To the Graduate Council:

I am submitting herewith a thesis written by Richard G. Burnette entitled "The Determination of Miscibility Relationships Among Mixtures Consisting of n-Butylcarbitol, Hydrocarbons, and Aqueous Sodium Salicylate Solutions." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

Milton H. Lietzke

Milton H. Lietzke, Major Professor

We have read this thesis
and recommend its acceptance:

William E Bull

James F. Kinstle

Accepted for the Council:

L Evans Post

Vice Chancellor
Graduate Studies and Research

Thesis
78
.T4
Cop. 2

THE DETERMINATION OF MISCIBILITY RELATIONSHIPS AMONG MIXTURES CONSISTING OF n-BUTYLCARBITOL, HYDROCARBONS, AND AQUEOUS SODIUM SALICYLATE SOLUTIONS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Richard G. Burnette

June 1978

1359423

ACKNOWLEDGMENT

The author wishes to express his thanks to Dr. M. H. Lietzke for providing the opportunity to work at Oak Ridge National Laboratory.

The author wishes to express his sincere appreciation to Dr. Patience Ho for her research direction and to Dr. Kurt A. Kraus for suggesting the problem based on previous work carried out at the Oak Ridge National Laboratory. Thanks are also due Phyllis Rafferty for assistance with the error calculation.

The theory section of this thesis was abridged from a thesis presented for the A.B. degree with Honors in Chemistry, Kenyon College, May 1977, by Michele Ann Moisio.

Special thanks are to be given to all the people at Oak Ridge National Laboratory. Their friendship and conversation made working a pleasure, not a task.

Special thanks are also to be given to Miss Carol Proaps for typing.

The author wishes to thank Kathy and Cus Clark for many evenings of excellent company and many mornings of excellent coffee.

This work was performed in the Chemistry Division of Oak Ridge National Laboratory, operated by Union Carbide Corporation for the U. S. Department of Energy, Dr. O. L. Keller, Division Director.

ABSTRACT

In the enhanced oil recovery process a cosolvent, for example an alcohol, is used to promote miscibility of the oil and an aqueous solution of a surfactant. In the Chemistry Division at the Oak Ridge National Laboratory a program of fundamental research is underway to investigate phase boundary relationships in model systems related to the enhanced oil recovery process. In these studies the model surfactants include the sodium salts of substituted aromatic sulfonic and carboxylic acids, while the hydrocarbons include both alkanes and various alkylbenzenes. For each system the minimum amount of cosolvent, for example, 1-butanol or n-butylcarbitol, needed to produce miscibility of the hydrocarbon and the aqueous solution of model surfactant is determined for various weight ratios of hydrocarbon to aqueous solution.

Each system thus contains four components: hydrocarbon, cosolvent, water, and the model surfactant. For convenience, however, the systems may be considered as pseudo-three component systems. For example, the three components may be chosen as hydrocarbon, cosolvent, and the aqueous solution. Alternatively, the components may be considered hydrocarbon, cosolvent, and water. In this latter case the effect of adding various amounts of the model surfactant on the phase boundary relationships in the hydrocarbon, cosolvent, water system is observed. This representation is referred to as the water basis.

In the present research miscibility relationships in systems containing an aqueous solution of sodium salicylate, n-butylcarbitol, and a series of hydrocarbons have been investigated. The hydrocarbons included both alkanes and alkylbenzenes. When the aqueous sodium

salicylate solution was treated as one component, then increasing the sodium salicylate concentration in the aqueous phase caused salting-in of the hydrocarbon, i.e., less cosolvent was required to produce miscibility of the hydrocarbon and the aqueous solution. On a water basis, however, both salting-in and salting-out effects were observed depending on the hydrocarbon.

At each fixed sodium salicylate concentration the effect of hydrocarbon chain length on the miscibility relationships was observed. It was found that in all cases the weight fraction of n-butylcarbitol required for miscibility gradually increased as the n-alkane chain length increased. For the alkylbenzenes, however, at aqueous sodium salicylate concentrations equal to zero or 1.0 molal, the amount of n-butylbarbitol required for miscibility at first decreased and then increased as the number of carbon atoms in the side chain on the benzene ring increased. At sodium salicylate concentrations of 2.5 molal and above, the amount of n-butylcarbitol required to produce miscibility of the aqueous solution and the hydrocarbon increased in all cases as the number of carbon atoms in the side chain increased. At any fixed sodium salicylate concentration the same amount of n-butylcarbitol was required to produce miscibility with either p-xylene or 1-phenylethane. Hence the number of alkyl carbon atoms on the benzene ring and not the arrangement was the important parameter.

