were typically conducted using solutions that were made up at a fixed water-to-oil ratio (volume water : volume oil = 1), unless otherwise specified. These solutions were prepared in 10-mL glass pipets that were sealed and equilibrated in approved safety ovens at the desired temperature condition. The relative volumes of the different phases were read and recorded at set time intervals until constant readings were obtained. These constant phase volume readings were then used to calculate the solubilization parameters of the oil ($\sigma_o = V_o/V_s$) and the brine ($\sigma_w = V_w/V_s$) in the microemulsion phase. Unusual phase

behavior such as the formation of gels, liquid crystalline phases, and precipitation was also recorded. Details regarding these calculations are discussed in an earlier report.[11]

Anionic surfactant component screening was conducted using bottle tests. Typically, the chemical solutions and the crude oil or alkane samples tested were mixed at a fixed water-to-oil volumetric ratio of 1. These bottles were then equilibrated at temperature, and observed solution behavior was recorded after a fixed time interval. The overall chemical system's tolerance to the salinity ranges tested was observed, and a qualitative description of the solution phase behavior for the different combinations of chemical systems was obtained. This type of screening was used in evaluating the potential of adding different types and concentrations of anionic surfactant to improve or modify the overall solution behavior of a base case chemical system, i.e., addition of ethoxylated sulfonates in the system 5 wt% TRS 10-410 and 3 wt% IBA, up to a maximum of 5 wt% total added surfactant concentration.

Phase Inversion Temperature (PIT) Measurements

The phase inversion temperatures (PIT) of the chemical systems studied were measured using a computer-controlled apparatus designed and constructed at NIPER.[12] The PIT is the temperature condition at which a water-in-oil emulsion changes into an oil-in-water emulsion or vice versa. This phase transition can be detected by measuring the electrical conductivity of a well-stirred mixture as a function of the temperature. The PIT experiment is routinely associated with measurement of the above phase transition for nonionic surfactants, and the technique has been used extensively by Shinoda to investigate surfactant-oil interaction.[13,14] Detailed discussions on the merits of PIT measurements, particularly in cases using nonionic surfactants, have been presented in the literature.[15,16]

Interfacial Tension (IFT) Measurements

The interfacial tension (IFT) of the different chemical systems tested was measured using a Model 300 Spinning Drop Interfacial Tensiometer, manufactured at University of Texas at Austin. These measurements were conducted using different equilibrated and non-equilibrated systems and different target crude oils at selected reservoir conditions. These measurements were taken after sufficient equilibration time had been allowed at the temperature conditions desired. Several measurements were taken until stable and reproducible IFT values were obtained. Other parameters needed in the calculation of the IFT, such as densities and refractive indices, were measured using a Mettler/Paar DMA 45

Calculating Digital Density Meter and a Bausch & Lomb Refractometer. Details of these procedures have been reported elsewhere.[17]

RESULTS AND DISCUSSION

Phase behavior studies were conducted using a surfactant system containing TRS 10-410 and IBA as the primary components with the addition of a series of ethoxylated surfactants. The primary surfactant system is a fairly well-studied system[4,5] and based on results of prior screening tests, it appears that the addition of ethoxylated secondary surfactants can enhance the salinity tolerance of the overall system.[3] Current work done on the TRS/IBA system is the determination of the phase behavior of the overall surfactant solution as a function of the amount and type of secondary surfactants added, using a series of ethoxylated anionic and nonionic surfactants. The optimum conditions were determined by means of several experimental methods, including, PIT, IFT and phase volume measurements at various salinities. Unless otherwise specified, these systems were tested with n-decane at 50° C.

For these studies, both nonionic and anionic surfactants were used, as well as combinations of the two types of surfactant. The objective of the study is to evaluate combinations of surfactants, anionic-nonionic as well as anionic-anionic mixtures, that have better salt tolerance and yield much improved phase behavior and oil/water solubilization capacity, comparable to or exceeding that of the original anionic formulation. Ethoxylated anionic and nonionic surfactants have been selected primarily because of the promising results shown by these types of surfactants in extending the range of primary sulfonate systems to higher salinity levels. Combinations of nonionic surfactants were used in these experiments to evaluate the possibility of utilizing these secondary surfactants as a means of achieving a balance between the affinity of the target chemical system for the oil-rich and water-rich phases that will yield more favorable overall solution behavior.

Addition of Nonionic Surfactant Components

Phase behavior studies were conducted using combinations of several surfactants containing ethoxylated nonionic surfactants. The initial group of nonionic surfactants tested included: Neodol 25-7, TDET TDA-60, and Trycol 5949. These surfactants have a similar range of molecular weight, 500 ± 25, and HLB value of about 12.1 to 12.5 (EO's of 7-8). The results using Neodol 25-7 [HLB 12.3] are presented in figures 1 to 7 and in Appendix A. Using these surfactants in combination with the base TRS 10-410/IBA

10

system with n-decane resulted in a shift in the mid-point salinity of the overall mixture to as high as 10% NaCl.

The results shown in figures 1 to 3 indicate that a favorable shift in optimal salinity (S*) levels was achieved with an increase in the proportion of ethoxylated nonionic surfactant in the system, i.e., 1:0, 3:1, 1:1, and 1:3. At the highest proportion of nonionic component tested, 1:3, the optimal salinity was as high as 15% NaCl, at a total surfactant concentration of 2 wt%. This relatively high optimal salinity level was offset though by the low value of the solubilization parameter of 2.5 mL/mL$_{surf}$.

Figure 1 shows a plot of the measured solubilization parameters and optimal salinity for the TRS 10-410/IBA [5:3] + N-25-7 system at several component proportions with n-decane. The extended width of the type-III region for this system was offset by the relatively low (2 to 4) oil solubilization parameters (V$_o$/V$_s$) measured, depending on the proportion of the ethoxylated component in the system. The width of this region is defined by an upper limit (S$^+$) and lower limit (S$^-$) in salinity, with ΔS being the difference between these two salinity limits. The V$_o$/V$_s$ and V$_w$/V$_s$ are the oil and water solubilization parameters determined from the phase volume measurements. These parameters are indicative of the amount of fluid, whether oil or water, present in the surfactant-rich middle
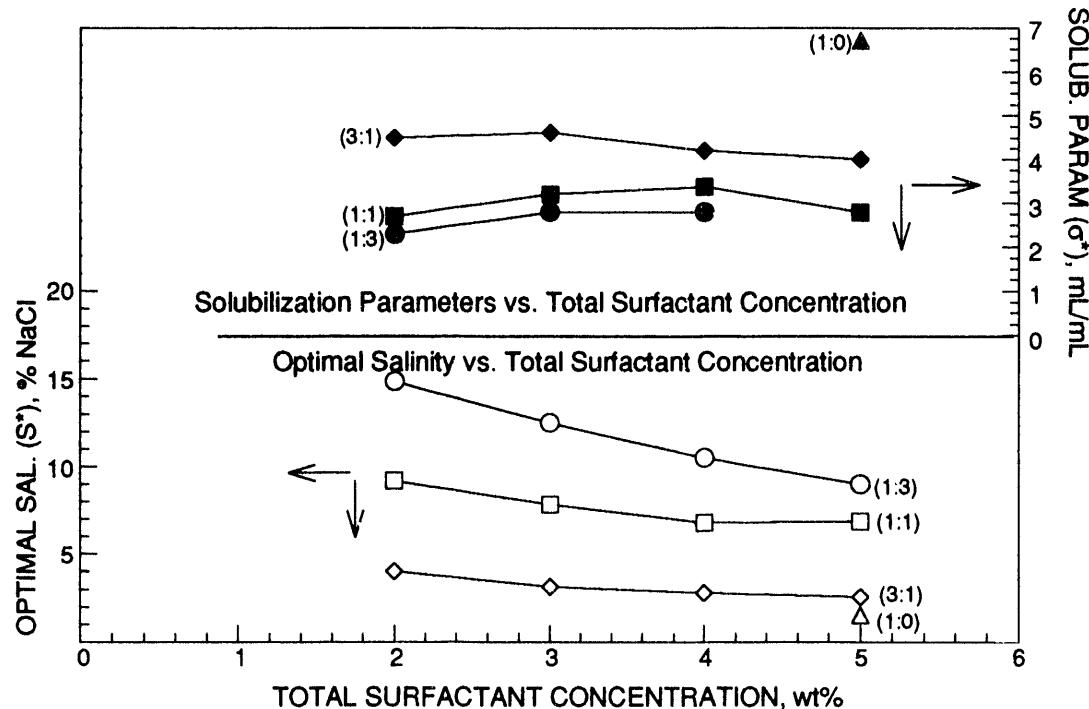
FIGURE 1. - Optimal salinity and solubilization parameters measured using TRS 10-410/IBA + N-25-7 system with n-decane at 50° C.

phase. Optimal conditions are determined from the salinity conditions (S*) where the degree of oil and water solubilization are approximate equal ($V_o/V_s \approx V_w/V_s$). The solubilization parameter at optimal salinity is designated as σ^*. These parameters were compared to that of the base system of TRS 10-410/IBA with n-decane (yielding a value >6 at optimum).

Overall the solubilization parameters measured at optimal salinity were considered low, ranging from about 2 to 5 mL/mL$_{surf}$, at all surfactant concentration levels tested. Only the mixtures with more anionic components, [3:1], had consistent moderate levels of solubilization parameters, about 4 to 5 mL/mL$_{surf}$, at relatively low optimal salinity levels of 2 to 4 wt% NaCl. The effect of the total surfactant concentration on optimal salinity also indicates an inverse dependence. The optimal salinity levels slightly increased with decreasing surfactant concentrations. This is somewhat contrary to the classical representation of the salinity requirement diagram (SRD) by Nelson,[18] but similar dependence of the optimal salinity with concentration was observed with synthetic oil-containing systems.[3,18] The plot in figure 2 shows an increase in the extent of the type-III window as a function of the increased proportion of nonionic surfactant component. These
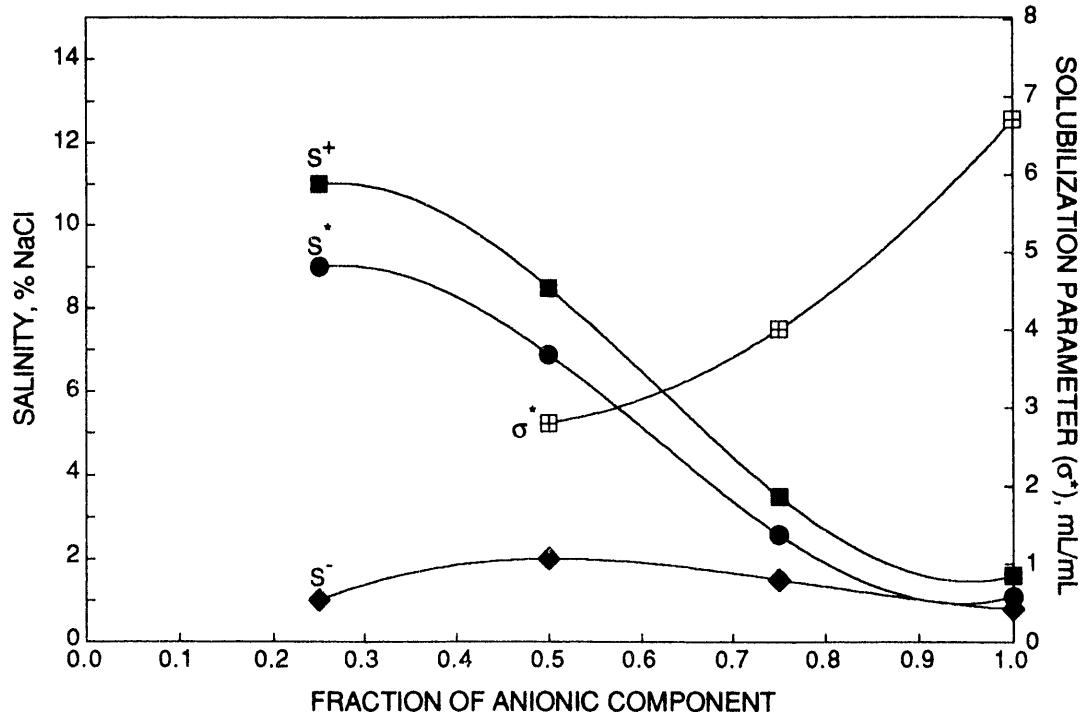
FIGURE 2. - Phase boundaries and solubilization parameters for the TRS 10-410/IBA + N-25-7 system with n-decane at 50° C and 5 wt% total surfactant concentration.

results show that the added ethoxylated surfactant did facilitate an improvement in the applicable range of salinity for this system, but the overall solubilization parameters obtained decreased in the process. Figure 3 shows that even at relatively low proportions of the nonionic component, i.e., 3:1, the resulting solubilization parameter was only about 4 mL/mL$_{surf}$, at an optimal salinity range of about 2.5 wt% NaCl.

The overall system containing N-25-7 appeared to be too hydrophilic. An alkane carbon number scan was conducted to find a combination where the selected surfactant system was better suited for the oil. It was determined that a C$_8$-oil component may be more suitable for this chemical system. The results using this oil showed that the chemical system's overall solubilization capacity did improve slightly, but this was coupled with a decrease in the optimal salinity levels by 1 to 2 wt% NaCl. Shortening the oil chain length shifted the surfactant's relative oil affinity favorably, as indicated by the positive change in oil solubilization. The lower optimal salinity condition was then necessary to maintain a balance of the surfactant's oil-water affinity at the new conditions. These results are presented in figures 4 and 5.

Figure 4 shows a plot of the optimal salinity and solubilization parameters as a
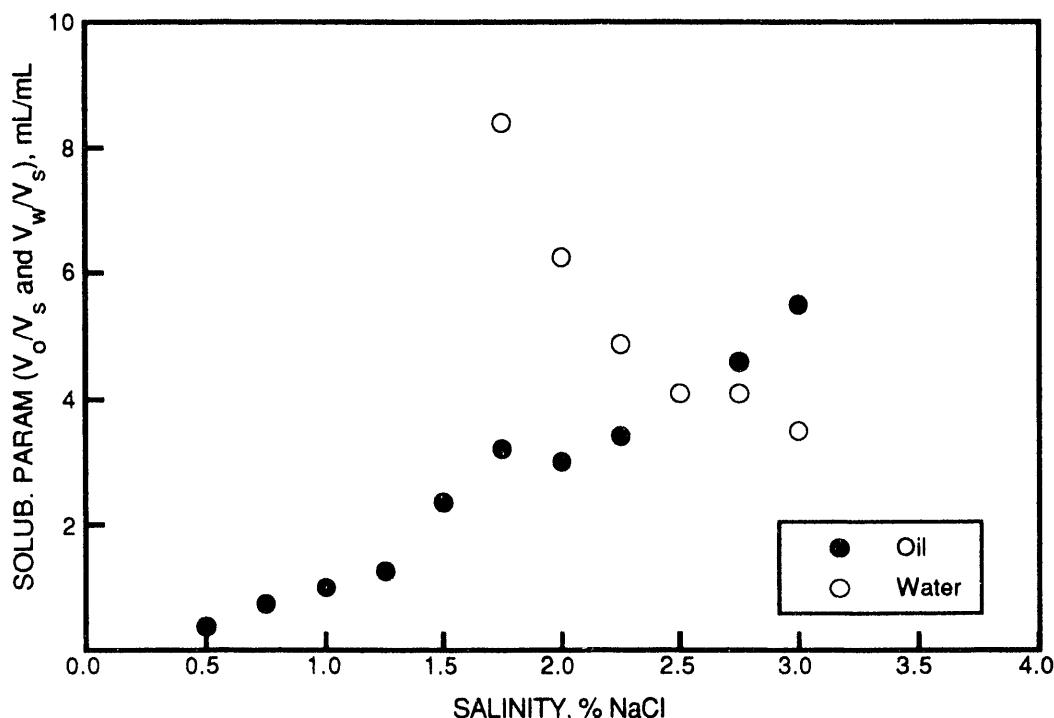
FIGURE 3. - Solubilization parameters for the [3:1] system of TRS 10-410/IBA + N-25-7 system with n-decane at 50° C and 5 wt% total surfactant concentration.
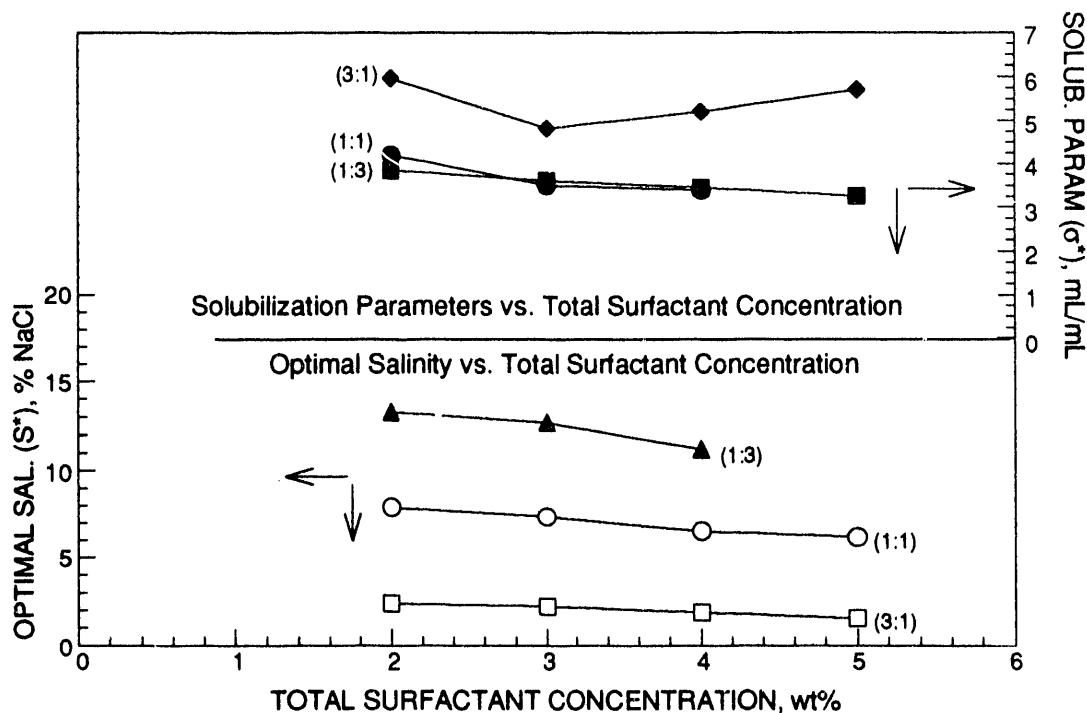
FIGURE 4. - Optimal salinity and solubilization parameters measured using TRS 10-410/IBA + N-25-7 system with n-octane at 50° C.

function of total surfactant concentration for the above-mentioned chemical system with n-octane. Figure 5 shows a plot of the phase boundaries for the same system. These results indicate that the presence of the nonionic component did improve the optimal salinity range of the overall system. These results also showed that using the n-octane as the oil resulted in a relatively higher degree of solubilization compared to the previous case. This improved degree of solubilization range of 3.5 to 6 mL/mL$_{surf}$ was offset though by a decrease in range of applicable optimal salinity. The results also indicate a narrower type-III window compared to the previous results. Other researchers have also observed that an extended type-III window often resulted in a drastic reduction in the capacity of the surfactant system for oil/water solubilization.[19]

The results from the study using the N-25-7 surfactant indicated that the overall chemical system may have been too hydrophilic in both cases when n-decane and n-octane were used. The first addition of this nonionic component to the TRS/IBA system resulted only in a relatively small increase in S*, with a corresponding large decrease in solubilization parameter, σ*, at optimal conditions. The effect with n-octane was slightly less than with n-decane.
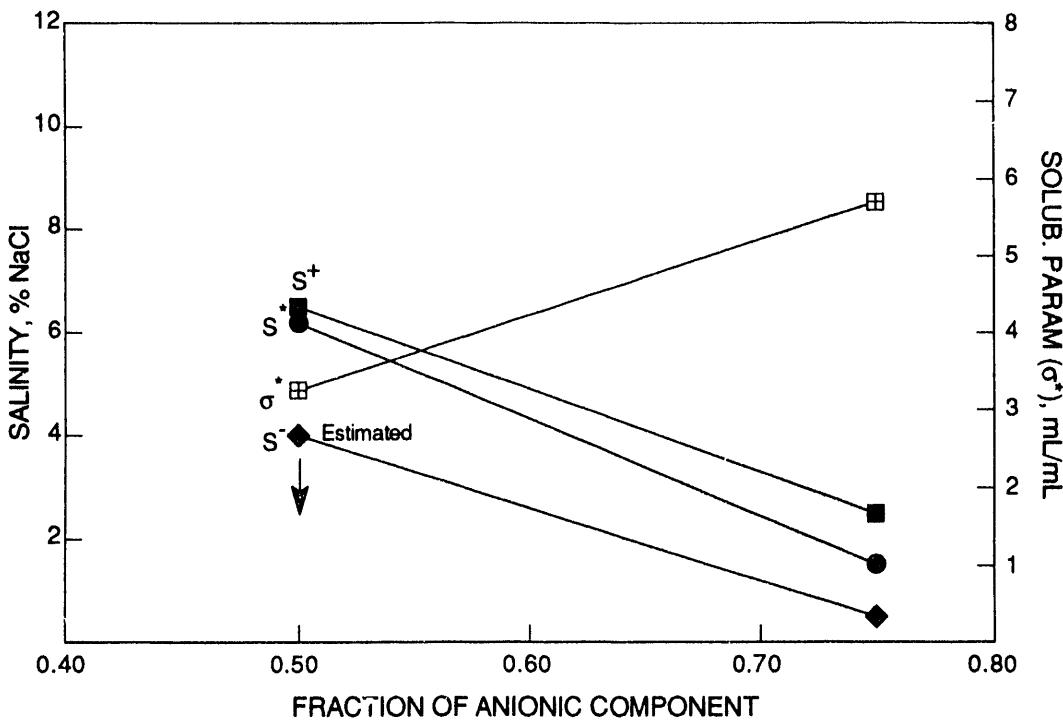
FIGURE 5. - Phase boundaries and solubilization parameters for the TRS 10-410/IBA + N-25-7 system with n-octane at 50° C and 5 wt% total surfactant concentration. Estimated points are approximate upper or lower limits observed in phase behavior tests.

Another secondary nonionic surfactant additive was then tested with a lower HLB. IGEPAL™ DM-530 [HLB 10.6] was used to evaluate any improvement in solubilization parameters at this HLB level. The results of these experiments are presented in figures 6 and 7. Figure 6 shows a summary plot of the optimal salinity and optimal oil/water solubilization parameters for this system as a function of the total surfactant concentration. The phase behavior using this system showed much improved oil solubilization parameters (>7 mL/mL$_{surf}$). The enhanced oil solubilization was offset though by a shift of the mid-point salinity of the overall mixture to much lower salinity ranges (about 1.5 to 6.0 % NaCl), compared to the previous results using N-25-7. The system showed a relatively hydrophobic behavior. These results, including the studies using N-25-7, showed the dependence of the optimal salinity on the proportion of nonionics in the chemical systems. The oil solubilization potential for both systems appeared to be somewhat insensitive to total surfactant concentration (within the tested limit of 2 to 5 wt%), while the favorable salinity range, ΔS and S*, showed slight inverse dependence on total concentration, as shown in figure 6. The results presented in figure 7 showed that the addition of the

15
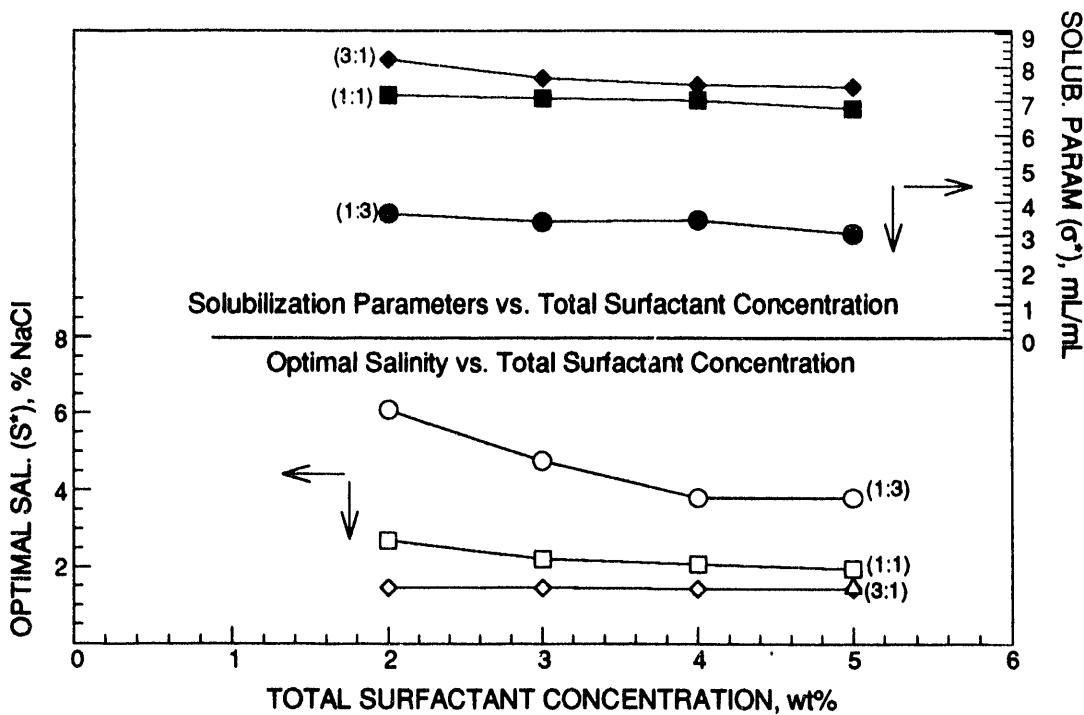
FIGURE 6. - Phase behavior measurements using TRS 10-410/IBA+DM-530 system with n-decane at 50° C.

DM-530 component can improve the range of optimal salinity for the overall system. This improvement in salinity range did not result in a marked decrease in solubilization parameters measured at optimal conditions. This figure shows that the solubilization parameters were similar, about 7 ± 0.5 mL/mL$_{surf}$, over the 0.5 to 1 range of anionic surfactant component proportions. Overall these results showed that a nonionic component can be used in combination with the primary anionic surfactant to improve the salinity tolerance range of the overall chemical system, while maintaining a comparable range of degree of solubilization capacity.

Figure 8 and 9 show plots of the effect of the increase in optimal salinity in the presence of the nonionic component on the corresponding oil/water solubilization parameters. These figure show plots of the change in degree of oil (decane) and water solubilization at optimal with respect to the increase in overall solution optimal salinity. Figure 8 shows the results of the tests containing various proportions of anionic:nonionic components at total surfactant concentrations from 2 wt% up to 5 wt%. Figure 9 shows a comparison the results of the studies using the N-25-7 and DM-530 with the TRS 10-410/IBA system at a fixed anionic:nonionic ratio of (1:3). These results show that the

16
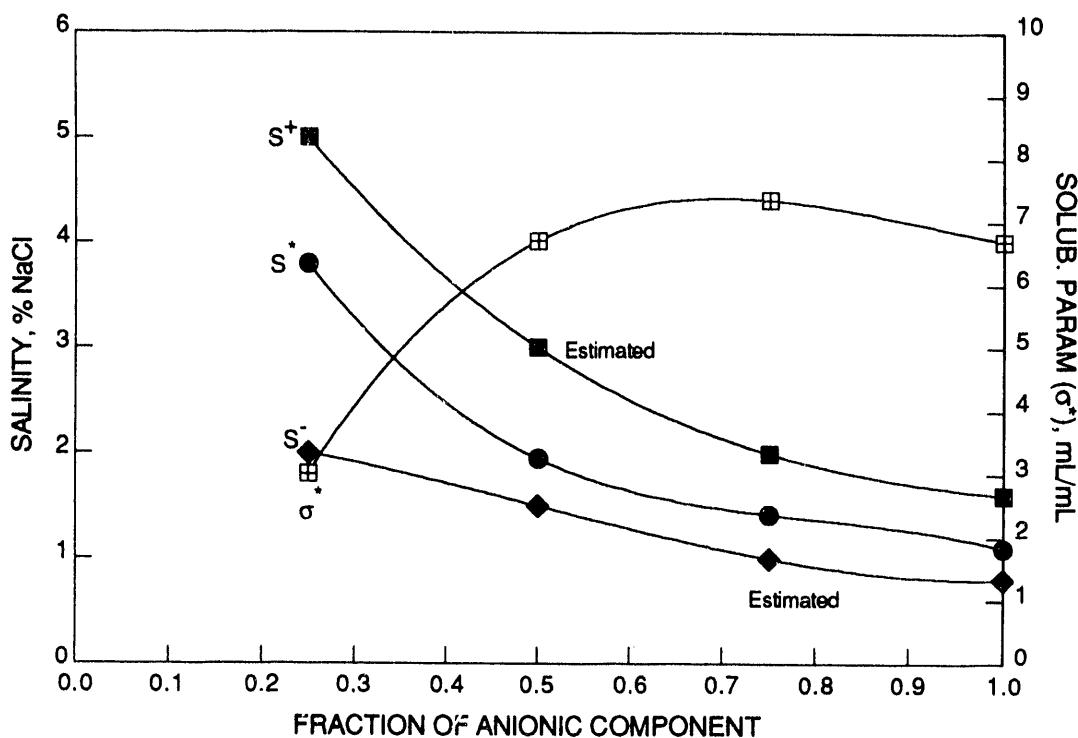
FIGURE 7. - Phase boundaries and solubilization parameters for TRS 10-410/IBA + DM-530 system with n-decane at 50° C and 5 wt% total surfactant concentration. Estimated points are approximate upper or lower limits observed in phase behavior tests.

addition of the nonionic component to the primary anionic surfactant system raises the optimal salinity (S^*) and the width of the type-III region (ΔS) of the overall solution. The corresponding increase in salinity conditions is offset though by a reduction in the optimal solubilization parameters (σ^*). Comparing the effect of the two nonionic components, the N-25-7 resulted in almost an immediate reduction in the degree of oil/water solubilization, while the DM-530 in limited cases actually resulted in an improvement in the σ^*. The addition of the N-25-7 resulted in higher overall levels of optimal salinity compared to systems containing DM-530. The selection of the additive nonionic component is therefore very important. The effect of total surfactant concentration appears to be relatively minor, although a trend in terms of an increase of optimal salinity and the width of the type-III window is indicated with a decrease in concentration. The total surfactant concentration level showed little effect on the degree of oil/water solubilization. These results indicate that for these type of systems, the dilution of the chemical slug may not have an adverse effect on its effectiveness as long as the slug remains relatively intact.
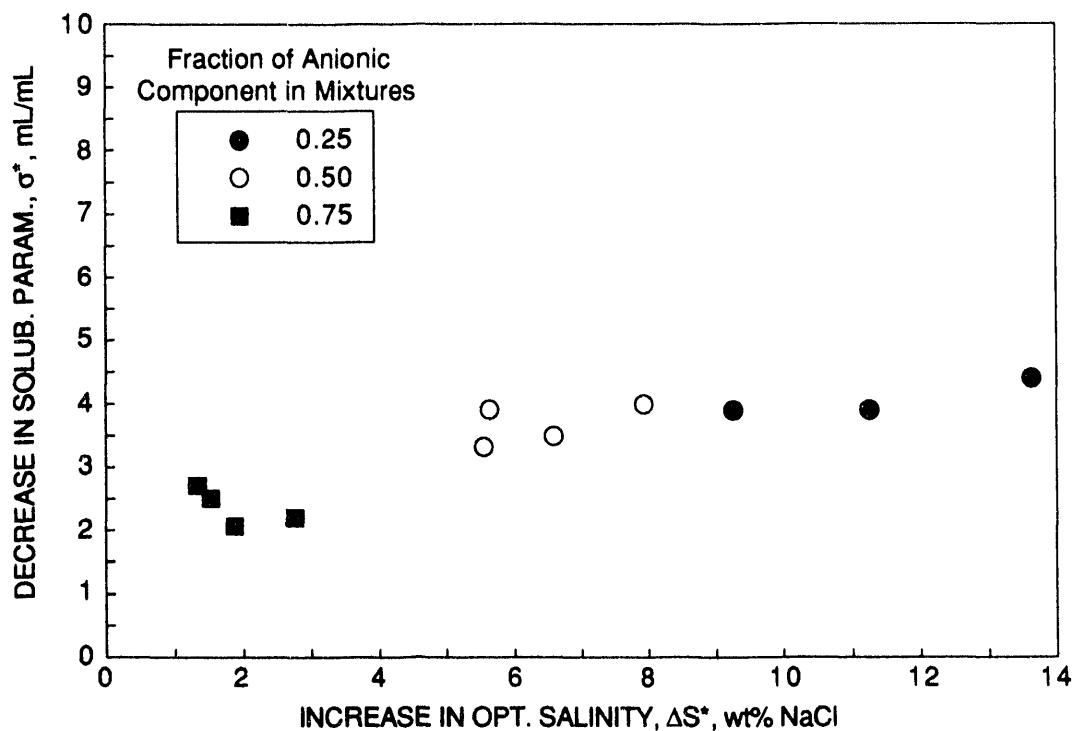
FIGURE 8. - Decrease in solubilization parameter as a function of increase in optimal salinity for TRS 10-410/IBA + N-25-7 system with n-decane at 50° C.
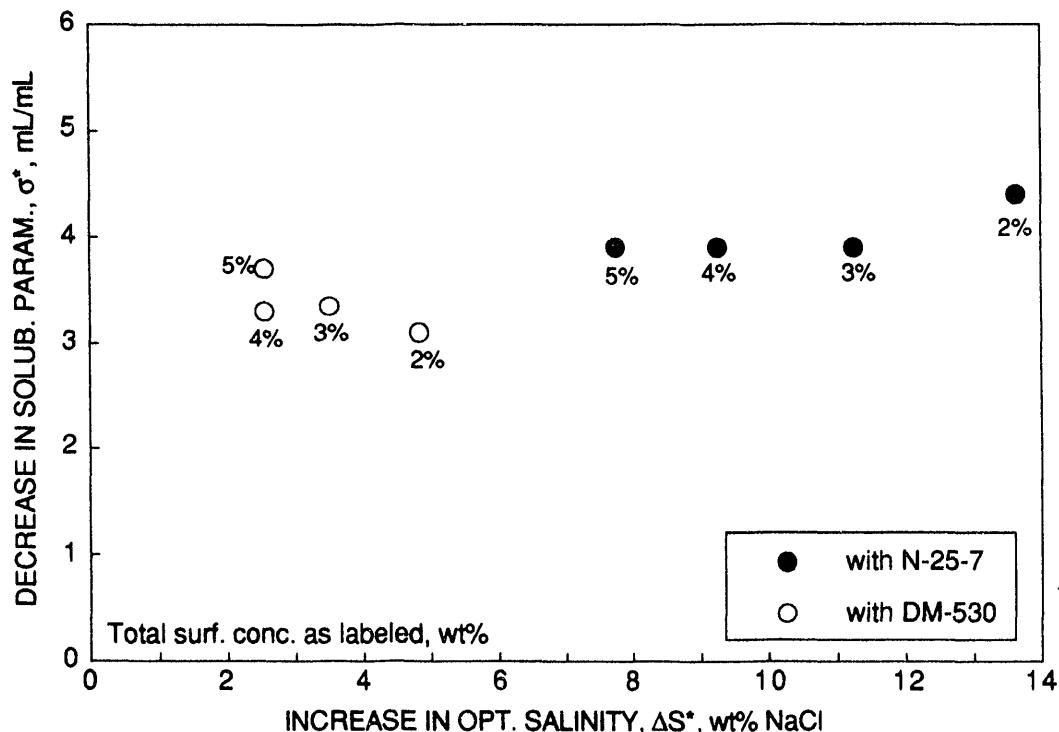
FIGURE 9. - Comparison of decrease in solubilization parameter as a function of increase in optimal salinity for (1) TRS 10-410/IBA + N-25-7 system and (2) TRS 10-410/IBA + DM-530 system with n-decane at 50° C.

Other systems containing nonionic surfactants of intermediate HLB values have also been studied in order to find systems where a favorable balance between salinity tolerance and oil solubilization can be maintained. These studies included a series of surfactants of different HLBs as well as combinations of these surfactants yielding different HLB levels. These tests provided screening information on which nonionics can be used in combination with the chosen base surfactant system.

A relatively fast screening method was needed to evaluate a series of combinations of different nonionic and anionic surfactants. The purpose of these tests was to screen these combinations to determine the range of optimal salinity of the overall chemical system based on the HLB parameter of the nonionic component. Considerable work has been done in the area of phase inversions with nonionic systems. The PIT method was selected as a means of screening these surfactant combinations for the range of applicable salinity levels.

Several nonionic surfactants were tested using the above-mentioned method including a series of Neodol®, Genapol® and Igepal surfactants, with an HLB range of 7.8 to 15.1. A list of the chemical systems studied was previously presented in table 3. These surfactants were tested in combination with a primary anionic surfactant system, TRS 10-410/IBA [1:1] at a fixed proportion of 1:1. These experiments were conducted to evaluate the overall solution behavior as a function of the amount and type of secondary surfactants added. The behavior of the solutions was also observed when only the nonionic surfactants were added. The PIT method proved to be a relatively fast screening method for estimating the relative proximity of optimum conditions for these solutions, at a given set of salinity and temperature. Although this type of screening was generally used on nonionic systems, for this study mixtures of anionic and nonionic as well as the individual nonionic systems were tested.

The results from the PIT studies are presented in figures 10 to 24 and in Appendix B. The results of these tests were compared to the results from conventional salinity scans of selected systems. The results of these comparisons will be discussed in a later section. From these relatively fast PIT screening studies, trends in relative proximity of optimal salinity conditions were studied and the dependence of solution behavior on the chemical structure of nonionic species was investigated. Figure 10 is a summary plot of the

optimum salinity of the different mixtures versus the HLB of the nonionic components at 50°C.

The linear alkyl alcohol ethoxylates, i.e., the Genapol® series, appear to exhibit a very distinct behavior from the dialkyl phenol surfactants such as the Igepal series, at similar HLB levels. The mixtures of dialkyl phenols exhibited a more significant dependence on the HLB value than the linear ethoxylates did. The contrast in the behavior of these two types of surfactants was more pronounced at lower HLB values and decreased at higher HLB values. This distinct behavior was also confirmed in mixtures containing a base primary sulfonate system of TRS 10-410/IBA in combination with these nonionic surfactants at a component ratio of 1:1. The mixtures containing the linear alkyl alcohol ethoxylates had higher optimal salinity ranges compared to the mixtures containing the other surfactant type, at similar HLB levels. The dependence of the optimal salinity on HLB of the mixtures containing the sulfonate and each of the two types of nonionics closely resembled the mixture behavior with the nonionic formulations alone. The trends in

FIGURE 10. - Optimal salinity (PIT-method) vs. HLB of nonionic surfactant component using (1) Genapol; (2) Igepal mixtures with and without TRS 10-410/IBA [1:1] at 50° C with n-decane. The no. labels shown on the graph correspond to the different chemical systems listed in table 3. The single component systems are also indicated; i.e., DM-530, 24-L-45, and others.

20

behavior almost parallel each other; the primary difference was that the mixtures containing the sulfonate system yielded much lower optimal salinity values overall. As an example, at an HLB value of 11.0 with n-decane at 50° C, the optimal salinities for the appropriate Genapol® mixture and the mixture of this nonionic with the primary sulfonate system were about 20 and 7 wt% NaCl, respectively. On the other hand, the optimal salinities for the Igepal mixtures and the mixture containing the sulfonate component were about 17 and 5.5 wt% NaCl at similar test conditions.

Figure 11 shows a plot of the optimum salinity of the different mixtures versus the HLB of the nonionic components at 60° C. At this temperature level, the observed optimal salinity ranges were considerably lower. The increase in temperature effectively shifted the relative affinity of the nonionic surfactant for the oil (increased affinity) and the water (decreased affinity).[15,19] Much lower optimal salinity levels were then necessary to rebalance the overall system. The distinct difference in trend between the two types of nonionic surfactants appears to have decreased with the rise in temperature level. At HLB levels greater than 11, the pattern of behavior of the two types of nonionics is similar, with and without the presence of the anionic surfactant system. The difference in behavior was
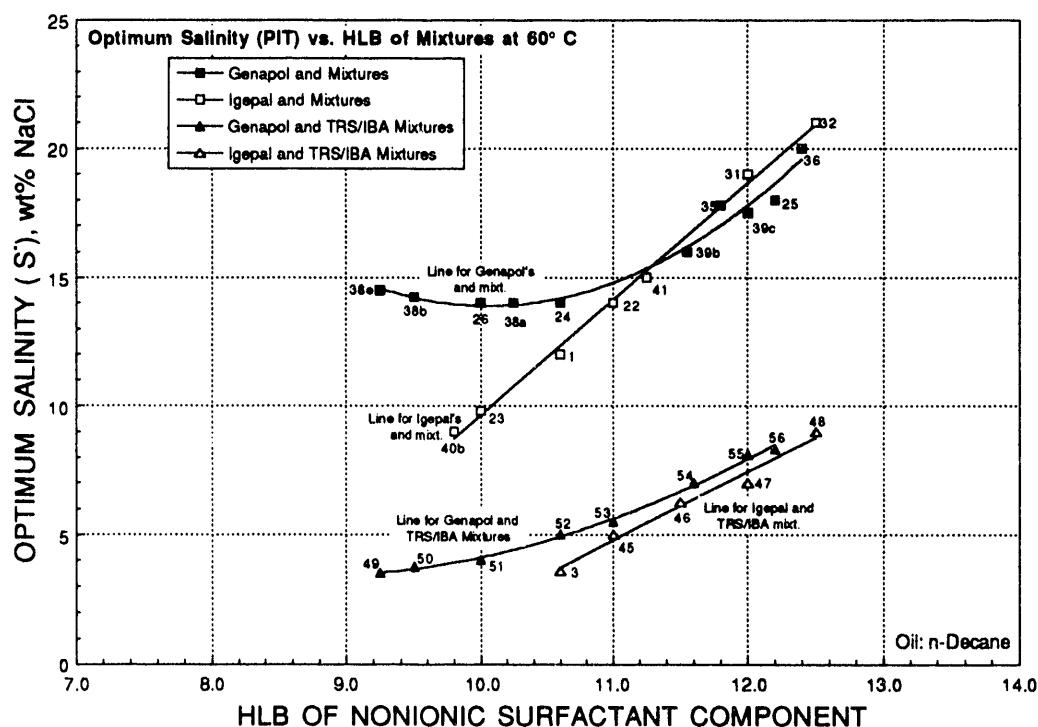

FIGURE 11. - Optimal salinity (PIT-method) vs. HLB of nonionic surfactant component using (1) Genapol; (2) Igepal mixtures with and without TRS 10-410/IBA [1:1] at 60° C with n-decane.

21

still very evident at the lower HLB levels, but to a lesser degree when the anionic surfactant was present. This difference in behavior when the anionic surfactant was present may be attributed to the relative effect of temperature of both the nonionic and anionic components' affinity for the oil and water phases. Nonionic surfactants have a tendency to be more lipophilic at higher temperatures; the opposite has been observed for anionic systems.[15,19] The presence of the anionic surfactant may have helped suppress some of the effects of the temperature on the anionic-nonionic mixed system, resulting in similar observations of behavior for both systems containing Igepal/TRS/IBA and those containing Genapol/TRS/IBA.

Additional PIT studies were conducted on similar chemical systems with different oils. Normal-octane was used in these studies and these results were compared to the results using n-decane. These results are presented in figures 12 and 13. Figure 12 shows a comparison plot of the optimum salinity of the different mixtures versus the HLB of the nonionic components at 50° C with (1) n-decane and (2) n-octane. Again for both cases, the two types of surfactants indicated a difference in dependence of optimal salinity with the HLB of the nonionic components in the system. The comparable results obtained using the
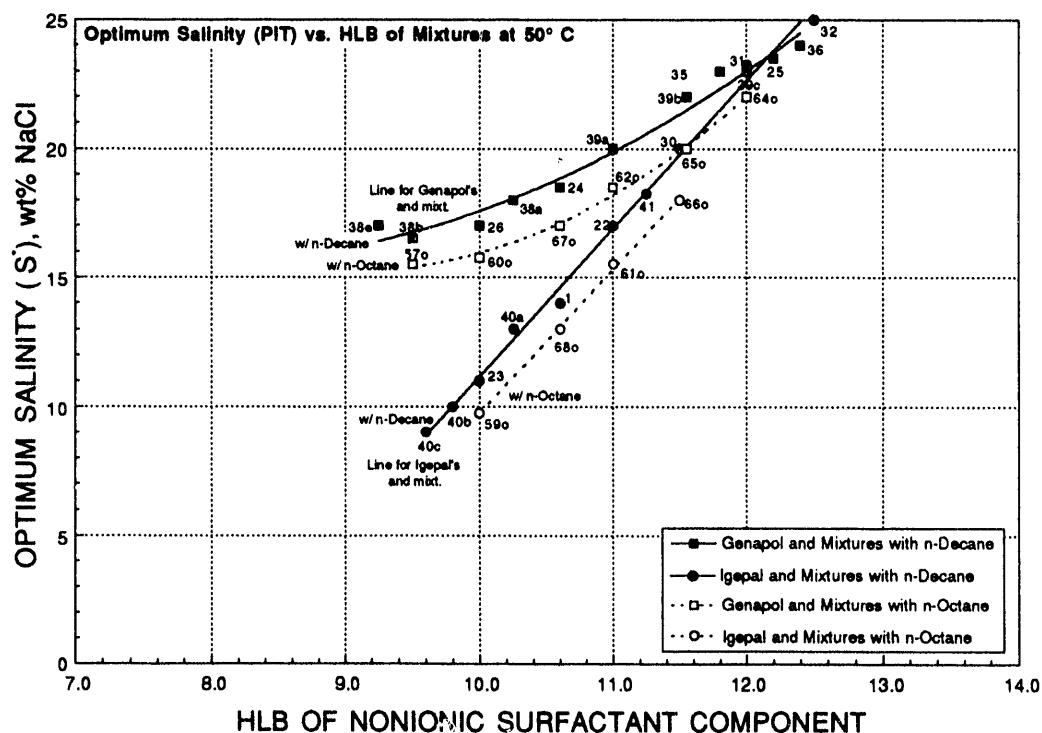

FIGURE 12. - Comparison of optimal salinity (PIT-method) vs. HLB of nonionic
surfactant component using (1) Genapol; (2) Igepal mixtures at 50°
C with n-decane and n-octane.