TABLE OF CONTENTS

CHAPTER		PAGE
I.	INTRODUCTION	1
	A. Theory	1
	B. Statement of the Research Problem	3
II.	EXPERIMENTAL DETAILS	5
	A. Equipment	5
	1. Equipment used to determine phase boundary diagrams	5
	2. Equipment used in Karl Fischer titrations	5
	B. Chemicals	6
	1. Chemicals used to determine phase boundary diagrams	6
	2. Chemicals used in Karl Fischer titrations	6
	C. Procedure	6
	1. Phase boundary diagram determinations	6
	2. Karl Fischer titrations	9
III.	DATA ANALYSIS	10
	A. Phase Boundary Diagram Calculations	10
	B. Error Analysis	11
IV.	EXPERIMENTAL RESULTS AND DISCUSSION	13
	A. Phase Boundary Curves	13
	B. Effect of Increasing the Aqueous Sodium Salicylate Concentration	22
	C. Effect of Increasing the Chain Length of n-Alkanes and Alkylbenzenes	25

CHAPTER PAGE

LIST OF REFERENCES 37

VITA 39

LIST OF TABLES

PAGE

I. Chemicals Used in Phase Diagram Determinations 8

II. Weight Fractions of n-Butylcarbitol and Hydrocarbons in Mixtures at Zero Molal Aqueous Sodium Salicylate . . 14

III. Weight Fractions of n-Butylcarbitol and Hydrocarbons in Mixtures at 1 Molal Aqueous Sodium Salicylate 16

IV. Weight Fractions of n-Butylcarbitol and Hydrocarbons in Mixtures at 2.5 Molal Aqueous Sodium Salicylate . . . 18

V. Weight Fractions of n-Butylcarbitol and Hydrocarbons in Mixtures at 6 Molal Aqueous Sodium Salicylate 20

VI. Minimum Weight Fractions of n-Butylcarbitol Necessary to Produce Miscibility in 1:1 Weight Fraction Mixtures of Hydrocarbons and Aqueous Sodium Salicylate. 23

VII. Minimum Weight Fractions of n-Butylcarbitol Necessary to Produce Miscibility in 1:1 Weight Fraction Mixtures of Hydrocarbons and Water. 24

LIST OF FIGURES

PAGE

1. Circuit diagram for amperometric Karl Fischer titrations 7
2. Minimum amount of n-butylcarbitol required to produce miscibility in 1:1 weight fraction mixtures of alkylbenzenes and water 27
3. Minimum amount of n-butylcarbitol required to produce miscibility in 1:1 weight fraction mixtures of n-alkanes and water 28
4. Effect of hydrocarbon chain length on miscibility in the butylcarbitol-1.0 molal aqueous sodium salicylate system (1:1 weight ratio of alkylbenzene and water and 1:1 weight ratio of alkylbenzene and aqueous solution) 29
5. Effect of hydrocarbon chain length on miscibility in the butylcarbitol-1.0 molal aqueous sodium salicylate system (1:1 weight ratio of n-alkanes and water and 1:1 weight ratio of n-alkanes and aqueous solution) 30
6. Effect of hydrocarbon chain length on miscibility in the butylcarbitol-2.5 molal aqueous sodium salicylate system (1:1 weight ratio of alkylbenzenes and water and 1:1 weight ratio of alkylbenzenes and aqueous solution) 31
7. Effect of hydrocarbon chain length on miscibility in the butylcarbitol-2.5 molal aqueous sodium salicylate system (1:1 weight ratio of n-alkanes and water and 1:1 weight ratio of n-alkanes and aqueous solution) 32

PAGE

8. Effect of hydrocarbon chain length on miscibility in the butylcarbitol-6 molal aqueous sodium salicylate system (1:1 weight ratio of alkylbenzenes and water and 1:1 weight ratio of alkylbenzenes and aqueous solution) . . . 33

9. Effect of hydrocarbon chain length on miscibility in the butylcaribtol-6 molal aqueous sodium salicylate system (1:1 weight ratio of n-alkanes and water and 1:1 weight ratio of n-alkanes and aqueous solution). 34

CHAPTER I

INTRODUCTION

A. Theory

Many studies of the effects of salts on the solubilities of nonelectrolytes in water have been carried out; however, the relationship of the salt effect to the salt concentration was first set forth by Setschenow[1] in his equation

$$\log \frac{S_o}{S} = k_s c, \tag{1}$$

where

S_o = solubility of nonelectrolyte in water,

S = solubility of nonelectrolyte in aqueous salt solution,

c = salt concentration in moles per liter,

and

k_s = a constant for a given salt-nonelectrolyte pair.

More recent quantitative theories predicting salt effects have been based on this equation.

In the early 1920's and 1930's many theories were proposed attempting to explain the mechanism by which a substance only slightly soluble in water became more soluble in an aqueous salt solution (salting-in). Bancroft's idea[2] was that the salt solution acted as a mixture of liquids, with the water and the salt together acting as solvent. Winsor[3] suggested the concept of the salt as a common solvent for water and water-insoluble organic compounds. Neither of these theories explained why some salts caused salting-in while others caused

salting-out. Debye and McAuley[4] proposed an explanation based upon the dielectric constant of the aqueous solution of the nonelectrolyte. The net result was that salting-in occurred when the dielectric constant of the solution was greater than that of water, and salting-out occurred when it was less. Later Debye gave another interpretation[5] of these phenomena based on the location of various species in solution. Salting-out was caused by water molecules clustering around the ions and thus reducing the amount of water available for dissolving the nonelectrolyte. Fewer molecules of the nonelectrolyte could dissolve with respect to the total amount of water present. In the case of salting-in, the nonelectrolyte clustered around the ions; thus more molecules of nonelectrolyte could dissolve with respect to the total amount of water present.