22

n-octane supports the indicated pattern difference between the two types of nonionics. The surfactant structure appears to have a significant effect on the HLB of the system,[15] and is not just a simple correlation as postulated by Griffin.[20] The results also show that a decrease in the carbon chain length of the oil results in a reduction of the effective salinity range at a specific calculated HLB value. This result is similar to observations made by other researchers.[15]

Figure 13 shows a comparison plot of the optimum salinity of the different mixtures versus the HLB of the nonionic components at 60° C with (1) n-decane and (2) n-octane. Again for both cases, the two types of surfactants indicated a difference in dependence of optimal salinity with the HLB of the nonionic components in the system, up to an HLB level of 11. Greater than 11, the pattern in behavior of the two types of nonionic surfactants was comparable. The results also showed that a decrease in the carbon chain length of the oil resulted in a reduction of the effective salinity range at a specific calculated HLB value. For both cases presented in figures 11 and 13, the difference in behavior dominated by the two types of nonionic surfactants appears to diminish at HLB levels above 11. This may indicate some possible shift in the structure-dependence of the
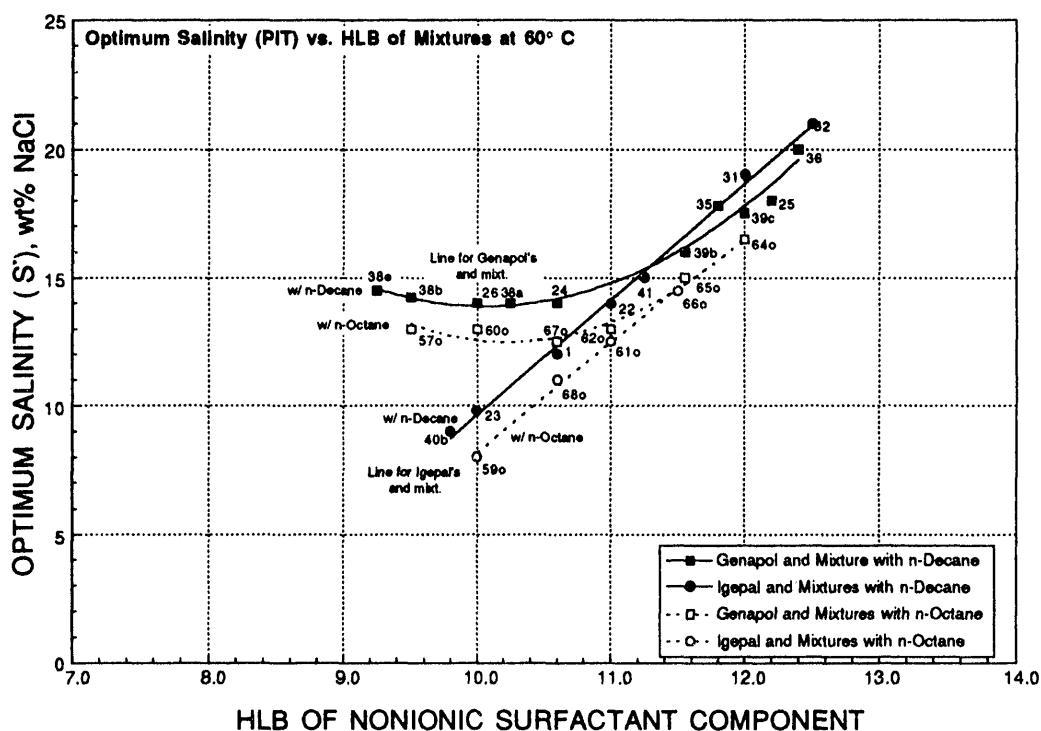

FIGURE 13. - Comparison of optimal salinity (PIT-method) vs. HLB of nonionic surfactant component using (1) Genapol; (2) Igepal mixtures at 60° C with n-decane and n-octane.

required HLB at this level.

Figures 14 to 17 show contour plots of the dependence of the PIT values of these systems with salinity and the HLB of the nonionic surfactant in the system. Figure 14 is the contour plot for the mixtures containing different combinations of Genapol surfactants with n-decane. These results indicate several trends in solution behavior from these types of systems. At a fixed salinity level, the results indicate a trend of higher PIT levels resulting from an increase in the HLB level of the nonionic surfactant. The overall chemical system is more hydrophilic at higher HLB values, such that an increase in temperature is necessary to achieve the required HLB, at fixed salinity levels. On the other hand, lower PIT levels were observed with an increase in salinity of the aqueous phase, at a fixed HLB level. The aqueous phase solubility and the lipophilic tendency of the surfactant are drastically affected by an increase in the salinity (electrolyte concentration) of the overall solution. The increase in salinity renders the chemical system more lipophilic. A reduction in temperature is needed to maintain a new balance between the oil and water affinity of the surfactant system. The results presented in figures 15 to 17 for the three other cases indicate the same trends. These results are similar to those previously reported by other researchers.
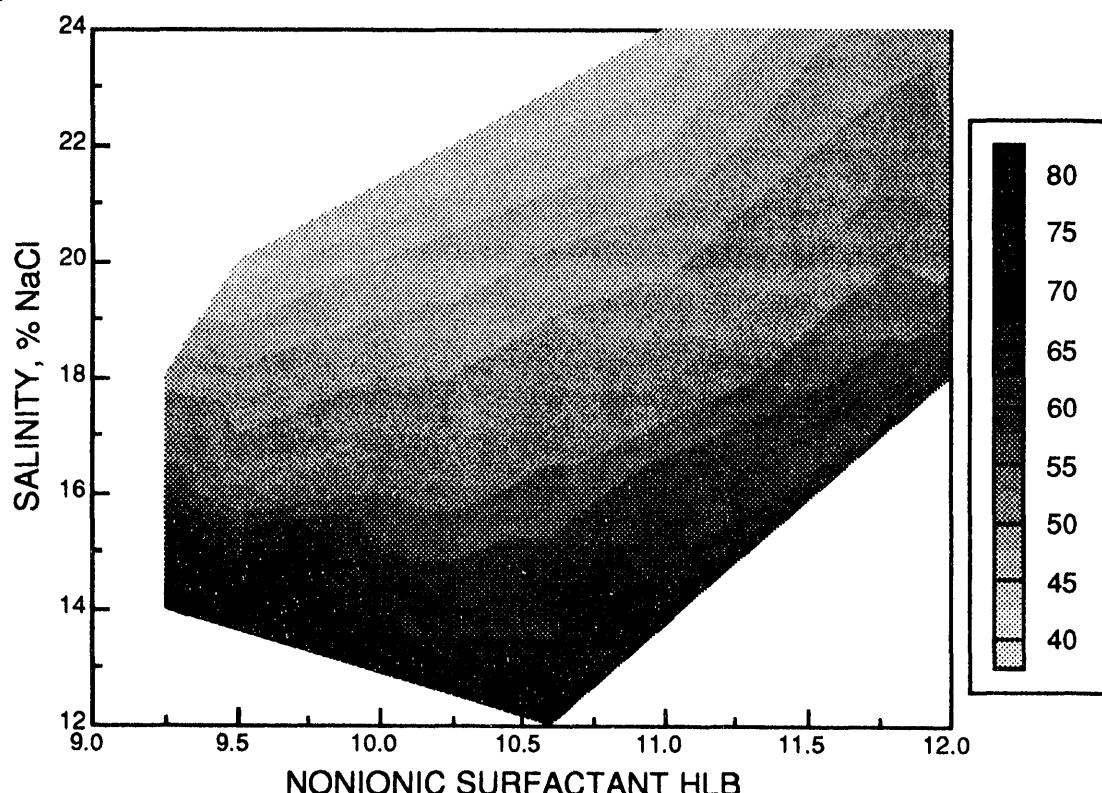

FIGURE 14. - Contour plot of PIT vs. salinity and nonionic surfactant HLB for the Genapol mixtures with n-decane. Legend scale is in °C.
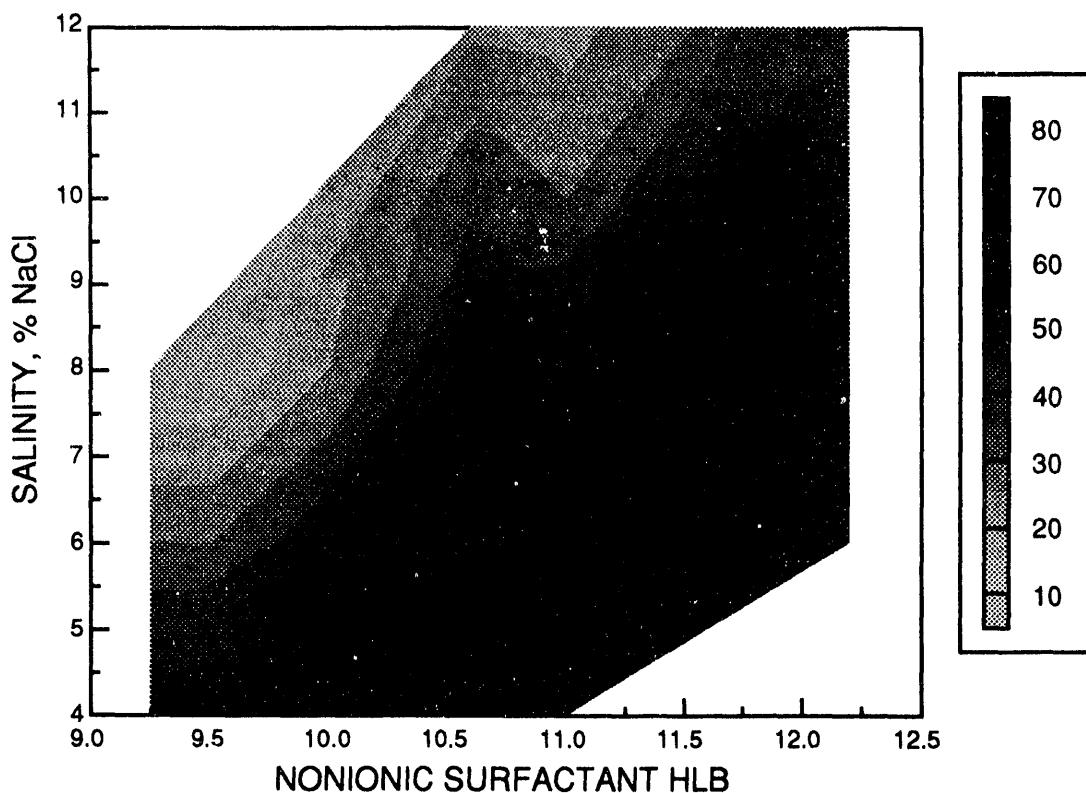
FIGURE 15. - Contour plot of PIT vs. salinity and nonionic surfactant HLB for the Genapol and TRS 10-410/IBA[1:1] mixtures with n-decane. Legend scale is in °C.
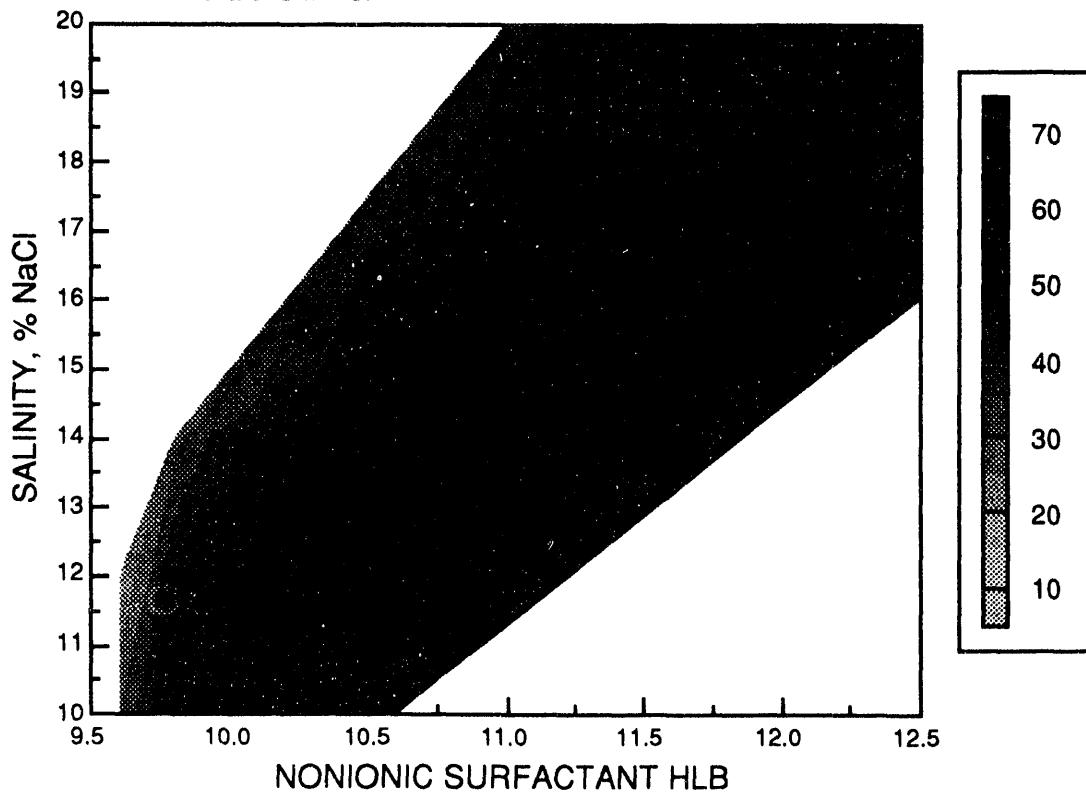

FIGURE 16. - Contour plot of PIT vs. salinity and nonionic surfactant HLB for the Igepal mixtures with n-decane. Legend scale is in °C.
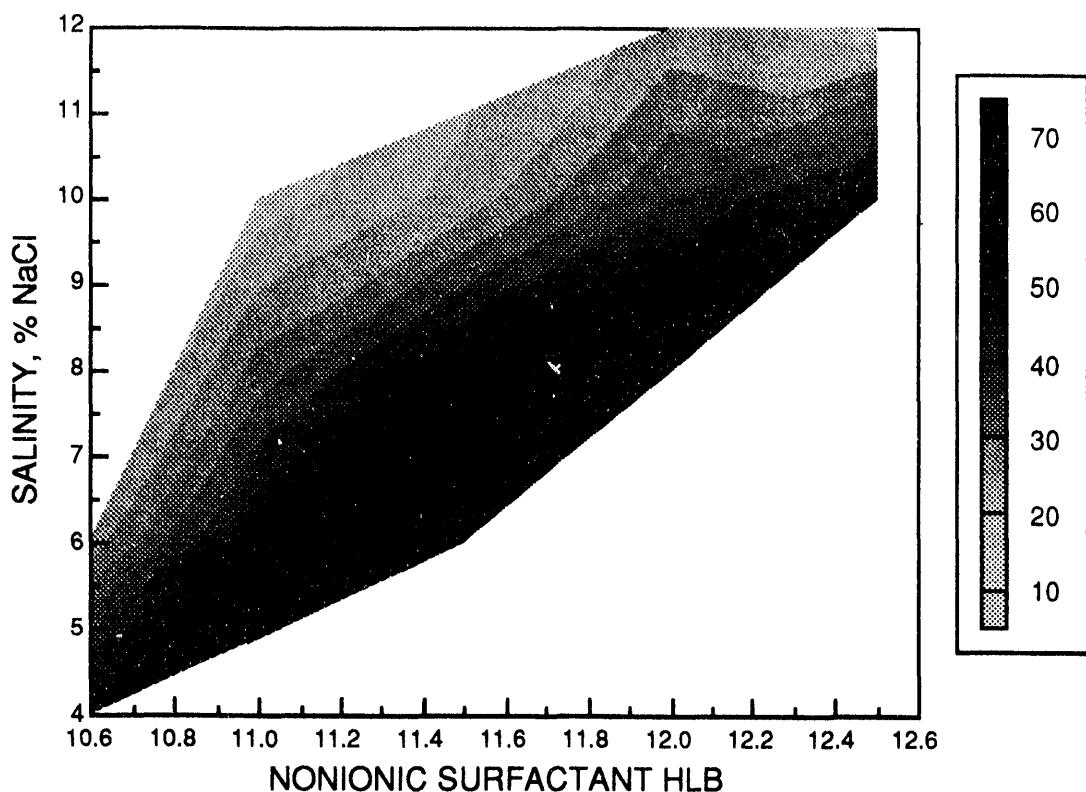
FIGURE 17. - Contour plot of PIT vs. salinity and nonionic surfactant HLB for the
Igepal and TRS 10-410/IBA[1:1] mixtures with n-decane. Legend
scale is in °C.

Figures 18 to 24 show plots of the dependence of the PIT values of these systems
with salinity and the HLB of the nonionic surfactant in the system. These figures provide a
better representation of the trends in PIT levels as a function of the HLB and salinity of the
chemical system. The general trends in the dependence of the PIT levels to salinity and
HLB observed for these systems are similar to the trends indicated in the previous contour
plots. At a fixed salinity level, the results indicate a trend of higher PIT levels resulting
from an increase in the HLB level of the nonionic surfactant. On the other hand, lower PIT
levels were observed with an increase in salinity of the aqueous phase, at a fixed HLB
level. A slight variation of these trends was observed though for the combinations using
Genapol surfactants. Figure 18 shows a plot of the results from this study. These results
also showed comparable results as far as the decrease in PIT levels with an increase in
salinity, at a fixed HLB value. A slight difference was observed on the dependence of the
PIT level with HLB, at a fixed salinity. At lower salinity ranges, 14% to 16% NaCl, the
PIT showed a decrease with an increase in HLB value. This is opposite to the trends noted
for the other systems, even the system containing the Genapol surfactant in the presence of
the anionic surfactant system. At salinity ranges between 18% and 20% NaCl, the PIT

26

levels appear to be insensitive to the HLB of the nonionic component in the system. At higher salinity ranges, greater than 20% NaCl, the results were similar to previous observations where the PIT levels increased with an increase in the HLB value. The above-mentioned transition in the PIT dependence on HLB and salinity for the Genapol series may have contributed to an alteration of solution behavior as presented in figures 11 and 13. As previously shown in these figures, the difference in the dominant solution behavior of the chemical systems containing these two types of nonionic surfactants appears to diminish at HLB levels greater that 11.
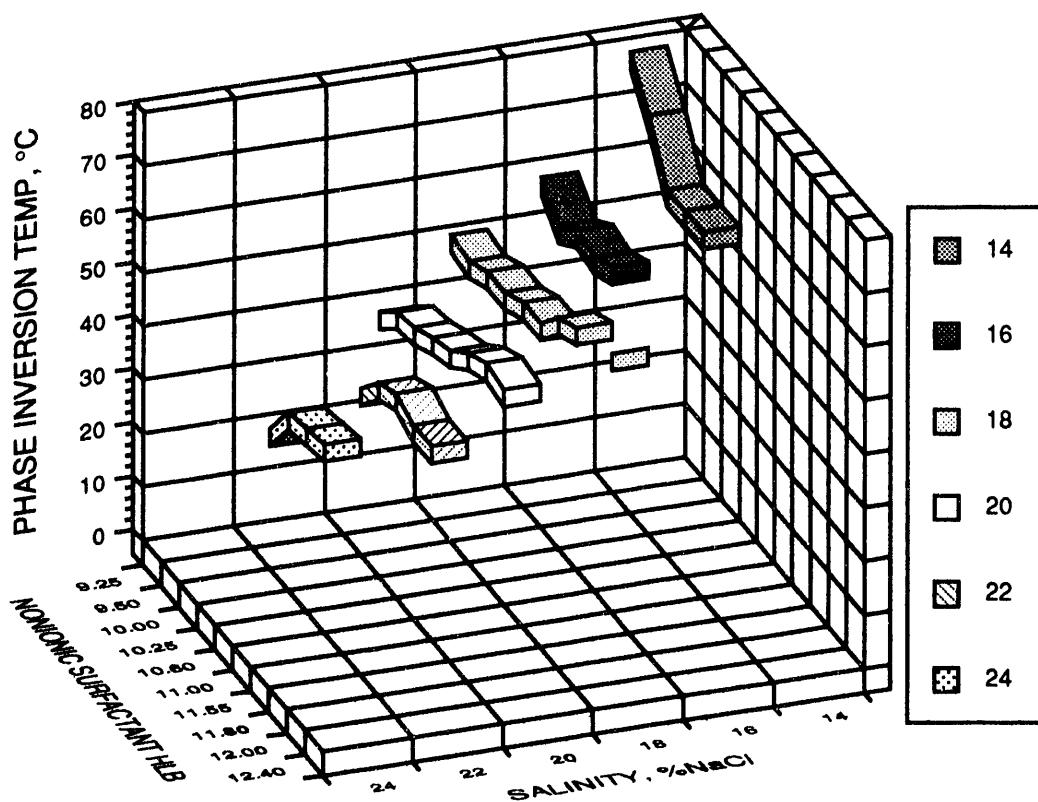

FIGURE 18. - 3-D Ribbon plot of PIT vs. salinity and nonionic surfactant HLB for the Genapol mixtures with n-decane. Legend scale is in wt% NaCl.
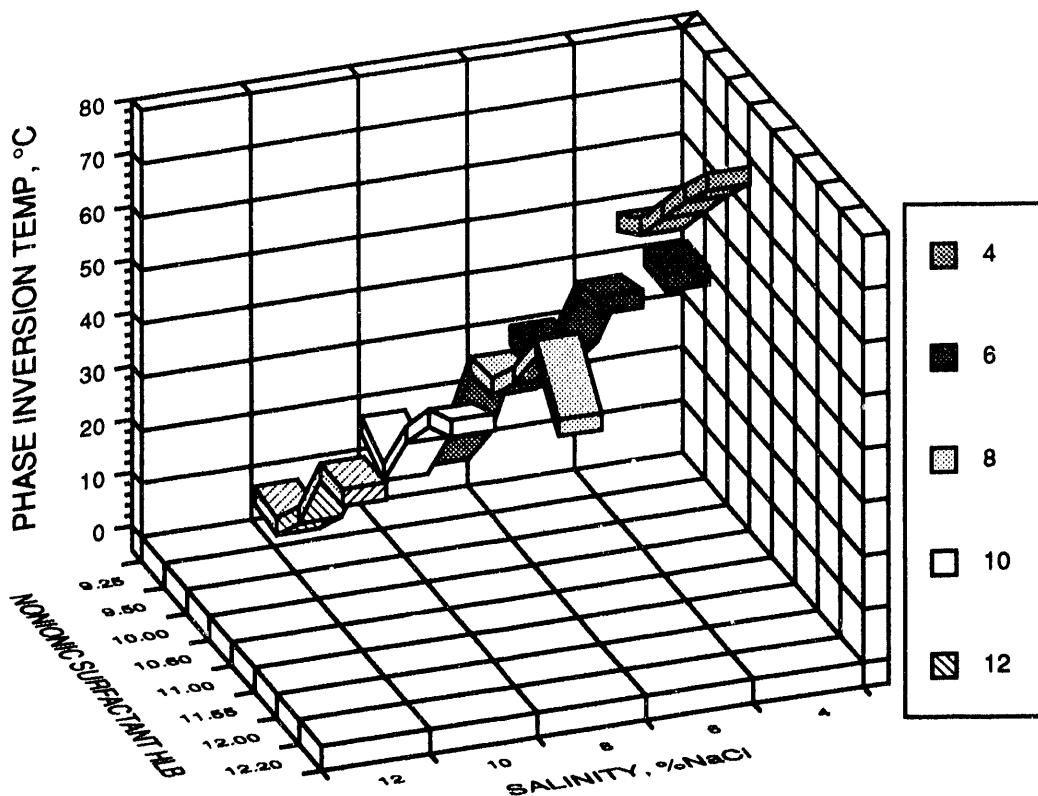
FIGURE 19. - 3-D Ribbon plot of PIT vs. salinity and nonionic surfactant HLB for the Genapol and TRS 10-410/IBA[1:1] mixtures with n-decane. Legend scale is in wt% NaCl.
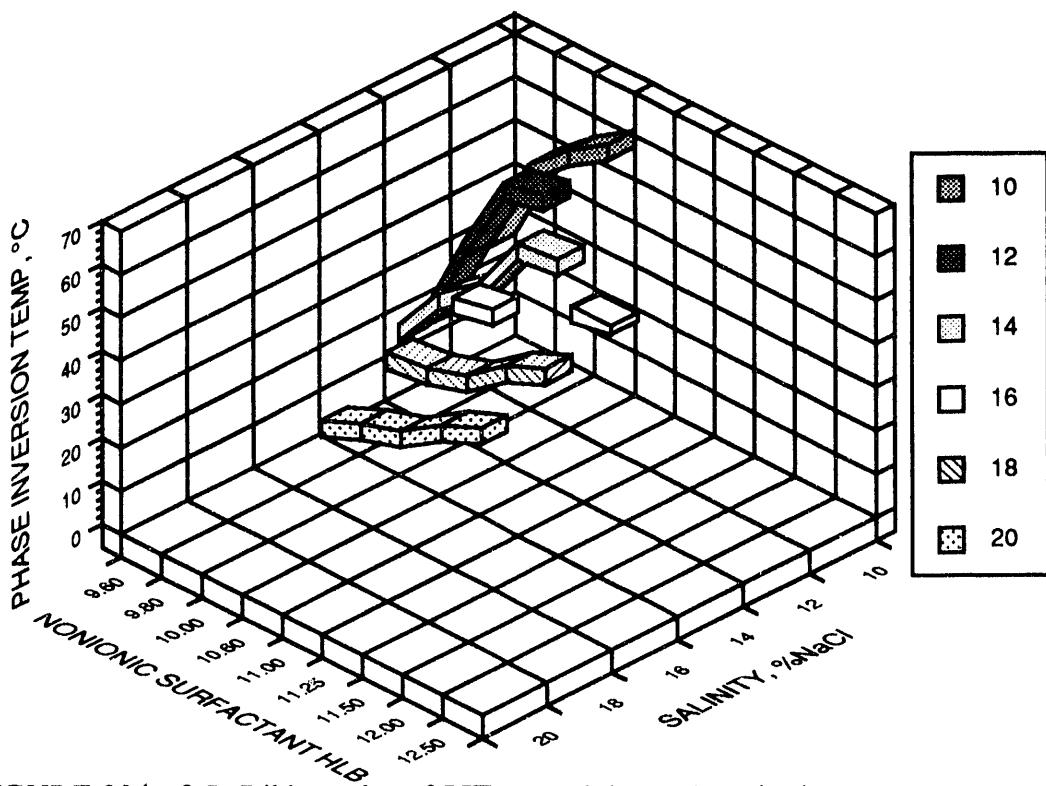

FIGURE 20.'- 3-D Ribbon plot of PIT vs. salinity and nonionic surfactant HLB for the Igepal mixtures with n-decane. Legend scale is in wt% NaCl.
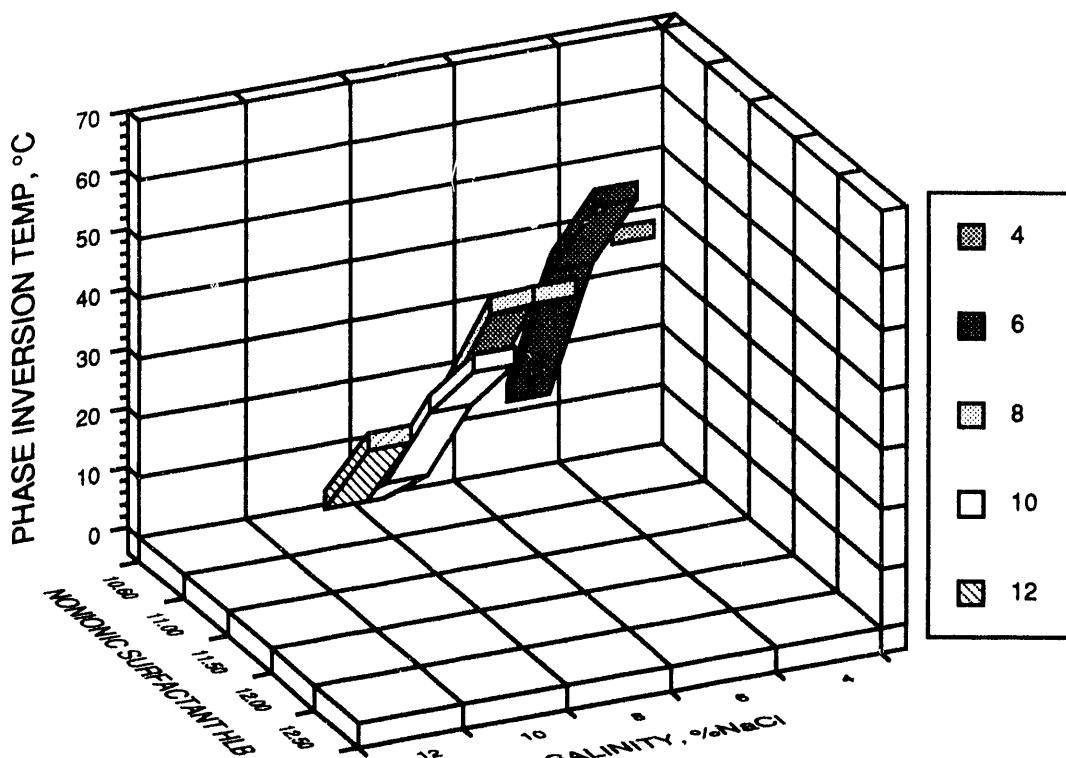
FIGURE 21. - 3-D Ribbon plot of PIT vs. salinity and nonionic surfactant HLB for the Igepal and TRS 10-410/IBA[1:1] mixtures with n-decane. Legend scale is in wt% NaCl.
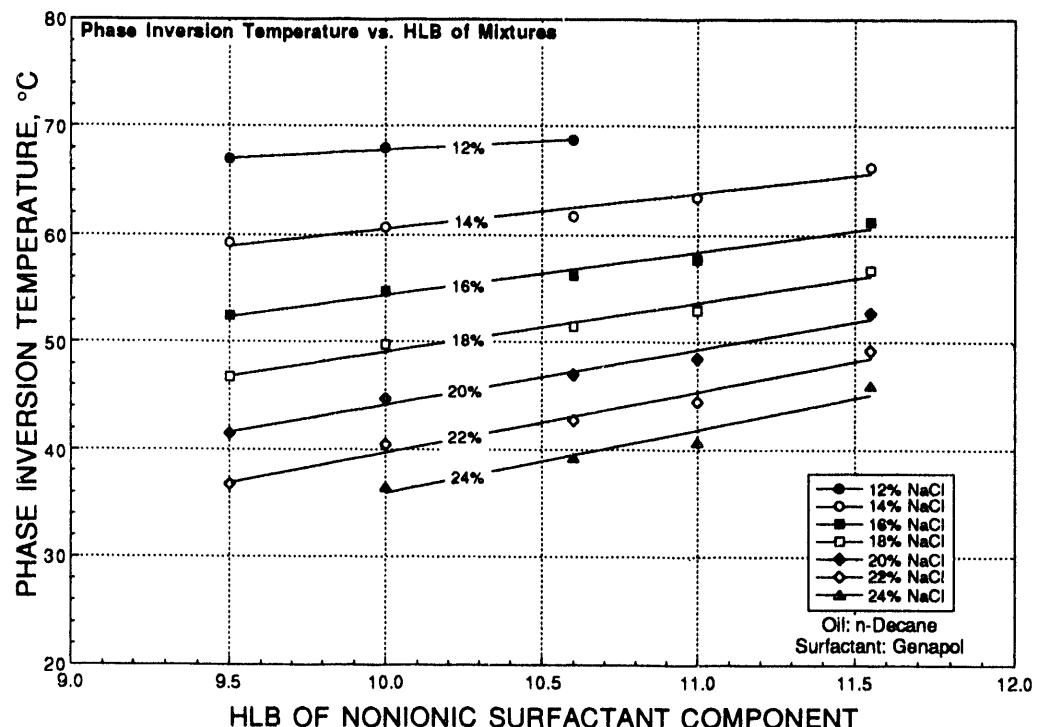

FIGURE 22. - Plot of PIT vs. nonionic surfactant HLB at different salinities for Genapol mixtures with n-decane.

29
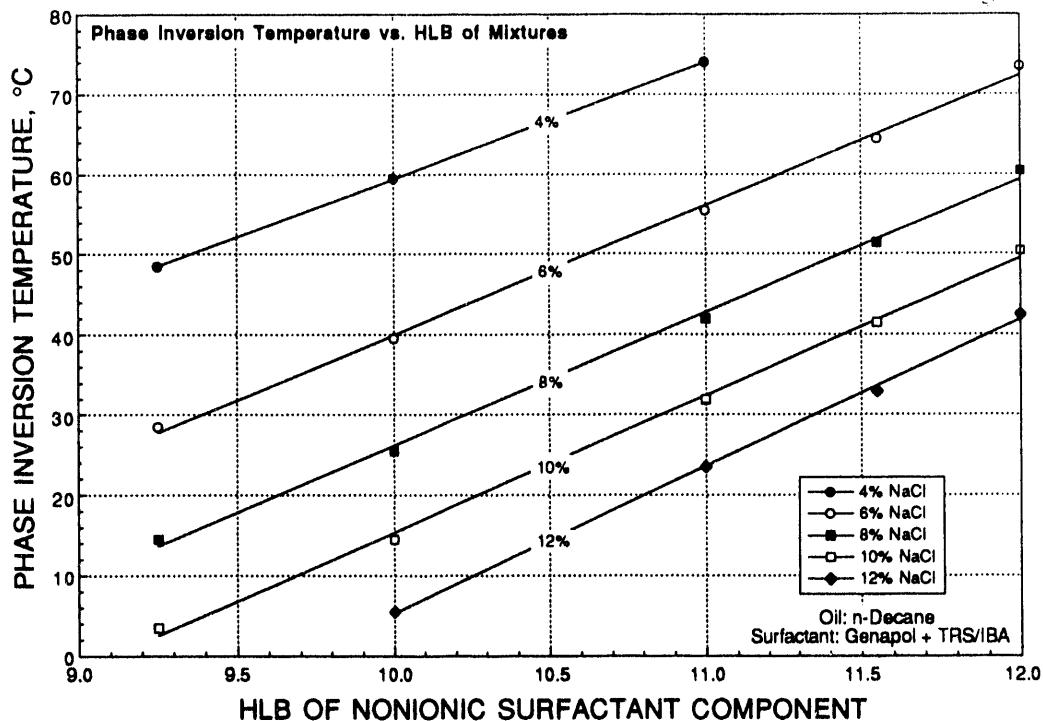
FIGURE 23. - Plot of PIT vs. nonionic surfactant HLB at different salinities for Genapol and TRS 10-410/IBA mixtures. (Oil: n-decane)
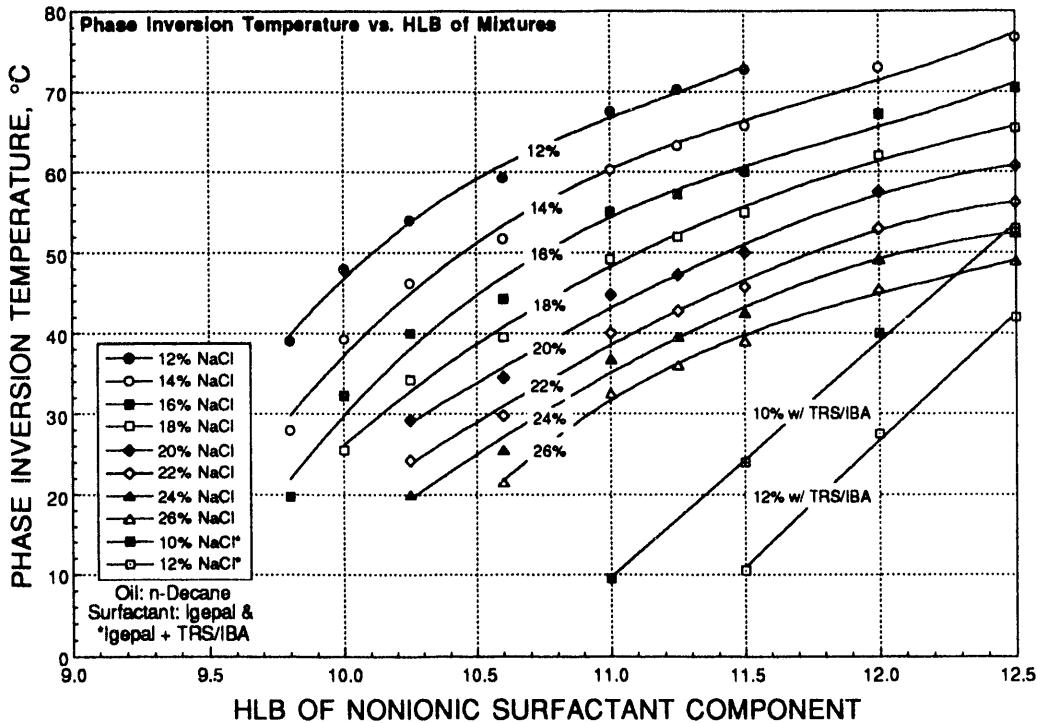

FIGURE 24. - Plot of PIT vs. nonionic surfactant HLB at different salinities for Igepal mixtures with and without TRS 10-410/IBA. (Oil: n-decane)

30

Salager and co-workers originally proposed general correlations to determine the optimum formulations of both anionic and nonionic surfactants. For anionic surfactant, i.e. alkyl aryl sulfonates, ester sulfates and carboxylates, it was suggested that the following correlation was applicable at optimum conditions[21]:

$$\text{Ln (S) - K*(EACN) - } f(A) + \sigma - a_T^*(T-25) = 0 \dots\dots\dots\dots\dots (1)$$

where S is the salinity of the aqueous phase in wt% NaCl; EACN is the Equivalent Alkane Carbon Number, which corresponds to the number of carbon atoms of the oil molecule; $f(A)$ is a parameter function of both the type and concentration of alcohol added to the mixture; σ is a parameter descriptive of the type of the surfactant; a_T is the temperature coefficient; and K is an adjustable parameter dependent on the hydrophilic part of the surfactant group and the type of electrolyte used.

The correlation for ethoxylated nonionic surfactants at optimum conditions was suggested to be of the form[19]:

$$\text{a - EON - k*(EACN) + } m_i^*C_{ai} + b^*S + C_T^*(T-28) = 0 \dots\dots\dots\dots (2)$$

where a is parameter dependent on the lipophilic tendency of the surfactant; EON is the average number of ethylene oxide in the surfactant molecule; k is a parameter constant; m_i is the coefficient dependent on the type of alcohol added; C_{ai} is the concentration of the alcohol; b is a coefficient based on the type of electrolyte in solution and C_T is the temperature coefficient.

For the types of nonionic surfactants used in this study, ethoxylated nonionics, the HLB is related to the EON parameter in equation (2) by the original expression proposed by Griffin[20]:

$$\text{HLB} = \frac{\text{wt\% EO}}{5} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

Equation (2) should be the correlation that aptly describes the behavior of the systems containing combinations of the nonionic surfactants used in this study. For mixtures of both anionic-nonionic systems some combination of the two equations should be descriptive of the behavior of these systems at optimum conditions. A more tractable approach would be based solely on the logarithmic form of the correlation, similar to

equation (1). As is shown in figures 10 to 13, the data presented did not seem to correspond well to a linear relationship of S^* similar to equation (2). An alternative form of equation (1) was used to represent the data presented in figures 10 to 13. Figures 25 through 28 show plots of the log of optimum salinity, ln (S^*), versus the HLB of the nonionic surfactant components of the systems tested with n-decane at 50° and 60° C. Figure 29 shows a similar plot of the systems tested with n-octane. These results show that the ln(S^*) appears to be a better parameter for correlation than the (S^*) form orginally suggested in equation (2). This was true for nonionic mixtures as well as anionic-nonionic mixtures.
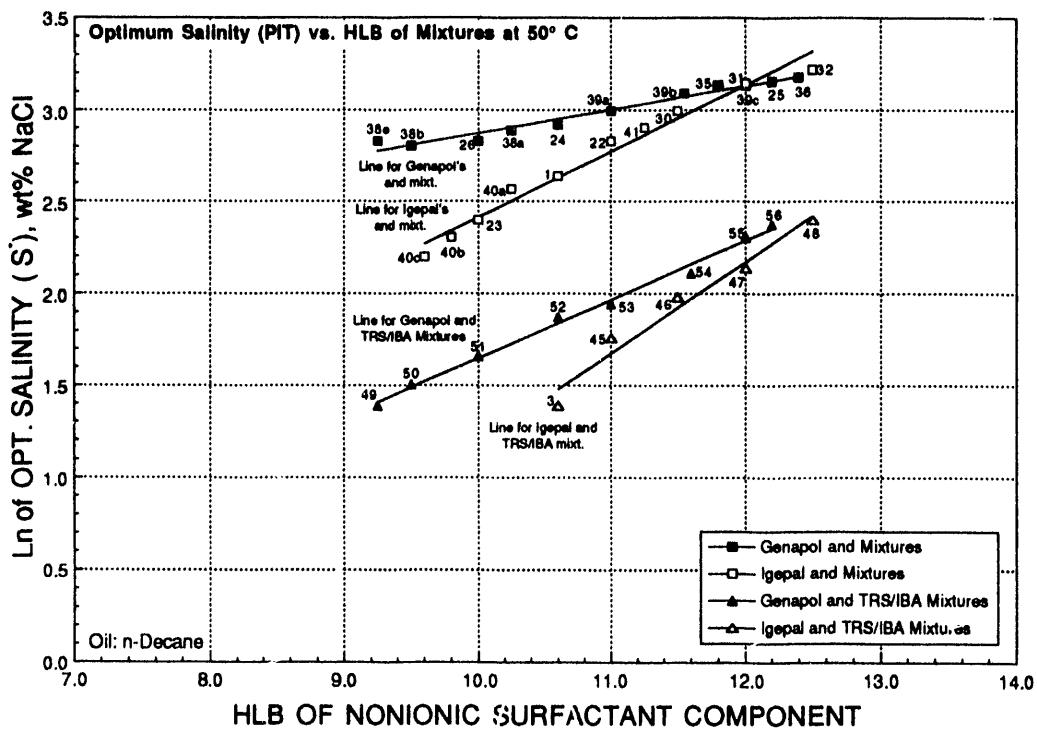

FIGURE 25. - Ln of optimal salinity vs. HLB of nonionic surfactant component using (1) Genapol; (2) Igepal mixtures with and without TRS 10-410/IBA [1:1] at 50° C with n-decane.
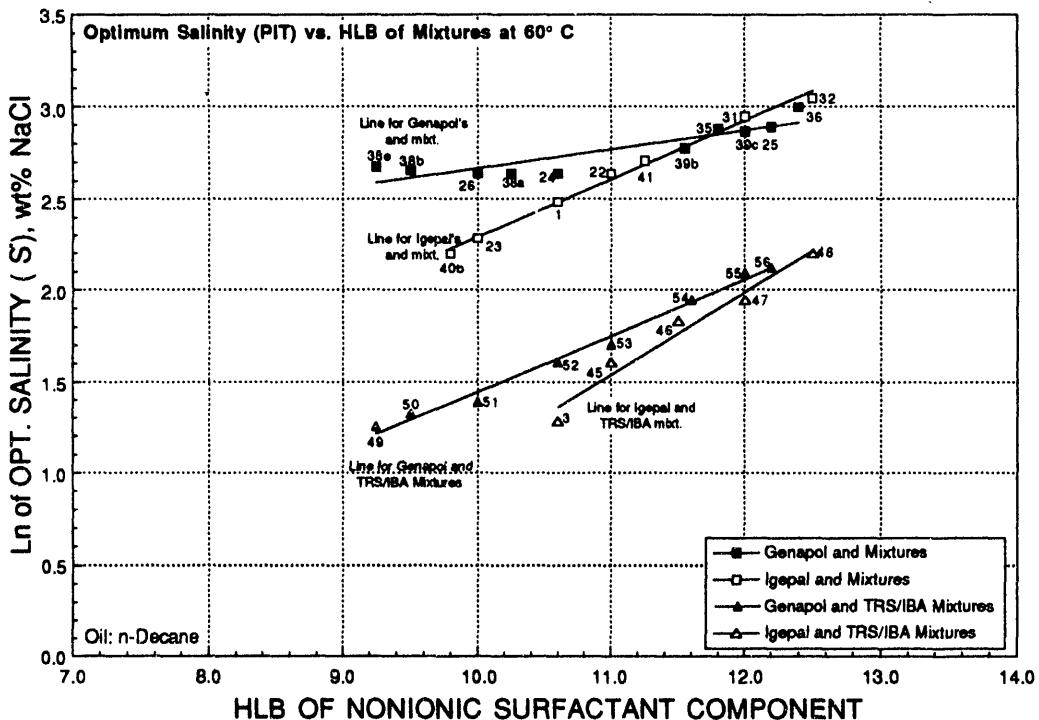
FIGURE 26. - Ln of optimal salinity vs. HLB of nonionic surfactant component using (1) Genapol; (2) Igepal mixtures with and without TRS 10-410/IBA [1:1] at 60° C with n-decane.
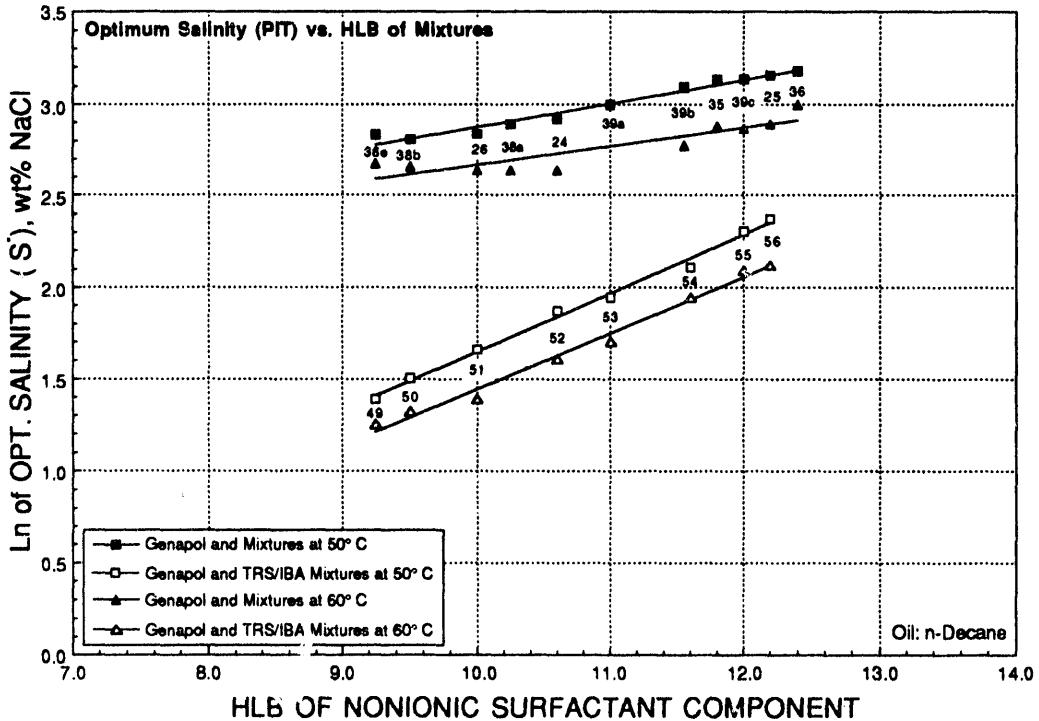

FIGURE 27. - Comparison of Ln of optimal salinity vs. HLB of nonionic surfactant component using Genapol mixtures with and without TRS 10-410/IBA [1:1] at 50° and 60° C with n-decane.
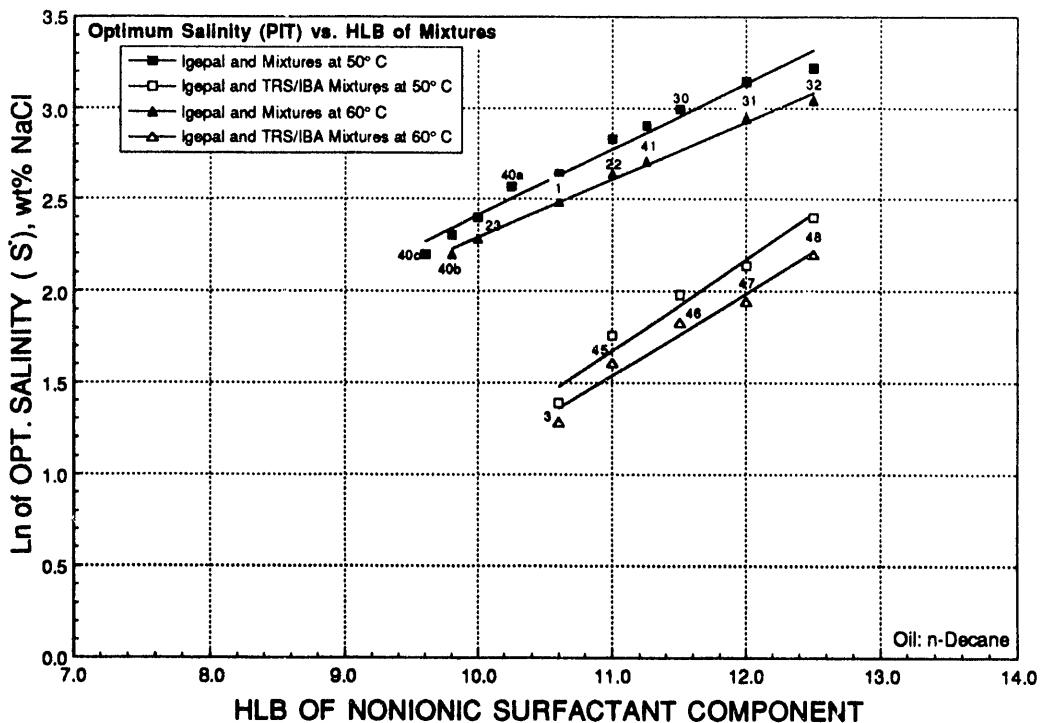
FIGURE 28. - Comparison of Ln of optimal salinity vs. HLB of nonionic surfactant component using Igepal mixtures with and without TRS 10-410/IBA [1:1] at 50° and 60° C with n-decane.
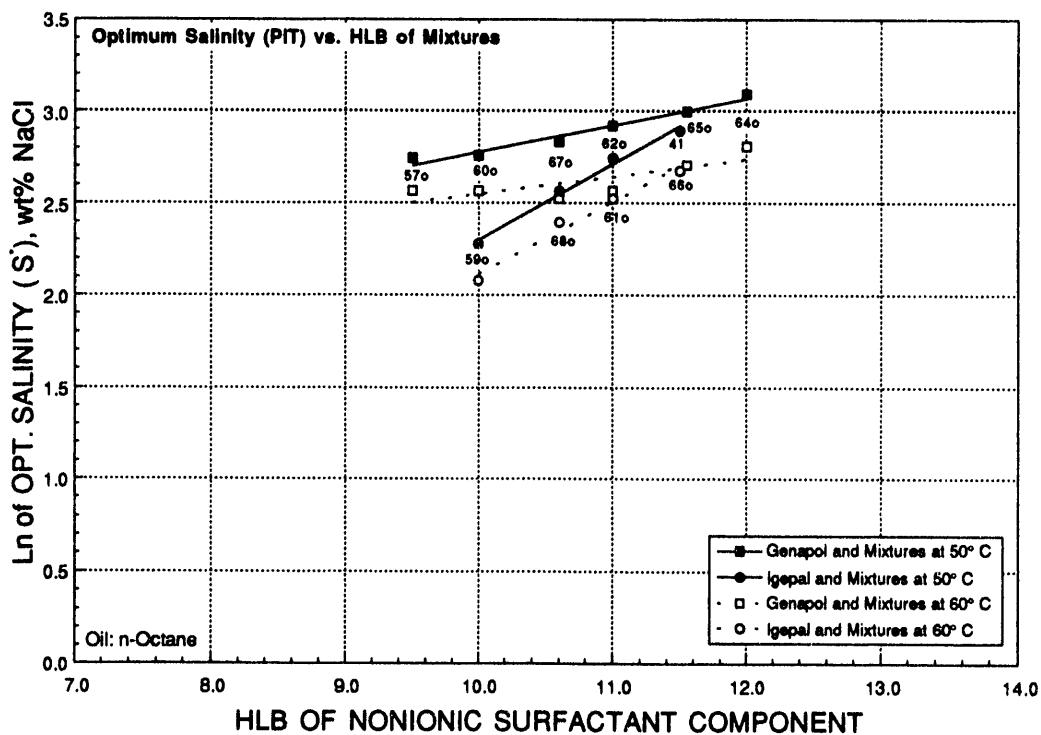

FIGURE 29. - Comparison of Ln of optimal salinity vs. HLB of nonionic surfactant component using (1) Genapol and (2) Igepal mixtures at 50° and 60° C with n-octane.

Figures 30 and 31 show plots of the ln(S*) versus temperature for the different HLB levels tested. Relatively linear relationships can be established between the ln(S*) of these mixtures with temperature. These lines have relatively similar slopes over a wide range of HLB values. These results lend further support to the prior observations that the logarithmic form of the correlation, similar to equation (1), more closely represents the data for the mixtures of nonionic-nonionic and anionic-nonionic surfactants obtained from the PIT screening studies.

Figure 32 shows a plot of the fractional increase in optimum salinity due to the addition of the nonionic surfactant. For this plot, the fractional increase in salinity was defined as:

$$\frac{\text{Fractional}}{\text{Increase}} = \left[\frac{\ln(S^*)_{\text{anionic+nonionic}} - \ln(S^*)_{\text{anionic}}}{\ln(S^*)_{\text{nonionic}} - \ln(S^*)_{\text{anionic}}} \right]_{\text{at T, }^{\circ}\text{C}} \quad \dots\dots (4)$$
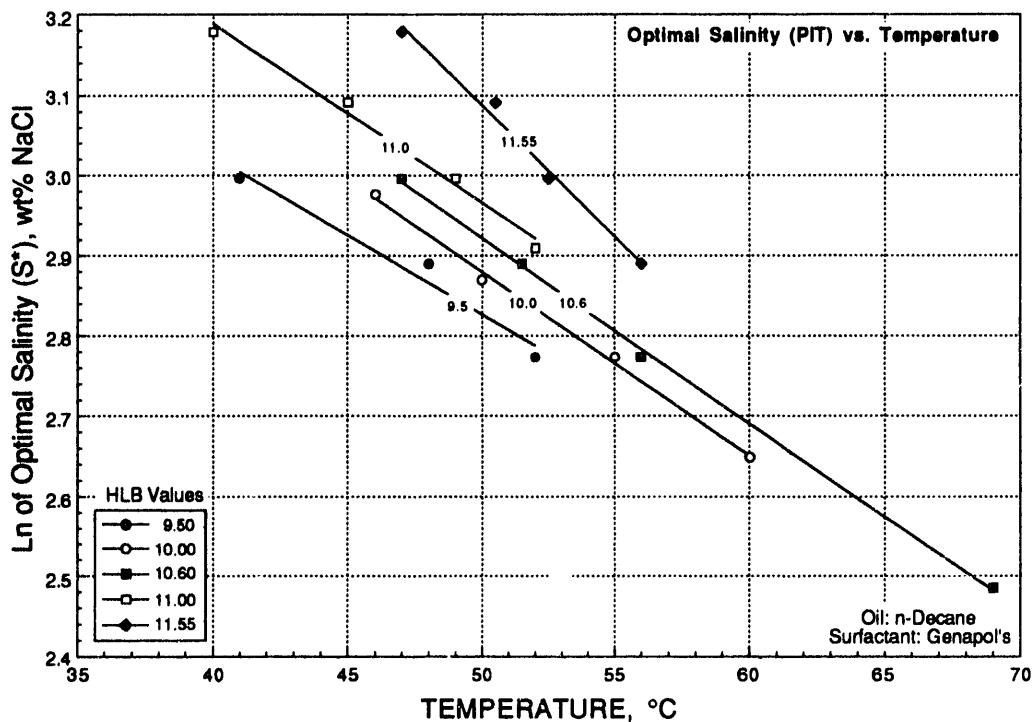

FIGURE 30. - Ln of optimal salinity vs. temperature using Genapol mixtures at different HLB values with n-decane.

Optimal Salinity (PIT) vs. Temperature

HLB Values
- 12.50
- 12.00
- 11.50
- 11.25
- 11.00
- 10.60
- 10.25
- 10.00
- 9.80

Oil: n-Decane
Surfactant: Igepal's
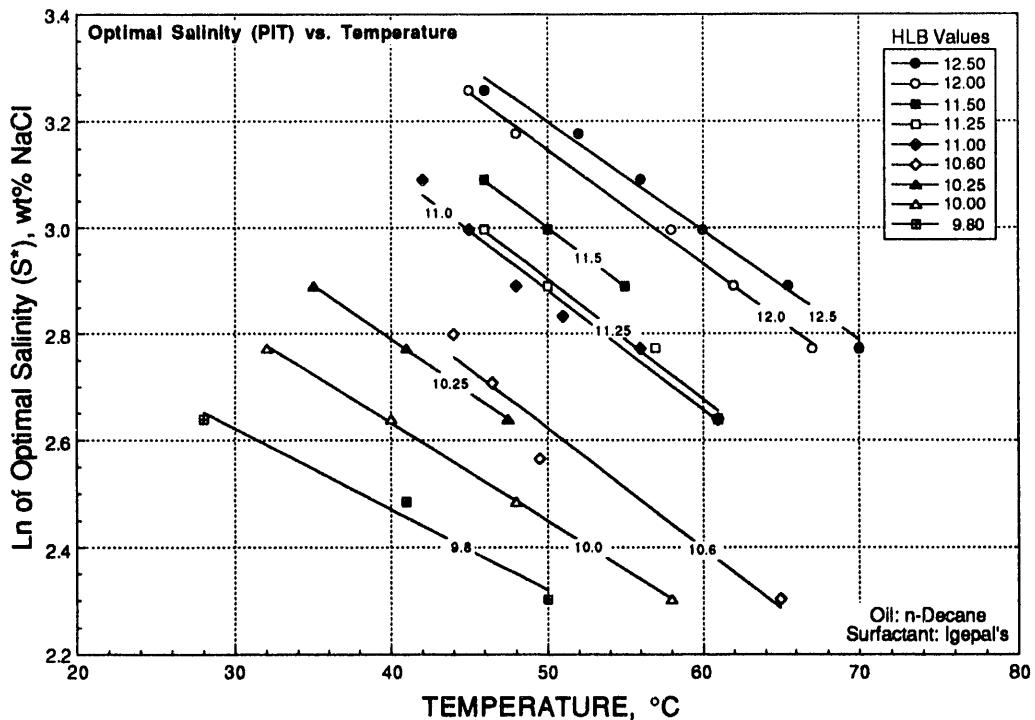
FIGURE 31. - Ln of optimal salinity vs. temperature using Igepal mixtures at different HLB values with n-decane.

These curves were generated using the ln(S*) vs. HLB linear equations derived from figures 25 through 29. The effect of the addition of the nonionic component to the primary surfactant component can be observed in this figure. Adding the nonionic surfactants to the primary TRS/IBA system (at 1:1 proportion) showed a corresponding increase in optimal salinity of the overall mixtures. At HLB $\approx 10 \pm 0.5$, the ln(S*) of the mixtures of anionic-nonionic systems was about 50% of the total difference between the ln(S*) of the purely nonionic system and the base case anionic system. The ln(S*)'s of these mixtures were less than 50% at HLB's < 10 and greater than 50% at higher HLB values. The effect of temperature on the difference in the fractional increase in optimal salinity, ln(S*), also appears to decrease with the HLB of the nonionic component. Figure 33 shows a plot of the results of the difference between the 50° and 60° isotherms. The effect of temperature on both systems appear to be relatively limited, ± 0.04, within the range of 50° to 60° C. Also evident in both cases, the effect of temperature on the difference in the fractional increase in optimal salinity appear to diminish with increasing HLB.
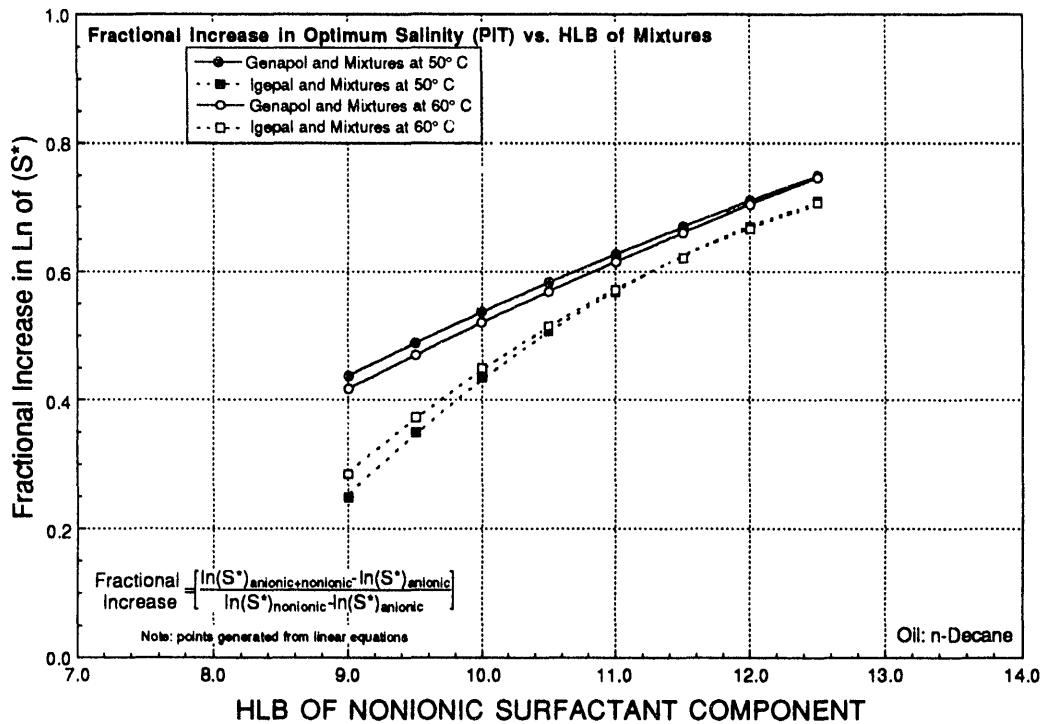
FIGURE 32. - Fractional increase in Ln of optimal salinity vs. HLB of nonionic component using (1) Genapol; (2) Igepal mixtures with and without TRS/IBA [1:1] at 50° and 60° C with n-decane.
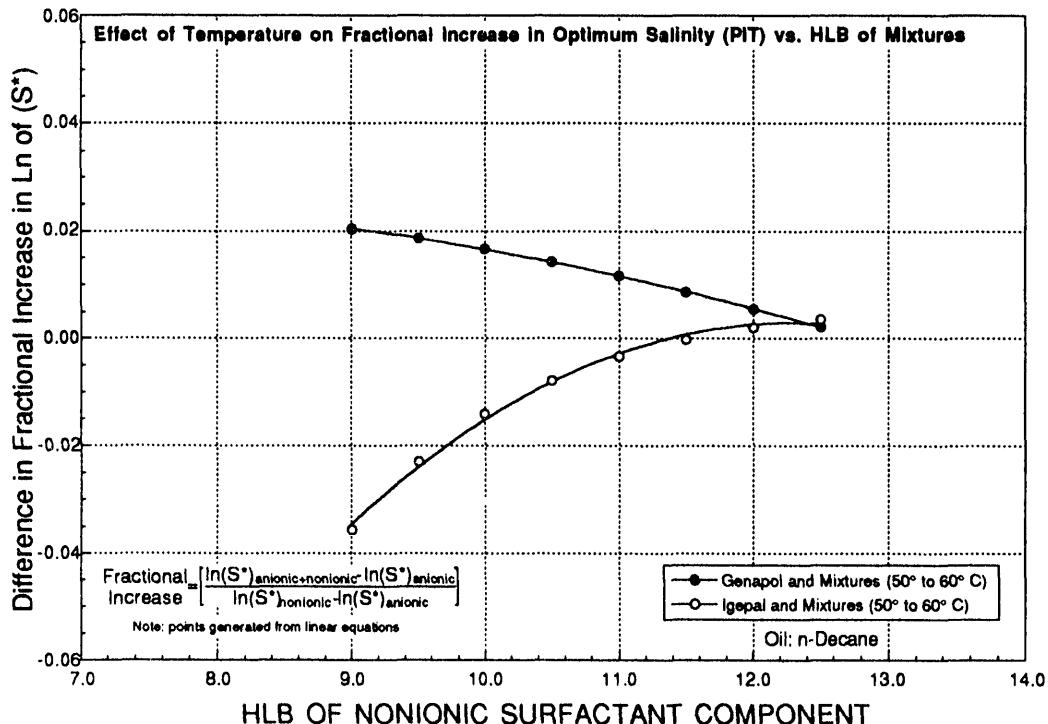

FIGURE 33. - Effect of temperature on the difference in fractional increase in Ln of optimal salinity vs. HLB of nonionic component using (1) Genapol; (2) Igepal mixtures with and without TRS/IBA [1:1] with n-decane.

Comparison of Methods of Nonionic and Anionic-Nonionic Surfactant Systems Screening

The PIT method has been shown to be a relatively fast screening method for determining approximate optimal conditions for candidate surfactant systems. Although the method was primarily used by Shinoda and others in screening nonionic surfactants,[13,14] it was also useful in identifying possible combinations of anionic-nonionic mixtures. The relative speed and ease by which the chemical systems were screened made it possible to evaluate a large number of combinations of several series of surfactants. Compared to the conventional way of screening using salinity scans, the PIT method allowed several surfactant systems to be screened in relatively short order. One drawback of the PIT method is the inability to quantify the solubilization capacity of each of the chemical formulations. One still would need the more time-consuming method of conducting a salinity scan to determine solubilization parameters. Using the two methods in sequence allowed the researcher a much better approach in optimizing chemical screening time and effort. To this effect, the optimal salinity regions mapped using the PIT method were used as reference points in narrowing down the scale needed to conduct a sufficient salinity scan. In an effort to validate the reliability of the optimal salinity regions mapped using the PIT method, comparisons were made of similar salinity regions identified using the conventional salinity scan on selected chemical systems. The results of these comparisons showed fairly good agreement between the salinity regions determined using both methods. These results support the possibility of utilizing the PIT method for initially identifying the salinity regions of interest, followed by additional studies including salinity scans and IFT measurements to determine oil-recovery potential.

Several examples are cited in the comparison of these two methods. Table 4 shows a listing for some of the comparisons that were made. The systems presented in this table have been described in table 3. In most of the selected systems tested, the difference between the optimal salinity regions determined by the two methods was within relatively narrow tolerance of ± 1.5 wt% NaCl. As an example, the optimum salinity measured from the phase behavior measurements was compared to the PIT measurement for the system containing 1 wt% N-25-7 and 1 wt% TRS 10-410/IBA (System 4), at a reference temperature of 50° C. The optimum salinity was experimentally determined to be about 9.25% NaCl using the conventional phase behavior measurements, compared to about 9 to 10% NaCl identified using the PIT experiment. Another example is the system containing 1 wt% DM-530 and 1 wt% of the primary surfactant (System 3) with n-decane. The optimum salinity was determined to be about 3.0% NaCl by salinity scan compared to 3.5

TABLE 4 - Comparison of surfactant screening methods

System	HLB	S^* by PIT	S^* by P.B.	Δ wt%	% diff	σ^* by P.B.
Genapol and Mixtures						
38b	9.5	16.50	17.60	1.10	6.25	3.0
26	10.0	17.00	18.20	1.20	6.59	1.9
39a	11.0	20.00	21.30	1.30	6.10	2.5
39c	12.0	23.00	22.80	-0.20	-0.88	2.2
40c	9.6	9.00	9.60	0.60	6.25	2.0
Igepal and Mixtures						
23	10.0	11.00	11.40	0.40	3.51	2.0
22	11.0	18.00	18.50	0.50	2.70	1.7
31	12.0	23.00	24.40	1.40	5.74	2.7
Genapol and TRS/IBA Mixtures						
50	9.5	4.50	5.28	0.78	14.77	1.7
51	10.0	5.25	6.10	0.85	13.93	2.3
53	11.0	7.00	7.80	0.80	10.26	2.6
55	12.0	10.00	11.27	1.27	11.27	2.7
Igepal and TRS/IBA Mixtures						
45	11.0	5.80	6.65	0.85	12.78	3.2
46	11.5	7.25	8.50	1.25	14.71	2.3
47	12.0	8.50	10.30	1.80	17.48	2.5

P.B. - by phase behavior measurement

to 4% NaCl using the PIT experiment. The estimate of the optimum salinity ranges using the PIT method also shows good agreement with extrapolated values of the optimum salinity for the individual nonionic surfactants with n-decane.

Anionic Surfactant Component Substitution

Limited phase behavior measurements have been performed using a series of AVANEL ethoxylated sulfonates in combination with the TRS 10-410 and IBA system. These surfactants have similar hydrocarbon chain length (C_{12}-C_{15}) and increasing degree of ethoxylation (3,7,9,15), as listed in table 2. The results of the preliminary study using this surfactant series combinations are presented in figure 34. For this study, salinity scans were conducted to determine the effect of the additive surfactants on the phase behavior of the overall system. This figure shows a qualitative representation of the estimated shift in the type-III phase behavior of the TRS 10-410/IBA system with and without the addition of the ethoxylated surfactants. The results showed a fairly moderate enhancement in the

Temperature = 50° C
Oil: n-Decane

100

VOLUME PERCENT

50

0

ΔS
5% TRS +
3% IBA +
3% S-150

ΔS
5% TRS +
3% IBA +
3% S-90

ΔS
5% TRS + 3% IBA

ΔS
5% TRS +
3% IBA +
3% S-70

ΔS
5% TRS +
3% IBA +
3% S-30

0.0   0.5   1.0   1.5   2.0   2.5   3.0
SALINITY, % NaCl
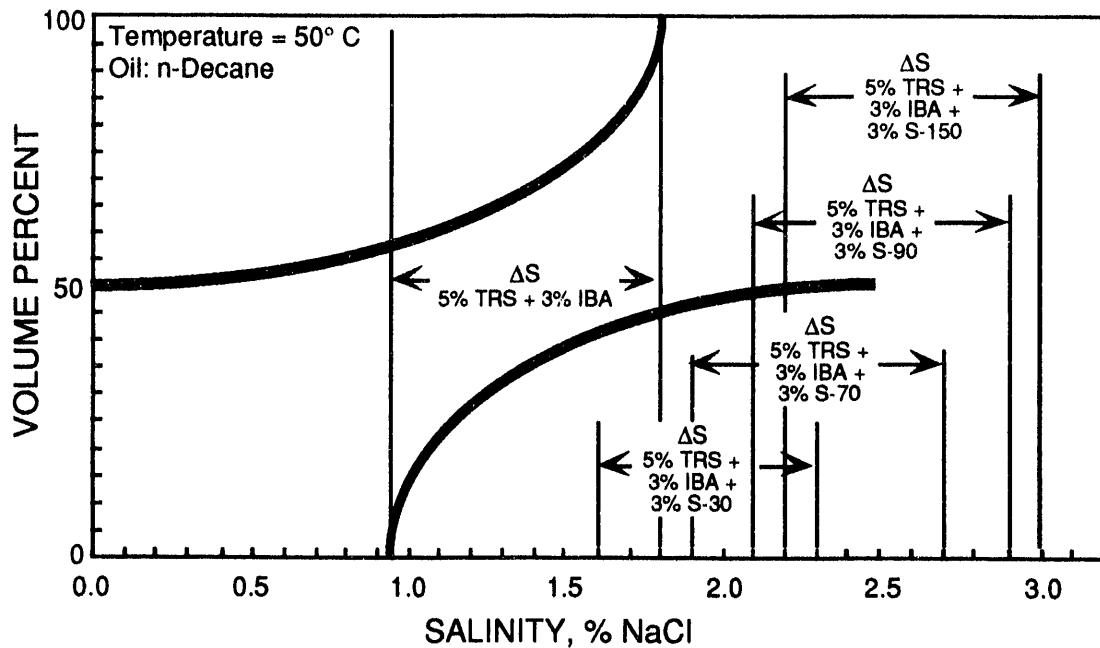
FIGURE 34. -   Phase behavior measurement using TRS 10-410/IBA + a series of ethoxylated sulfonates with n-decane at 50° C.

salinity tolerance of the overall solution, up to 4.0 % NaCl, with the mid-point salinity shifted to about 2.5% NaCl. The order of shift in salinity tolerance followed the order of increasing degree of ethoxylation in the surfactant. This range of improvement in salinity tolerance was similar to results of studies conducted last year on this type of secondary surfactant.[3] Several combinations of these surfactants were tested with n-decane. Additional work will be needed to evaluate combinations that will extend the salinity range of these systems beyond the limits presently obtained. Other samples of ethoxylated anionic surfactants need to be obtained to evaluate the effects of additional parameters such as alkane chain length, degree of ethoxylation, and type of head group on overall solution behavior.

Summary of Mixed Surfactant Studies

Mixed surfactant systems containing a primary anionic surfactant component in combination with a series of ethoxylated anionic and nonionic surfactants have been studied to evaluate potential for yielding improved solution behavior and oil/water solubilization capacity. These systems were screened for combinations of surfactant components that jointly yield high oil recovery potential as well as improved adaptability to different ranges of conditions. The effects of parameters such as (a) anionic and nonionic component substitution, (b) salinity, (c) ratio of the surfactant components, (d) total surfactant

concentration, (e) hydrocarbon chain length, and (e) surfactant type on the behavior of the overall surfactant system were studied. The dependence of the solution behavior on the structure of the surfactant, type of additive, type of oil, proportion of the different surfactant components, salinity, HLB, and temperature was observed.

The results clearly showed that the ethoxylated surfactants, both anionic and nonionic, can improve the overall phase behavior of the chemical systems tested. The degree of enhancement was dependent on the degree of ethoxylation of the surfactant. For both ethoxylated anionic and nonionic surfactants, increasing the degree of ethoxylation resulted in a relative increase in the optimum salinity range of the overall solution, up to a certain limit. The addition of the nonionic surfactants yielded much higher salinity ranges compared to the limited results from the ethoxylated anionic surfactants tested. The proportion of the ethoxylated component to the primary sulfonate component was critical in identifying a balance between the solubilization capacity of the system versus the enhancement in salinity tolerance. The total surfactant concentration was also a parameter that can significantly affect the performance of these mixed system. A shift in the range of salinity tolerance was observed as a function of the total surfactant concentration. As the total concentration decreased, the favorable salinity region appeared to have slightly increased. This is somewhat contrary to the classical representation of the SRD by Nelson, but similar dependence of the optimal salinity with concentration was observed with synthetic oil-containing systems.

As previously observed by other researchers, a marked improvement in salinity tolerance resulted in a drastic decrease in the solubilization capacity of some of the chemical systems studied. In certain combinations of anionic-nonionic surfactants though, it was possible to enhance the salinity tolerance of the mixtures without a negative effect on the system's oil/water solubilization capacity. Under these conditions, the optimal solubilization parameters were determined to be comparable or exceeded that of the original primary anionic system at much higher optimal salinity levels. These results support the possibility that combinations of these types of surfactants can yield much improved solution behavior without altering the capacity of the overall system to solubilize the oil-rich and water-rich phases.

Several observations were made during the PIT screening of the nonionic surfactant additives. There was a difference in behavior, dependence of optimal salinity on HLB, observed for the two types of nonionic surfactants tested. The linear alkyl alcohol ethoxylates, i.e., the Genapol® series, appear to exhibit a very distinct behavior from the

dialkyl phenol surfactants such as the Igepal series, at similar HLB levels. The mixtures of dialkyl phenols exhibited a more significant dependence on the HLB value than the linear ethoxylates did. The contrast in the behavior of these two types of surfactants was more pronounced at lower HLB values and decreased at higher HLB values. This distinct behavior was also confirmed in mixtures containing a base primary sulfonate system of TRS 10-410/IBA in combination with these nonionic surfactants at a component ratio of 1:1. The mixtures containing the linear alkyl alcohol ethoxylates had higher optimal salinity ranges compared to the mixtures containing the other surfactant type, at similar HLB levels. The dependence of the optimal salinity on HLB of the mixtures containing the sulfonate and each of the two types of nonionics closely resembled the mixture behavior with the nonionic formulations alone. The trends in behavior almost parallel each other, the primary difference was that the mixtures containing the sulfonate system yielded much lower optimal salinity values overall. At higher temperature levels, in this case 60° C, the distinct difference in trend between the two types of nonionic surfactants appears to have decreased with the rise in temperature level. At HLB levels greater than 11, the pattern of behavior of the two types of nonionics is similar, with and without the presence of the anionic surfactant system. The difference in behavior was still very evident at the lower HLB levels, but to a lesser degree when the anionic surfactant was present. This difference in behavior when the anionic surfactant was present may be attributed to the relative effect of temperature of both the nonionic and anionic components' affinity for the oil and water phases. Nonionic surfactants have a tendency to be more lipophilic at higher temperatures; the opposite has been observed for anionic systems. The presence of the anionic surfactant may have helped suppress some of the effects of the temperature on the anionic-nonionic mixed system, resulting in similar observations of behavior for both systems containing Igepal/TRS/IBA with those containing Genapol/TRS/IBA.

Screening tests using a different hydrocarbon also indicated a difference in the dependence of optimal salinity with the HLB and type of the nonionic components in the system. The comparable results obtained using the n-octane support the indicated pattern difference between the two types of nonionics. The difference in dependence of optimal salinity with the HLB of the nonionic components in the system was observed up to an HLB level of 11. Greater than 11, the pattern in behavior of the two types of nonionic surfactants was comparable. The surfactant structure appears to have a significant effect on the HLB of the system, and is not just a simple correlation as postulated by Griffin[20], at certain HLB ranges. At higher HLB levels, some possible alteration in the structure-dependence of the required HLB may be present.

Other observations that were made will provide some information on combinations of formulations and conditions that may be applicable for certain reservoirs. Contour plots and spatial maps of the these mixtures have been made that will be useful in identifying conditions where some of these can be used. Decreasing the carbon chain length of the oil results in a reduction of the effective salinity range at a specific calculated HLB value. The reduction in salinity was necessary to rebalance the overall system due to the shift in the oil affinity of the system. At a fixed salinity, the PIT of the system increases with the nonionic component HLB. The higher temperature range was necessary to offset the relative higher hydrophilic tendency of the solution. Increasing the temperature shifts or balances the oil-water affinity of the higher HLB system. On the other hand, altering the salinity at a fixed HLB renders the system more lipophilic, such that a reduction in PIT was needed to improve the hydrophilic tendency of the system. Combinations of anionic-nonionic systems appear to behave similarly to the behavior exhibited by the predominantly nonionic systems. Additional experiments with different primary anionic surfactants will be conducted to observe any alteration in the overall solution behavior with these types of combinations.

The results showed that a trend can be observed, in terms of a qualitative dependence of the salinity tolerance on the molecular weight, surfactant type, and concentration of the surfactant components in the system. The ethoxylated sulfates were better than the ethoxylated sulfonates in improving the tolerance of the overall chemical system, with the primary component being a sulfonate-type surfactant. The results showed that for both cases when ethoxylated sulfonates and ethoxylated sulfates were added to a primary sulfonate surfactant system such as TRS 10-410, the MW and the branching-structure of these ethoxylated components affected the overall salinity tolerance of the surfactant mixture. Shorter hydrocarbon chain length and branching in the secondary ethoxylated surfactants favored improved solubility and salinity tolerance of the overall chemical system.

The PIT method has also been shown to be a relatively fast screening method for determining approximate optimal conditions for candidate surfactant systems. Although primarily directed toward screening nonionic surfactants, it was also very useful in identifying possible combinations of anionic-nonionic mixtures. The speed and ease by which the different chemical systems were screened made it possible to evaluate a significant number of combinations of several series of surfactants. Comparisons were made of similar salinity regions identified using both the conventional salinity scan as well as the PIT method on selected chemical systems. The results of these comparisons showed

fairly good agreement between the salinity regions determined using both methods. One drawback of the PIT method is that the method does not have provisions for measuring the solubilization parameters of each of the chemical formulations. Salinity scans still need to be conducted to measure oil/water solubilization parameters. With this in mind, the results from the PIT studies can be used as reference points to determine the salinity ranges needed for the more time-consuming salinity scans.

DEVELOPMENT OF SURFACTANT FLOODING FORMULATION FOR NAVAL PETROLEUM RESERVE No. 3

NIPER's efforts in developing other cost-effective chemical flooding technologies have also been focused on the use of alkaline-enhanced surfactant flooding technology for the recovery of light crude oils. NPR No. 3 is one of the targets for this technology. The primary targets for chemical EOR are believed to be the Shannon and Frontier (or 2nd Wall Creek) formations. Both of these formations still have relatively high oil saturations. Particular emphasis is being placed on the Frontier formation, since production has been so low and is rapidly becoming uneconomical.[8]

Discussion

Two crude oil samples that were received from NPR No. 3 have been tested at NIPER. The first sample was shipped to NIPER in 1989.[22] We believe this sample (oil sample No. 1) was stock tank oil that was predominantly from the Shannon formation, but may have been co-mingled production. This oil had essentially no acid content (i.e., acids that could be measured by titration with KOH) and the gravity was 34.1° API. The second sample (oil sample No. 2), from the southern area of 2nd Wall Creek (well 62-AX-3), was received in 1992. The acid number of the 2nd Wall Creek oil sample was 0.15 mg KOH/gm oil, and the gravity was 33.1° API. Experiments conducted with these oil samples are summarized below.

Figure 35 shows the dynamic IFT between oil sample No.1 and aqueous solutions of Stepan Petrostep B-100 surfactant at two pH levels. B-100 is an anionic surfactant with molecular weight of 420. The IFT was significantly lower under alkaline conditions than non-alkaline conditions, and the IFT under alkaline conditions was about 1 μN/m, which is extremely favorable to mobilization of residual oil. A high-permeability (811 mD) Berea sandstone core was used for the coreflood conducted with oil sample No. 1 (Coreflood TP-1, table 5). The chemical formulation contained 0.1% Petrostep B-100 surfactant, 0.3%

NaCl, and a pH 9.5 carbonate mixture. Deionized water (DIW) was used for the formulation. Oil recovery (after waterflooding to residual oil saturation) was 60.8% of the oil that remained after waterflood. This high oil recovery is an example of the oil recovery that can be obtained when good conformance and good mobility control are maintained.

The Frontier formation has been waterflooded during the past 15 years with water from the Madison limestone aquifer. Analyses of Madison water furnished by the U.S. Geological survey vary considerably.[23] A composite analysis is given in table 6. The compositions of two synthetic Madison waters are also given in table 6. The exact water composition will be an important parameter for field test design. However, for the laboratory results now being discussed, the more important parameter is the level of divalent ions. Divalent ion level is especially critical for ASP flooding.

TABLE 5. - Corefloods conducted with oil from NPR-3.

| Coreflood | ASP solutions | | | S_{oi},% | S_{owf},% | S_{ocf},% | R_{eff},% |
	Surfactant	%	pH				
TP-1	B-100	0.1	9.5	73.6	39.6	15.5	60.8
TP-2	XP-100	0.25	11.0	63.8	38.5	32.1	16.6
TP-3	XP-100	0.25	11.2	81.4	39.2	28.4	27.6

ASP solutions contain surfactant, alkali, and polyacrylamide polymer
S_{oi} = initial oil saturation
S_{owf} = oil saturation after waterflood
S_{ocf} = oil saturation after chemical (ASP) flood

TABLE 6. - Chemical composition of Madison limestone aquifer water.

| Constituent | Composition, mg/L | | |
	USGS Analysis	Synthetic	Softened
Ca^{++}	307-366	305	0
Mg^{++}	28-60	46	0
Na^+	452-738	822	2530
K^+	36-73	-	-
HCO_3^-	98-133	117	117
$SO_4^=$	900-1560	942	2707
Cl^-	322-1050	593	0
F^-	3-5	–	–
*$B_4O_7^=$	1	1	1
TDS	2600-3290	2857	5334

* as boron

45
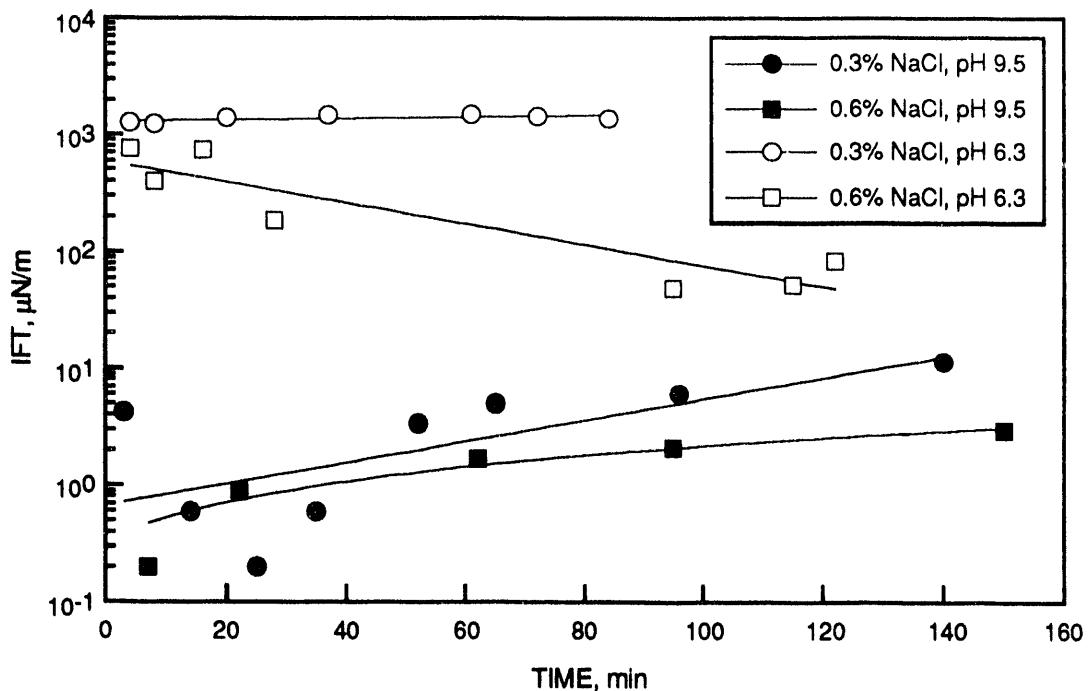
FIGURE 35. - IFT between oil sample No. 1 and 0.1% B-100 surfactant in a pH 9.5 carbonate mixture.

Chemical compatibility tests showed that produced Madison water is incompatible with most alkalis. The tests were limited to the weak alkalis, which react the least with reservoir rock. Some $NaHCO_3$, up to 0.3%, could be dissolved in Madison water without precipitation of carbonate salts. There was no tolerance to Na_2CO_3. Sodium tripolyphosphate (STPP), which is a complexing agent as well as a weak alkali, also caused precipitation. The adverse precipitation that occurs between alkalis and Madison water can be eliminated by softening the water. Na_2CO_3 could be dissolved in softened Madison water without carbonate precipitation occurring.

The IFT behaviors between oil sample No. 2 and several alkali-surfactant mixtures formulated with softened Madison water are shown in figures 36-38. Figure 36 shows the IFT between oil sample No. 2 and aqueous solutions of Chevron Chaser™ XP-100 surfactant. XP-100 is an anionic surfactant with molecular weight of 434. Make-up water was softened, synthetic Madison aquifer water. Notice that the minimum IFT was obtained with 2.0% sodium carbonate; and was about 1 μN/m, which is very favorable for oil mobilization.

46
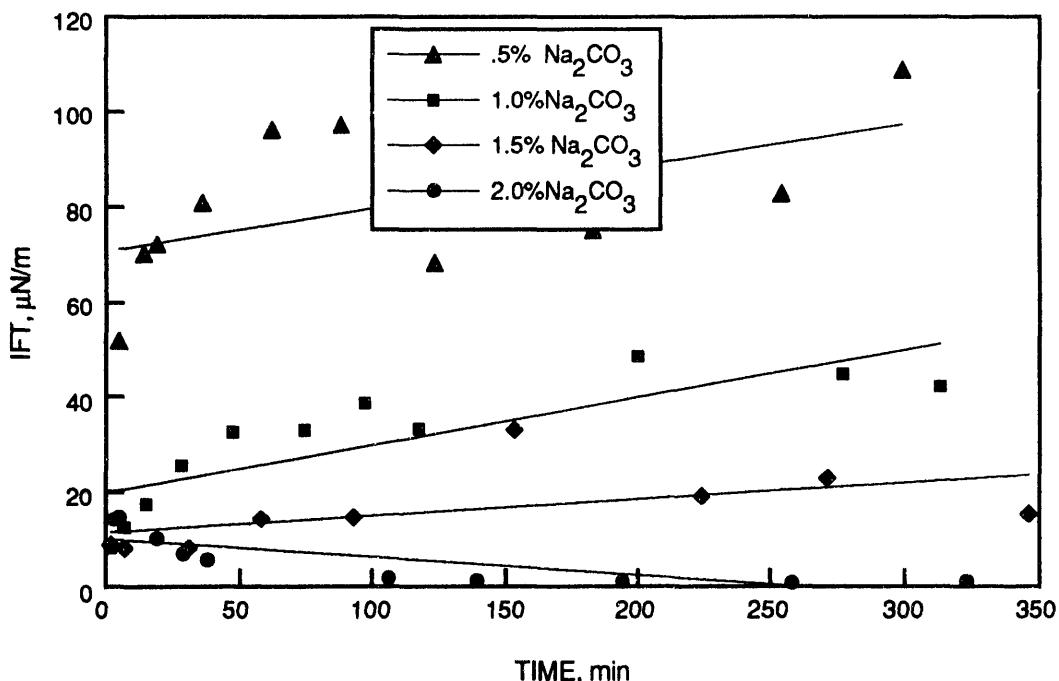
FIGURE 36. - IFT between oil sample No. 2 and 0.25% XP-100 surfactant and sodium carbonate in synthetic softened Madison limestone aquifer water.

Figure 37 shows the IFT between oil sample No. 2 and aqueous solutions of Chevron Chaser™ CF-100 surfactant. Make-up water was softened, synthetic Madison aquifer water. Chaser™ CF-100, which is a recent addition to the line of Chevron EOR surfactants, is very similar to XP-100. CF-100 is slightly more salt tolerant than XP-100. IFT shows the same trend as with XP-100, with the lowest IFT values at higher Na_2CO_3 concentrations.

Figure 38 shows the IFT behavior between oil sample No. 2 and a mixture that contained 0.25% Stepan Petrostep™ B-105 surfactant. B-105 is a very salt tolerant surfactant mixture with a molecular weight of about 424. Low IFT values occurred only at very high concentrations of Na_2CO_3. Concentrations of Na_2CO_3 greater than 5% are probably unrealistic because of economic considerations.

47
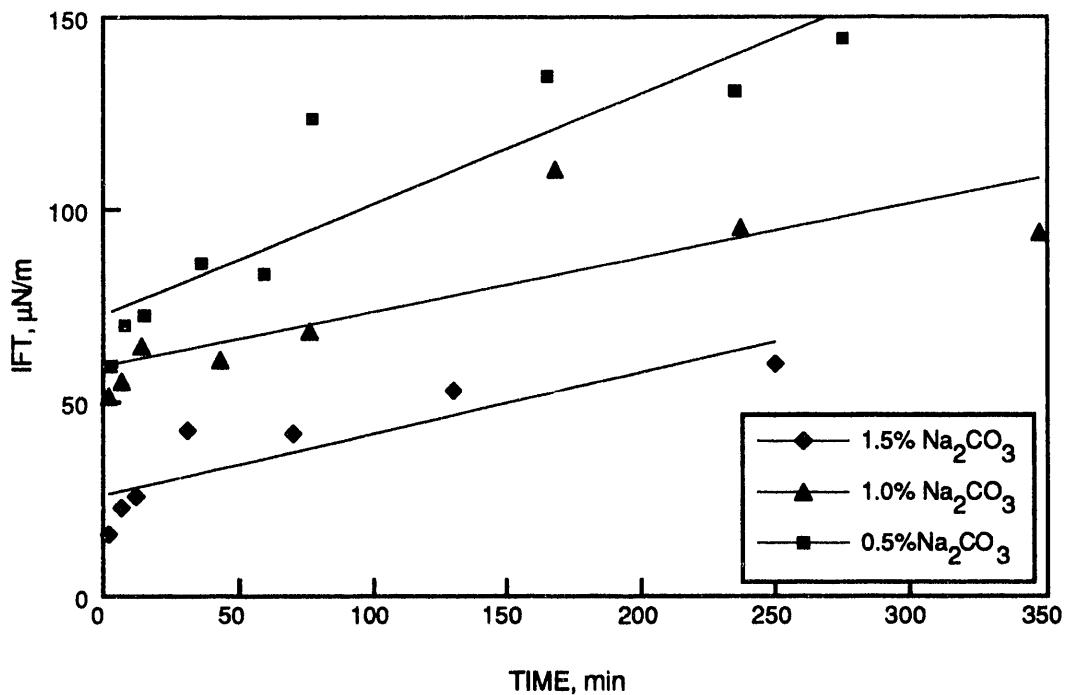
FIGURE 37. - IFT between oil sample No. 2 and 0.25% CF-100 surfactant and sodium carbonate in synthetic softened Madison limestone aquifer water.
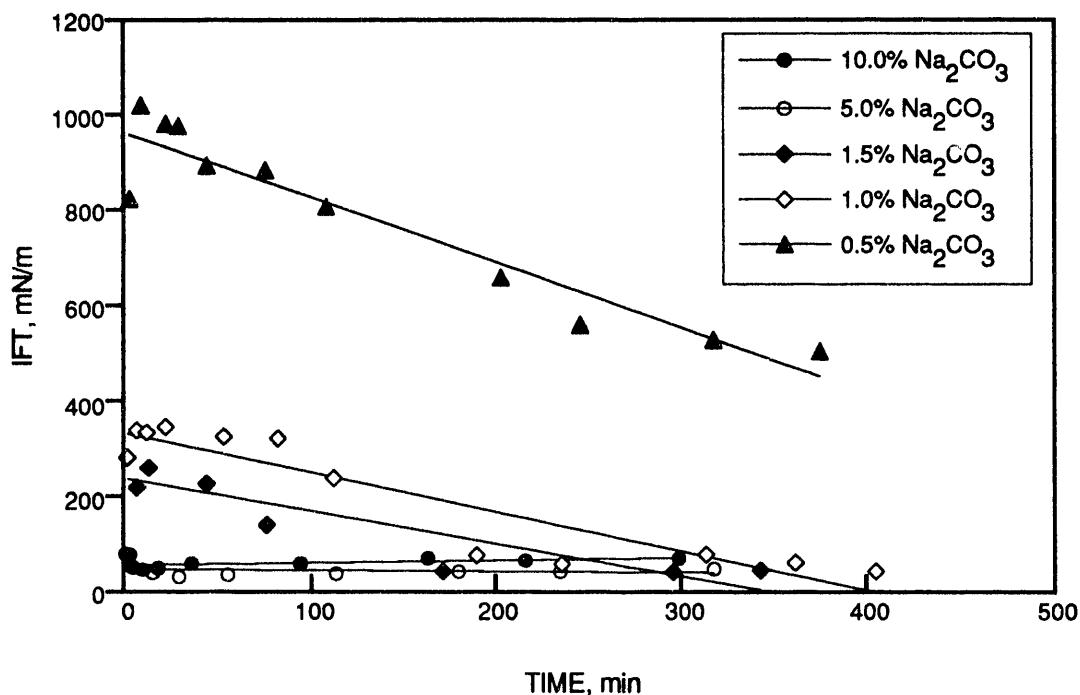
FIGURE 38. - IFT between oil sample No. 2 and 0.25% B-105 surfactant and sodium carbonate in synthetic softened Madison limestone aquifer water.