During the past thirty years theories have been proposed explaining salting-in and salting-out phenomena. Conway, Desnoyers, and Smith[6] expanded the electrostatic theory; their work, however, yielded k_s values which agreed with experimental values only to a first approximation. McDevit and Long[7,8] attempted to explain the diversity in the effects of different salts by focusing on the volume change occurring when the salt was added to water. Although k_s values obtained by McDevit and Long were better than those obtained from the expanded electrostatic theory, the results were far from satisfactory. One of the more successful theories was the scaled-particle theory.[6,9] Based on a statistical mechanical treatment[10,11] of fluid structure, this theory predicted k_s values more accurately than did the McDevit-Long theory in two-thirds of the cases,[6] particularly for nonelectrolytes

of small size. The most recent explanation of salting-in and salting-out phenomena was that of Aveyard and Heselden.[12] If the addition of salt decreased the solution surface tension, salting-in occurred; if the addition increased the solution surface tension, salting-out occurred.

The above theories pertain to solutions consisting of salt, water, and one nonelectrolyte; hence they are not strictly applicable to the present research involving two nonelectrolytes. Nevertheless, any theoretical considerations of these four-component systems will certainly contain elements from the theories describing the much simpler three-component systems.

B. Statement of the Research Problem

A study of phase boundary relationships in pseudo-three component systems containing a hydrocarbon, a cosolvent, and an aqueous solution of a sodium benzenesulfonate has been underway for about two years in the Chemistry Division of the Oak Ridge National Laboratory. This work has been carried out by Dr. Patience C. Ho. In addition, an extensive study was made of the effect of various inorganic solutes on the miscibility relations in a series of hydrocarbon-alcohol-water mixtures by Michele A. Moisio while a participant in the Great Lakes College Association Science Semester at ORNL during the Fall of 1976. These studies were continued after Ms. Moisio returned to Kenyon College and described in a thesis presented by her for the A.B. degree with Honors in Chemistry. On the basis of results obtained in these studies and preliminary results by Ms. Moisio, the systems described in this thesis were chosen for study.

In the present research a study has been made of miscibility relationships in systems containing an aqueous solution of sodium salicylate (chosen because of its high solubility in water), n-butylcarbitol, and a series of hydrocarbons, including both n-alkanes and alkylbenzenes.

CHAPTER II

EXPERIMENTAL DETAILS

A. Equipment

1. Equipment Used to Determine Phase Boundary Diagrams

All phase boundary diagram determinations were carried out in test tubes that had specially designed caps. Each cap contained a silicone septum through which chemicals could be injected.

Disposable Pasteur pipets were used to add the aqueous salt solutions and the hydrocarbons to the test tubes. The alcohol was added dropwise from a syringe inserted through the cap.

To insure solution homogeneity after each addition of alcohol, each test tube was placed on a Vortex-Genie. The solution was swirled for several seconds.

The temperature of all solutions was maintained at 25.0°C by placing the test tubes in a constant temperature water bath. With a sensitivity of $\pm$ 0.05 degree, the thermoregulator was able to control the bath temperature to within $\pm$ 0.1 degree.

2. Equipment Used in Karl Fischer Titrations

The Karl Fischer[13] amperometric titrations for the determination of the water content in the chemicals were carried out in a closed system continuously flushed with dry nitrogen. The end point was determined by the "dead stop" technique.

A 10-milliliter, bottom-filling buret was used to add the Karl Fischer reagent. Titrations were carried out in a 250-milliliter, round-bottom flask. The bottom of this flask contained two sealed-in platinum electrodes. These electrodes were connected to a microammeter, a 100,000 ohm potentiometer, and a standard 1.5 volt dry cell battery. Figure 1 shows a typical circuit diagram.

B. Chemicals

1. Chemicals Used to Determine Phase Boundary Diagrams

Table I contains a listing of chemicals, manufacturers, and purities. All chemicals were used without further purification or drying.

2. Chemicals Used in Karl Fischer Titrations

A highly concentrated Karl Fischer reagent, which consisted of iodine, pyridine, sulfur dioxide, and methanol, was obtained from Fisher Scientific Company. After dilution with anhydrous methanol, this reagent was used in the Karl Fischer titrations.

C. Procedure

1. Phase Boundary Diagram Determinations

A series of test tubes plus caps were weighed on a Mettler balance. Then various amounts of aqueous sodium salicylate were added to the tubes. After reweighing, various amounts of a particular hydrocarbon were added and the tubes weighed for a third time. The solutions were then thermostatted at 25.0°C for thirty minutes in a

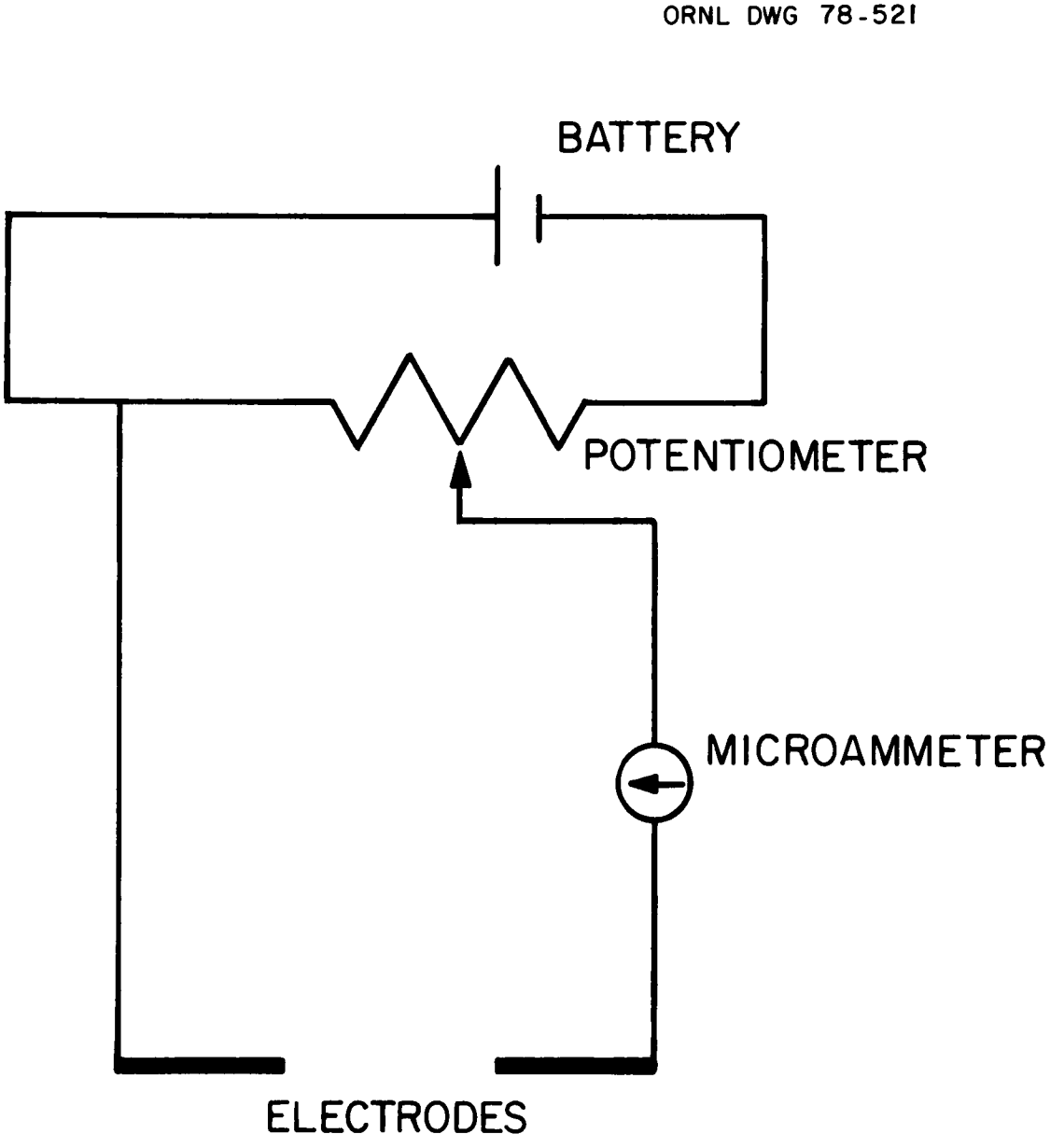


Figure 1. Circuit diagram for amperometric Karl Fischer titrations.

TABLE I

CHEMICALS USED IN PHASE DIAGRAM DETERMINATIONS

Name	Manufacturer	Purity
Benzene	Mallinckrodt	Analytical reagent
Toluene	Fisher Scientific Co.	Certified A.C.S.
1-Phenylethane	Matheson Coleman and and Bell (MC/B)	-
p-Xylene	MC/B	-
1-Phenylbutane	MC/B	-
Cyclohexane	MC/B	-
1-Phenylhexane	Aldrich	97%
1-Phenylheptane	Aldrich	96%
1-Phenyloctane	Aldrich	99%
1-Phenylnonane	Aldrich	97%
1-Phenyldecane	Aldrich	-
n-Heptane	Mallinckrodt	Analytical reagent
n-Nonane	Aldrich	99%
n-Undecane	Aldrich	99%
n-Tridecane	Aldrich	99+%
n-Pentadecane	Aldrich	98%
n-Hexadecane	Aldrich	Spectrophotometric grade (99+%)
Sodium salicylate	MC/B	-
n-Butylcarbitol	Fisher Scientific Co.	Certified A.C.S.

constant temperature water bath. In each test tube two distinct liquid phases were present. After the thirty minutes had elapsed, n-butylcarbitol was added until a single phase resulted.