Low-permeability cores were used for corefloods TP-2 and TP-3, which were conducted with oil sample No. 2. The permeabilities of these cores, 12 and 50 mD, respectively, are representative of the north part of the 2nd Wall Creek reservoir. In coreflood TP-2, tertiary oil recovery was 16.6% of the waterflood residual oil saturation. Coreflood results are shown in figure 39. During chemical flooding, pressure across the core rose to a very high level, about 220 psi, then remained high during injection of the brine post-flush. In this coreflood, even though a low-molecular weight polymer was used, mobility control was lost due to polymer filtration that was observed on the core face. The high pressure differential across the core during and after polymer injection was caused by poor polymer propagation during the coreflood. This problem is not uncommon when core permeability is low.

In coreflood TP-3, polymer injectivity was much better. Coreflood results shown in figure 40 reveal that pressure increased during chemical flooding, but then returned to a level that was lower than before chemical flooding. The effective permeability to brine was greater after chemical flooding as a result of lower oil saturation. In this coreflood, chemical flooding produced 27.6% of the waterflood residual oil saturation.
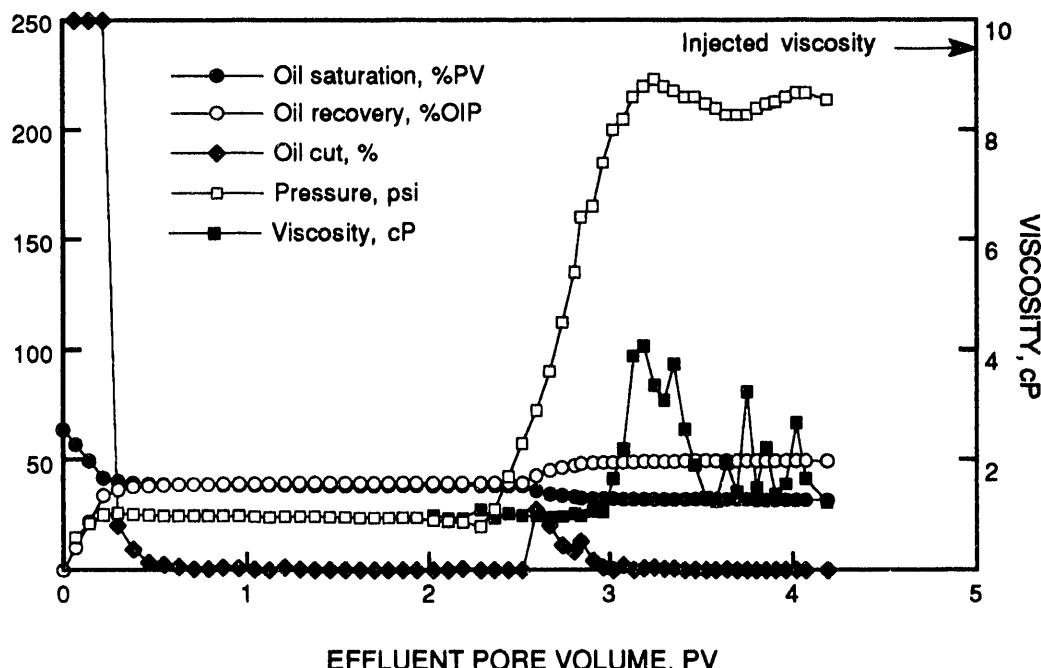
FIGURE 39. - Coreflood TP-2 conducted with oil sample No. 2.
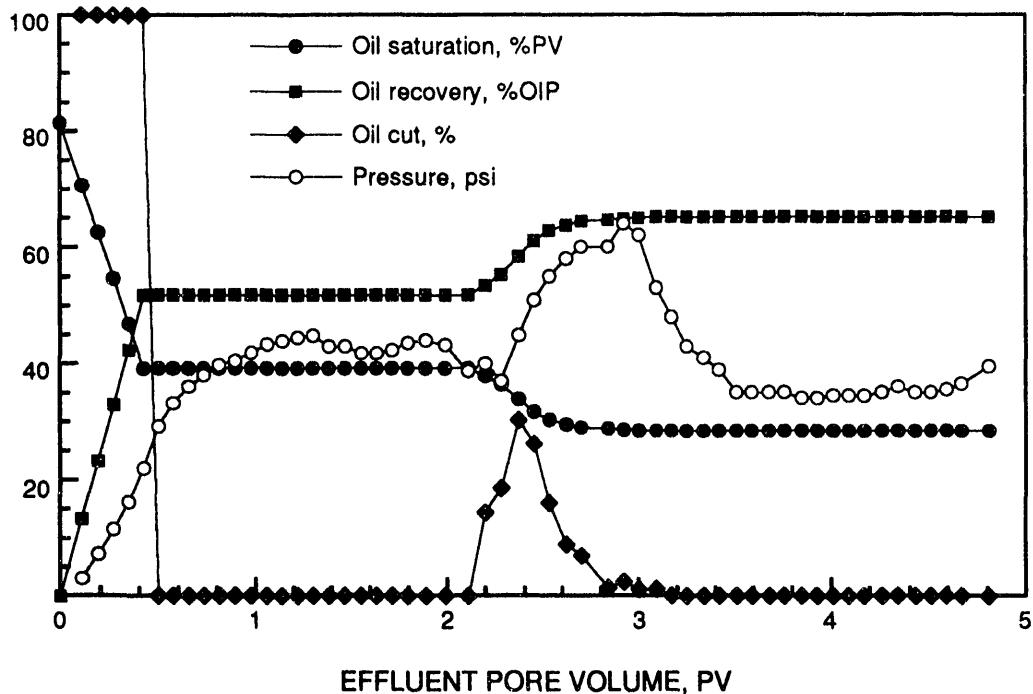
FIGURE 40. - Coreflood TP-3 conducted with oil sample No. 2.

Oil saturation is currently about 45% in 2nd Wall Creek reservoir. Based on coreflood TP-3 results, total recovery (starting at 45% oil saturation) would be projected to be about 37% of the current oil-in-place. The coreflood results are encouraging; they indicate that oil recovery from 2nd Wall Creek can be greater than 37% of the current oil-in-place. It is important that mobility control is maintained during chemical flooding, and polymer selection is important because of the low permeability of the 2nd Wall Creek reservoir.

The Frontier formation has been waterflooded with Madison water for several years. Due to the high ion-exchange capacity of Frontier formation rock, the reservoir has undoubtedly become hardened. Calcium and magnesium from the Madison water have replaced sodium in ion-exchange sites on the reservoir rock. Therefore, chemical formulations made-up with unsoftened water have an appeal because potential adverse reactions with the divalent ions on the reservoir rock should be eliminated. Figures 41 through 43 show the dynamic IFT behavior between oil sample No. 2 and low concentrations of synthetic surfactants dissolved in unsoftened Madison water. With unsoftened water, NaCl instead of Na_2CO_3 was used for ionic strength adjustment.

Figure 41 illustrates the very high optimal salinity for B-105 surfactant. Similar results have been observed in earlier studies.[3] Very low IFT values were not measured, except at very high NaCl concentrations. Surfactants XP-100 and CF-100 were insoluble in unsoftened water, and co-surfactants were required to solubilize these surfactants in unsoftened water. The IFT values shown in figures 42 and 43 are encouraging. Very low IFT values were not obtained, but further adjustment of the surfactant: co-surfactant ratio and of salinity would likely yield a low-concentration surfactant mixture that gives low IFT in unsoftened water.

In order to successfully apply chemical flooding in NPR No. 3, some form of remediation to redirect fluid flow away from fractures is needed. This is especially true for the 2nd Wall Creek reservoir, which is of special interest for the application of some form of EOR. The best approach is probably to test gel treatments while waterflooding, then decide whether to proceed with a combination of gel treatments and chemical injection. It is possible that a careful geological study of the reservoir might reveal an area that can be successfully chemical flooded without gel treatment.
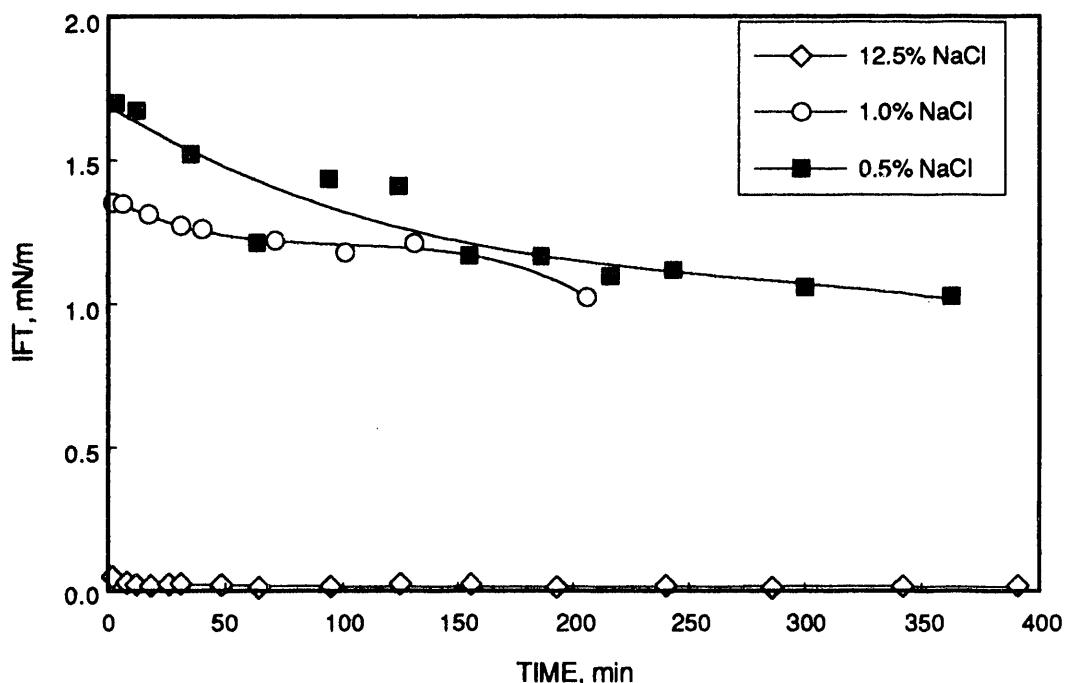
FIGURE 41. - IFT between oil sample No. 2 and 0.25% B-105 surfactant and sodium chloride in synthetic Madison limestone aquifer water.
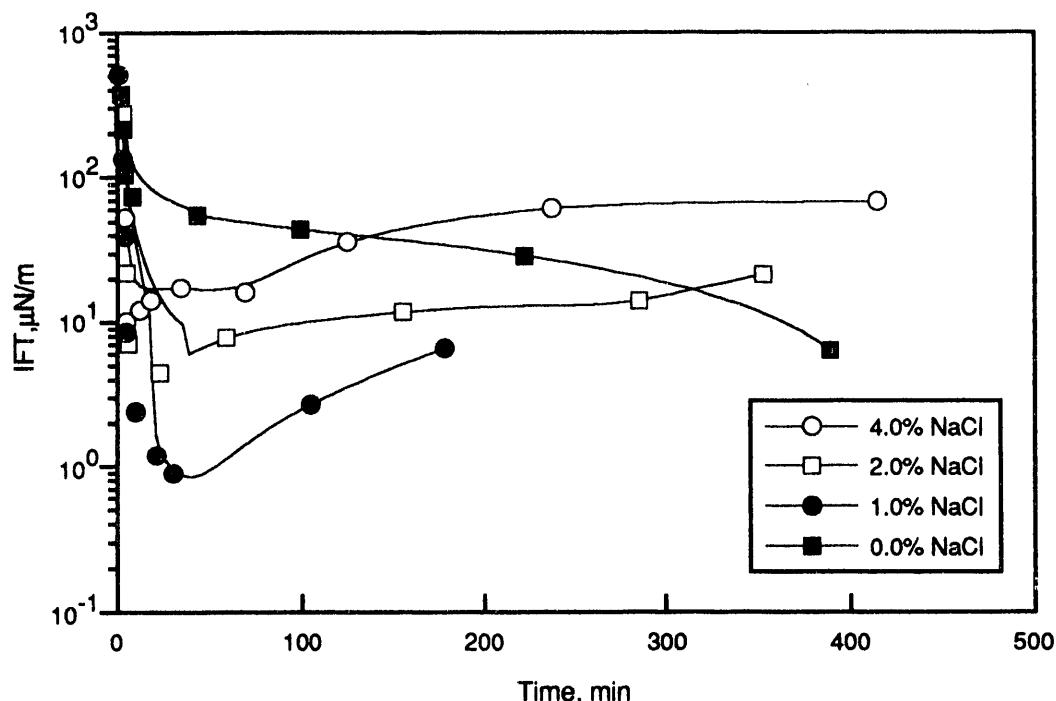
FIGURE 42. - IFT between oil sample No. 2 and 0.25% XP-100 surfactant + 0.1% CA-207 and sodium chloride in synthetic Madison limestone aquifer water.
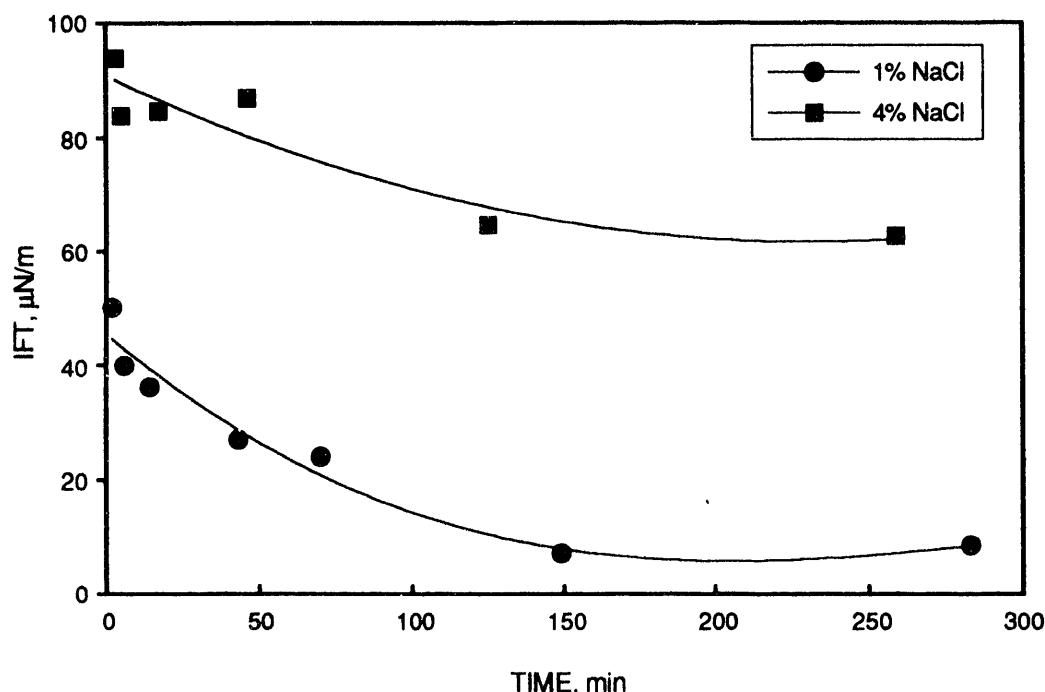
FIGURE 43. - IFT between oil sample No. 2 and 0.25% XP-100 surfactant + 0.1% Neodol 45-13 co-surfactant and sodium carbonate in synthetic Madison limestone aquifer water.

The economics of ASP flooding are more favorable than for traditional chemical flooding methods because low IFT values are achievable with a low surfactant concentration. The 2nd Wall Creek reservoir is a desirable target because, since only 17% of the OOIP has been recovered, the current oil saturation should be high. Chemical costs for ASP flooding should be between about $600 and $1800 per acre-ft of floodable sand. The exact cost will depend on many variables, such as polymer concentration, surfactant concentration, and the particular surfactants and polymers selected for the project. Polymer selection is especially important because of low permeability in the north area of the 2nd Wall Creek reservoir. Since the 2nd Wall Creek reservoir may soon be abandoned, all of the oil produced during an ASP project would be considered incremental oil, and the chemical cost could be as low as $2- $4 per barrel. These estimates are based on prior field work and computer simulations for other fields.[24]

Summary and Conclusions

Experiments performed at NIPER have shown that surfactant-enhanced alkaline flooding has good potential for the recovery of oil from NPR No. 3 reservoirs. Recovery of oil from the 2nd Wall Creek reservoir, which is an especially attractive candidate for EOR, can be increased by application of surfactant-enhanced alkaline flooding. Due to low permeability in the north section of the 2nd Wall Creek reservoir, particular attention must be given to selecting the polymer that will be used for mobility control during chemical flooding. The highly fractured nature of NPR No. 3 reservoirs must also be considered. In order to successfully apply chemical flooding in the 2nd Wall Creek reservoir, some form of remediation is needed to redirect fluid flow away from fractures. The best approach is probably to test gel treatments while continuing to waterflood, then decide whether to proceed with a combination of gel treatments and chemical injection. A careful geological study of NPR No. 3 reservoirs is also recommended because it might reveal an area that can be successfully chemical flooded without gel treatment.

REFERENCES

1. U.S. Department of Energy. Oil Research Program Implementation Plan. Department of Energy Report No. DOE/FE-0188P, April 1990.
2. Strycker, A. Selection of Temperature, Salinities, and API Gravities for Laboratory Surfactant Screening Studies. Department of Energy Report No. NIPER-424, Nov. 1989.

3. Llave, F. M., B. L. Gall, T. R. French, L. A. Noll and S. A. Munden. Phase Behavior and Oil Recovery Investigations Using Mixed and Alkaline-Enhanced Surfactant Systems. Department of Energy Report No. NIPER-567, Feb. 1992.

4. Glinsmann, G. R. Aqueous Surfactant Systems for InSitu Multiphase Microemulsion Formation. U.S. Patent No. 4,125,156. Nov. 14, 1978.

5. Boneau, D. F. and R. L. Clampitt. A Surfactant System for the Oil-Wet Sandstone of the North Burbank Unit. J. P. T., May 1977. pp. 501-506.

6. Bansal, V. K. and D. O. Shah. The Effect of Ethoxylated Sulfonates on Salt Tolerance and Optimal Salinity of Surfactant Formulations for Tertiary Oil Recovery. SPE Journal, June 1978, pp. 167-172.

7. Doll, T. E. Polymer Mini-Injectivity Test: Shannon Reservoir, Naval Petroleum Reserve No. 3, Natrona County, WY. Pres. at the Rocky Mountain Regional Meeting in Casper WY, May 1984, SPE paper 12925.

8. Jackson, Susan. Personal Communication. 1992.

9. French, T. R. and C. B. Josephson. Alkaline Flooding Injection Strategy. NIPER Topical Report No. NIPER-563, submitted for review September 1991.

10. French, T. R. Design and Optimization of Phosphate-Containing Alkaline Flooding Formulations. Department of Energy Report No. NIPER-446, Sept. 1989.

11. Lorenz, P. B. and S. Brock. Surfactant and Cosurfactant Properties of Mixed and Polysulfonated Surfactant by Phase Volume Measurements. Department of Energy Report No. NIPER-256, October 1987.

12. Llave, F. M. and D. K. Olsen Development of an Automated System for Phase Inversion Temperature Measurements. Department of Energy Report No. NIPER-318, June 1988.

13. Shinoda, K. and H. Arai. The Correlation Between Phase Inversion Temperature in Emulsion and Cloud Point in Solution of Nonionic Emulsifier. J. Phys. Chem., v. 68, 1964, pp. 3485-3490.

14. Shinoda, K. and M. Kuneida. Conditions to Produce So-called Microemulsions: Factors to Increase the Mutual Solubility of Oil and Water by Solubilizer. J. Coll. and Interface Sci., v. 42, 1973, p. 381.

15. Marzall, L. HLB of Nonionic Surfactants: PIT and EIP Methods. Nonionic Surfactants: Physical Chemistry, ed. by M. J. Schick., Marcel Dekker, Inc. New York, 1987, pp. 493-547.

16. Salager, J. L., and R. E. Anton. Physico-Chemical Characterization of a Surfactant: A Quick and Precise Method. J. Disp. Sci. and Tech. v. 4(3), 1983, pp. 253-273.

17. Llave, F. M., B. L. Gall, and L. A. Noll. Mixed Surfactant Systems for Enhanced Oil Recovery. Department of Energy Report No. NIPER-497, Dec. 1990.

18. Nelson, R. Salinity-Requirement Diagram - A Useful Tool in Chemical Flood Research and Development. SPEJ, April 1982, pp. 259-270.

19. Bourrel, M., J. L. Salager, R. S. Schechter, and W. H. Wade. A Correlation for Phase Behavior of Nonionic Surfactants. J. Coll. and Interface Sci. v. 75 (2), June 1980.

20. Griffin, W. C., Classification of Surface-Active Agents by "HLB". J. Soc. of Cosm. Chem., v. 1, 1949, pp. 311-326.

21. Salager, J. L., J. Morgan, R. S. Schechter, W. H. Wade, and E. Vasquez. . A Correlation for Phase Behavior of Nonionic Surfactants. SPEJ. v. 19, 1978, pp 242.

22. French, T. R., C. B. Josephson, and D. B. Evans. The Effects of Alkaline Additives on the Performance of Surfactant Systems Designed to Recover Light Crude Oil. Department of Energy Report No. NIPER-506, Oct. 1990. Revised Jan. 1991.

23. Water-Resources Activities of the U. S. Geological Survey in Wyoming, October 1989 Through September 1991. U. S. Geological Survey Open-File Report 91-226.

24. French, T. R. and T. E. Burchfield. Design and Optimization of Alkaline Flooding Formulations. Pres. at the Seventh Joint SPE/DOE Symposium on Enhanced Oil Recovery. Tulsa, OK., April 1990. SPE/DOE paper 20238.

APPENDIX

Appendix A show plots of the results of the phase behavior studies conducted on combinations of several nonionic surfactants with a primary anionic surfactant system. The width of the type-III region is defined by an upper limit (S^+) and lower limit (S^-) in salinity, with ΔS being the difference between these two salinity limits. The V_o/V_s and V_w/V_s are the oil and water solubilization parameters determined from these phase volume measurements. These parameters are indicate the amount of oil or water, up-take in the surfactant-rich middle phase. Optimal conditions are determined from the salinity conditions (S^*) where the degree of oil and water solubilization are approximate equal ($V_o/V_s \approx V_w/V_s$). The solubilization parameter at optimal salinity is designated as σ^*. These results are for total surfactant concentration levels from 2 wt% to 4 wt%.
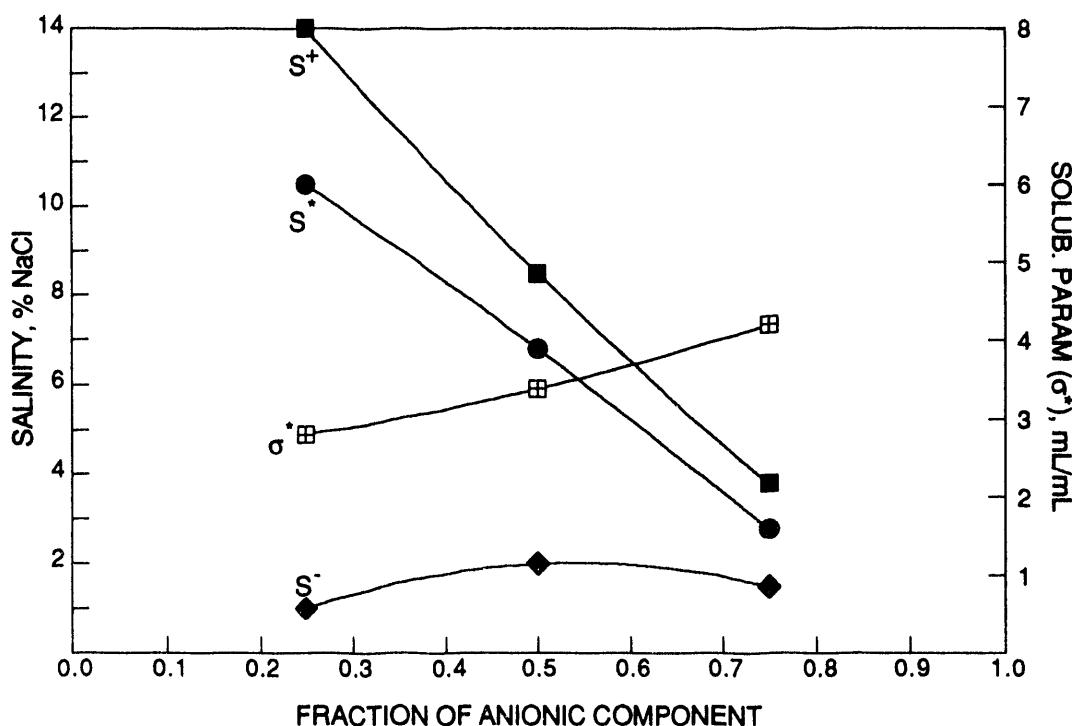
FIGURE A1. - Solubilization parameters for TRS 10-410/IBA + N-25-7 system
with n-decane at 50° C and 4 wt% total surfactant concentration.
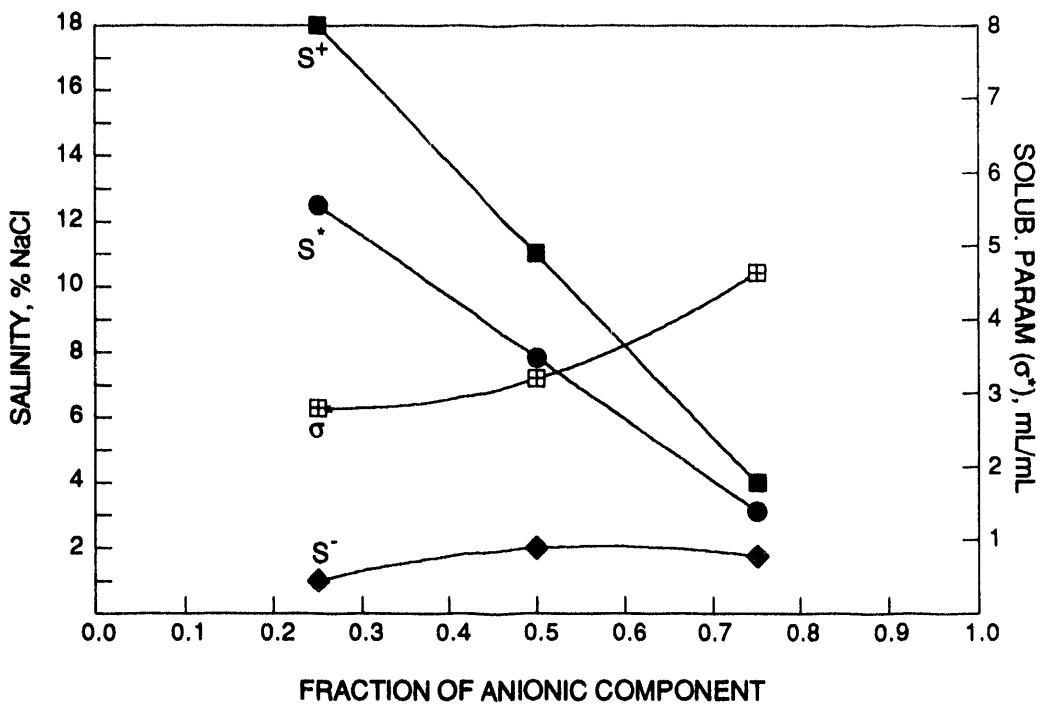
FIGURE A2. - Solubilization parameters for TRS 10-410/IBA + N-25-7 system with n-decane at 50° C and 3 wt% total surfactant concentration.
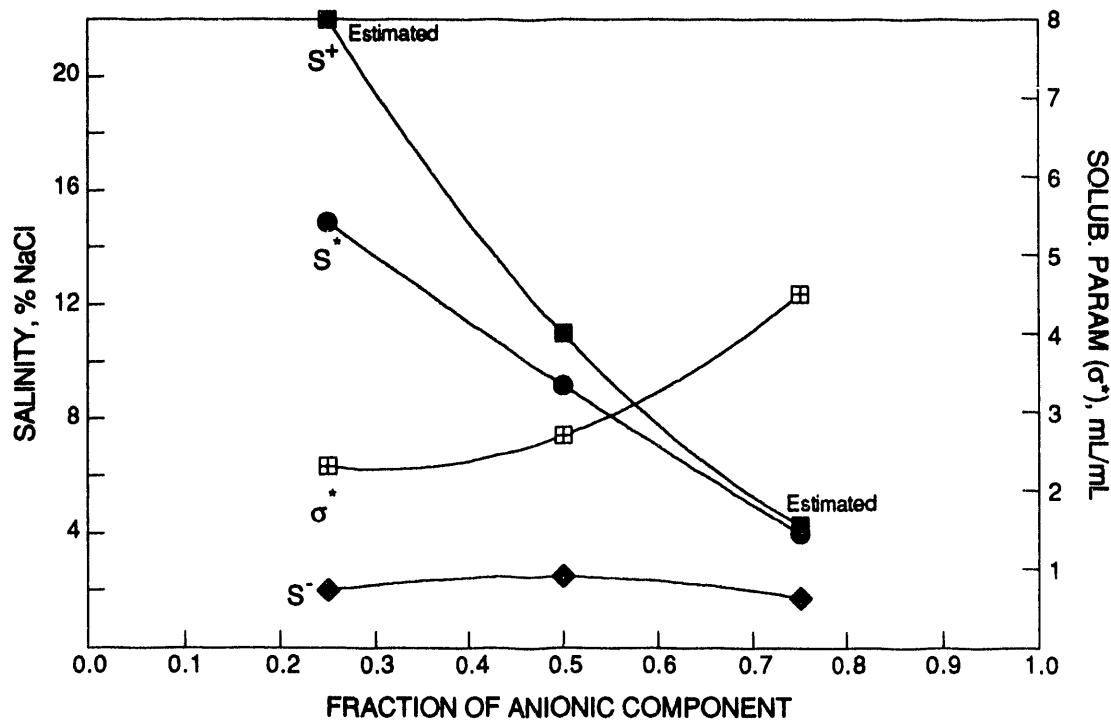
FIGURE A3. - Solubilization parameters for TRS 10-410/IBA + N-25-7 system with n-decane at 50° C and 2 wt% total surfactant concentration.

58
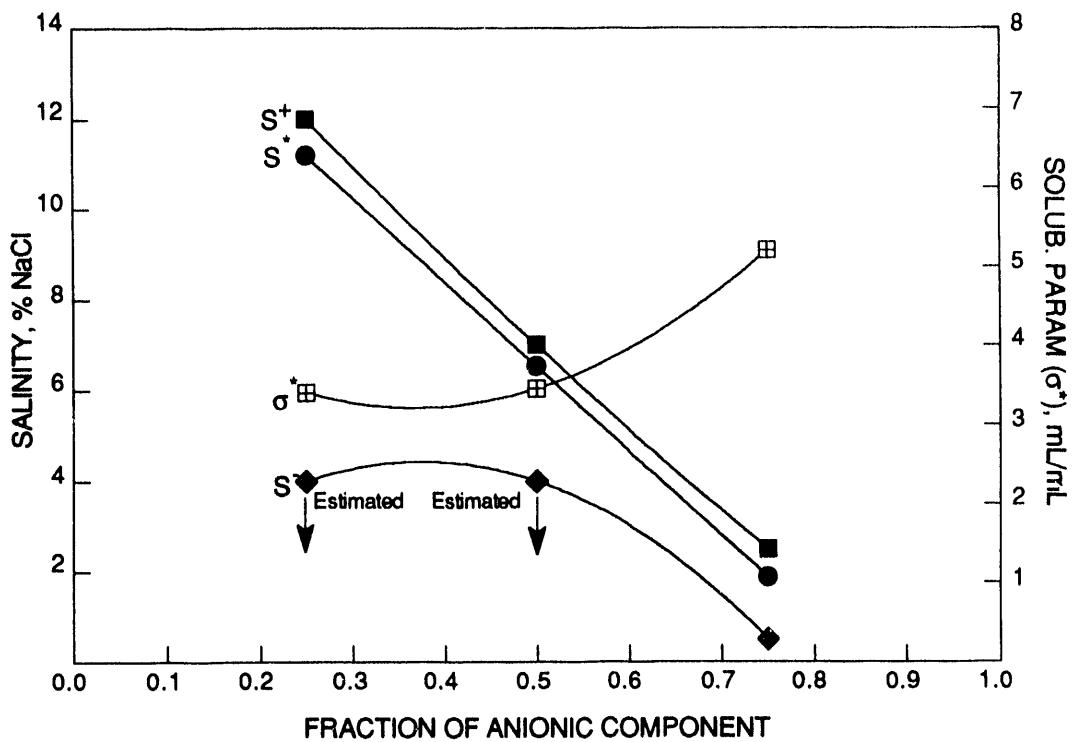
FIGURE A4. - Solubilization parameters for TRS 10-410/IBA + N-25-7 system
with n-octane at 50° C and 4 wt% total surfactant concentration.
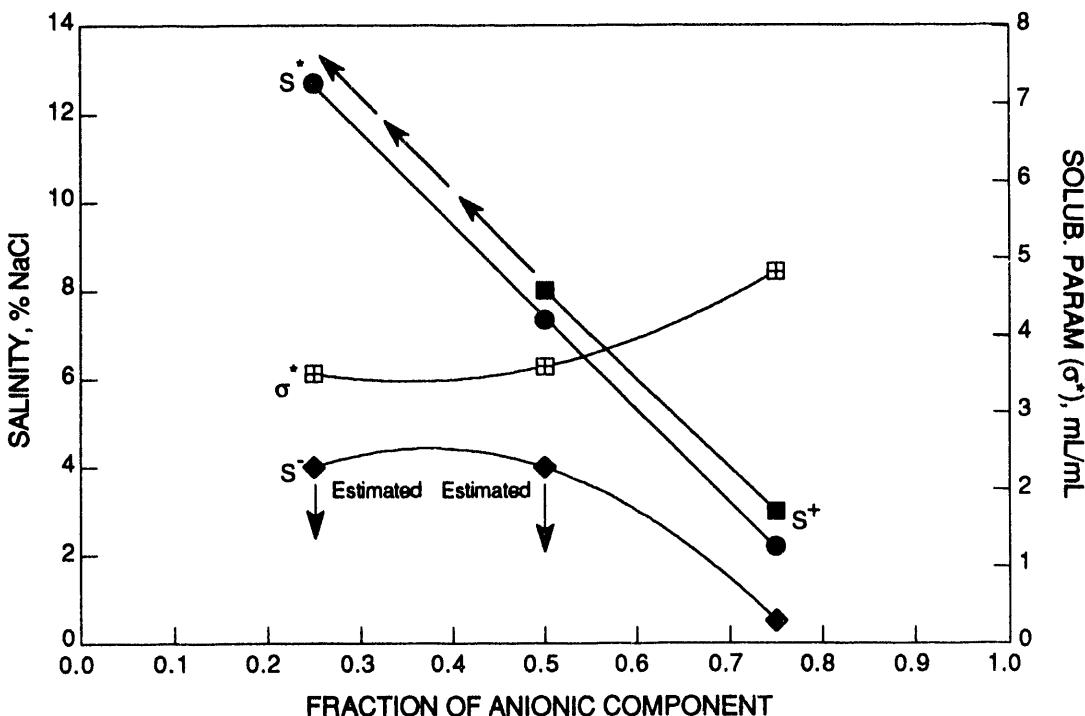
FIGURE A5. - Solubilization parameters for TRS 10-410/IBA + N-25-7 system
with n-octane at 50° C and 3 wt% total surfactant concentration.
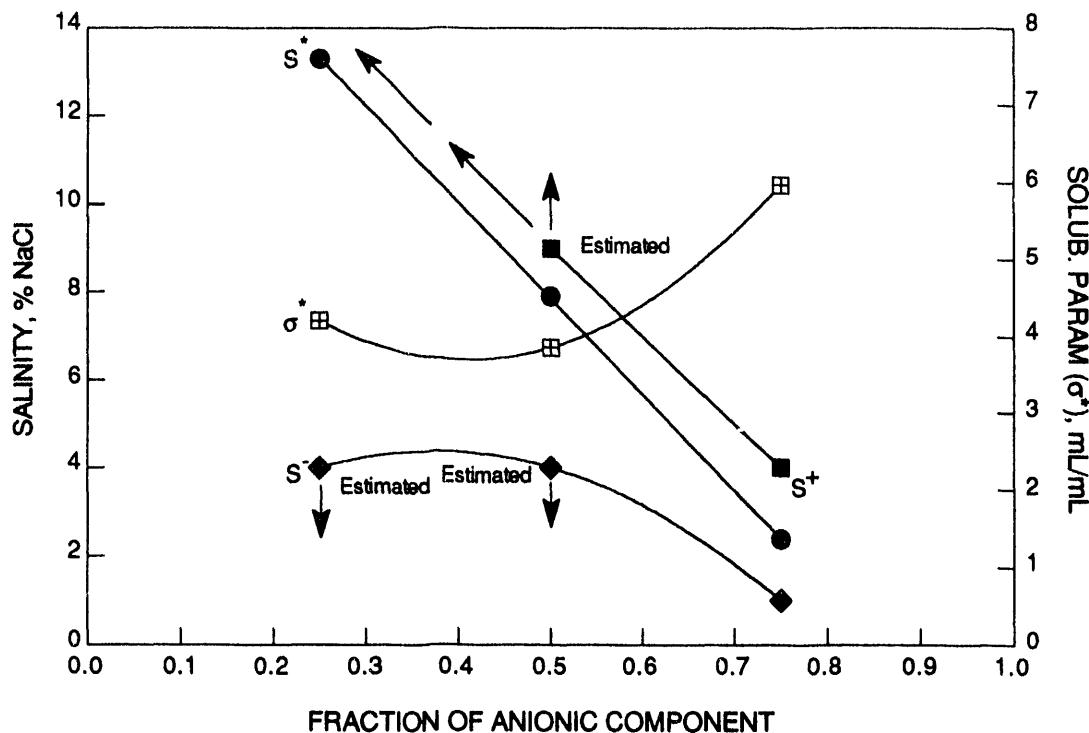
FIGURE A6. - Solubilization parameters for TRS 10-410/IBA + N-25-7 system with n-octane at 50° C and 2 wt% total surfactant concentration.
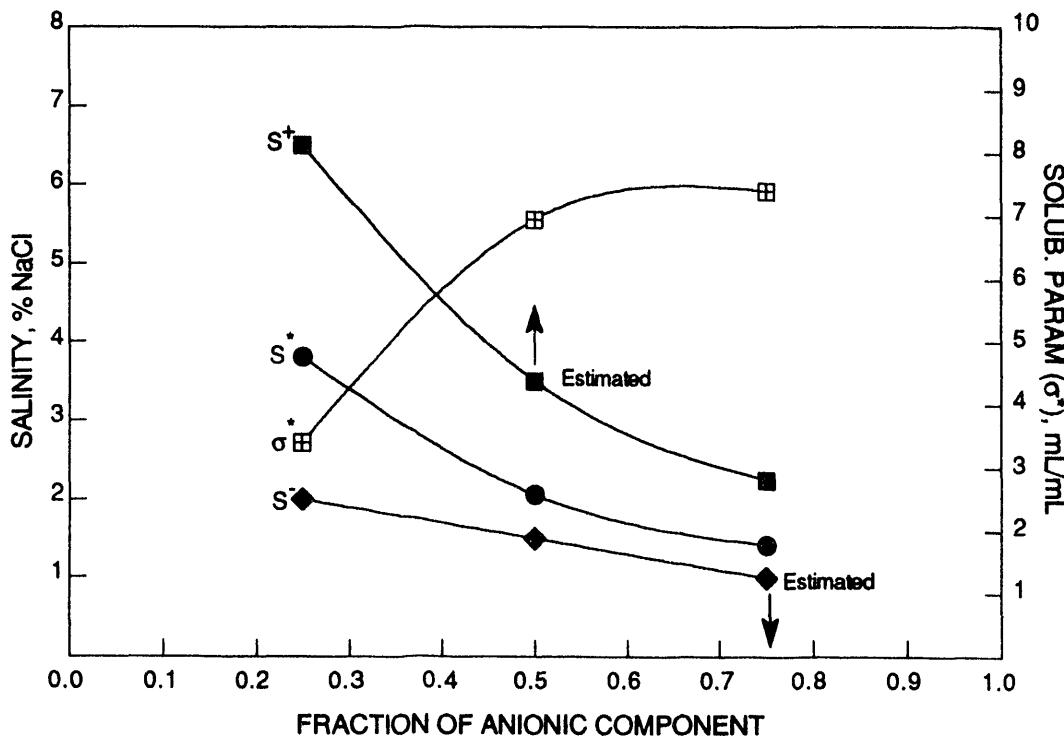
FIGURE A7. - Solubilization parameters for TRS 10-410/IBA + DM-530 system with n-decane at 50° C and 4 wt% total surfactant concentration.
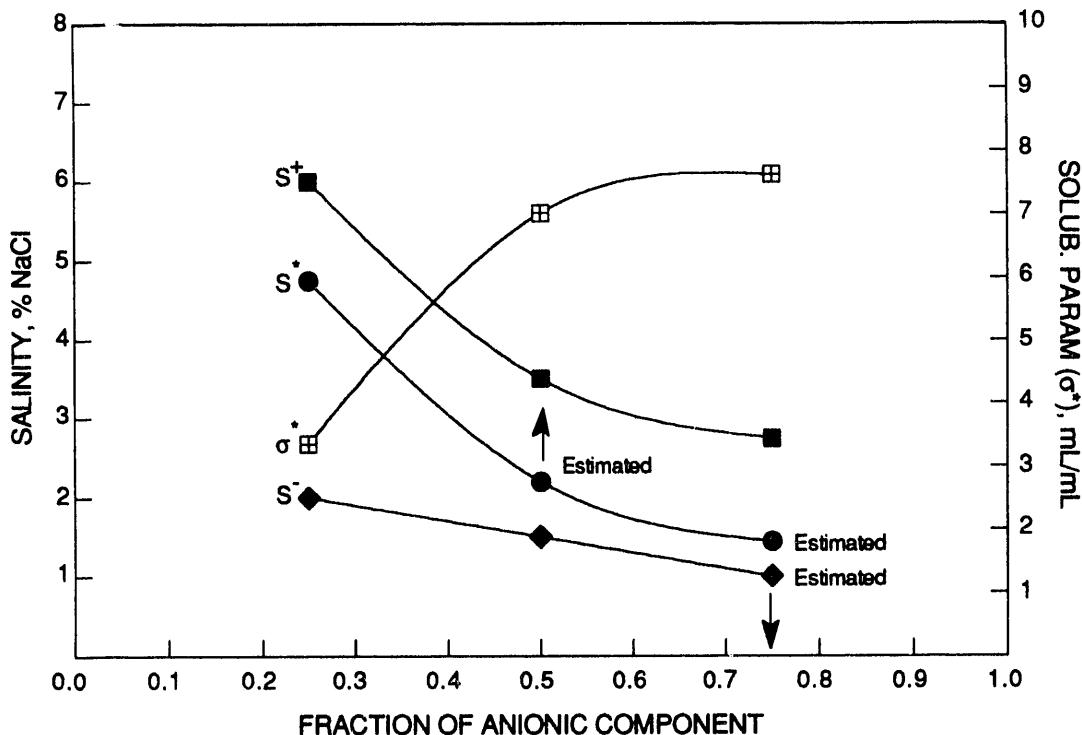
FIGURE A8. - Solubilization parameters for TRS 10-410/IBA + DM-530 system with n-decane at 50° C and 3 wt% total surfactant concentration.
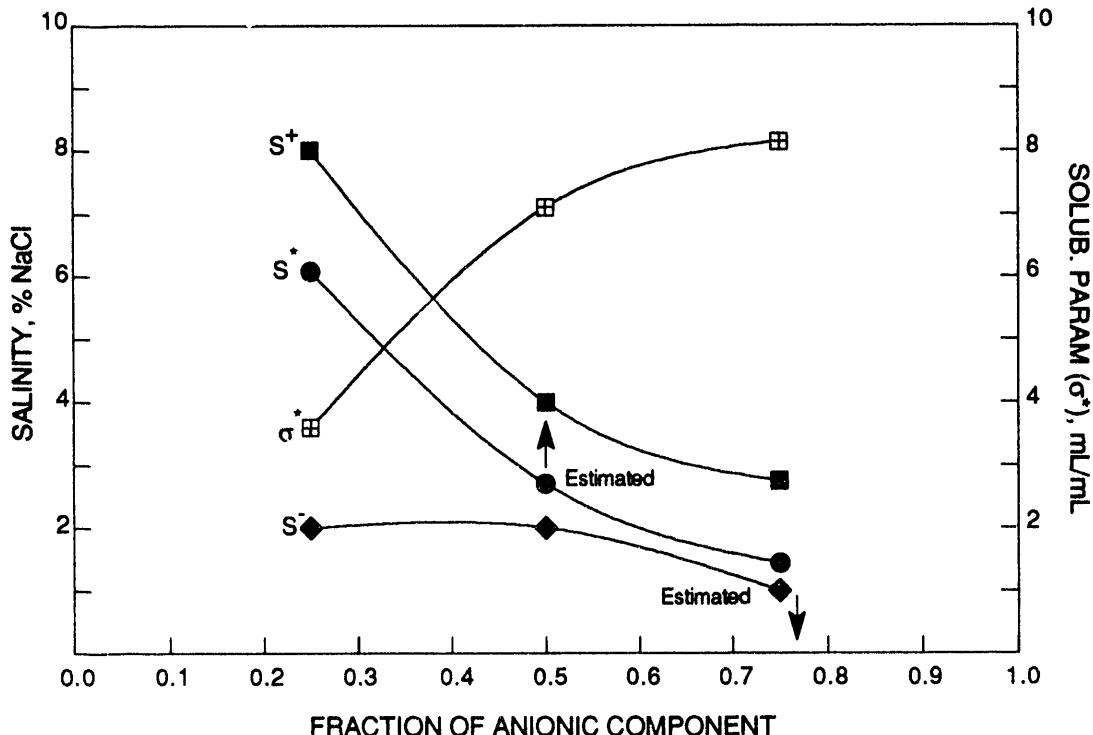
FIGURE A9. - Solubilization parameters for TRS 10-410/IBA + DM-530 system with n-decane at 50° C and 2 wt% total surfactant concentration.

Appendix B show plots of the results of the phase inversion temperature (PIT) measurements conducted on combinations of anionic and nonionic surfactants. These plots show traces of the solution conductivity as a function of temperature and salinity. The PIT is approximated based on the narrow range in temperature where a dramatic change in solution conductivity occurs. This difference in solution conductivity is attributed to the transition of the high conducting oil-in-water (O/W) microemulsion to a poorly-conducting water-in-oil (W/O) microemulsion with an increase in temperature. The distinct narrow range of temperature where the transition occurs indicates the relative proximity of the optimal condition of the surfactant-oil system. Given a fixed temperature to consider, in this case 50° C, the optimal condition is estimated as the salinity level where a reduction (1/2 to 1 order of magnitude) in solution conductivity is observed.
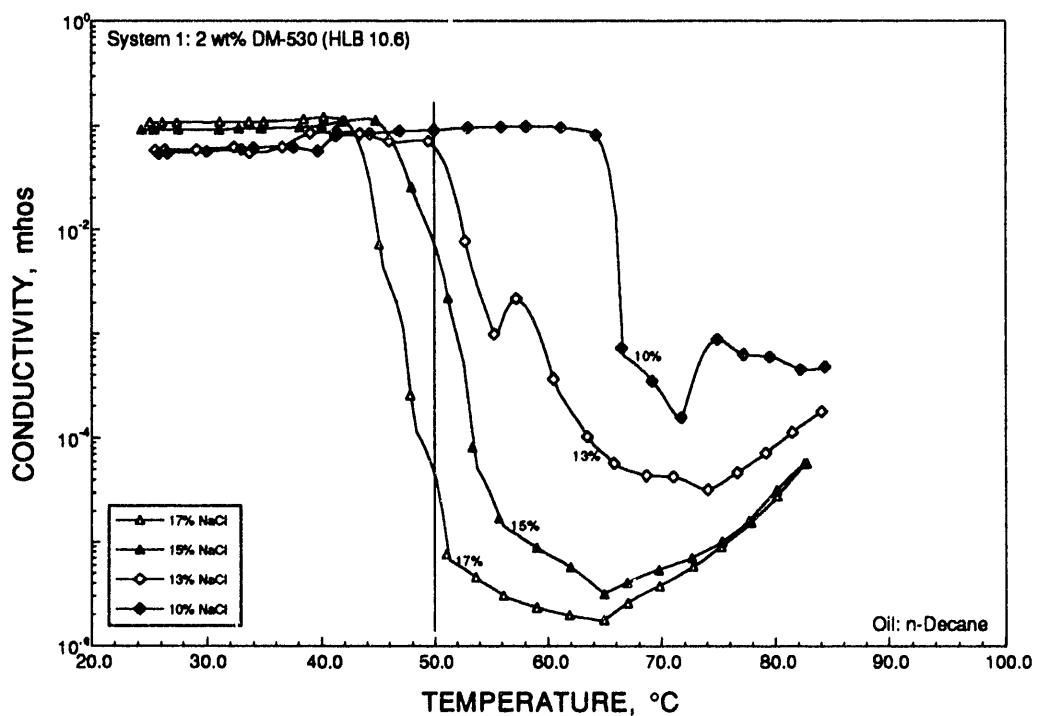
FIGURE B1. - Phase inversion temperature (PIT) for System 1 with n-decane.
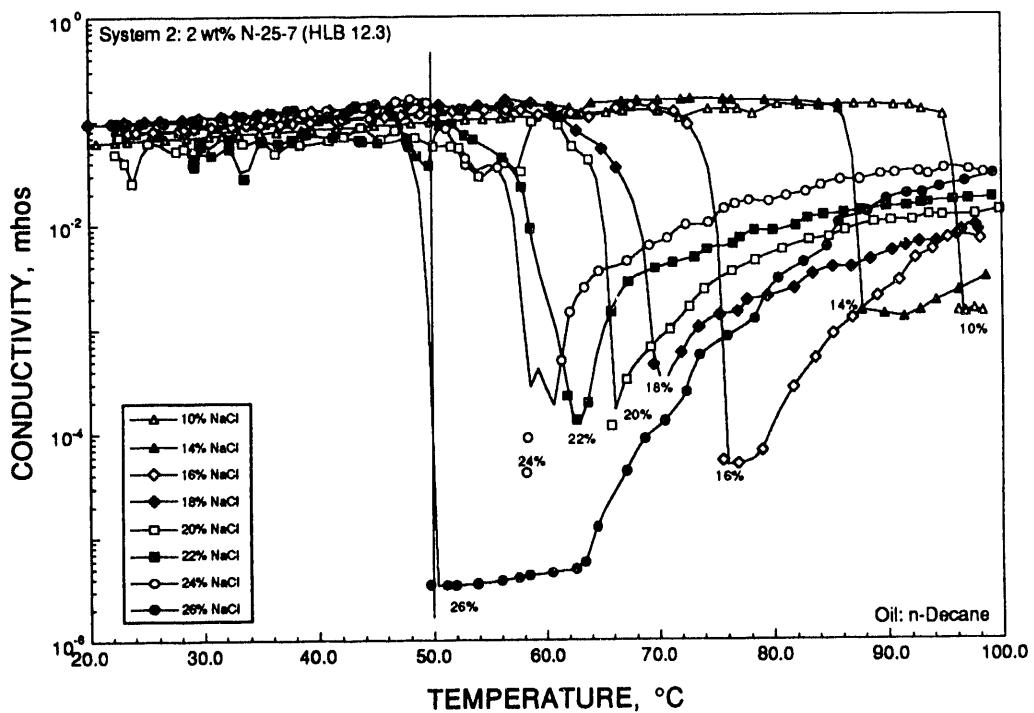
FIGURE B2. - Phase inversion temperature (PIT) for System 2 with n-decane.
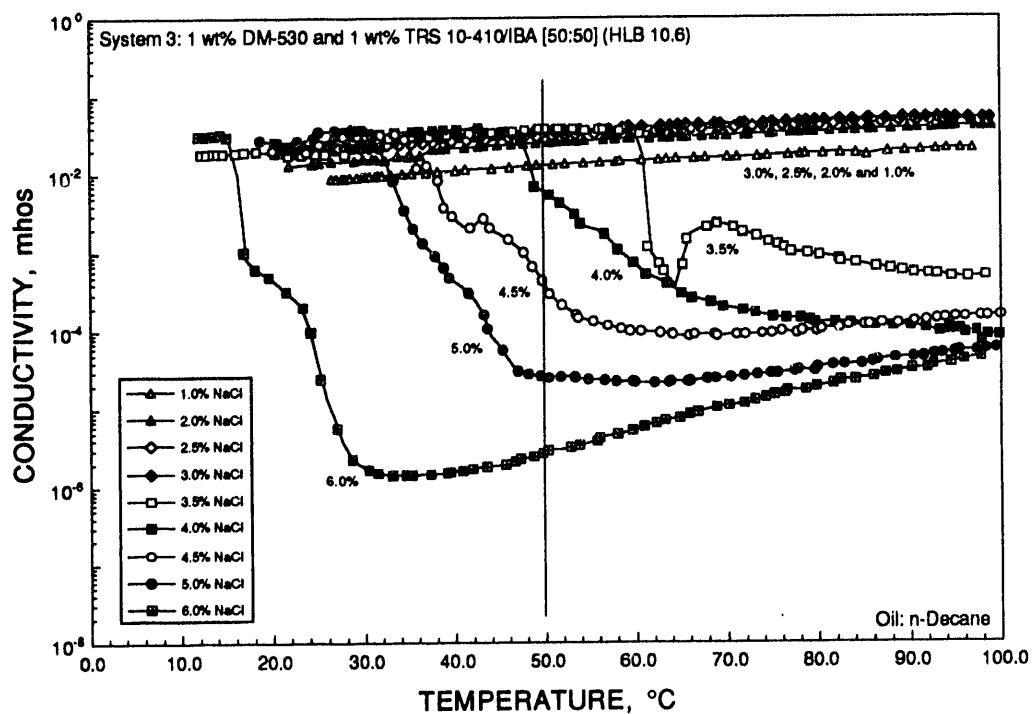
FIGURE B3. - Phase inversion temperature (PIT) for System 3 with n-decane.
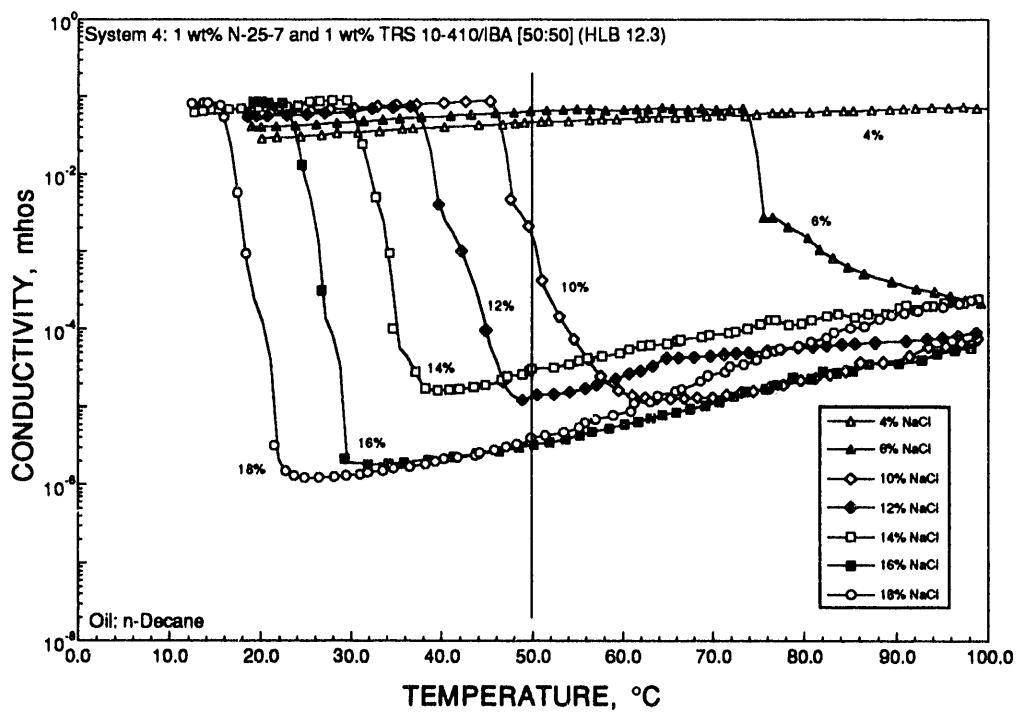
FIGURE B4. - Phase inversion temperature (PIT) for System 4 with n-decane.
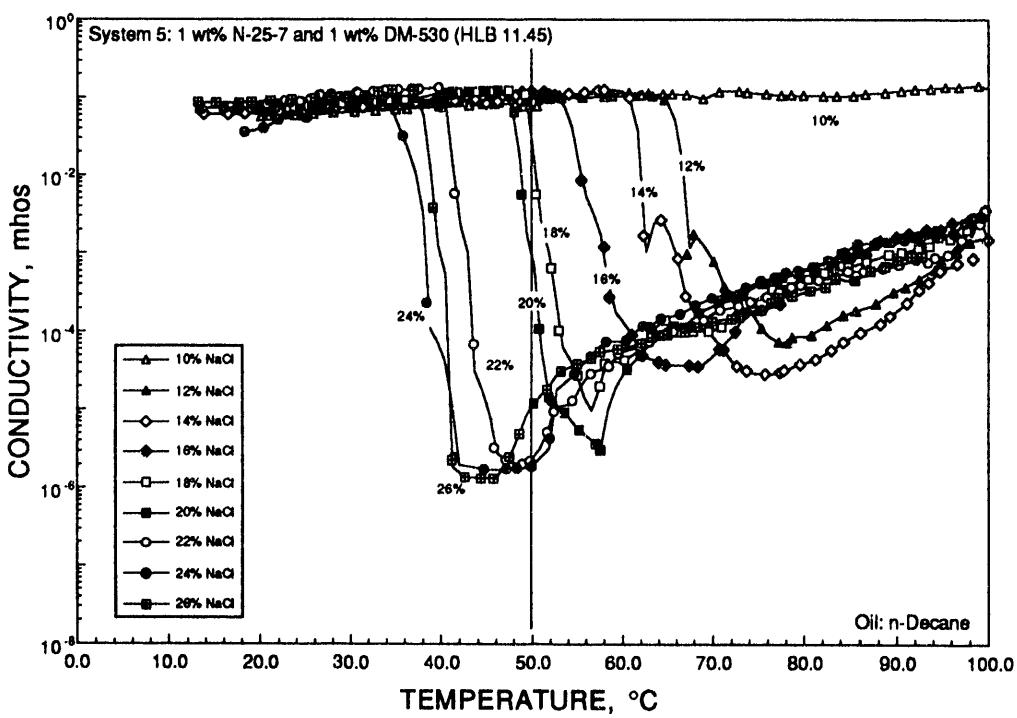
FIGURE B5. - Phase inversion temperature (PIT) for System 5 with n-decane.

64
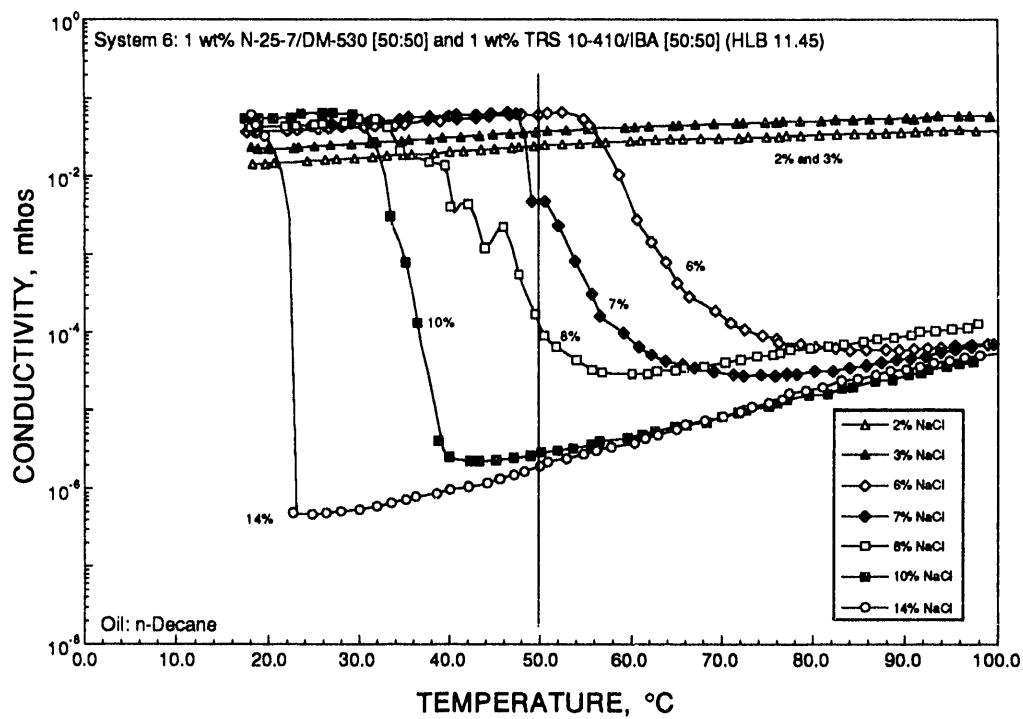
FIGURE B6. - Phase inversion temperature (PIT) for System 6 with n-decane.
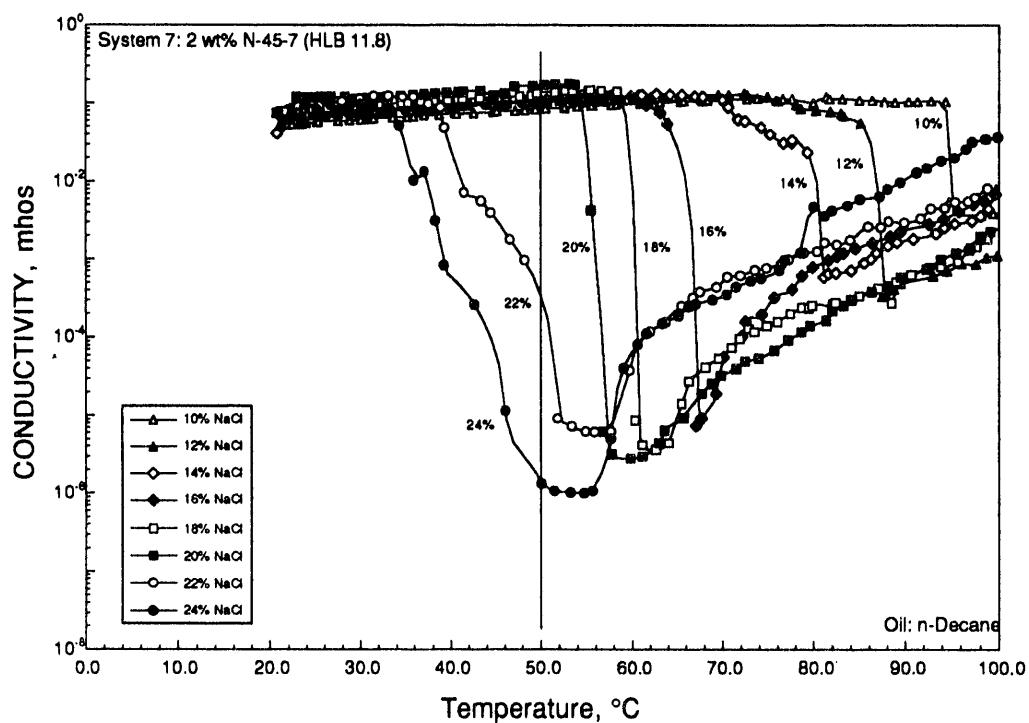
FIGURE B7. - Phase inversion temperature (PIT) for System 7 with n-decane.
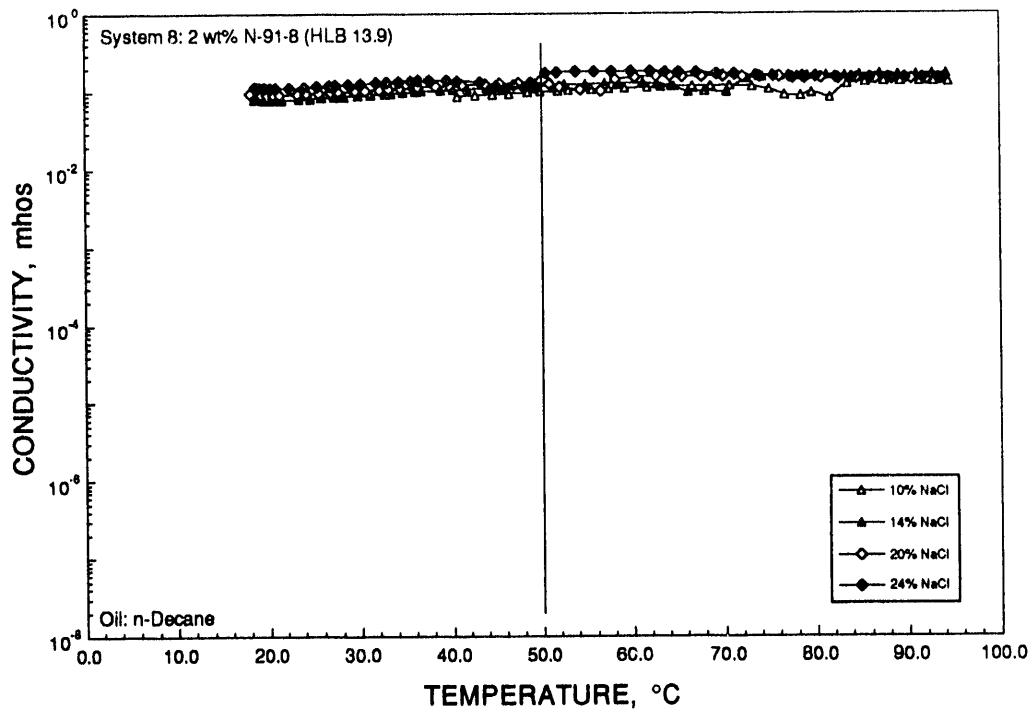
FIGURE B8. - Phase inversion temperature (PIT) for System 8 with n-decane.
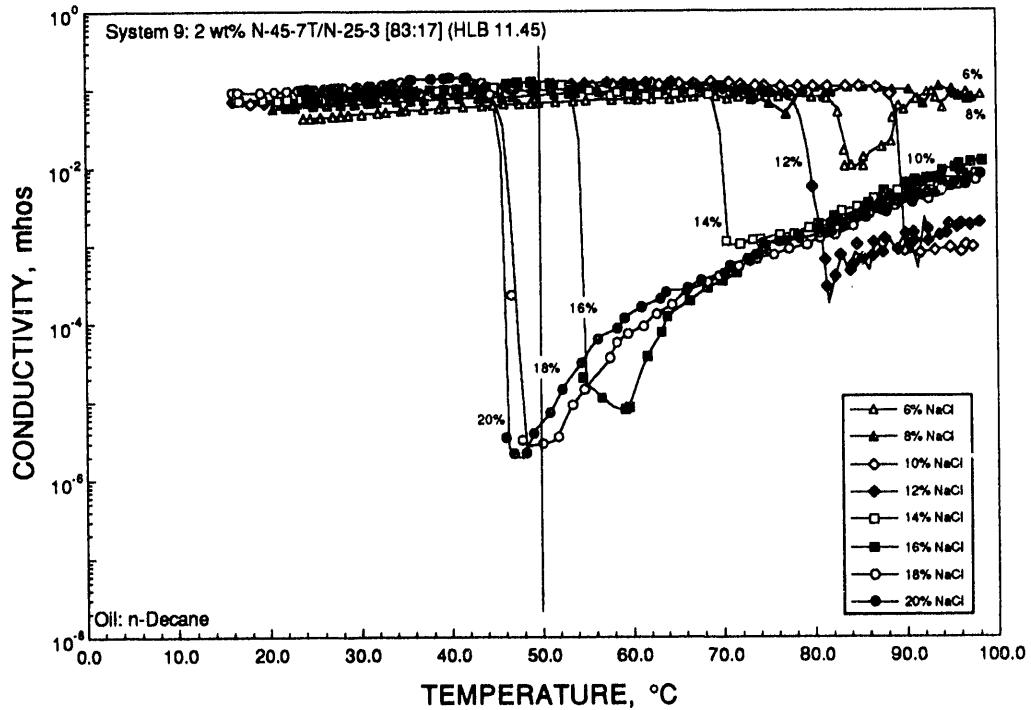
FIGURE B9. - Phase inversion temperature (PIT) for System 9 with n-decane.

66
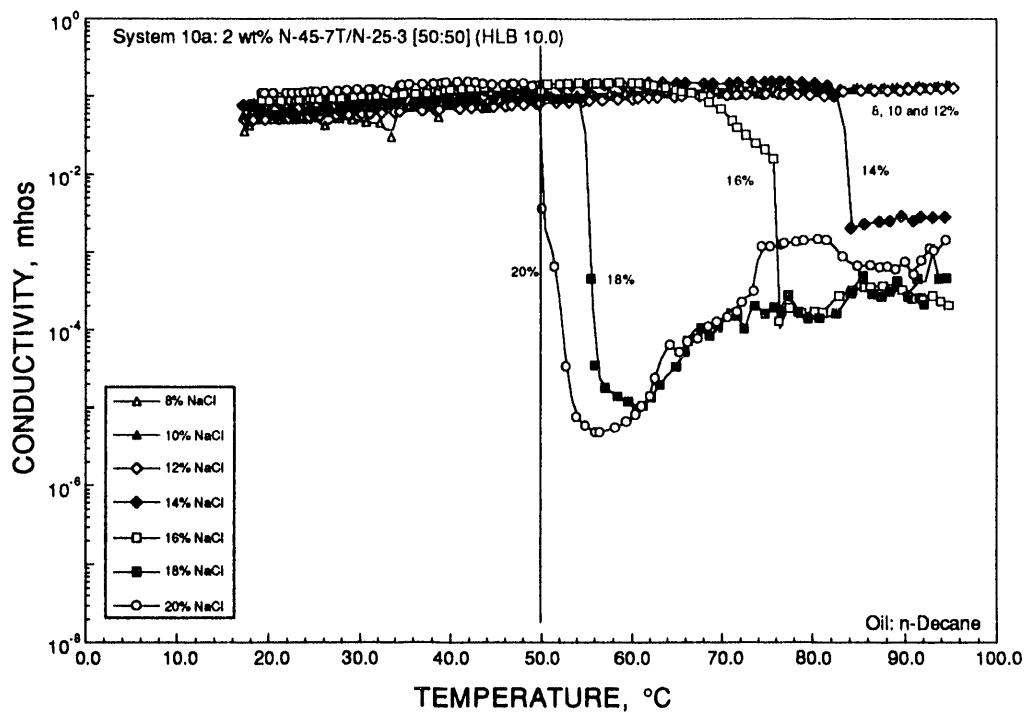
FIGURE B10a. - Phase inversion temperature (PIT) for System 10a with n-decane.
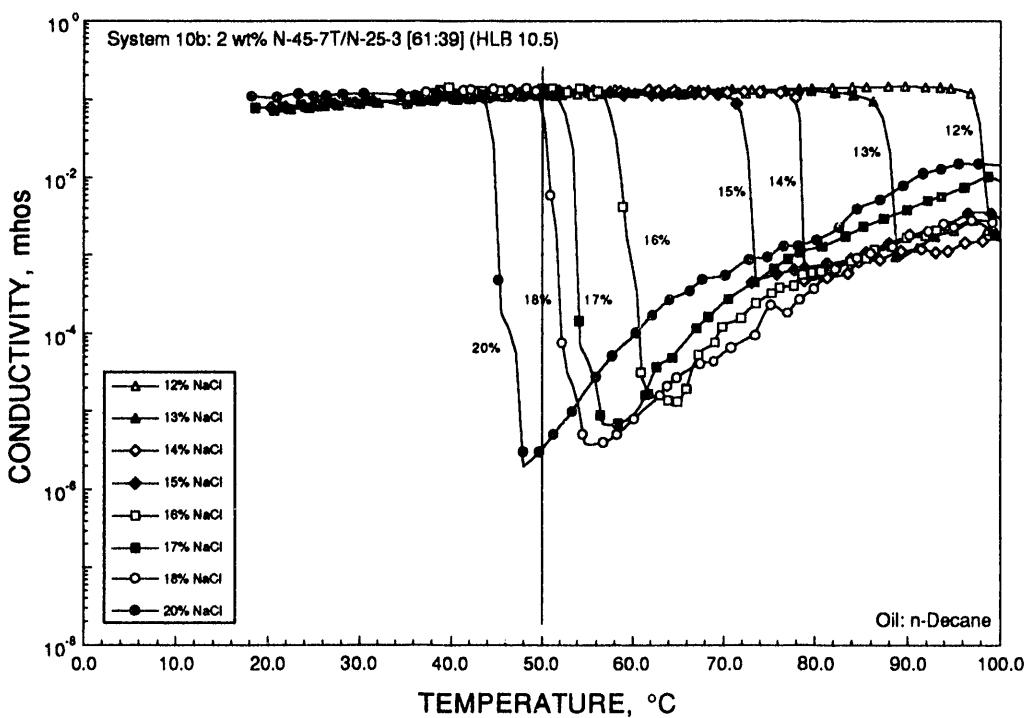
FIGURE B10b. - Phase inversion temperature (PIT) for System 10b with n-decane.
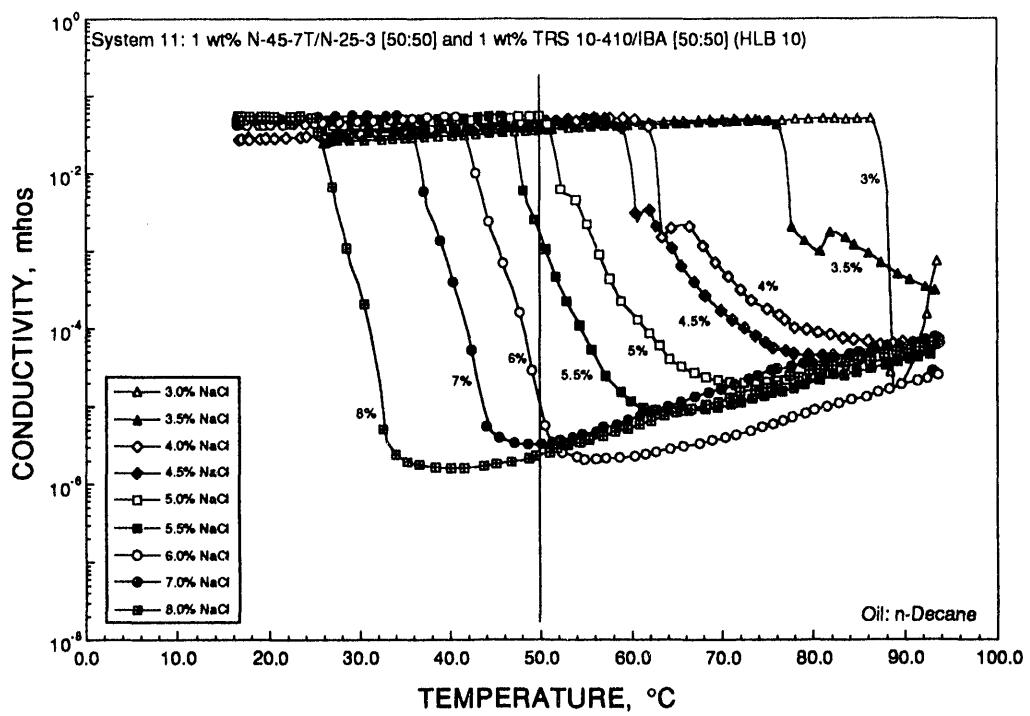
FIGURE B11. - Phase inversion temperature (PIT) for System 11 with n-decane.
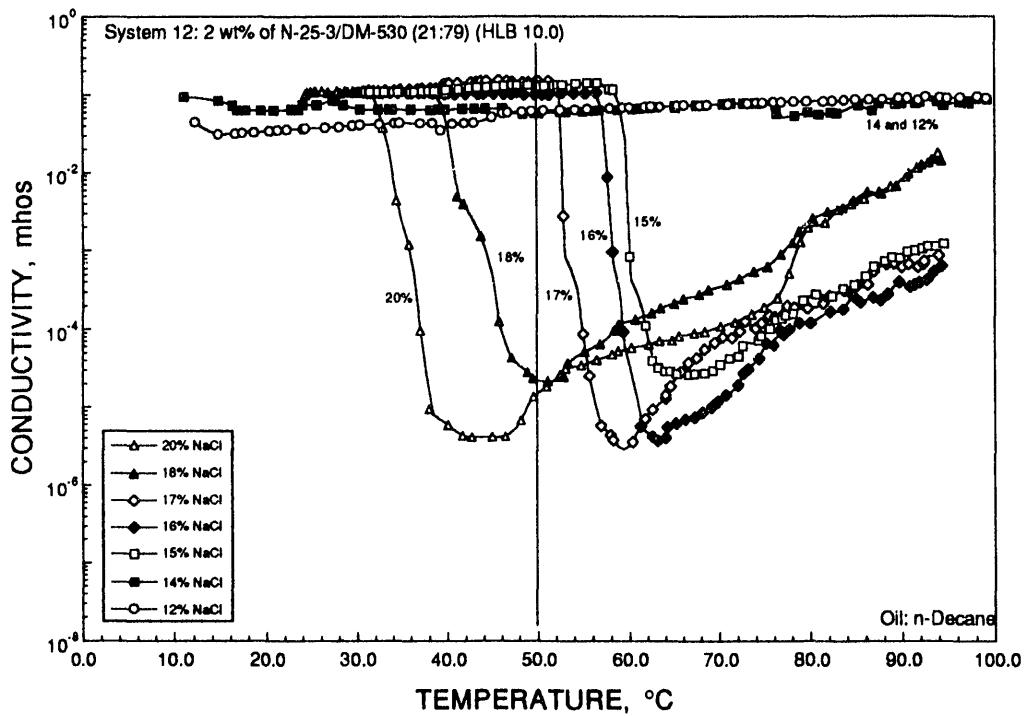
FIGURE B12. - Phase inversion temperature (PIT) for System 12 with n-decane.
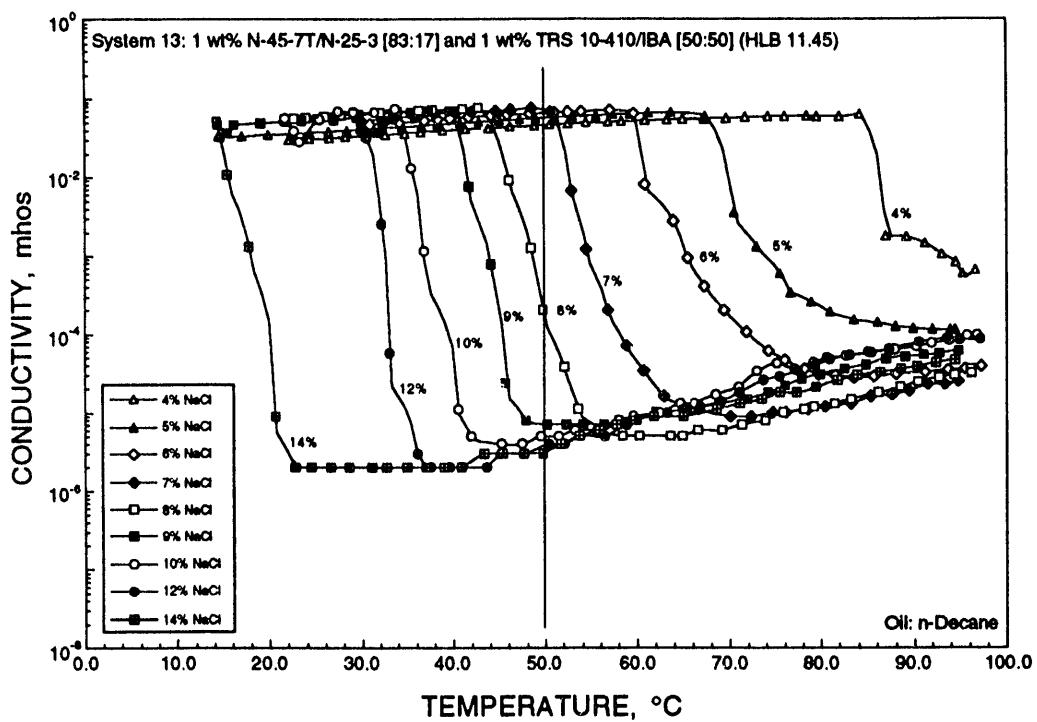
FIGURE B13. - Phase inversion temperature (PIT) for System 13 with n-decane.
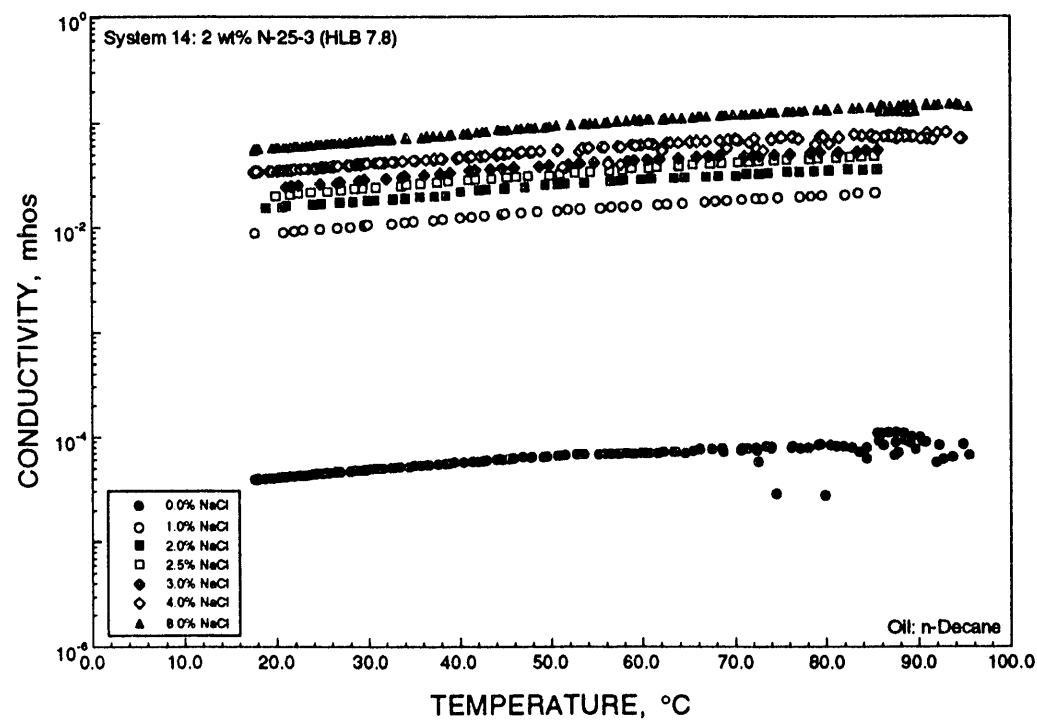

FIGURE B14. - Phase inversion temperature (PIT) for System 14 with n-decane.
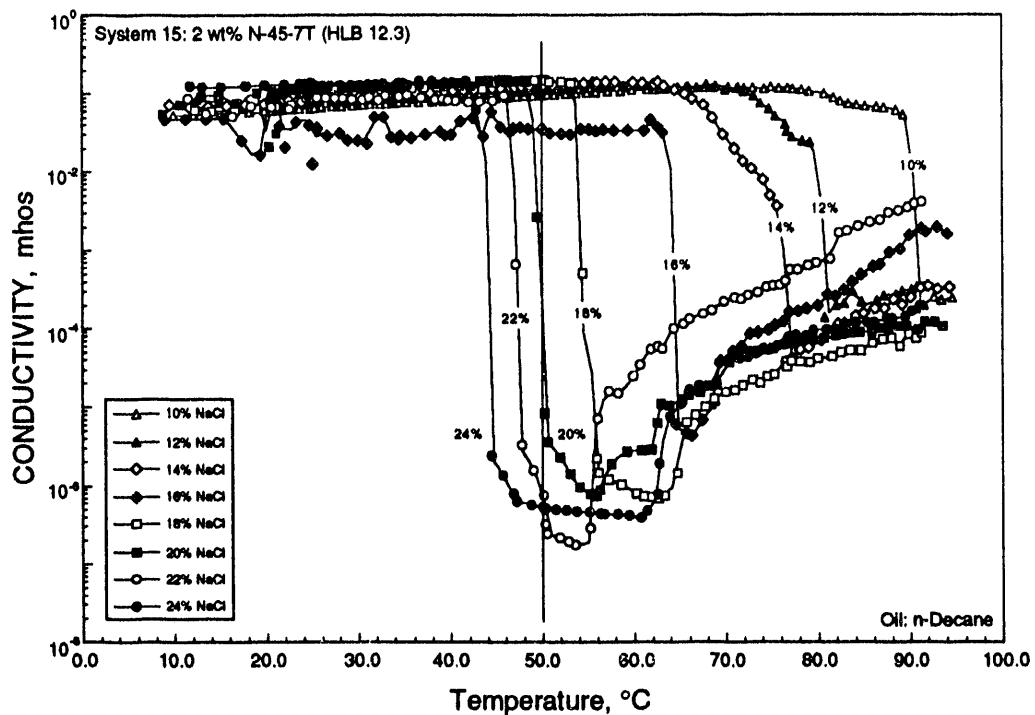
FIGURE B15. - Phase inversion temperature (PIT) for System 15 with n-decane.
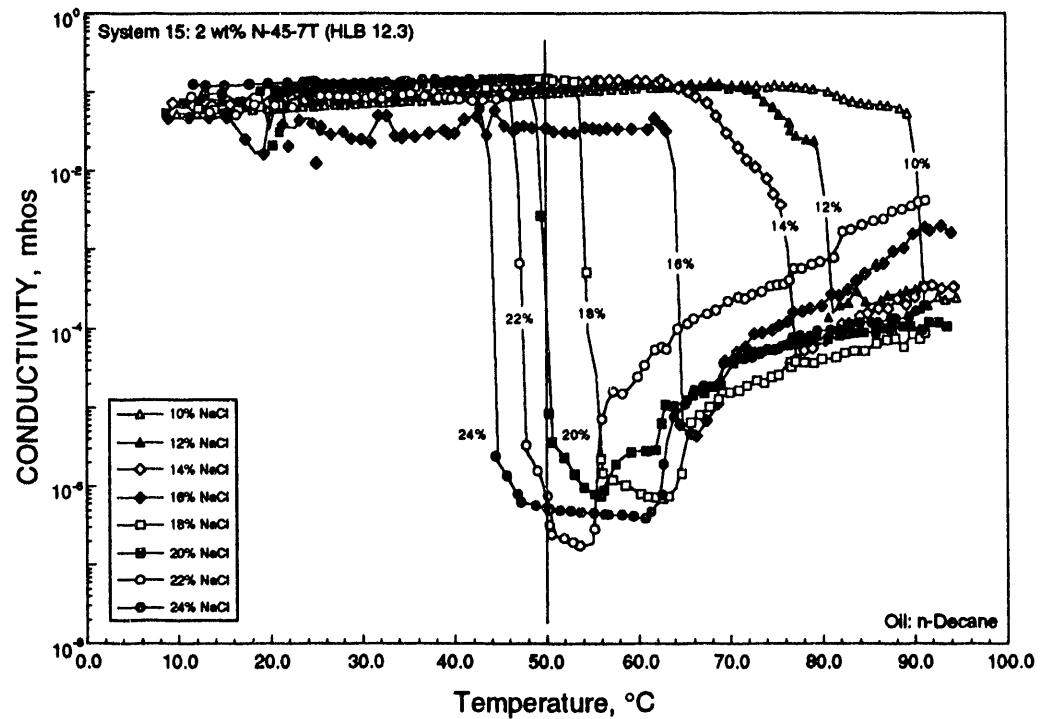
FIGURE B16. - Phase inversion temperature (PIT) for System 16 with n-decane.