Upon completion of the titrations, the test tubes were again thermostatted and then examined for the presence of two phases. Additional n-butylcarbitol was added if necessary. The test tubes were allowed to air dry and then were weighed. From the weights of the various components the phase boundary diagrams were calculated.

2. Karl Fischer Titrations

To standardize the Karl Fischer reagent, milligram samples of water were added to the flask containing the two platinum electrodes. Karl Fischer reagent was then added dropwise from the buret. During the titration no current flowed through the circuit due to the absence of free iodine. At the endpoint there was a surge of current due to cathode depolarization by free iodine. The microammeter was used to signify the end of the titration. Calculations were done in terms of grams of water per milliliter of Karl Fischer reagent. Due to small sample sizes and barely adequately reproducibility, at least ten determinations on the Karl Fischer reagent were performed.

CHAPTER III

DATA ANALYSIS

A. Phase Boundary Diagram Calculations

To calculate F_a, the weight fraction of n-butylcarbitol, F_b, the weight fraction of hydrocarbon, and F_c, the weight fraction of water in the mixtures, the equations

$$F_a = [(1 - e)a]/[a + b + c\ (\frac{1000}{1000 + 160.11\ d})], \tag{2}$$

$$F_b=[(1 - f)b]/[a + b + c\ (\frac{1000}{1000 + 160.11\ d})], \tag{3}$$

and

$$F_c = [ea + fb + c\ (\frac{1000}{1000 + 160.11\ d})]/[a + b + c\ (\frac{1000}{1000 + 160.11\ d})] \tag{4}$$

were used, where

a = weight of n-butyl carbitol,

b = weight of hydrocarbon,

c = weight of aqueous sodium salicylate,

d = molality of aqueous sodium salicylate,

e = weight fraction of water in n-butylcarbitol

f = weight fraction of water in the hydrocarbon, and

160.11 = the molecular weight of sodium salicylate.

F_a, F_b, and F_c were plotted on triangular co-ordinate graph paper. Through these points the phase boundary diagrams were drawn.

For a number of mixtures, phase boundary diagrams were obtained by treating the aqueous sodium salicylate solutions as single components instead of considering only the water contained in these solutions.

B. Error Analysis

The experimental uncertainties associated with the quantities a, b, and c were determined. The weight of the hydrocarbon and the weight of aqueous sodium salicylate had uncertainties of $\pm$ 0.0002 g. This value was determined by repeatedly weighing a test tube and then calculating S, the standard deviation, from the formula

$$S = \{[n \sum_{i=1}^{n} X_i^2 - (\sum_{i=1}^{n} X_i)^2]/n(n-1)\}^{1/2}, \tag{5}$$

where n is the number of experimental points and X_i is the ith experimental point. The weight of the n-butylcarbitol also had this uncertainty; however, there was another important source of error. One could quite easily add one drop too much or one drop too little. Consequently the average weight of a drop falling from the syringe needle was determined. This weight was 0.0050 g; hence the total uncertainty in the weight of the n-butylcarbitol was $\pm$ 0.0052 g.

To obtain ΔF_a, the uncertainty in the calculated weight fraction of n-butylcarbitol, a standard procedure involving partial differentiation was employed.

$$\Delta F_a = \left(\frac{\partial F_a}{\partial a}\right)_{b,c} \Delta a + \left(\frac{\partial F_a}{\partial b}\right)_{a,c} \Delta b + \left(\frac{\partial F_a}{\partial c}\right)_{a,b} \Delta c, \tag{6}$$

where

$\Delta a = \pm$ 0.0052 g, the uncertainty of the n-butylcarbitol weight,

$\Delta b = \pm$ 0.0002 g, the uncertainty of the hydrocarbon weight,

$\Delta c = \pm$ 0.0002 g, the uncertainty of the aqueous sodium salicylate weight,

$$\left(\frac{\partial F}{\partial a}\right)_{b,c} = (1 - e)/\left[a + b + c\left(\frac{1000}{1000 + 160.11d}\right)\right] -$$

$$(1 - e)a/\left[a + b + c\left(\frac{1000}{1000 + 160.11d}\right)\right]^2, \tag{7}$$

$$\left(\frac{\partial F}{\partial b}\right)_{a,c} = -(1 - e)a/\left[a + b + c\left(\frac{1000}{1000 + 160.11d}\right)\right]^2, \tag{8}$$

and

$$\left(\frac{\partial F}{\partial c}\right)_{a,b} = -(1 - e)a/\left\{\left(\frac{1000}{1000 + 160.11d}\right)\right.$$

$$\left.\left[a + b + c\left(\frac{1000}{1000 + 160.11d}\right)\right]^2\right\}. \tag{9}$$

To obtain the uncertainty associated with points estimated from the phase boundary graphs, the actual values of plotted data points were compared to the estimated values.

CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

A. Phase Boundary Curves

Tables II through V contain data which describe the phase boundary curves for all systems studied. The data presented in the tables were calculated by treating the water in the aqueous sodium salicylate solutions as one component in the mixture; thus each system consisted of n-butylcarbitol, a hydrocarbon, and water. Only the weight fraction of the hydrocarbon and the weight fraction of n-butylcarbitol are given, for the sum of all three weight fractions equals unity.

For each phase boundary curve, measurements at the points at which the curve intersects the baseline were not made. Measurements were made, however, over a wide range of the central part of the phase diagrams.

The phase boundary diagrams for benzene and toluene were quite similar. At 6.0 molal aqueous sodium salicylate, the curves were almost symmetrical. In each case the curve was skewed slightly to the right. At 2.5 molal sodium salicylate the curves were symmetrical. In fact, the curves were nearly flat over a wide region. At 1.0 molal the curves were quite asymmetrical; they rose steeply at first, leveled off, and then began to drop slowly at the point corresponding to 1:1 weight fraction mixtures of hydrocarbons and water. For mixtures containing no sodium salicylate, the curves were skewed slightly to the left.

TABLE II

WEIGHT FRACTIONS OF n-BUTYLCARBITOL AND HYDROCARBONS IN MIXTURES AT ZERO MOLAL AQUEOUS SODIUM SALICYLATE

F_a^1	F_b^2	F_a	F_b	F_a	F_b
Benzene		Toluene		1-Phenylethane	
0.169	0.825	0.137	0.858	0.192	0.802
0.397	0.565	0.368	0.599	0.369	0.589
0.509	0.398	0.492	0.411	0.458	0.441
0.550	0.308	0.527	0.324	0.487	0.353
0.555	0.213	0.528	0.221	0.486	0.218
0.476	0.119	0.462	0.110	0.426	0.116
0.311	0.039	0.307	0.037	0.295	0.036
0.150	0.007	0.164	0.006	0.177	0.006
p-Xylene		1-Phenylbutane		1-Phenylhexane	
0.173	0.820	0.152	0.844	0.127	0.870
0.348	0.616	0.291	0.672	0.264	0.697
0.457	0.441	0.387	0.510	0.398	0.502
0.493	0.286	0.452	0.329	0.502	0.294
0.468	0.188	0.455	0.196	0.529	0.175
0.427	0.118	0.417	0.121	0.511	0.097
0.288	0.038	0.314	0.039	0.423	0.034
0.181	0.007	0.231	0.007	0.292	0.006
Cyclohexane		1-Phenylheptane		1-Phenyloctane	
0.094	0.902	0.130	0.864	0.138	0.855
0.223	0.736	0.255	0.708	0.295	0.668
0.404	0.486	0.472	0.389	0.461	0.436
0.485	0.350	0.544	0.240	0.535	0.318
0.530	0.219	0.562	0.163	0.599	0.190
0.488	0.103	0.561	0.119	0.594	0.078
0.353	0.036	0.508	0.055	0.503	0.029
0.207	0.006	0.354	0.011	0.349	0.005
1-Phenylnonane		1-Phenyldecane		n-Heptane	
0.128	0.867	0.134	0.860	0.124	0.870
0.392	0.556				
0.295	0.669	0.431	0.507	0.431	0.526
0.483	0.427	0.589	0.297	0.666	0.209
0.564	0.307	0.653	0.183	0.682	0.146
0.648	0.151	0.672	0.125	0.668	0.096
0.621	0.062	0.658	0.064	0.638	0.071
0.550	0.026	0.551	0.022	0.547	0.033
		0.407	0.005	0.284	0.004

TABLE II (Continued)

F_a	F_b	F_a	F_b	F_a	F_b
n-Nonane		n-Undecane		n-Tridecane	
0.119	0.876	0.173	0.821	0.119	0.878
0.470	0.492	0.407	0.572	0.606	0.371
0.688	0.236	0.732	0.206	0.762	0.192
0.737	0.119	0.772	0.143	0.814	0.089
0.550	0.018	0.783	0.094	0.815	0.060
0.356	0.004	0.738	0.047	0.786	0.036
		0.622	0.016	0.708	0.015
		0.324	0.001	0.538	0.004
b-Pentadecane		n-Hexadecane			
0.179	0.818	0.422	0.571		
0.613	0.371	0.711	0.272		
0.795	0.166	0.819	0.147		
0.837	0.100	0.858	0.081		
0.846	0.068	0.859	0.478		
0.829	0.038	0.839	0.029		
0.758	0.016	0.769	0.012		
0.599	0.004	0.640	0.003		

[1]Weight fraction of n-butylcarbitol.
[2]Weight fraction of hydrocarbon.