70
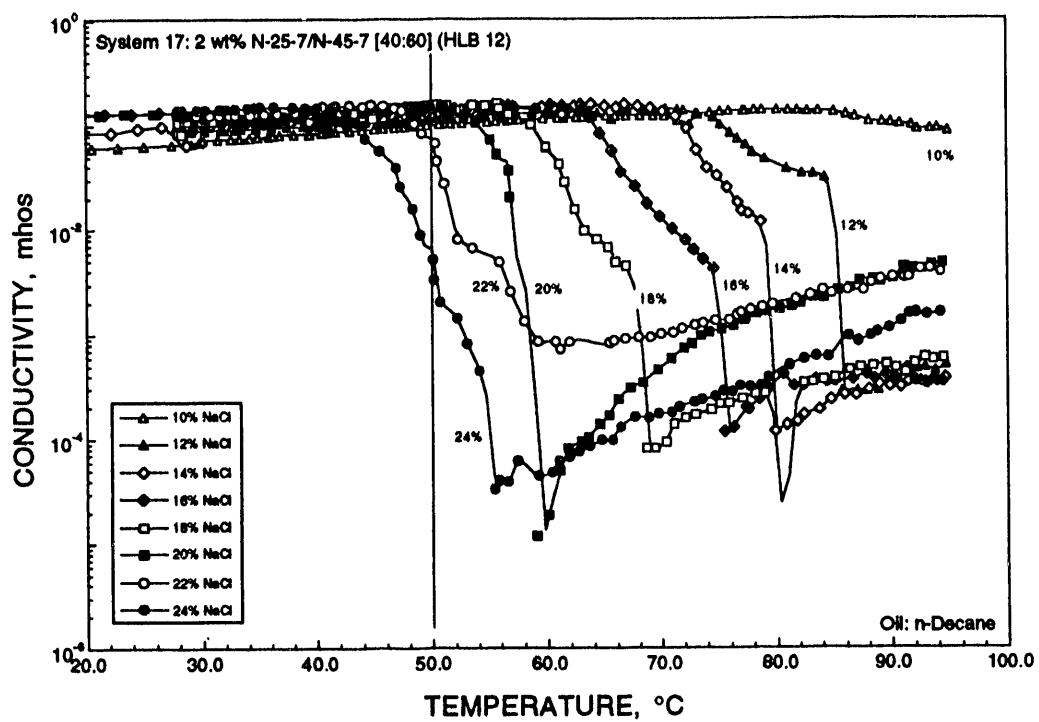
FIGURE B17. - Phase inversion temperature (PIT) for System 17 with n-decane.
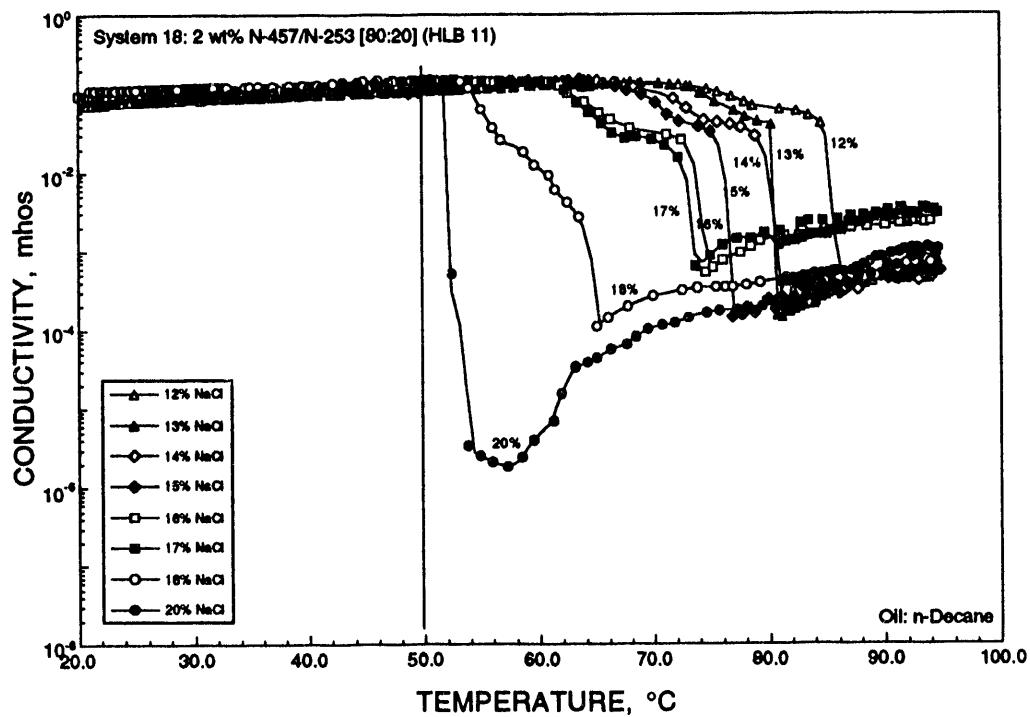
FIGURE B18. - Phase inversion temperature (PIT) for System 18 with n-decane.
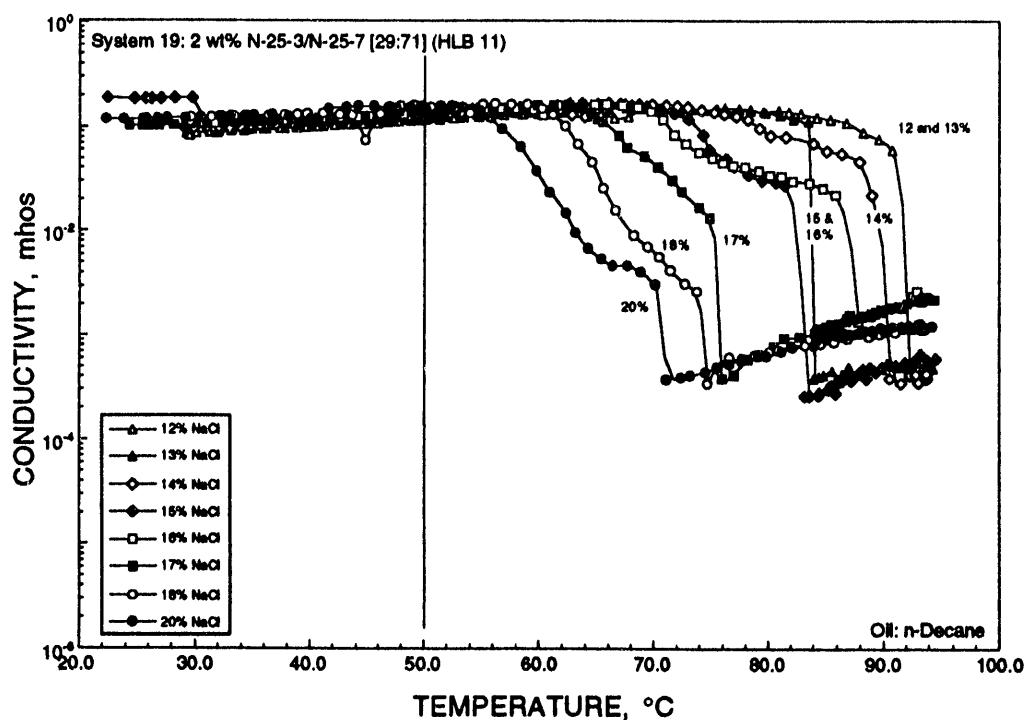
FIGURE B19. - Phase inversion temperature (PIT) for System 19 with n-decane.
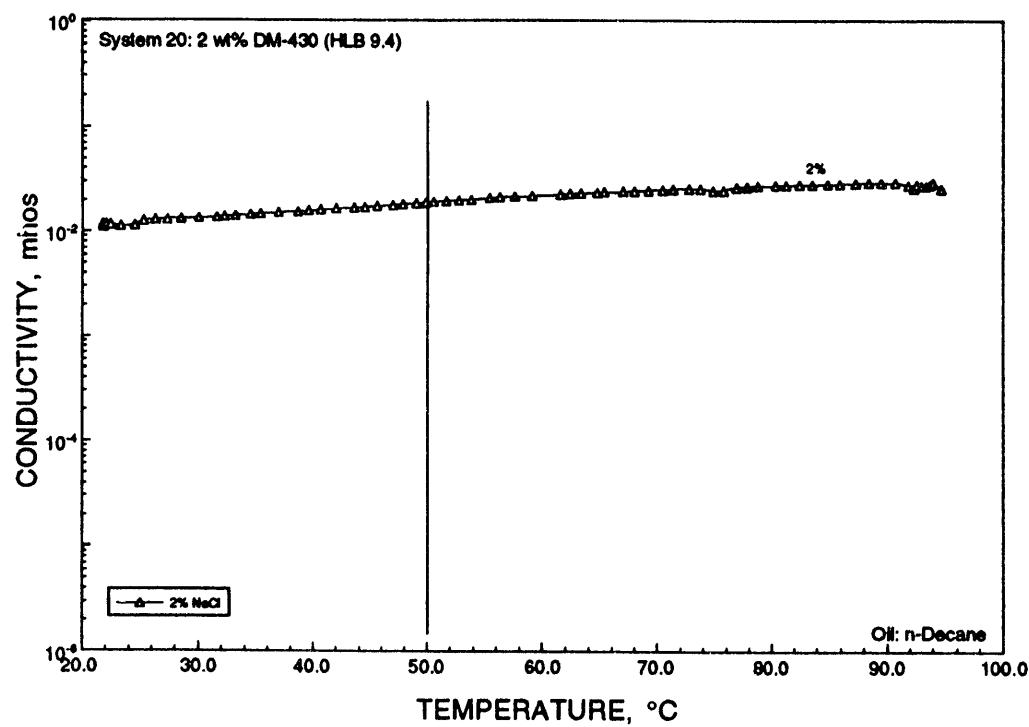
FIGURE B20. - Phase inversion temperature (PIT) for System 20 with n-decane.
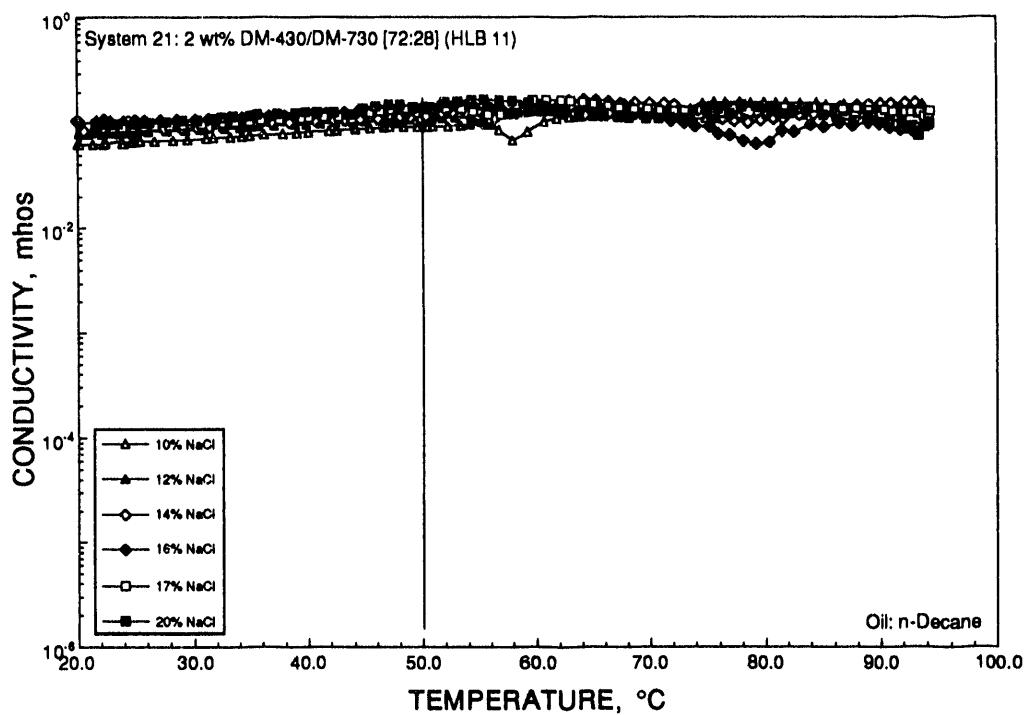
FIGURE B21. - Phase inversion temperature (PIT) for System 21 with n-decane.
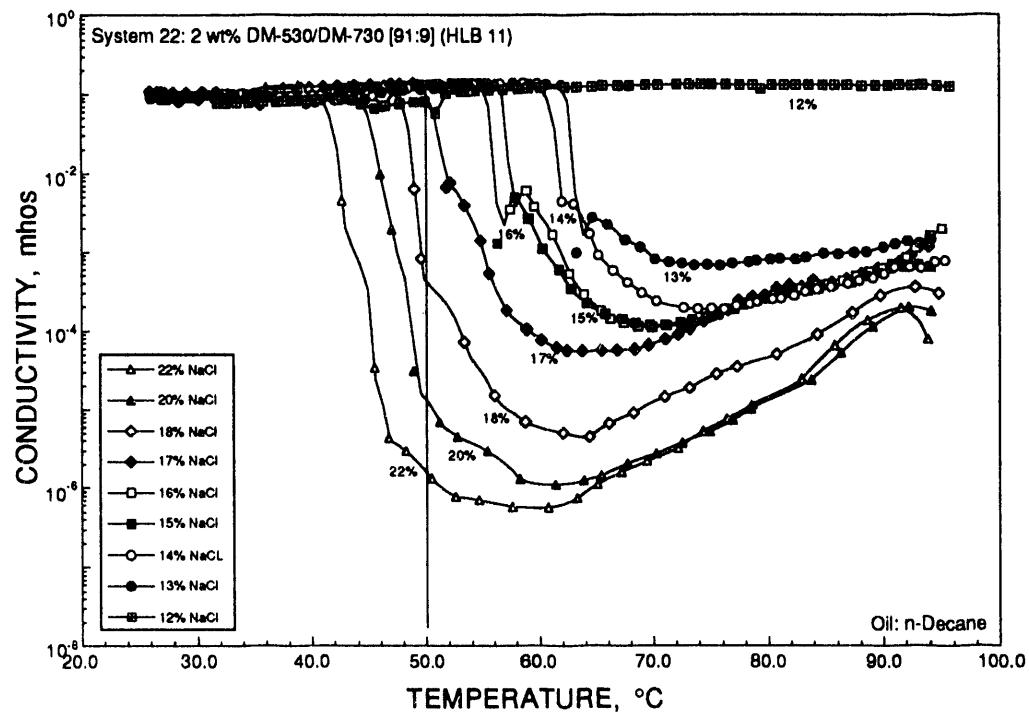
FIGURE B22. - Phase inversion temperature (PIT) for System 22 with n-decane.
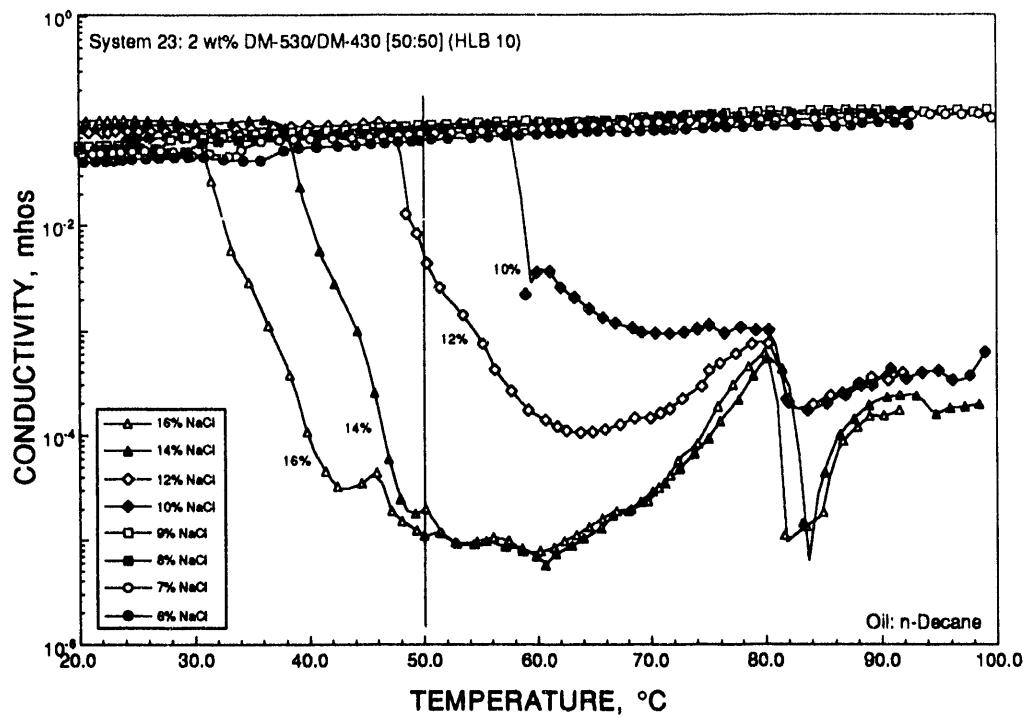
FIGURE B23. - Phase inversion temperature (PIT) for System 23 with n-decane.
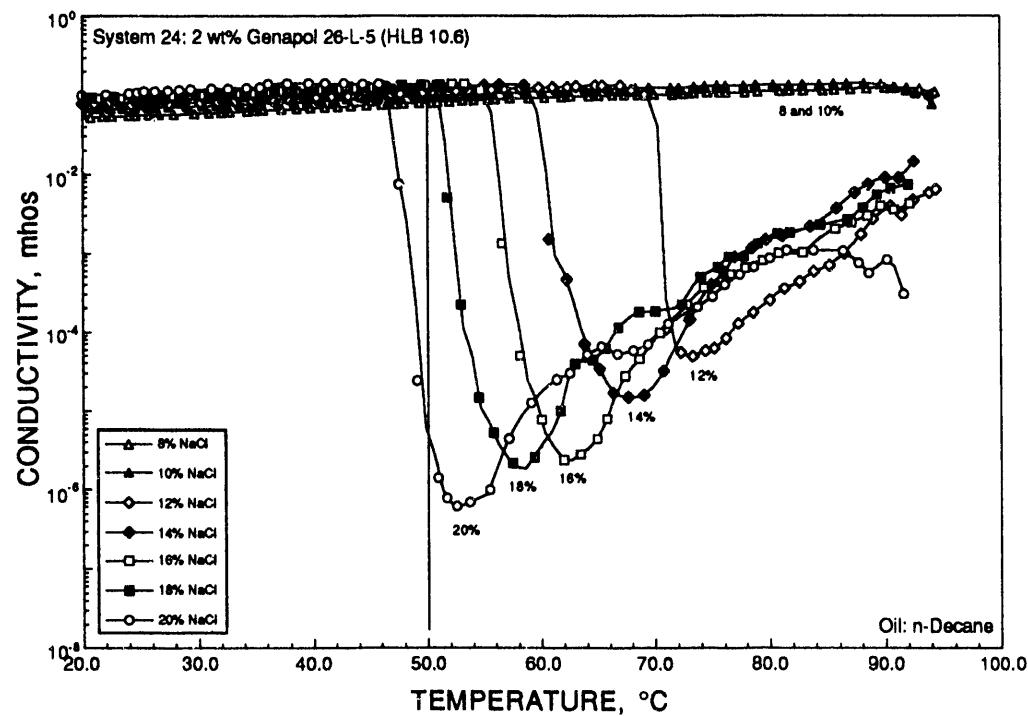
FIGURE B24. - Phase inversion temperature (PIT) for System 24 with n-decane.
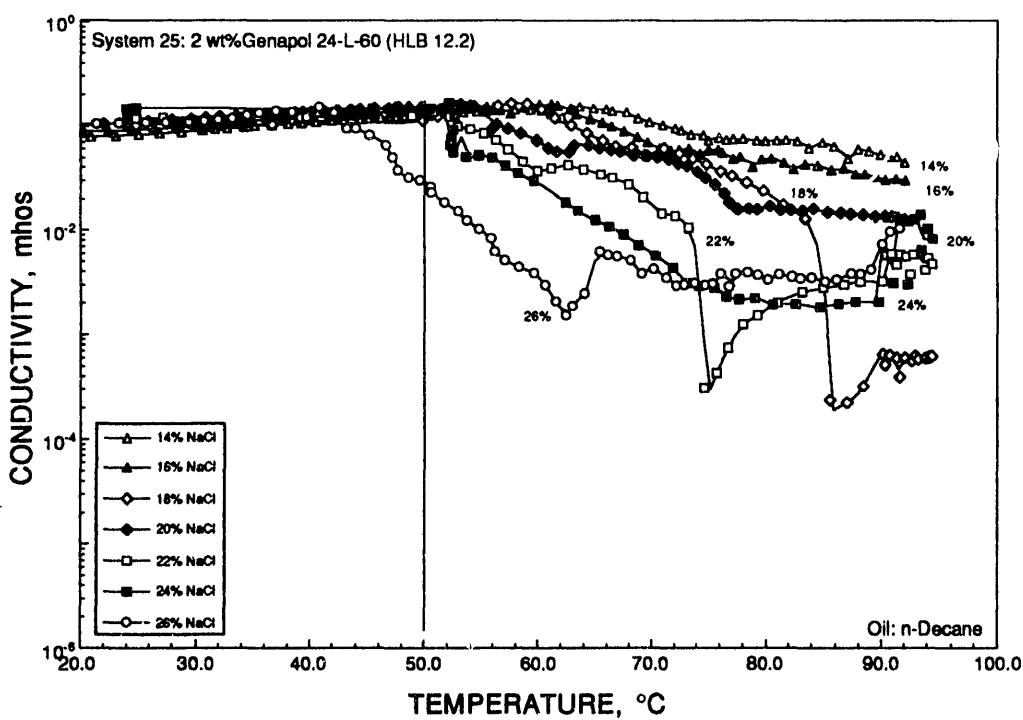
FIGURE B25. - Phase inversion temperature (PIT) for System 25 with n-decane.
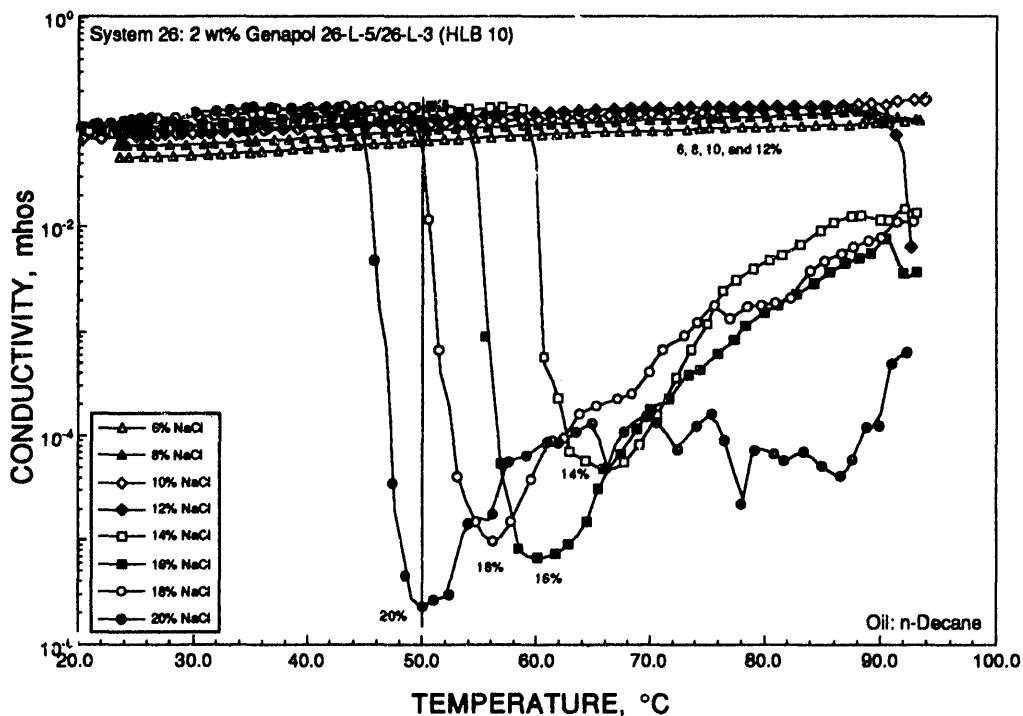

FIGURE B26. - Phase inversion temperature (PIT) for System 26 with n-decane.
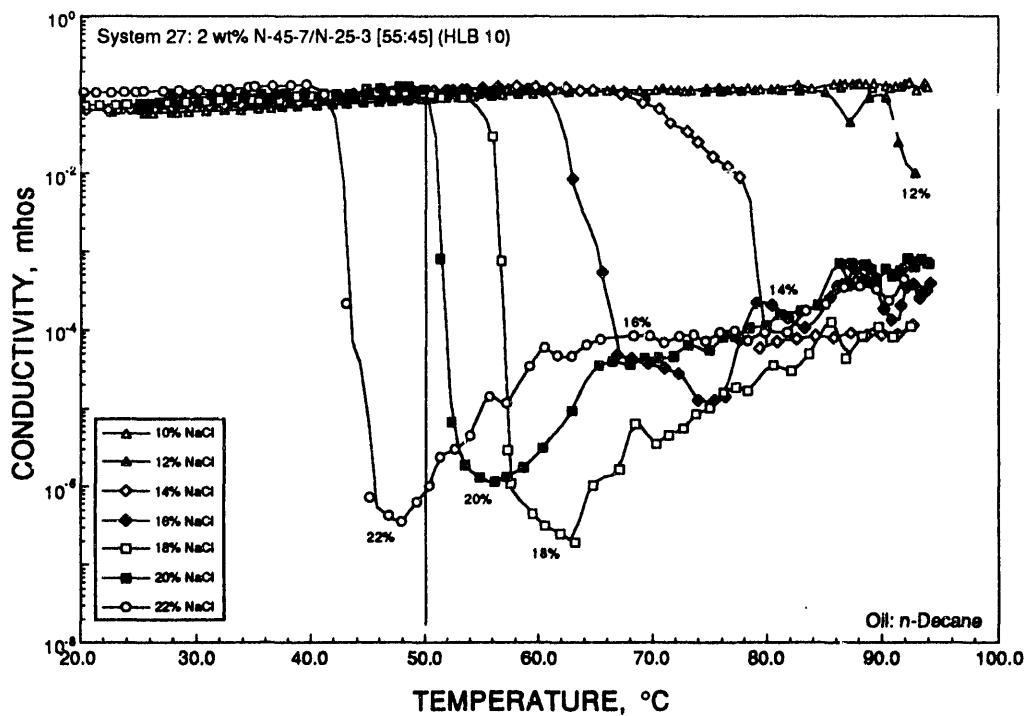
FIGURE B27. - Phase inversion temperature (PIT) for System 27 with n-decane.
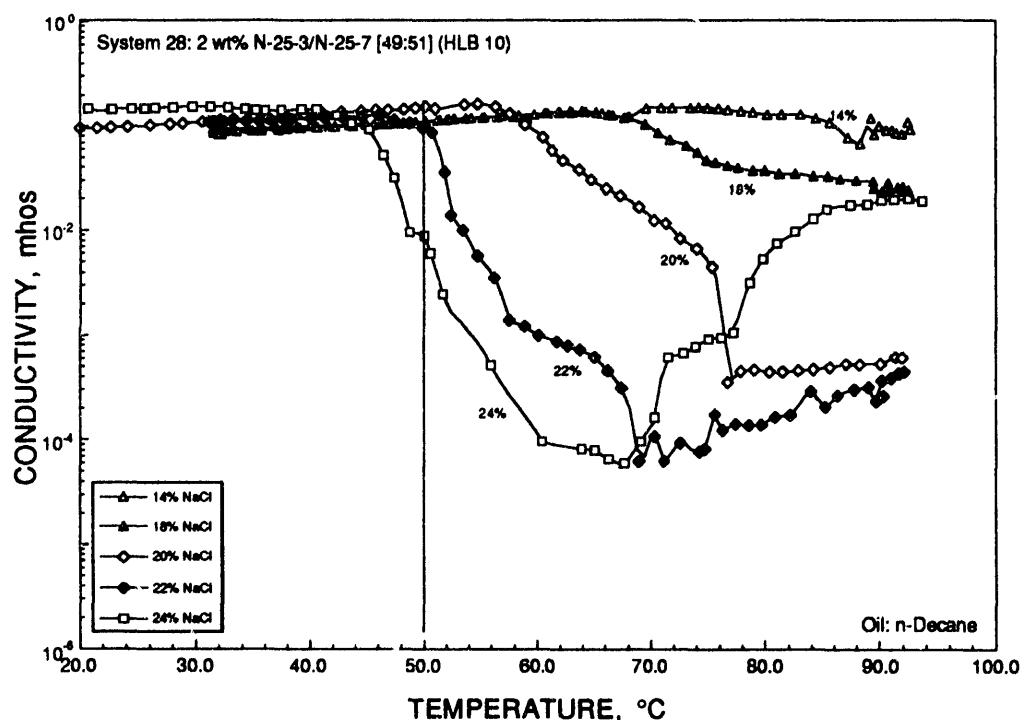

FIGURE B28. - Phase inversion temperature (PIT) for System 28 with n-decane.
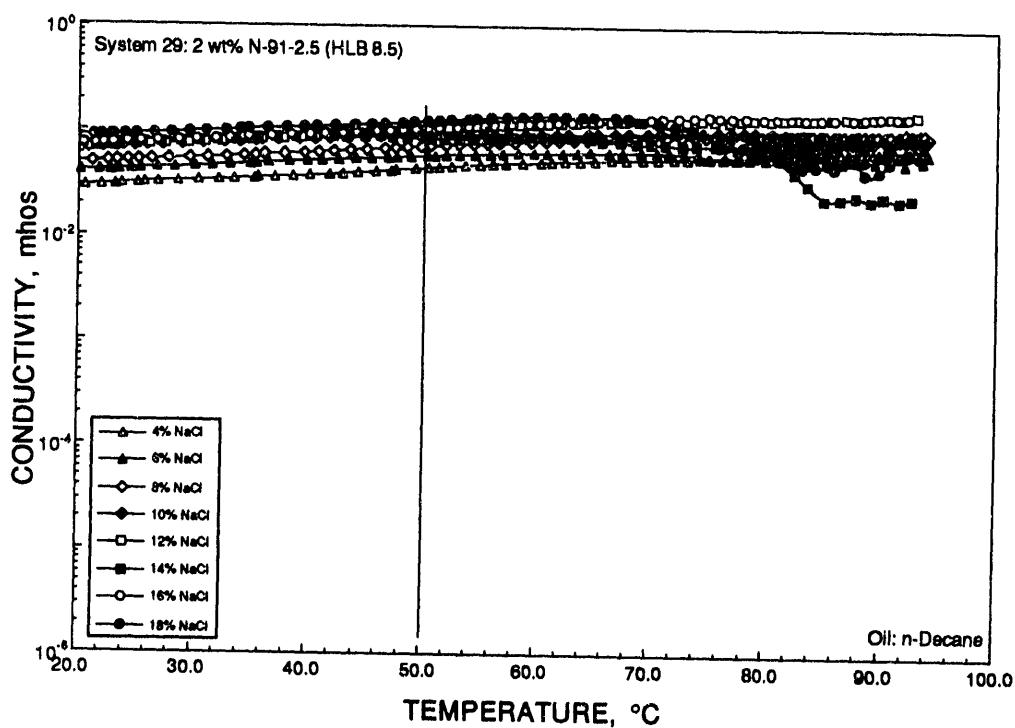
FIGURE B29. - Phase inversion temperature (PIT) for System 29 with n-decane.
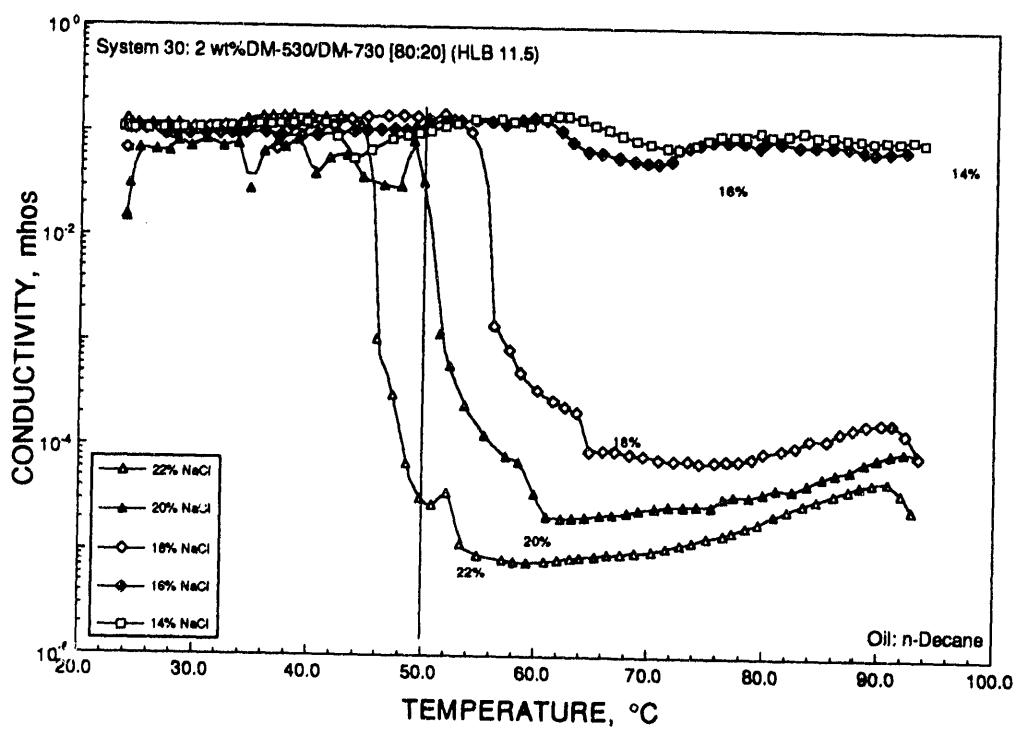
FIGURE B30. - Phase inversion temperature (PIT) for System 30 with n-decane.
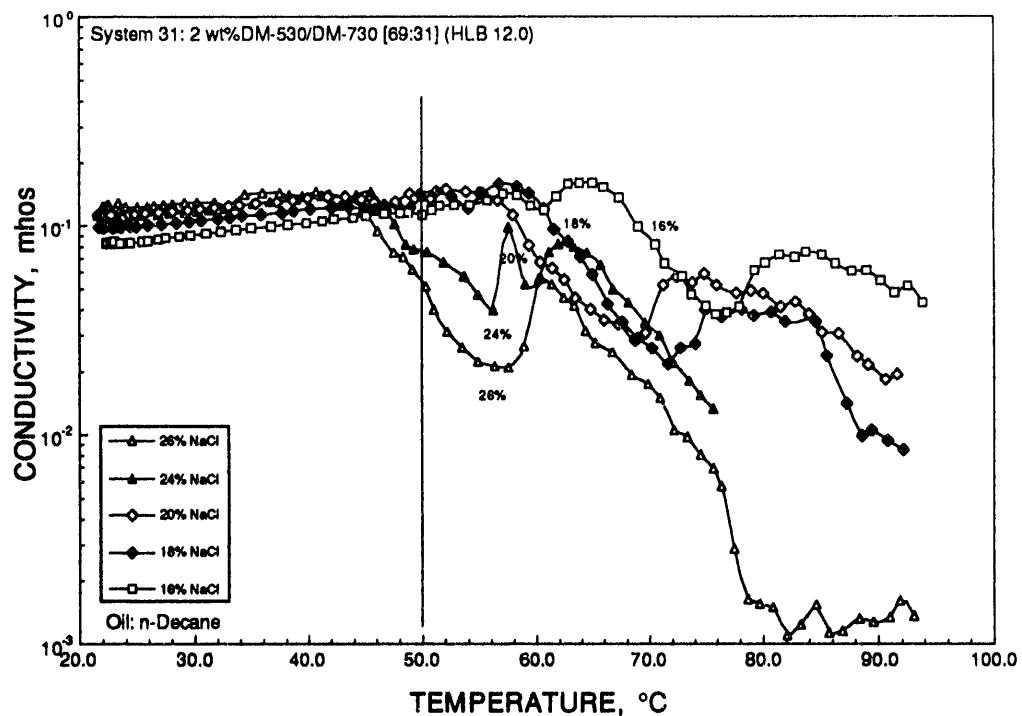
FIGURE B31. - Phase inversion temperature (PIT) for System 31 with n-decane.
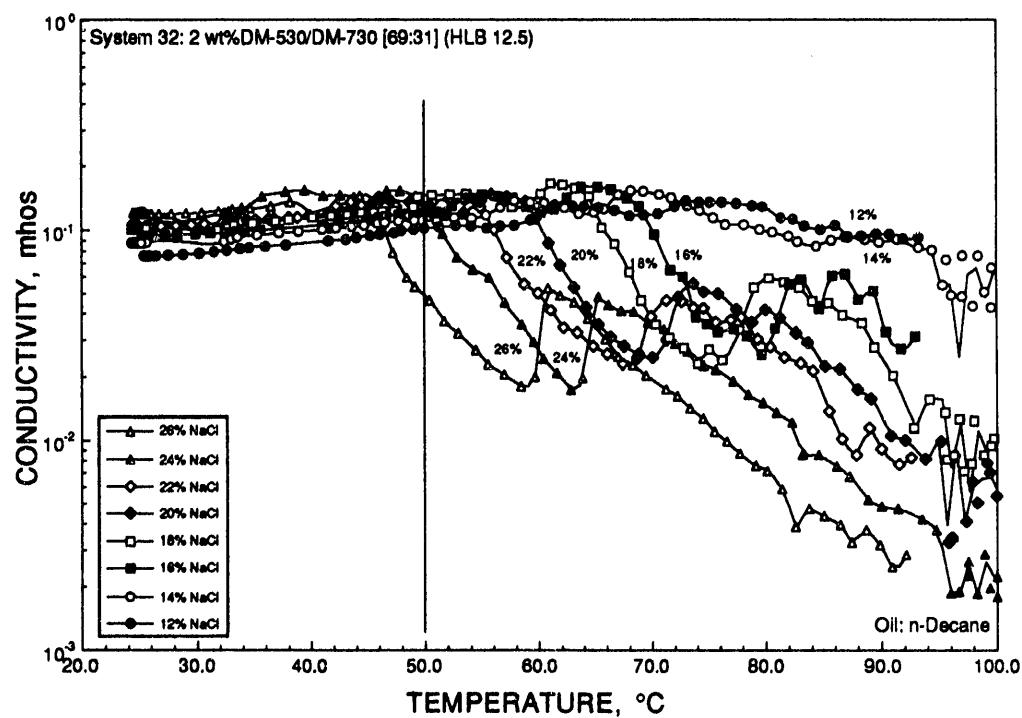
FIGURE B32. - Phase inversion temperature (PIT) for System 32 with n-decane.
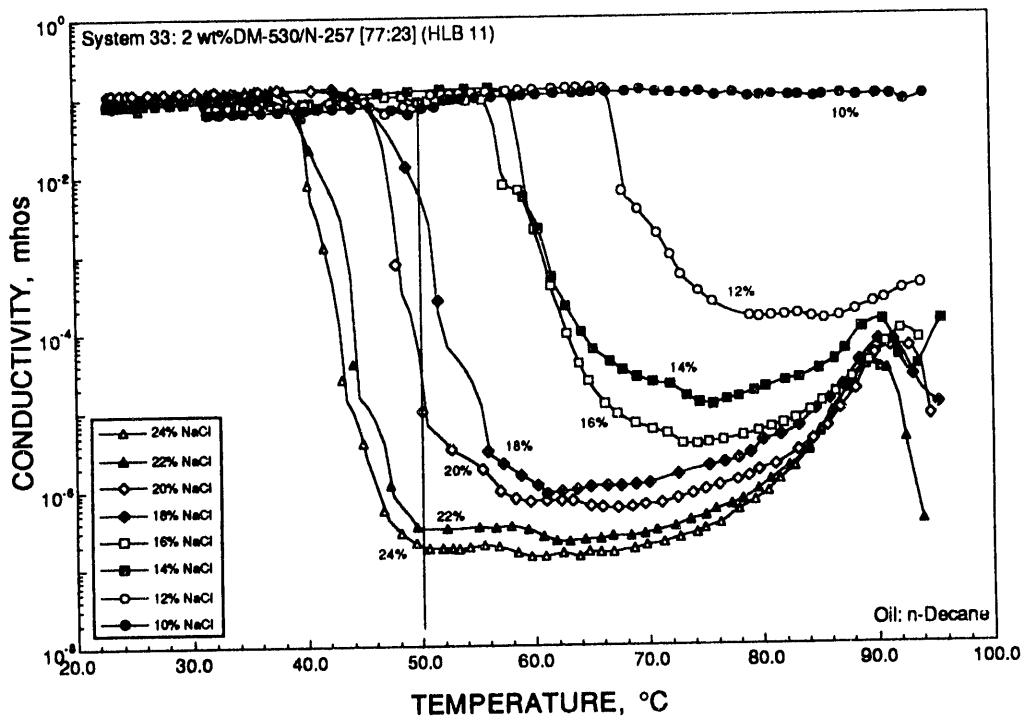
FIGURE B33. - Phase inversion temperature (PIT) for System 33 with n-decane.
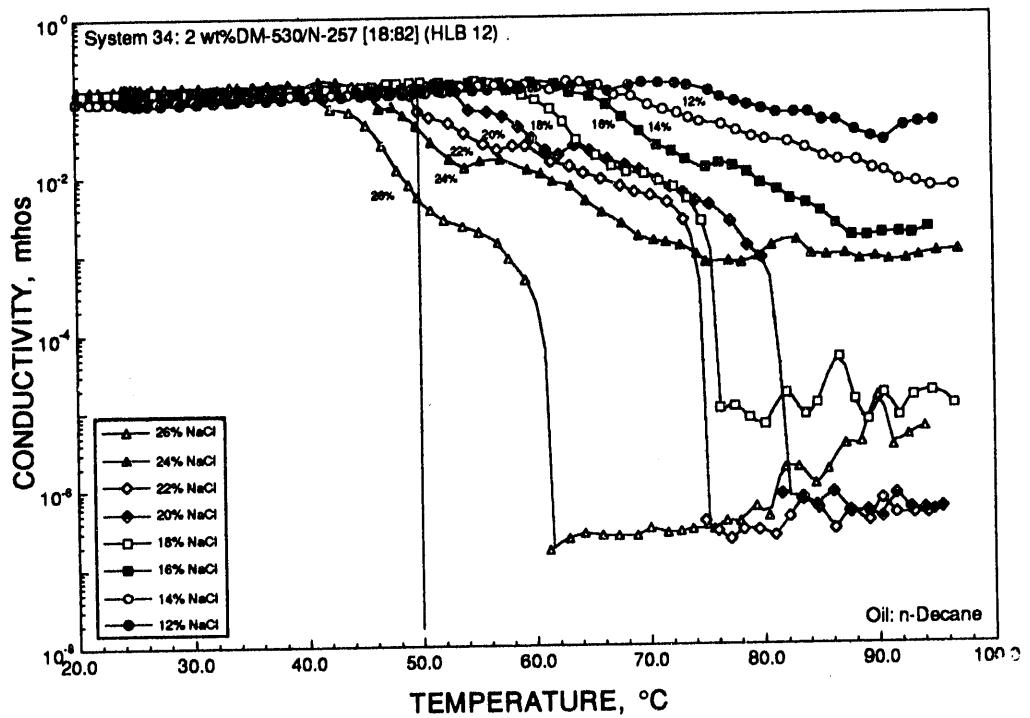

FIGURE B34. - Phase inversion temperature (PIT) for System 34 with n-decane.
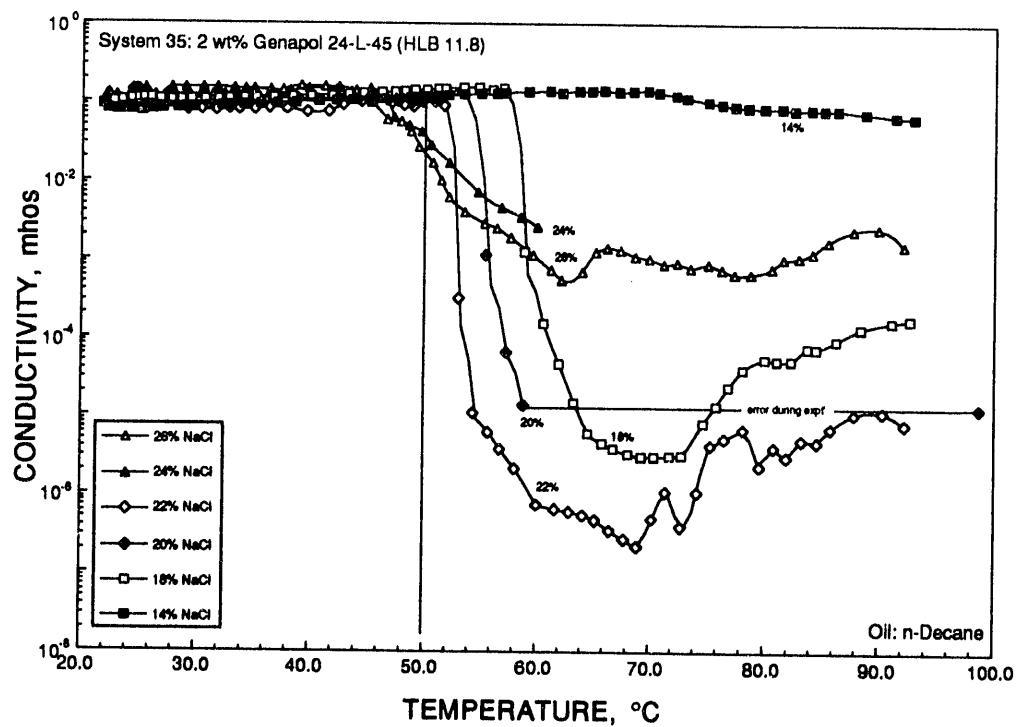
FIGURE B35. - Phase inversion temperature (PIT) for System 35 with n-decane.
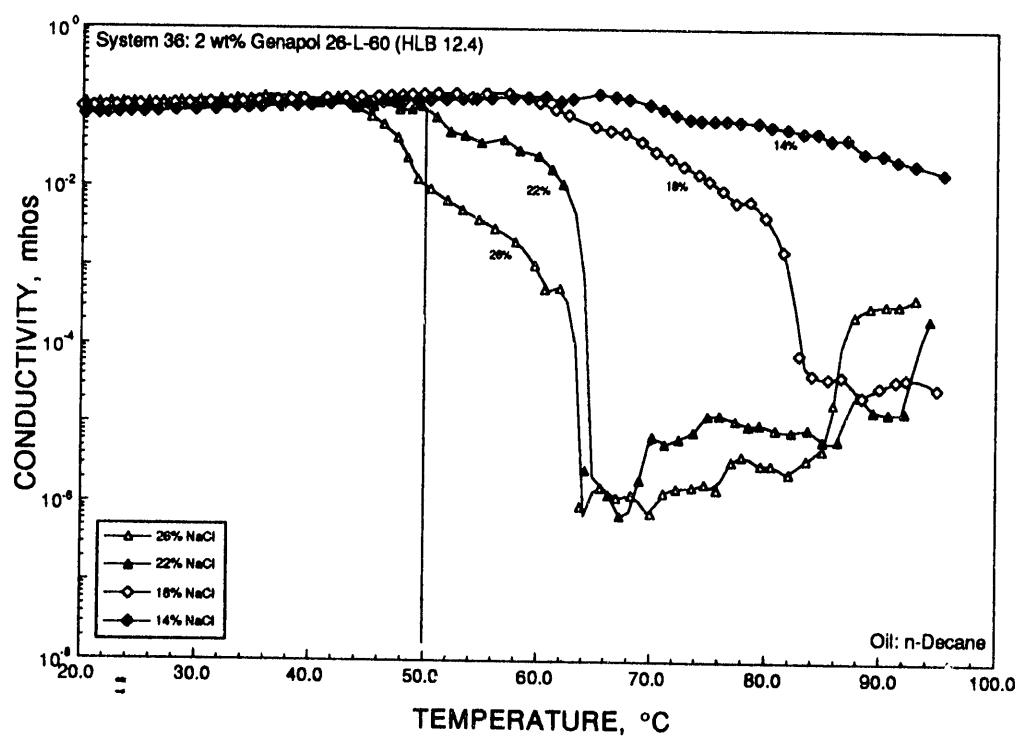
FIGURE B36. - Phase inversion temperature (PIT) for System 36 with n-decane.