TABLE III

WEIGHT FRACTIONS OF n-BUTYLCARBITOL AND HYDROCARBONS IN MIXTURES AT 1 MOLAL AQUEOUS SODIUM SALICYLATE

F_a^1	F_b^2	F_a	F_b	F_a	F_b
Benzene		Toluene		1-Phenylethane	
0.101	0.897	0.103	0.895	0.082	0.916
0.342	0.630	0.292	0.673	0.258	0.713
0.384	0.516	0.313	0.634	0.344	0.565
0.402	0.379	0.346	0.516	0.394	0.378
0.352	0.266	0.349	0.227	0.364	0.153
0.278	0.151	0.375	0.290	0.307	0.055
0.211	0.056	0.283	0.096	0.198	0.010
0.123	0.010	0.222	0.031		
		0.146	0.008		
p-Xylene		1-Phenylbutane		1-Phenylhexane	
0.128	0.869	0.116	0.882	0.108	0.889
0.263	0.702	0.242	0.730	0.244	0.725
0.360	0.541	0.350	0.565	0.385	0.528
0.403	0.380	0.433	0.371	0.472	0.364
0.365	0.151	0.461	0.232	0.537	0.191
0.276	0.044	0.452	0.130	0.525	0.113
0.192	0.008	0.372	0.046	0.440	0.040
		0.255	0.008	0.312	0.007
Cyclohexane		1-Phenylheptane		1-Phenyloctane	
0.088	0.908	0.047	0.952	0.050	0.948
0.254	0.707	0.237	0.731	0.248	0.723
0.401	0.499	0.452	0.425	0.409	0.515
0.518	0.292	0.536	0.270	0.503	0.379
0.54]	0.182	0.563	0.188	0.566	0.266
0.502	0.102	0.553	0.099	0.600	0.193
0.392	0.044	0.457	0.032	0.605	0.039
0.225	0.006	0.320	0.008	0.524	0.039
				0.381	0.008

TABLE III (Continued)

F_a	F_b	F_a	F_b	F_a	F_b
1-Phenylnonane		1-Phenyldecane		n-Heptane	
0.069	0.930	0.054	0.945	0.083	0.916
0.279	0.694	0.288	0.682	0.399	0.571
0.441	0.488	0.553	0.349	0.639	0.266
0.527	0.371	0.645	0.205	0.684	0.166
0.633	0.197	0.665	0.086	0.684	0.122
0.635	0.080	0.430	0.008	0.662	0.093
0.570	0.037			0.585	0.047
0.425	0.010			0.282	0.006
n-Nonane		n-Undecane		n-Tridecane	
0.079	0.920	0.008	0.917	0.189	0.808
0.432	0.538	0.475	0.502	0.536	0.448
0.638	0.303	0.690	0.265	0.724	0.242
0.733	0.161	0.774	0.142	0.802	0.136
0.735	0.093	0.786	0.087	0.792	0.057
0.708	0.063	0.760	0.056	0.733	0.023
0.591	0.026	0.643	0.022	0.562	0.006
0.376	0.005	0.462	0.006		
n-Pentadecane		n-Hexadecane			
0.072	0.928	0.399	0.595		
0.594	0.391	0.688	0.297		
0.764	0.205	0.812	0.158		
0.826	0.120	0.857	0.089		
0.843	0.074	0.860	0.054		
0.838	0.046	0.844	0.035		
0.742	0.014	0.773	0.014		
0.651	0.007	0.691	0.006		

[1]Weight fraction of n-butylcarbitol.
[2]Weight fraction of hydrocarbon.

TABLE IV

WEIGHT FRACTIONS OF n-BUTYLCARBITOL AND HYDROCARBONS IN MIXTURES AT 2.5 MOLAL AQUEOUS SODIUM SALICYLATE

F_a^1	F_b^2	F_a	F_b	F_a	F_b
Benzene		Toluene		1-Phenylethane	
0.171	0.822	0.075	0.922	0.118	0.879
0.218	0.758	0.207	0.776	0.192	0.781
0.271	0.642	0.267	0.681	0.259	0.651
0.298	0.556	0.344	0.383	0.322	0.526
0.318	0.406	0.350	0.306	0.377	0.349
0.308	0.212	0.333	0.176	0.383	0.183
0.233	0.069	0.271	0.066	0.318	0.063
0.110	0.012	0.168	0.016	0.200	0.011
p-Xylene		1-Phenylbutane		1-Phenylhexane	
0.148	0.846	0.141	0.854	0.124	0.872
0.218	0.740	0.194	0.786	0.209	0.765
0.273	0.642	0.288	0.640	0.356	0.564
0.347	0.460	0.394	0.436	0.463	0.382
0.386	0.302	0.463	0.262	0.529	0.235
0.393	0.191	0.466	0.164	0.538	0.144
0.315	0.060	0.395	0.056	0.472	0.053
0.199	0.011	0.285	0.013	0.335	0.010
Cyclohexane		1-Phenylheptane		1-Phenyloctane	
0.084	0.913	0.098	0.898	0.032	0.967
0.216	0.752	0.226	0.748	0.218	0.759
0.393	0.518	0.526	0.306	0.401	0.529
0.471	0.399	0.572	0.160	0.473	0.422
0.527	0.259	0.563	0.118	0.583	0.236
0.519	0.125	0.540	0.073	0.597	0.098
0.408	0.045	0.409	0.018	0.553	0.054
0.194	0.007	0.241	0.002	0.385	0.008