80
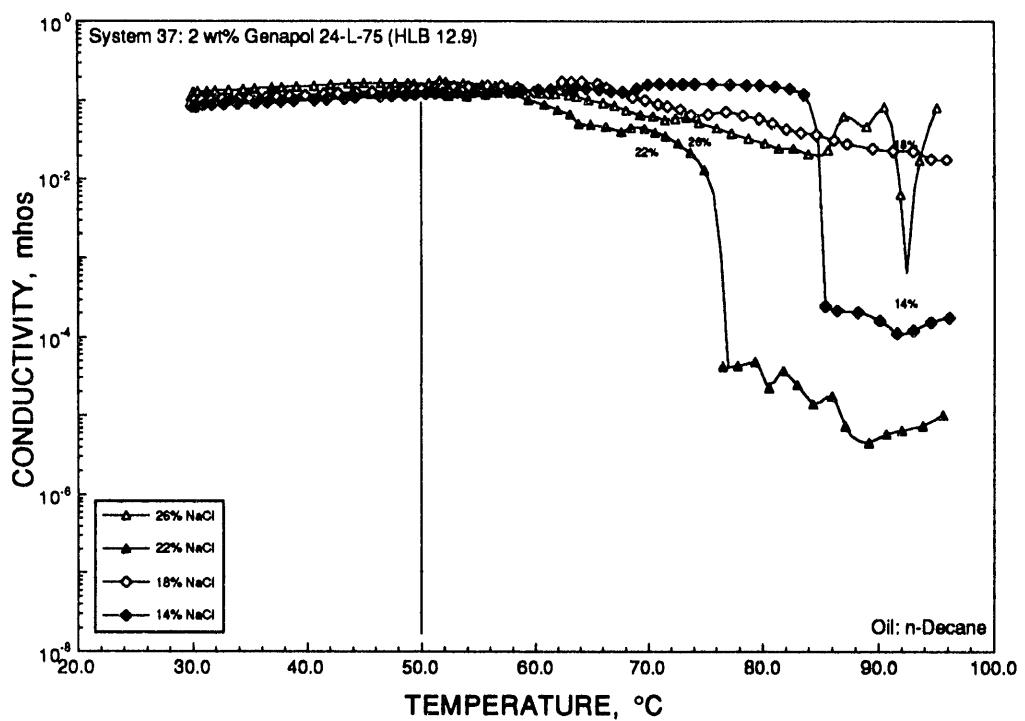
FIGURE B37. - Phase inversion temperature (PIT) for System 37 with n-decane.
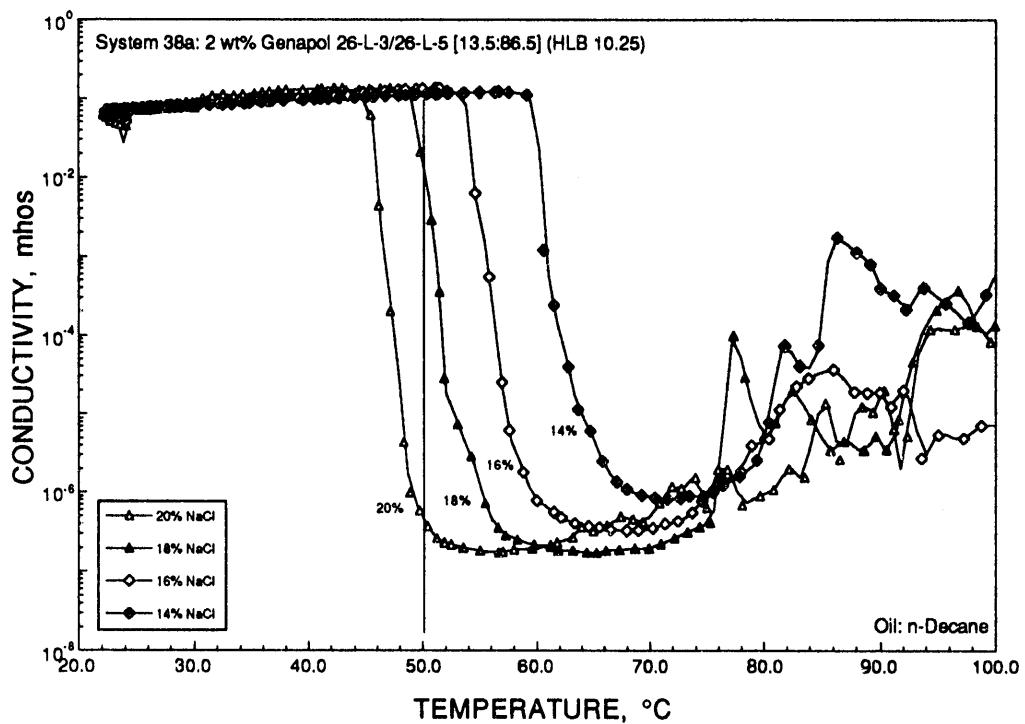
FIGURE B38a. - Phase inversion temperature (PIT) for System 38a with n-decane.
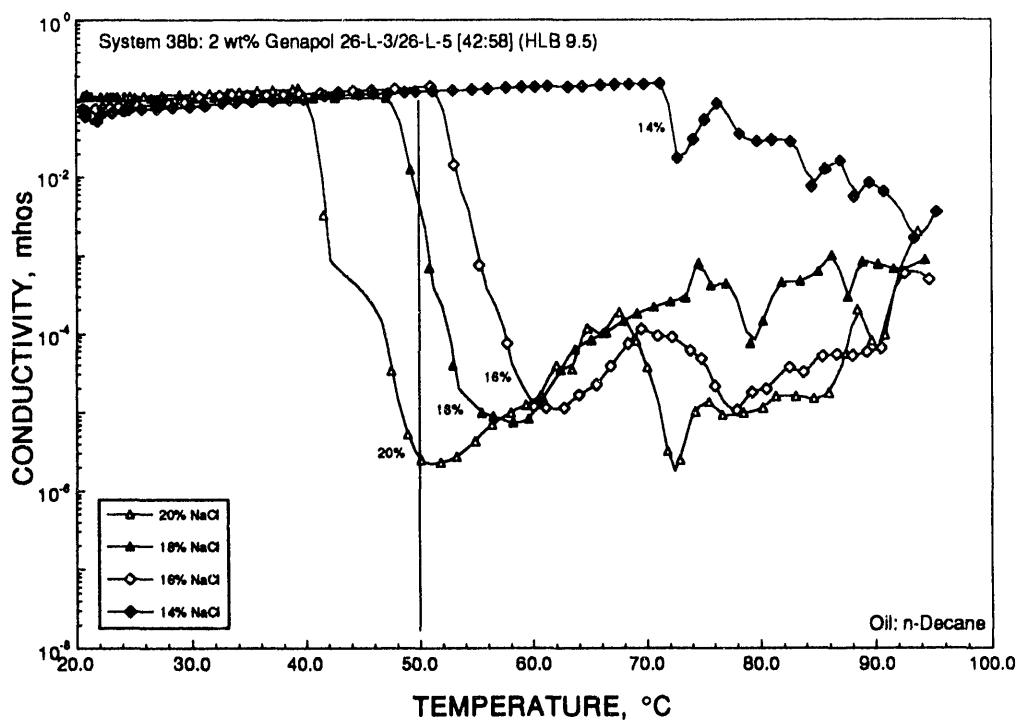
FIGURE B38b. - Phase inversion temperature (PIT) for System 38b with n-decane.
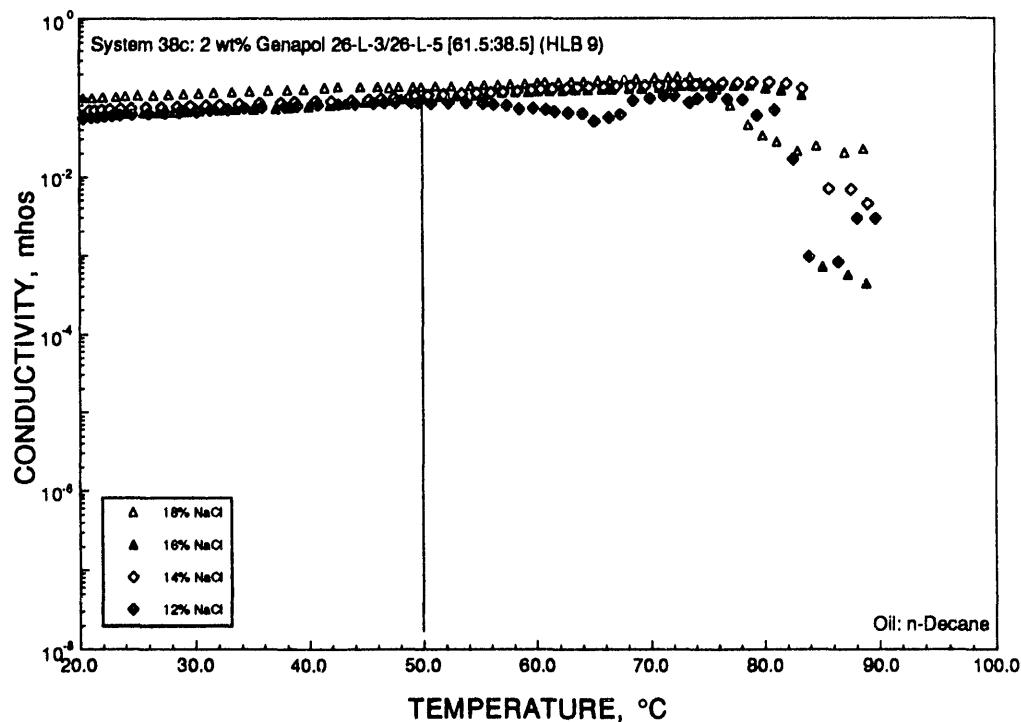
FIGURE B38c. - Phase inversion temperature (PIT) for System 38c with n-decane.

82
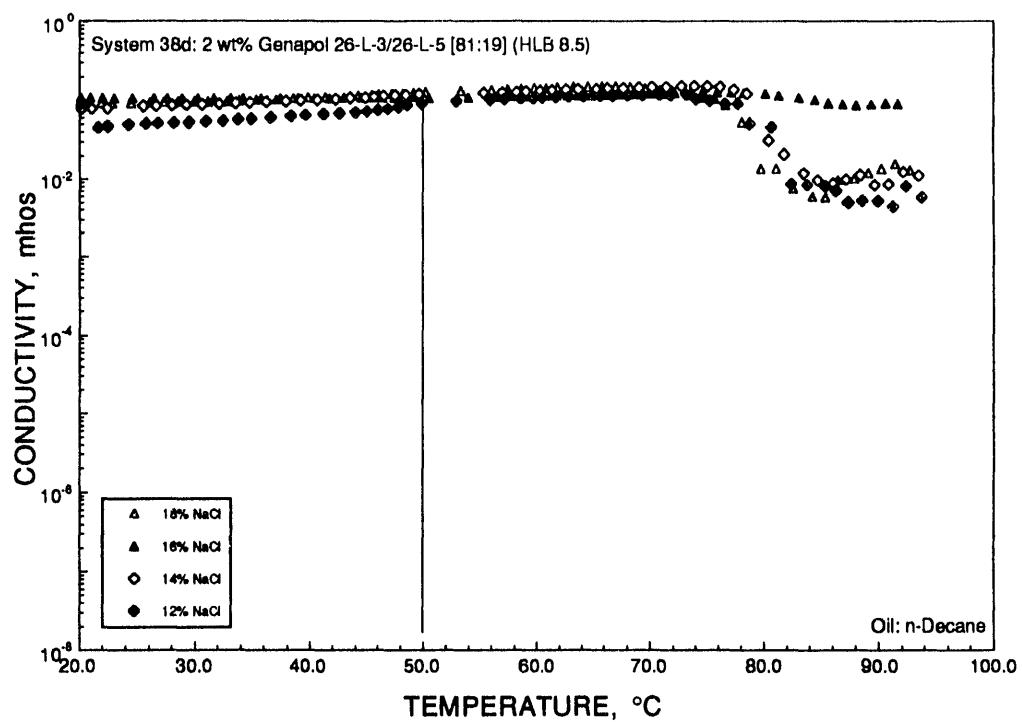
FIGURE B38d. - Phase inversion temperature (PIT) for System 38d with n-decane.
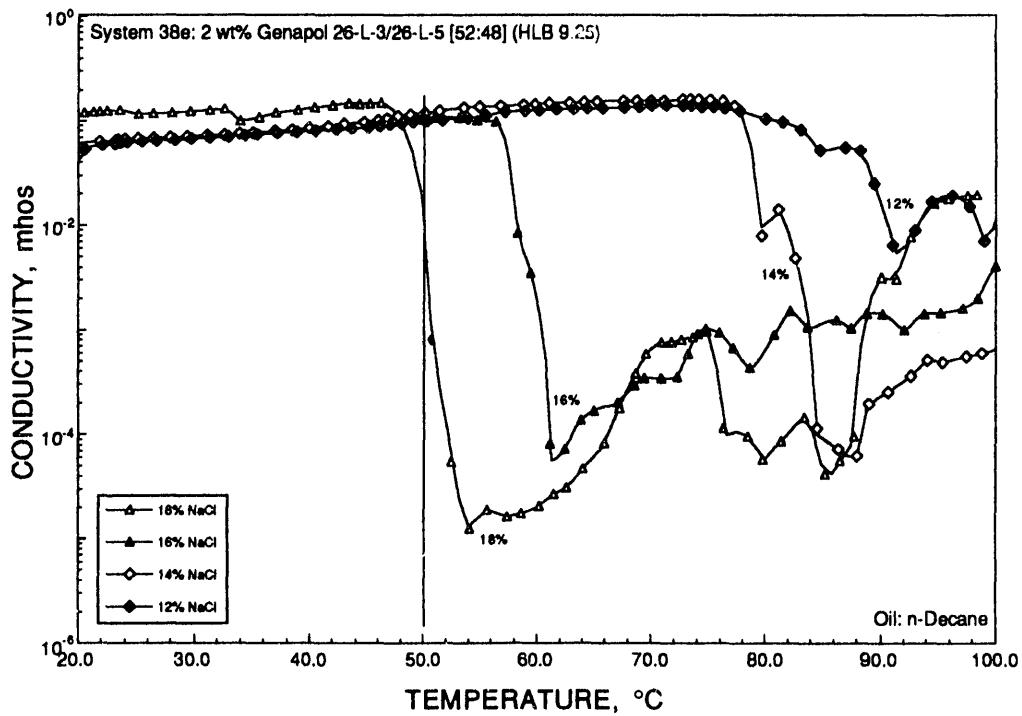
FIGURE B38e. - Phase inversion temperature (PIT) for System 38e with n-decane.
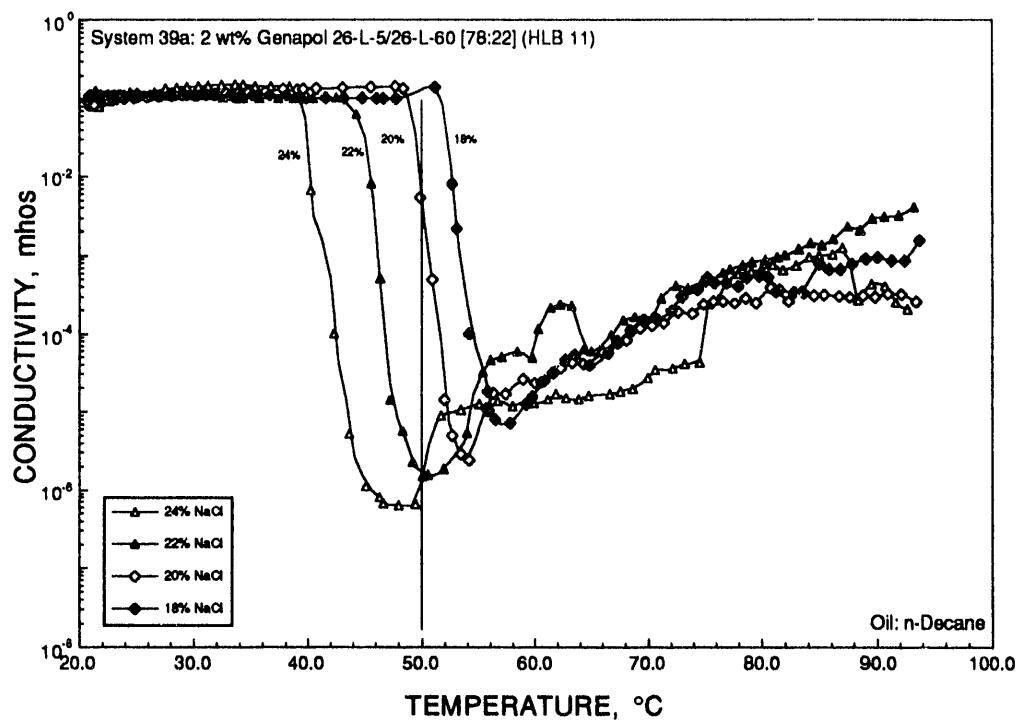
FIGURE B39a. - Phase inversion temperature (PIT) for System 39a with n-decane.
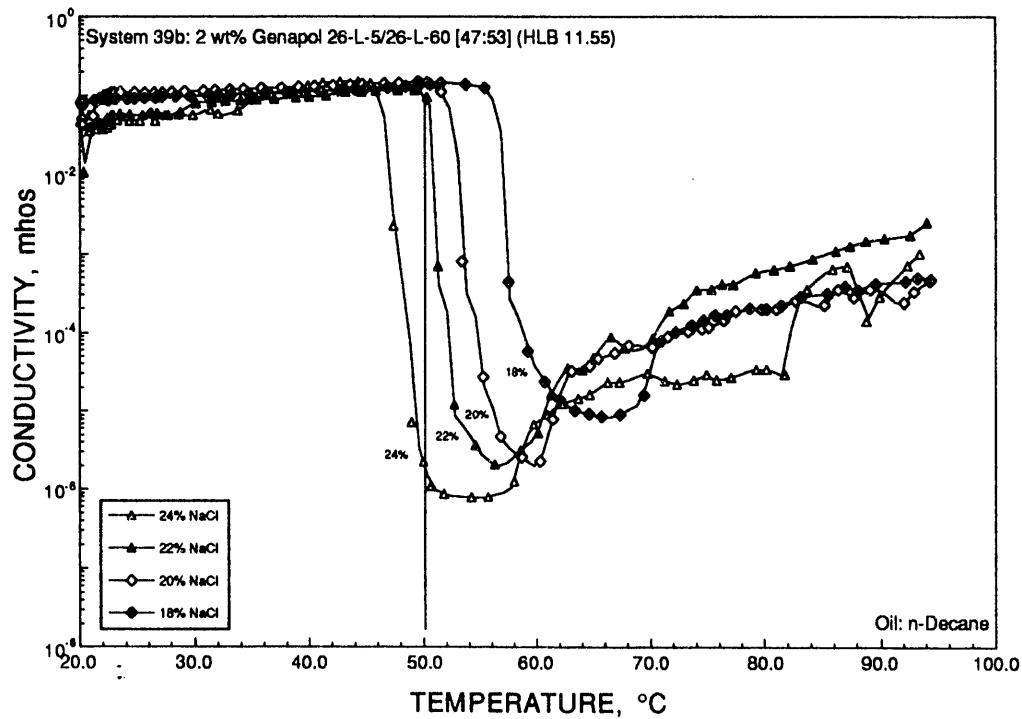
FIGURE B39b. - Phase inversion temperature (PIT) for System 39b with n-decane.
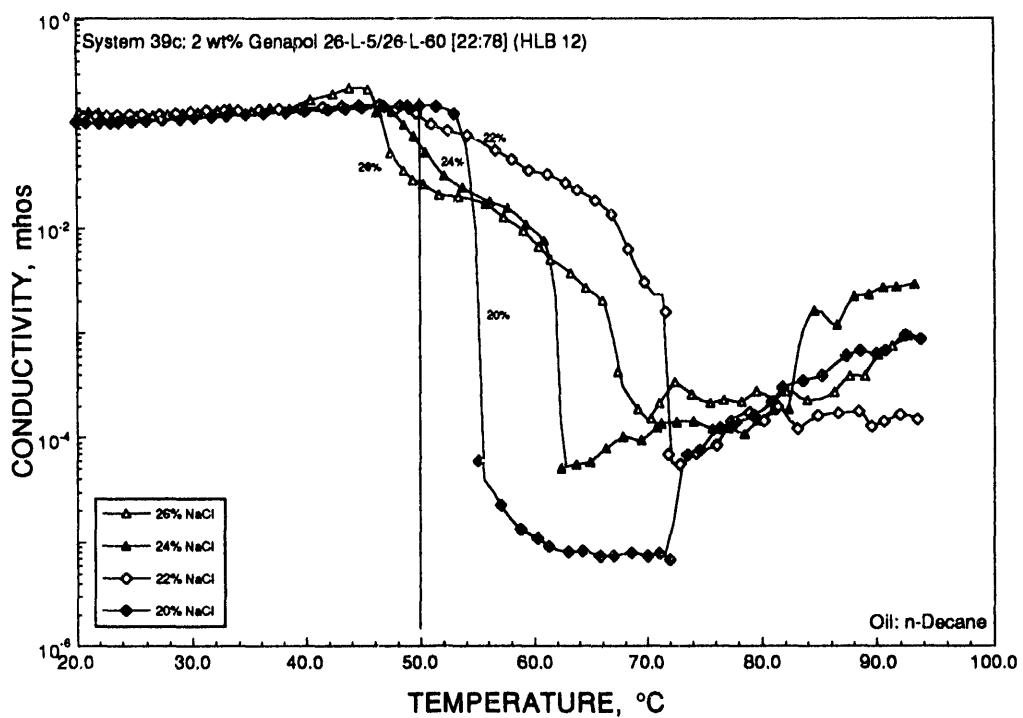
FIGURE B39c. - Phase inversion temperature (PIT) for System 39c with n-decane.
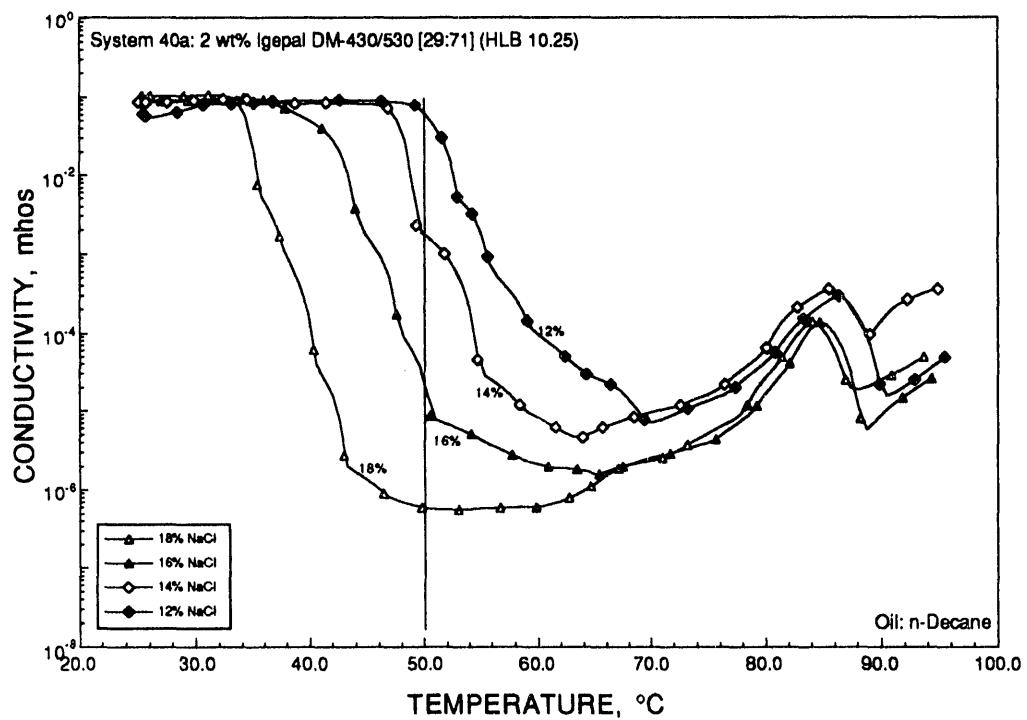
FIGURE B40a. - Phase inversion temperature (PIT) for System 40a with n-decane.
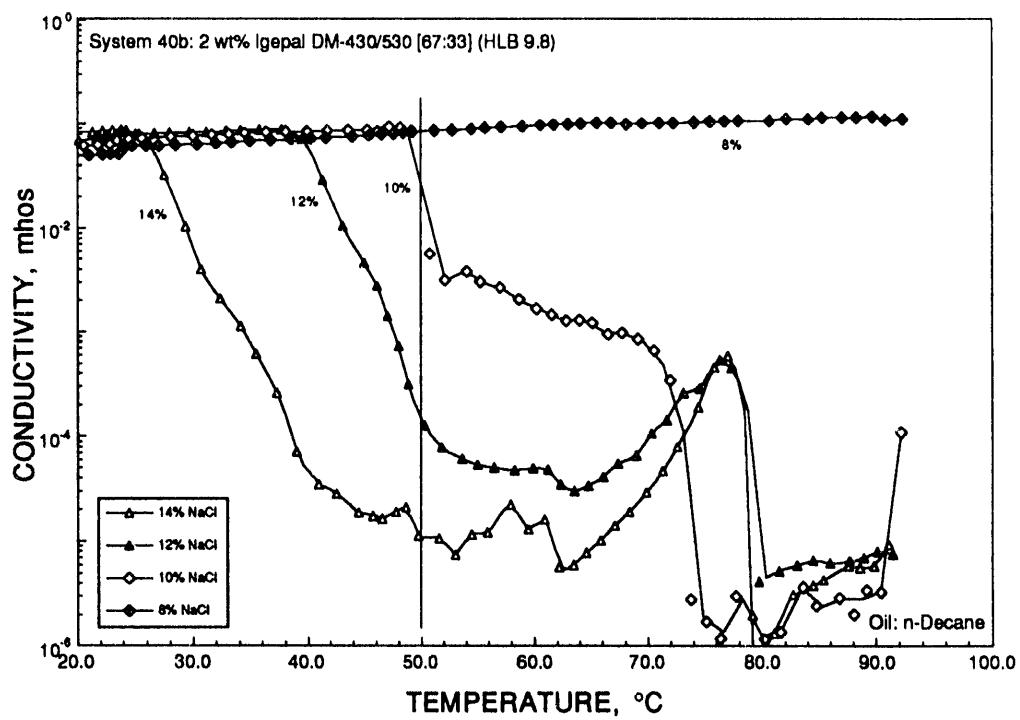
FIGURE B40b. - Phase inversion temperature (PIT) for System 40b with n-decane.
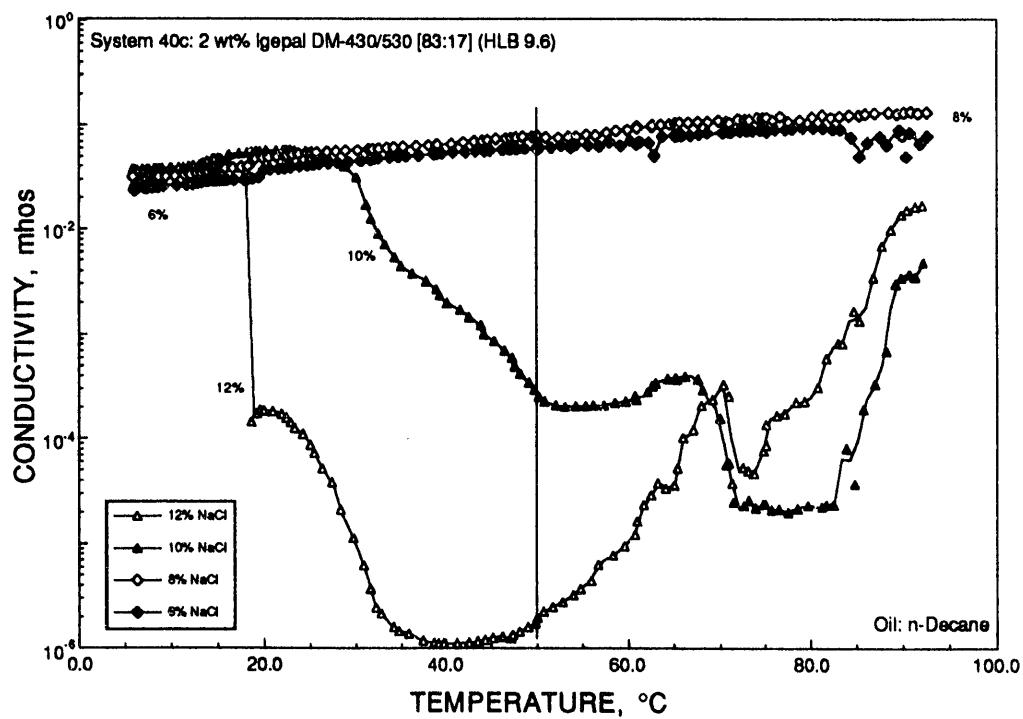
FIGURE B40c. - Phase inversion temperature (PIT) for System 40c with n-decane.
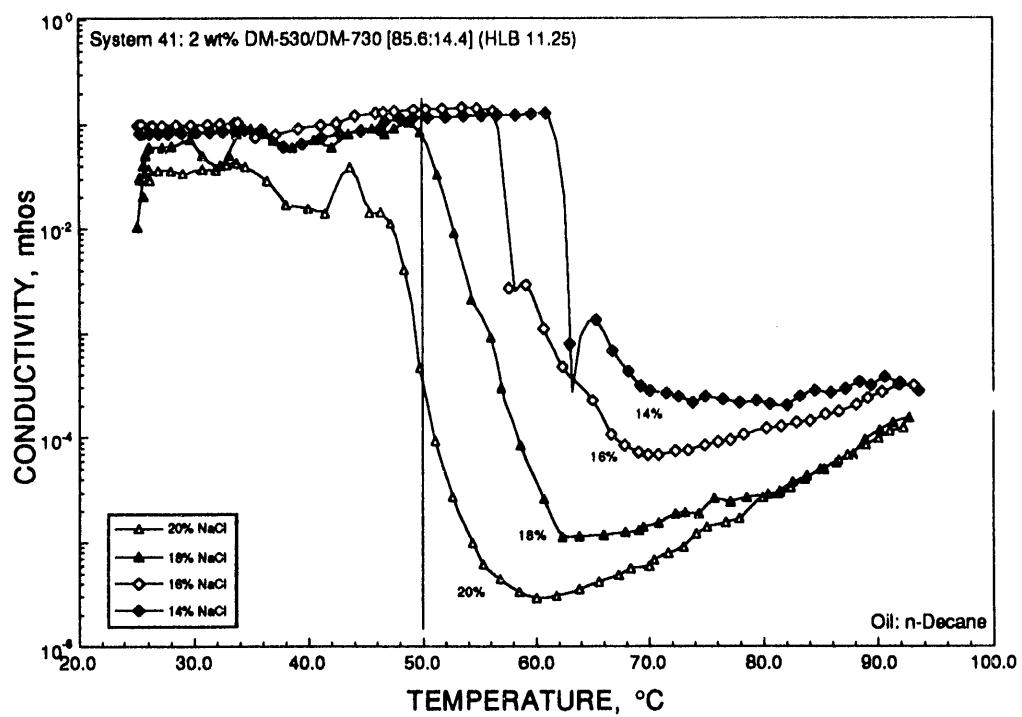
FIGURE B41. - Phase inversion temperature (PIT) for System 41 with n-decane.
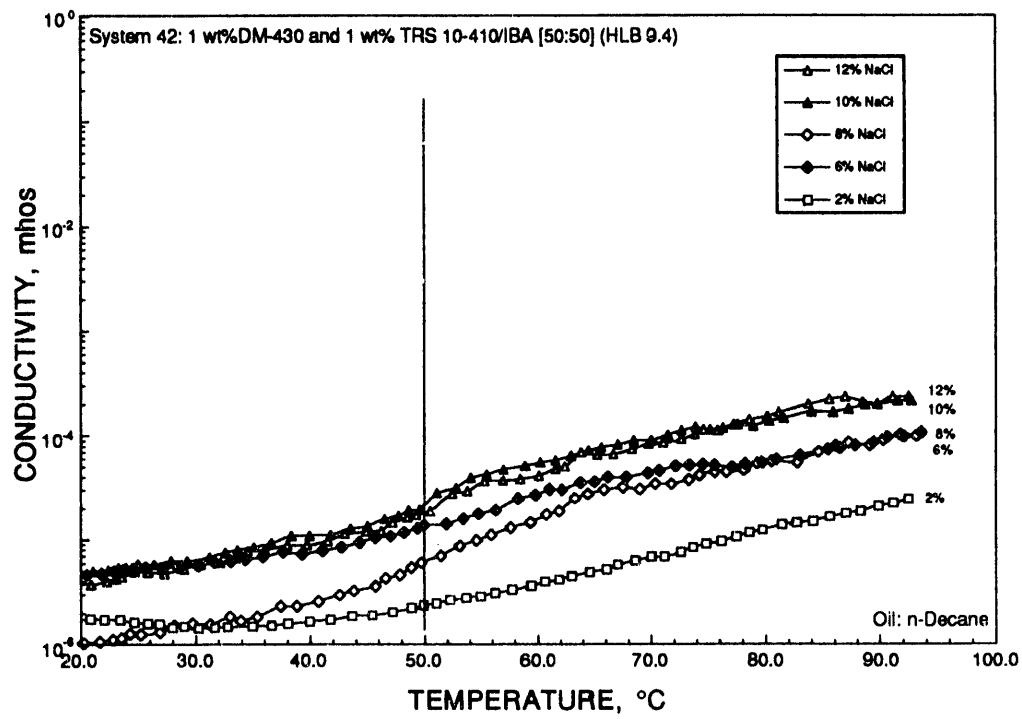
FIGURE B42. - Phase inversion temperature (PIT) for System 42 with n-decane.
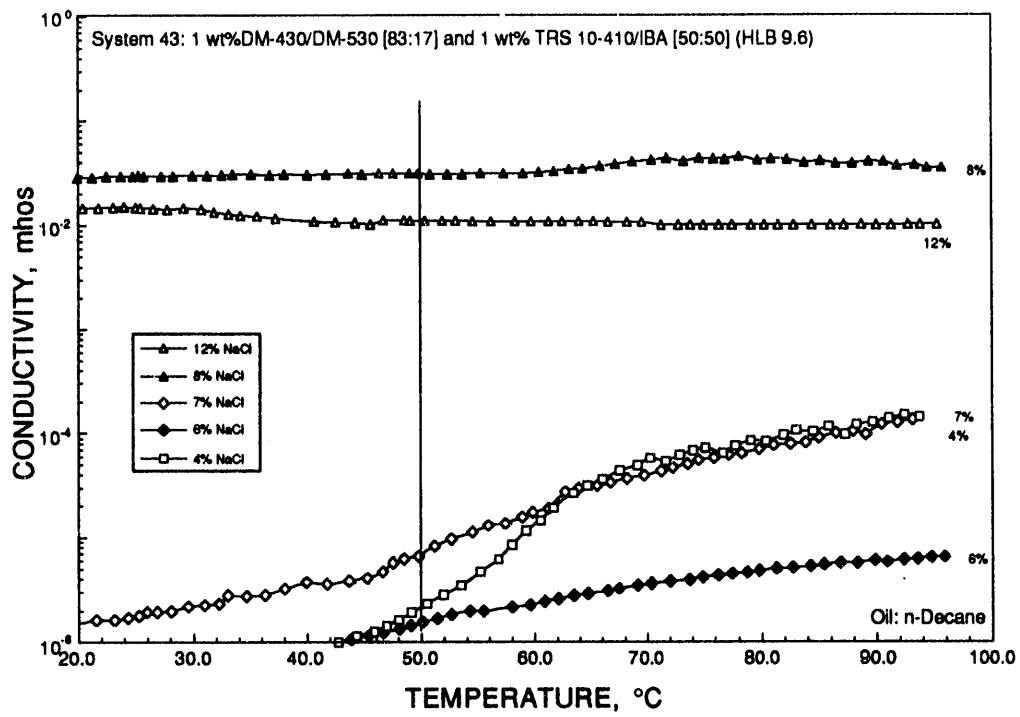
FIGURE B43. - Phase inversion temperature (PIT) for System 43 with n-decane.
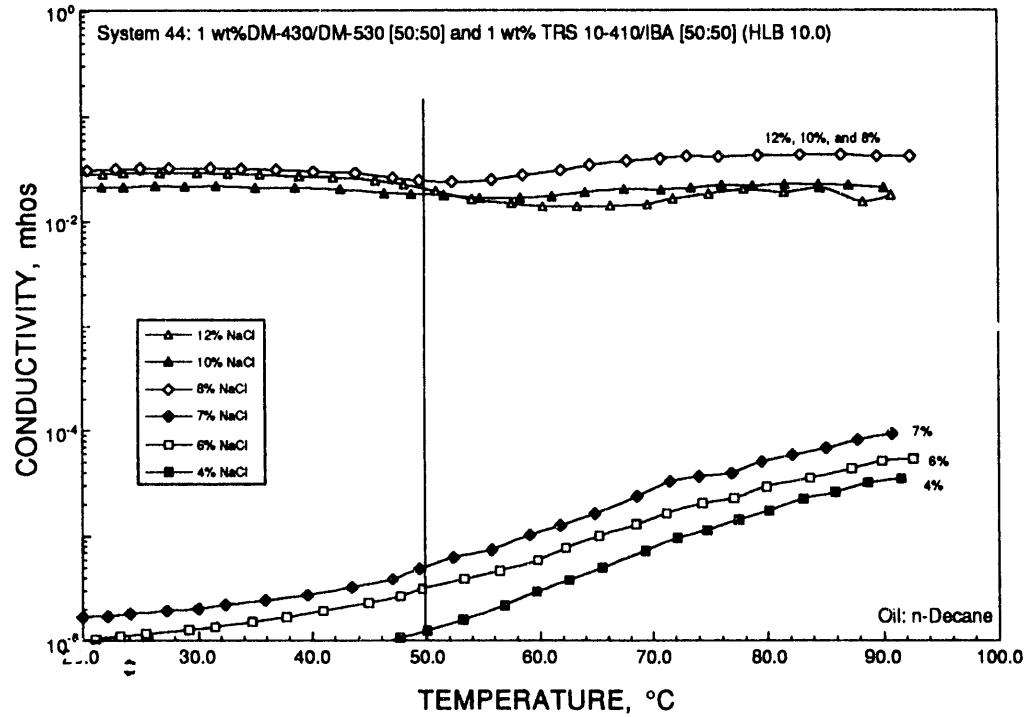
FIGURE B44. - Phase inversion temperature (PIT) for System 44 with n-decane.

88
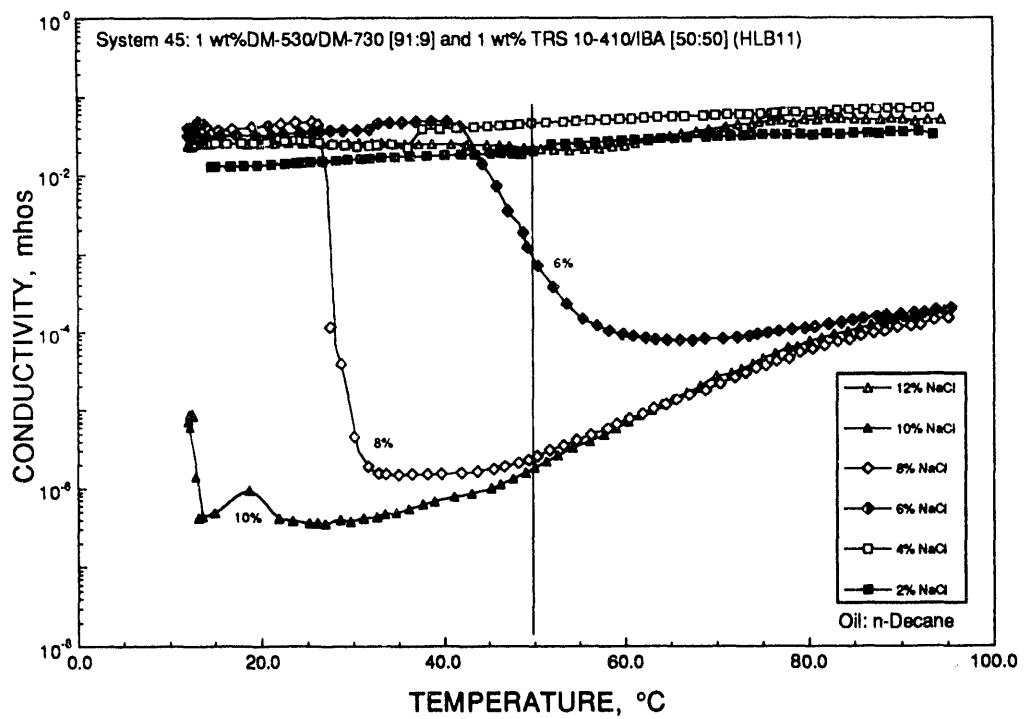
FIGURE B45. - Phase inversion temperature (PIT) for System 45 with n-decane.
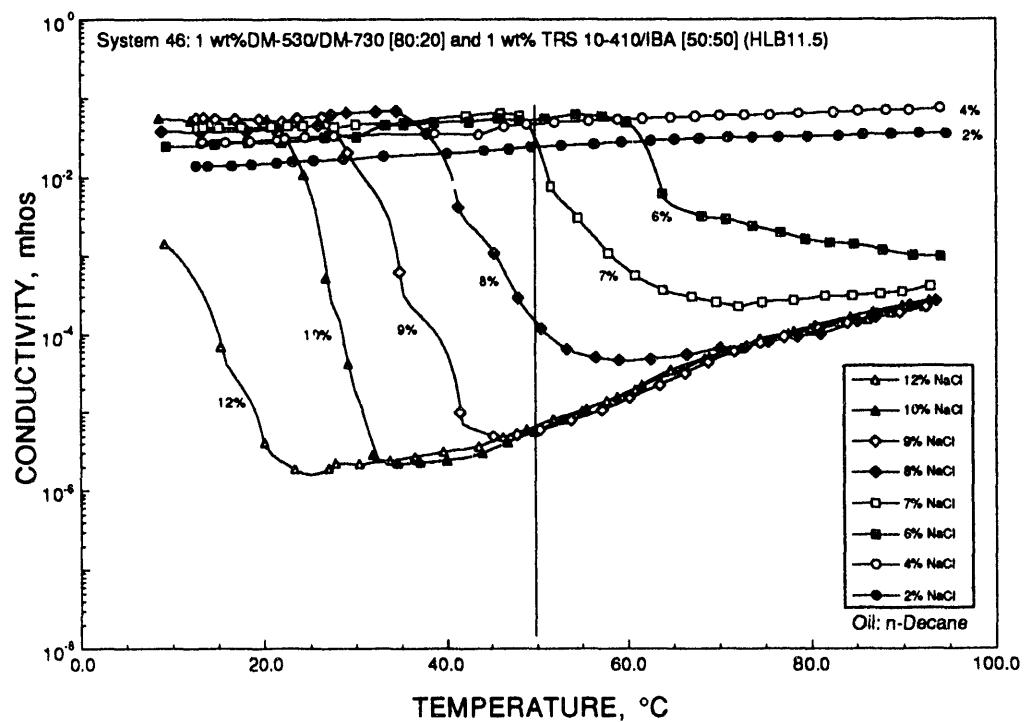
FIGURE B46. - Phase inversion temperature (PIT) for System 46 with n-decane.
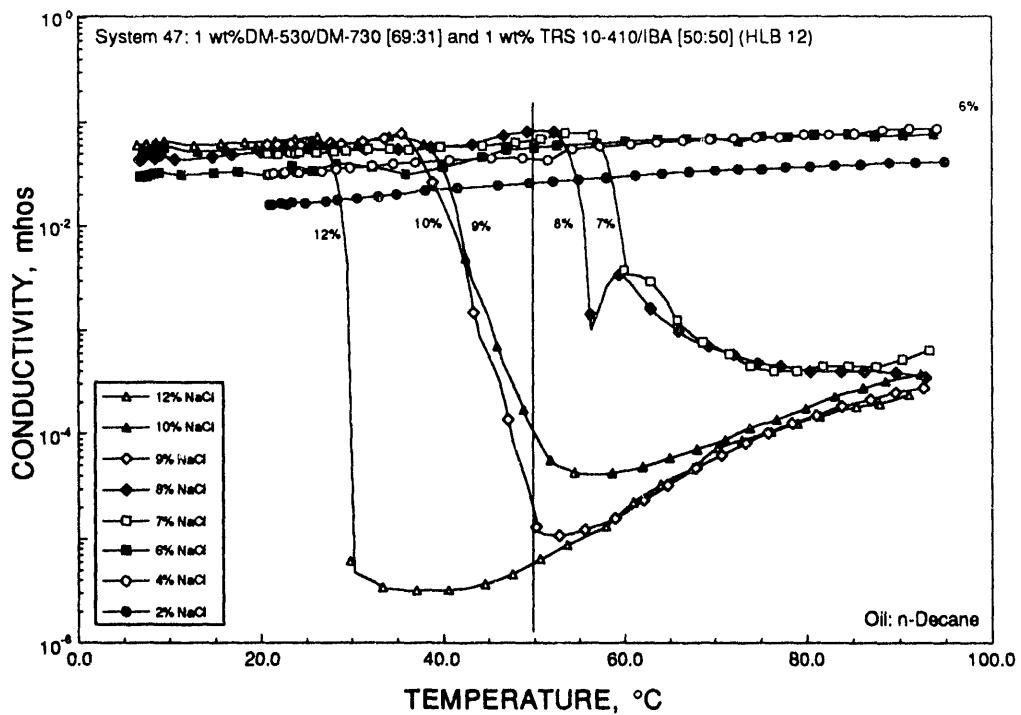
FIGURE B47. - Phase inversion temperature (PIT) for System 47 with n-decane.
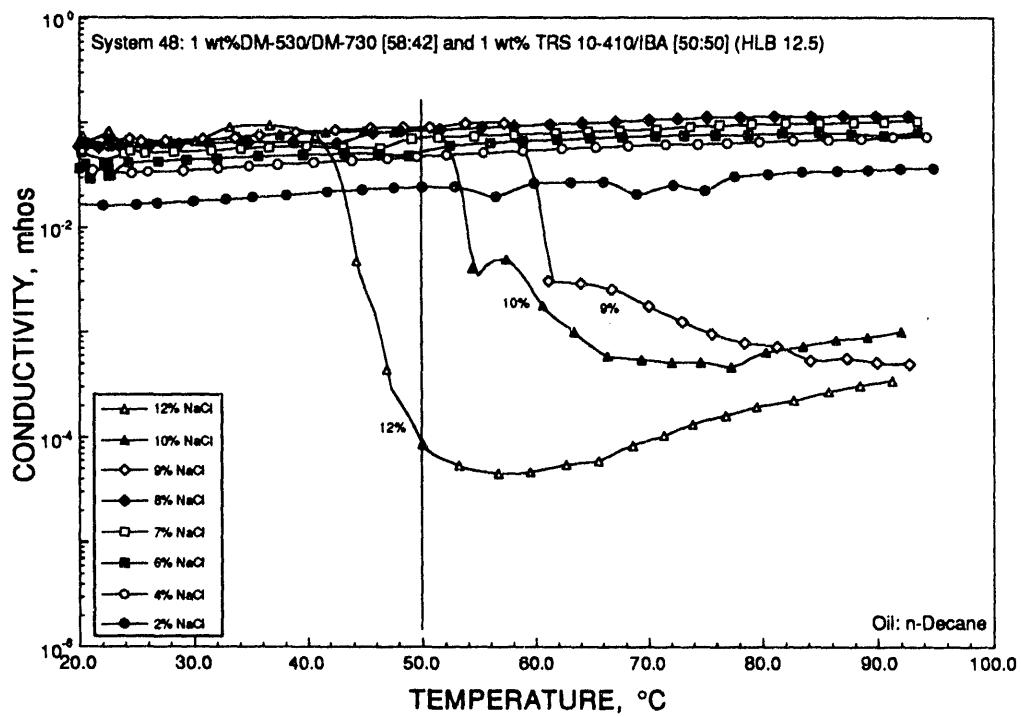
FIGURE B48. - Phase inversion temperature (PIT) for System 48 with n-decane.

90
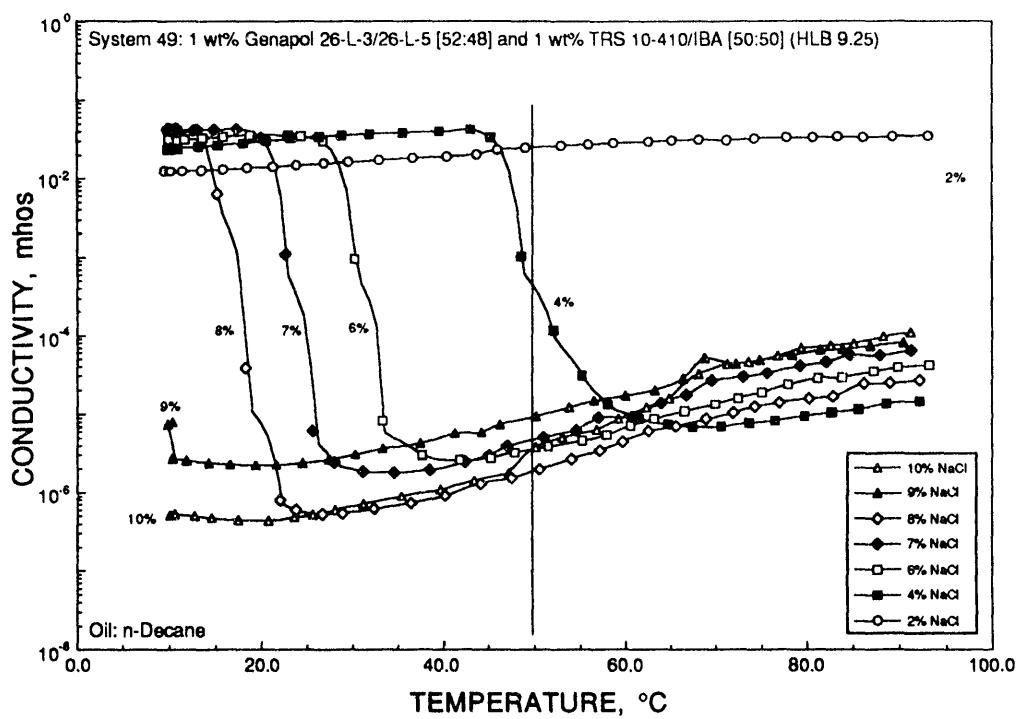
FIGURE B49. - Phase inversion temperature (PIT) for System 49 with n-decane.
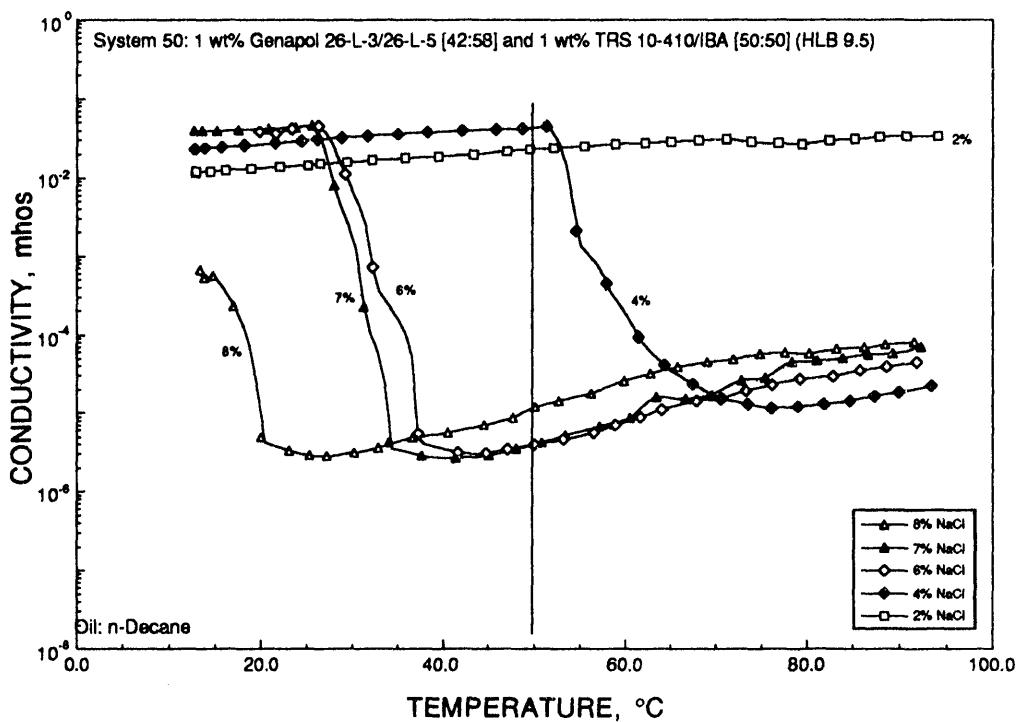
FIGURE B50. - Phase inversion temperature (PIT) for System 50 with n-decane.
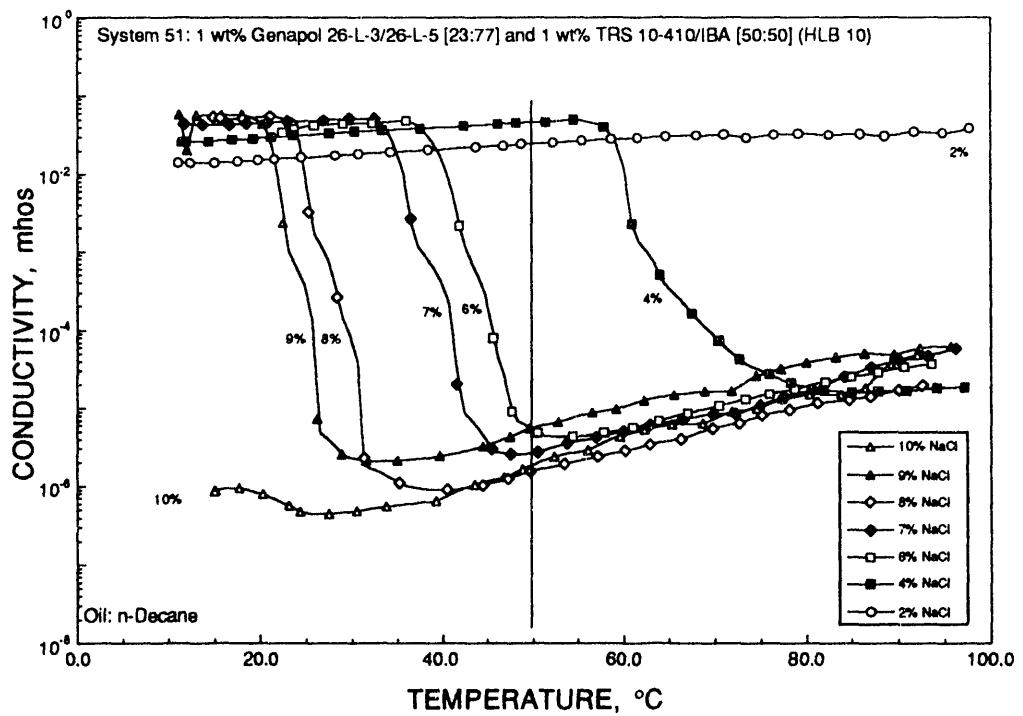
FIGURE B51. - Phase inversion temperature (PIT) for System 51 with n-decane.
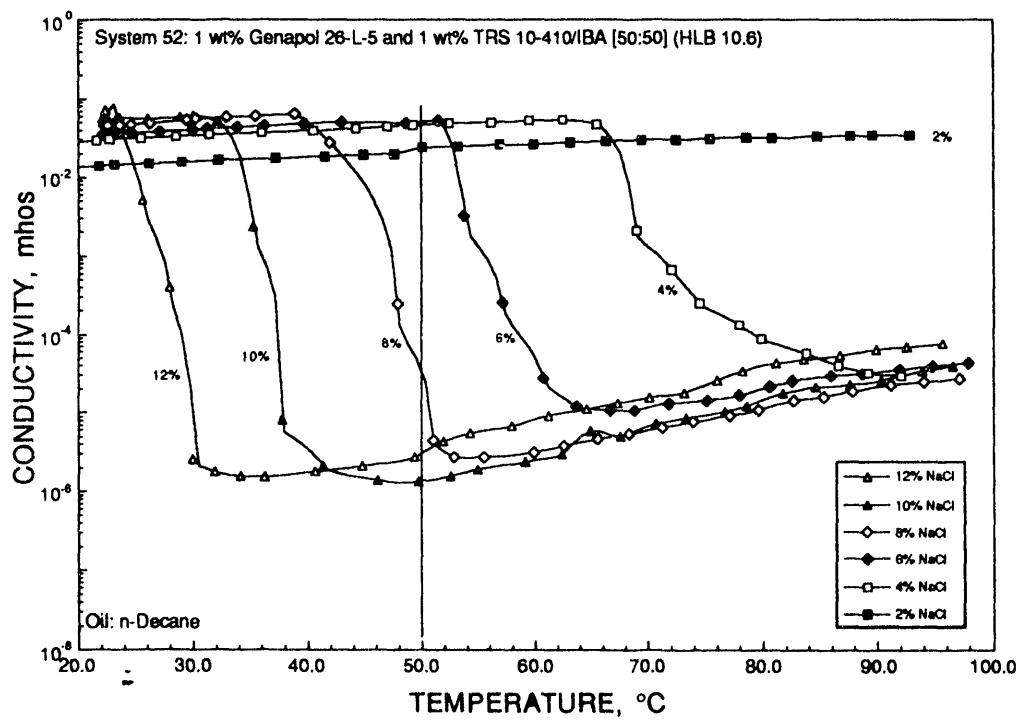
FIGURE B52. - Phase inversion temperature (PIT) for System 52 with n-decane.
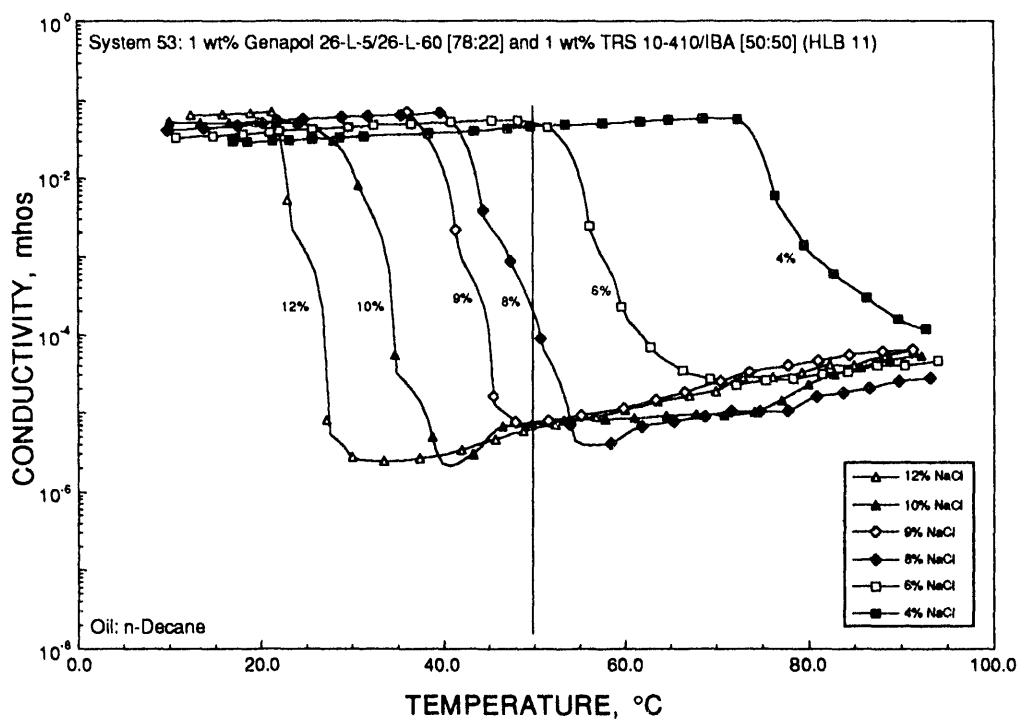
FIGURE B53. - Phase inversion temperature (PIT) for System 53 with n-decane.
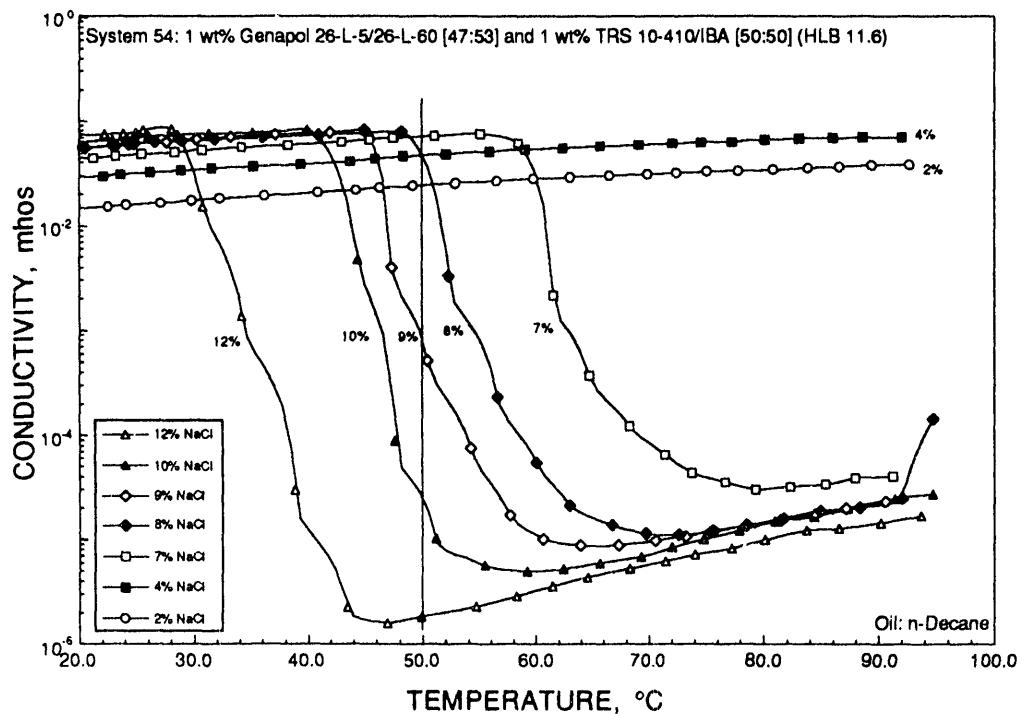
FIGURE B54. - Phase inversion temperature (PIT) for System 54 with n-decane.
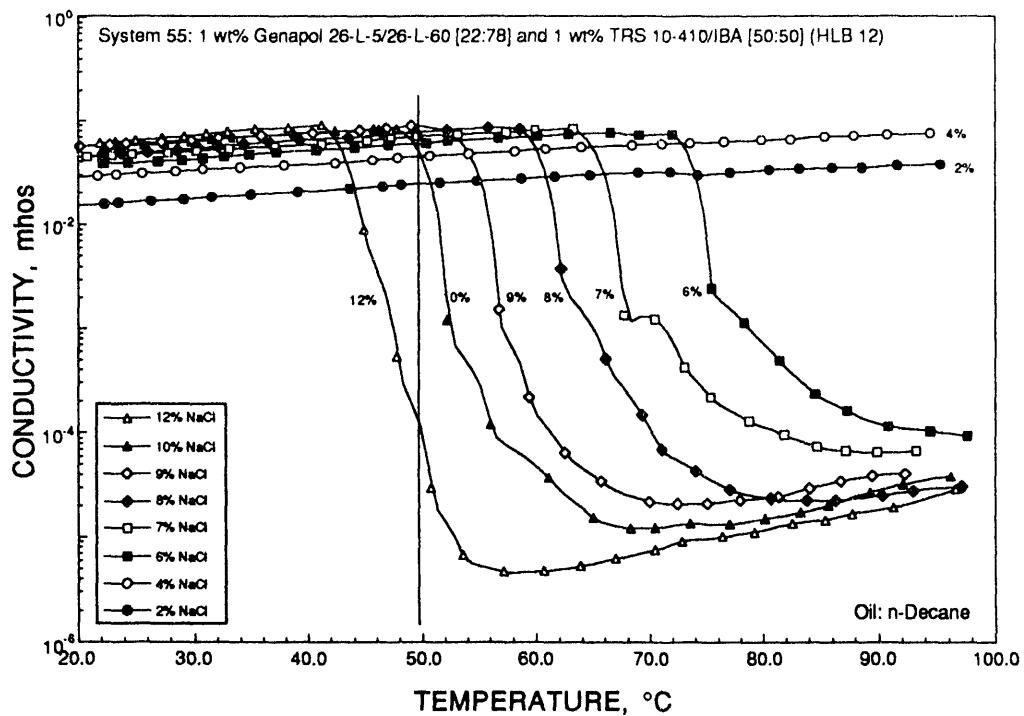
FIGURE B55. - Phase inversion temperature (PIT) for System 55 with n-decane.
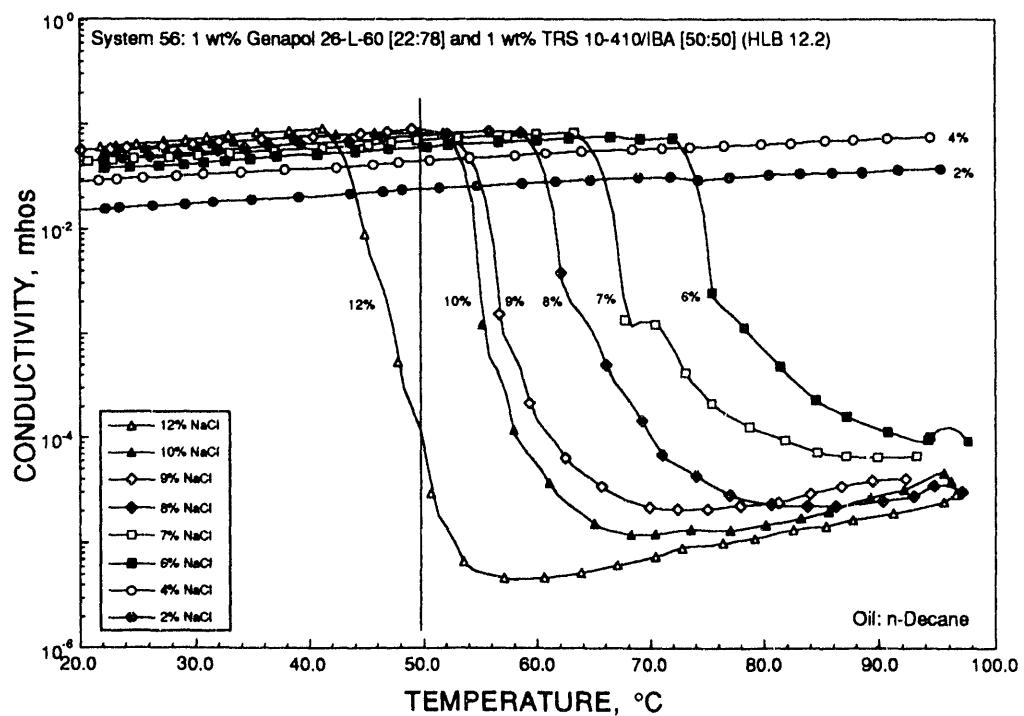
FIGURE B56. - Phase inversion temperature (PIT) for System 56 with n-decane.
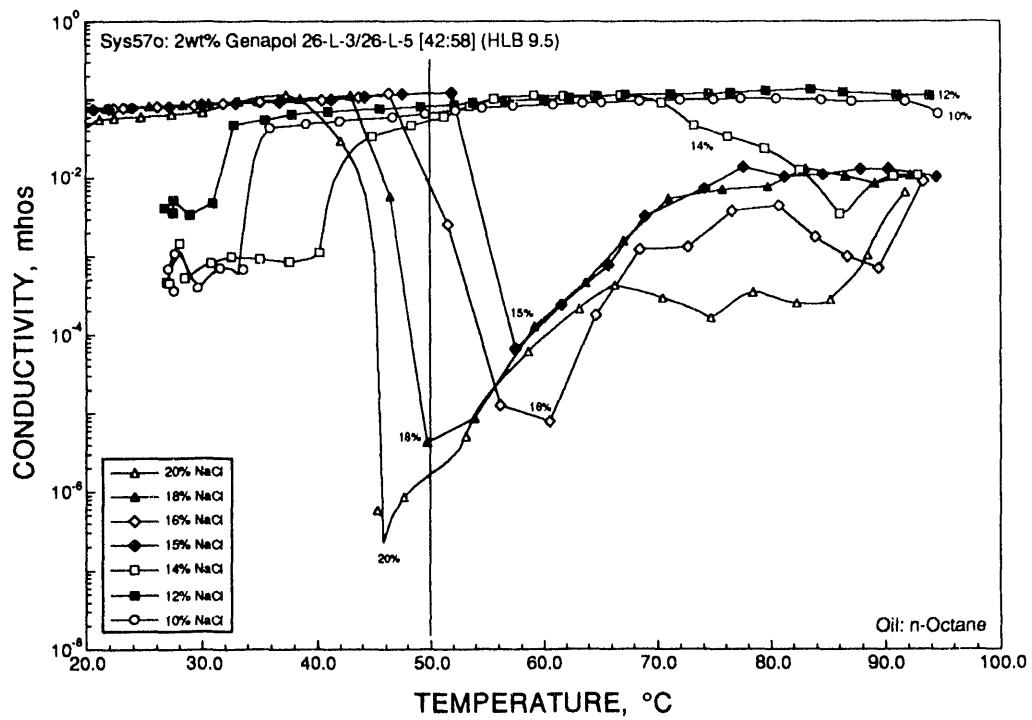
FIGURE B57o. - Phase inversion temperature (PIT) for System 57o with n-octane.
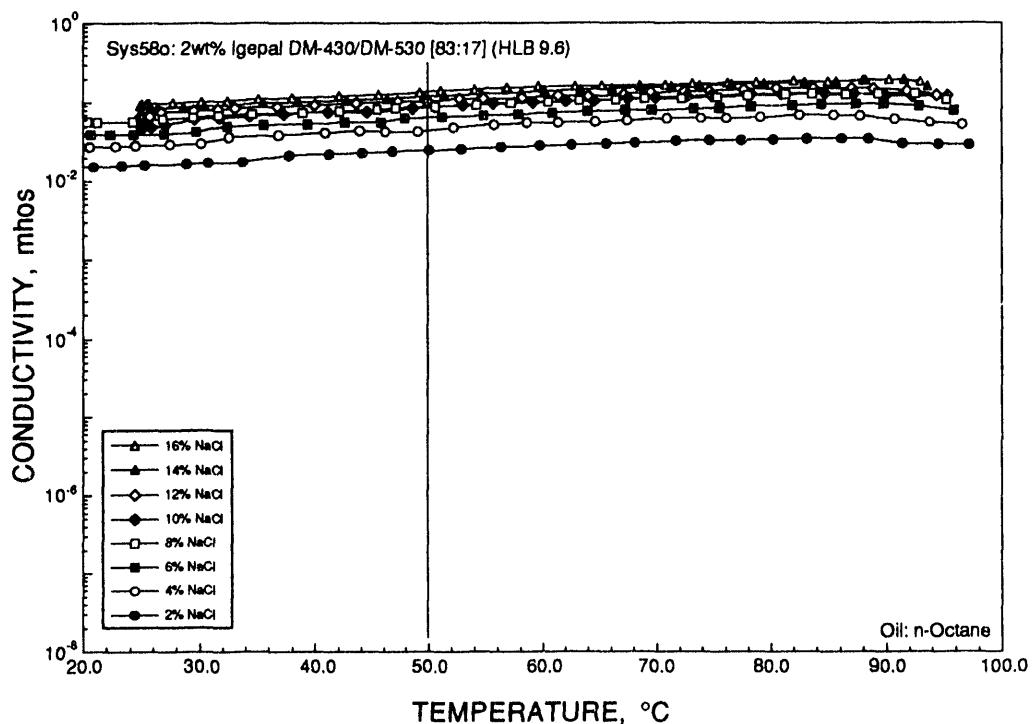
FIGURE B58o. - Phase inversion temperature (PIT) for System 58o with n-octane.
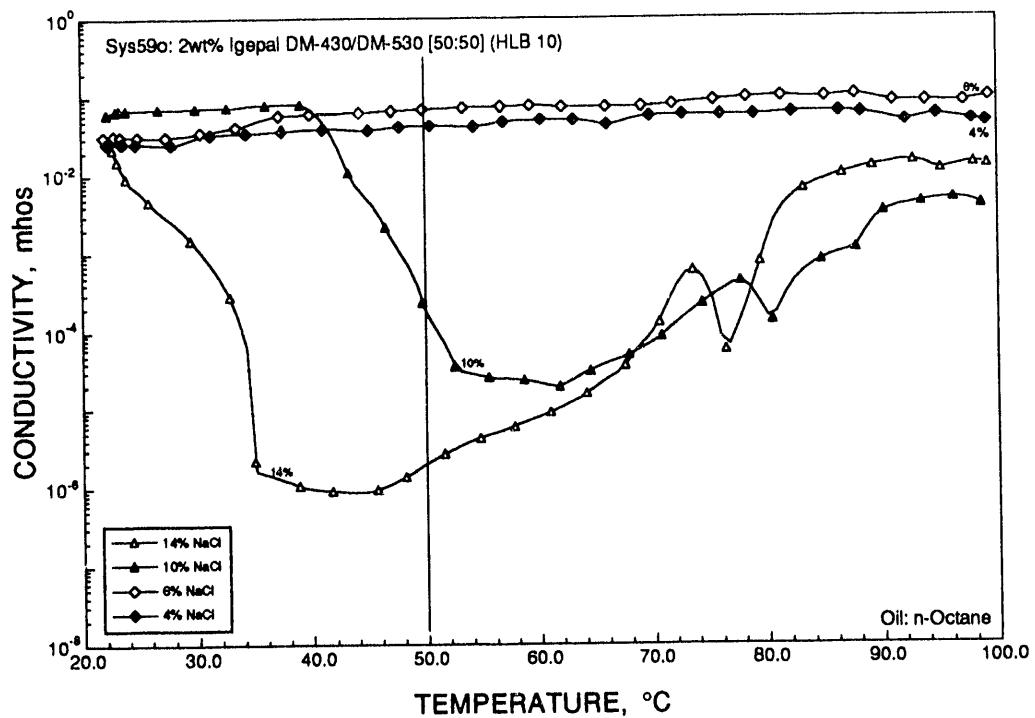
FIGURE B59o. - Phase inversion temperature (PIT) for System 59o with n-octane.
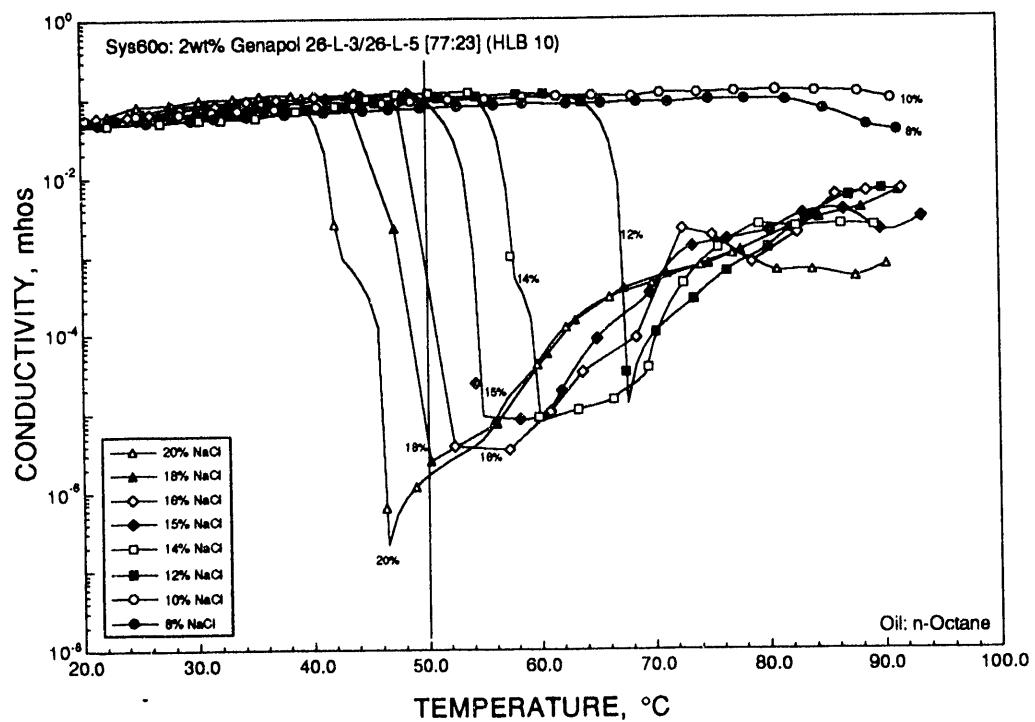
FIGURE B60o. - Phase inversion temperature (PIT) for System 60o with n-octane.
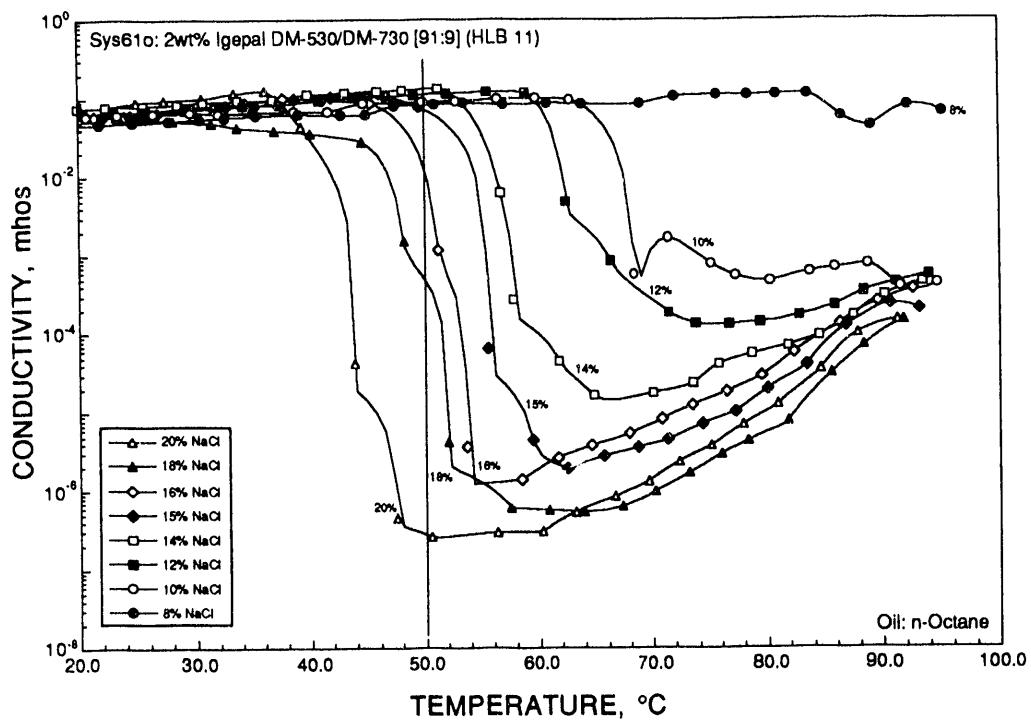
FIGURE B61o. - Phase inversion temperature (PIT) for System 61o with n-octane.
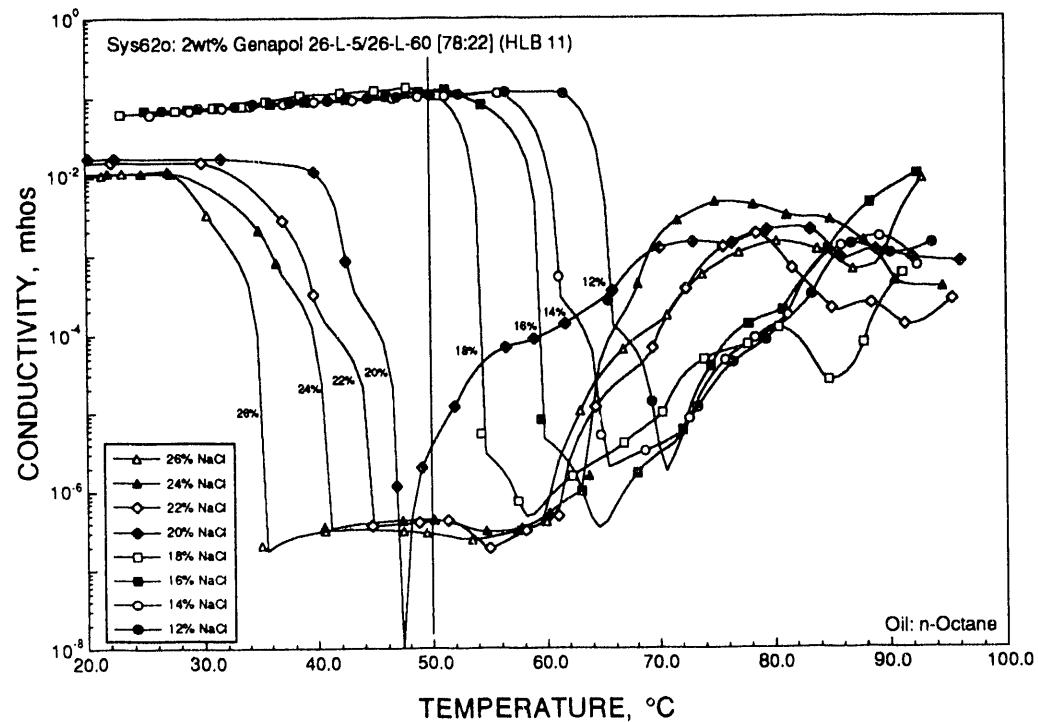
FIGURE B62o. - Phase inversion temperature (PIT) for System 62o with n-octane.
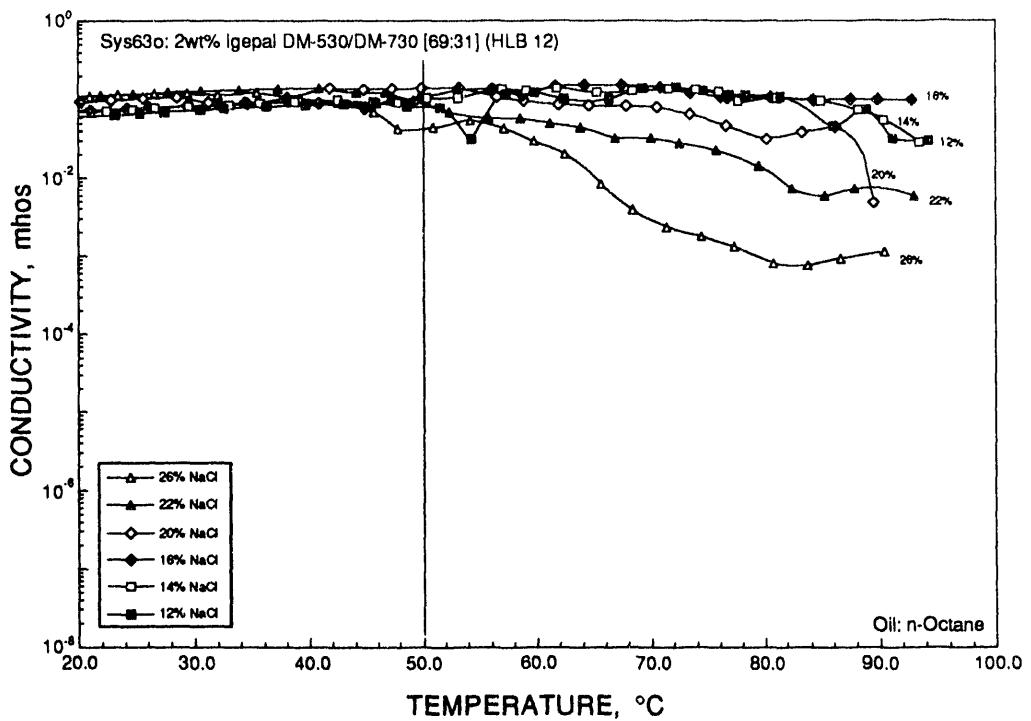
FIGURE B63o. - Phase inversion temperature (PIT) for System 63o with n-octane.
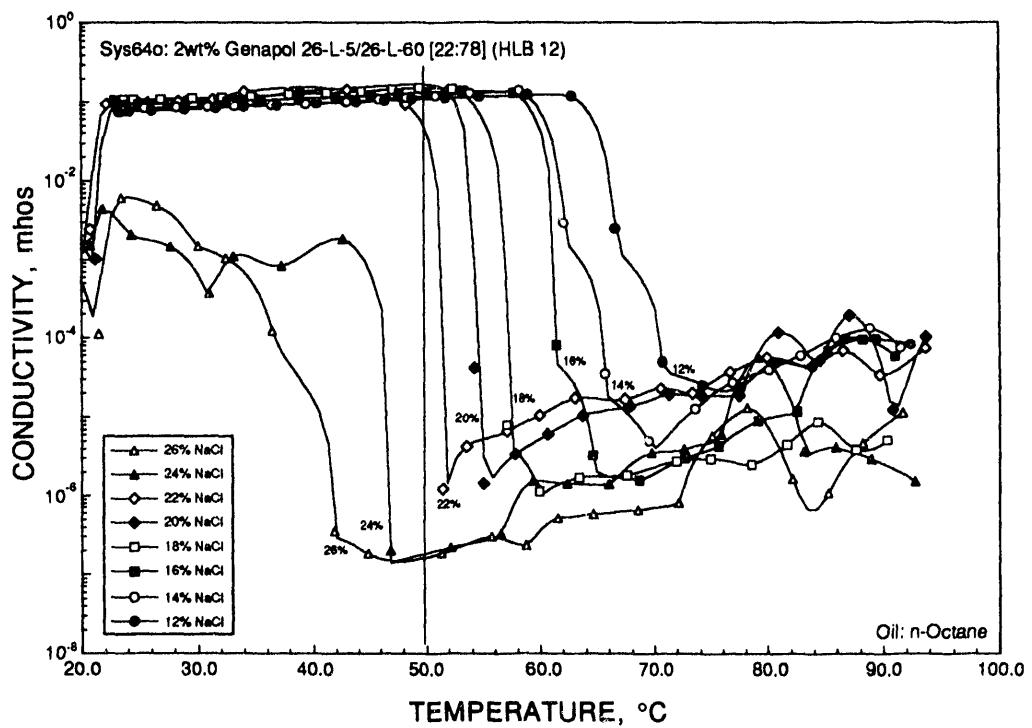

FIGURE B64o. - Phase inversion temperature (PIT) for System 64o with n-octane.
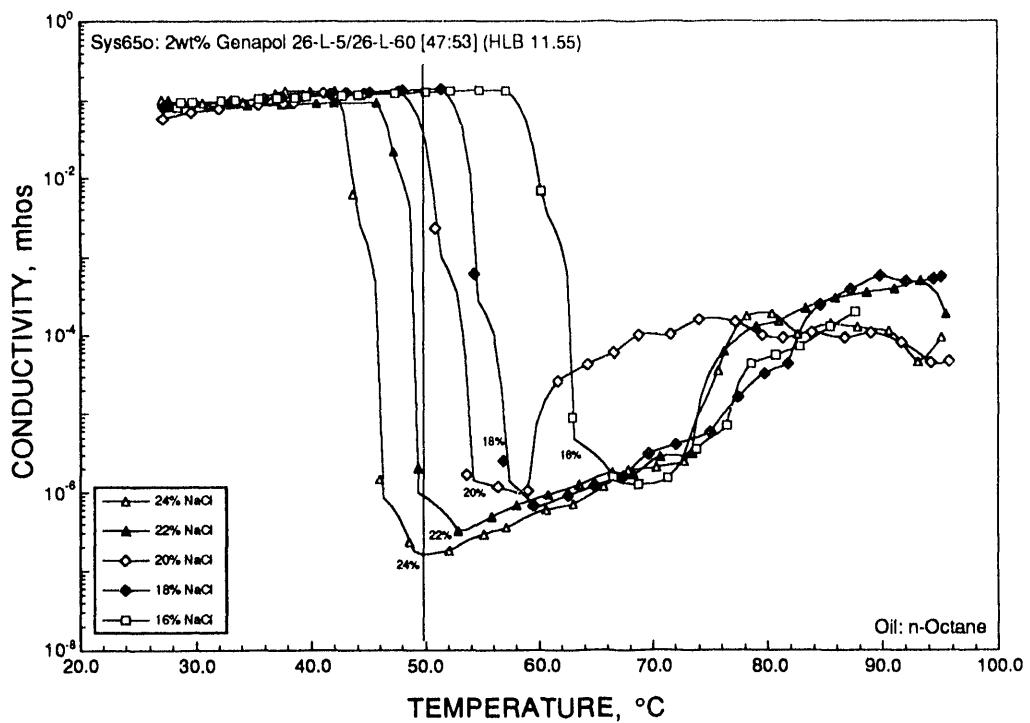
FIGURE B65o. - Phase inversion temperature (PIT) for System 65o with n-octane.
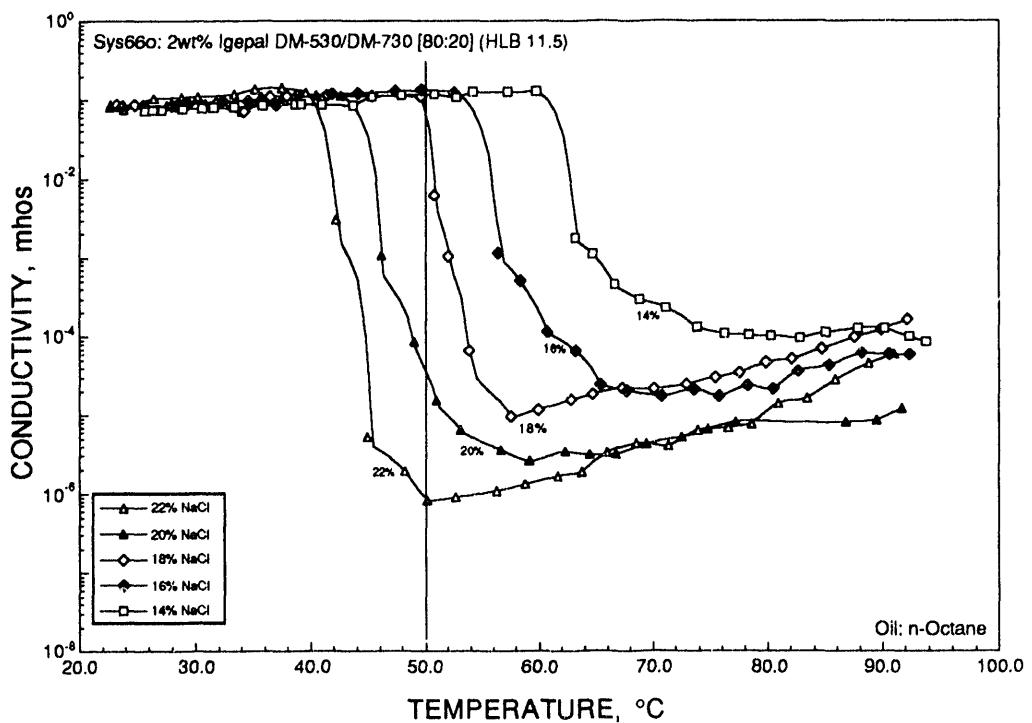
FIGURE B66o. - Phase inversion temperature (PIT) for System 66o with n-octane.
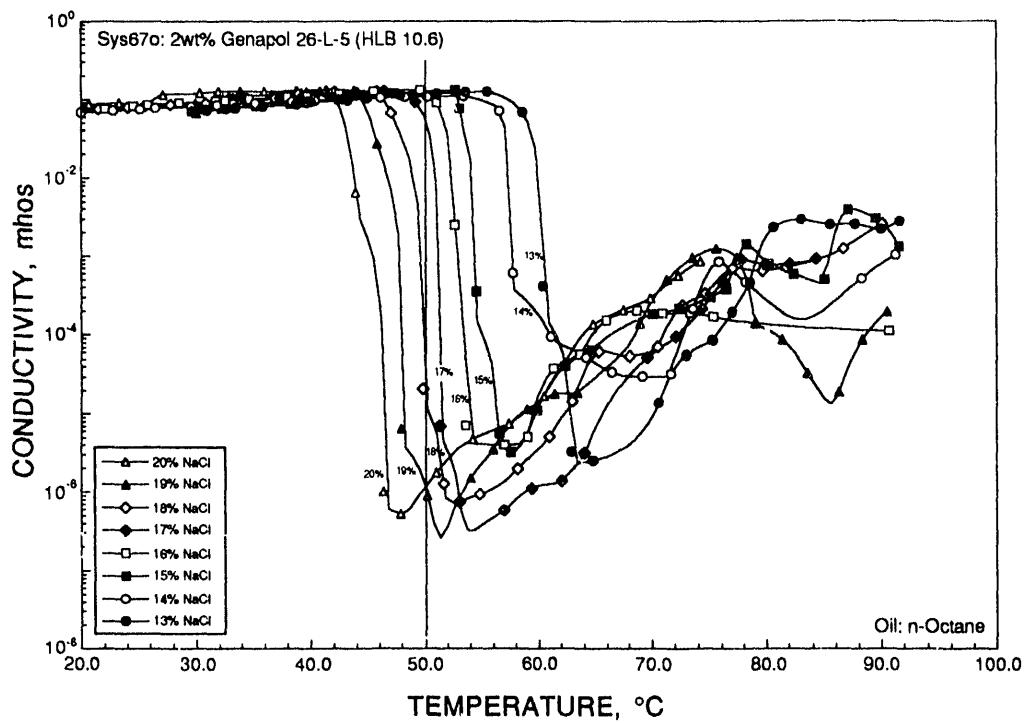
FIGURE B67o. - Phase inversion temperature (PIT) for System 67o with n-octane.
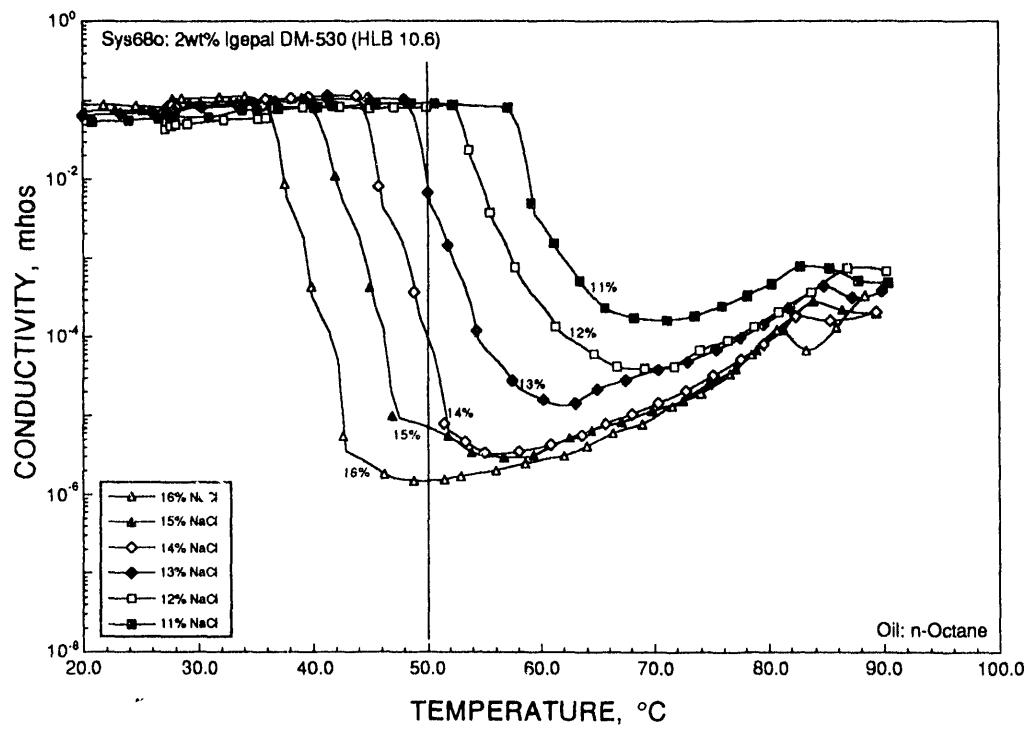
FIGURE B68o. - Phase inversion temperature (PIT) for System 68o with n-octane.

END

DATE
FILMED

4 / 7 / 93