TABLE IV (Continued)

F_a	F_b	F_a	F_b	F_a	F_b
1-Phenylnonane		1-Phenyldecane		n-Heptane	
0.073	0.925	0.062	0.937	0.079	0.920
0.274	0.704	0.388	0.570	0.344	0.628
0.433	0.503	0.519	0.399	0.621	0.296
0.505	0.411	0.619	0.254	0.677	0.198
0.627	0.216	0.656	0.189	0.688	0.147
0.649	0.089	0.668	0.136	0.676	0.100
0.575	0.040	0.646	0.069	0.607	0.054
0.442	0.008	0.470	0.010	0.532	0.035
				0.322	0.007
n-Nonane		n-Undecane		n-Tridecane	
0.138	0.858	0.232	0.763	0.257	0.738
0.367	0.612	0.670	0.287	0.506	0.480
0.650	0.293	0.736	0.205	0.710	0.260
0.732	0.168	0.778	0.133	0.798	0.147
0.738	0.097	0.771	0.063	0.822	0.092
0.715	0.067	0.643	0.028	0.811	0.055
0.600	0.026	0.422	0.006	0.732	0.024
0.392	0.005			0.550	0.007
n-Pentadecane		n-Hexadecane			
0.101	0.898	0.285	0.712		
0.581	0.406	0.656	0.332		
0.731	0.240	0.801	0.174		
0.834	0.050	0.853	0.101		
0.770	0.021	0.863	0.064		
0.602	0.006	0.854	0.041		
		0.801	0.021		
		0.635	0.005		

[1]Weight fraction of n-butylcarbitol.
[2]Weight fraction of hydrocarbon.

TABLE V

WEIGHT FRACTIONS OF n-BUTYLCARBITOL AND HYDROCARBONS IN MIXTURES AT 6 MOLAL AQUEOUS SODIUM SALICYLATE

F_a^1	F_b^2	F_a	F_b	F_a	F_b
Benzene		Toluene		1-Phenylethane	
0.053	0.946	0.064	0.935	0.046	0.953
0.134	0.829	0.230	0.664	0.201	0.730
0.236	0.620	0.309	0.497	0.266	0.618
0.294	0.473	0.342	0.397	0.362	0.423
0.309	0.403	0.359	0.298	0.407	0.227
0.315	0.229	0.349	0.177	0.349	0.085
0.247	0.102	0.280	0.081	0.200	0.017
0.083	0.019	0.131	0.016	0.080	0.004
p-Xylene		1-Phenylbutane		1-Phenylhexane	
0.088	0.909	0.064	0.935	0.102	0.896
0.129	0.853	0.246	0.691	0.188	0.794
0.210	0.725	0.368	0.493	0.367	0.581
0.321	0.523	0.457	0.310	0.443	0.433
0.393	0.346	0.484	0.184	0.529	0.270
0.419	0.217	0.428	0.068	0.554	0.163
0.355	0.085	0.294	0.016	0.506	0.066
0.192	0.016	0.183	0.005	0.357	0.015
Cyclohexane		1-Phenylheptane		1-Phenyloctane	
0.063	0.936	0.066	0.933	0.038	0.961
0.170	0.809	0.163	0.815	0.137	0.854
0.333	0.604	0.378	0.538	0.324	0.624
0.433	0.470	0.500	0.367	0.385	0.543
0.525	0.318	0.552	0.268	0.560	0.293
0.555	0.163	0.571	0.205	0.614	0.131
0.461	0.061	0.582	0.147	0.575	0.062
0.226	0.013	0.523	0.054	0.427	0.014
		0.445	0.025		
		0.248	0.005		

TABLE V (Continued)

F_a	F_b	F_a	F_b	F_a	F_b
1-Phenylnonane		1-Phenyldecane		n-Heptane	
0.073	0.926	0.085	0.913	0.079	0.920
0.211	0.774	0.311	0.657	0.366	0.608
0.369	0.585	0.460	0.477	0.625	0.301
0.470	0.458	0.644	0.221	0.684	0.197
0.600	0.268	0.668	0.159	0.695	0.157
0.649	0.122	0.674	0.117	0.692	0.119
0.610	0.058	0.619	0.045	0.623	0.061
0.459	0.012	0.490	0.013	0.417	0.015
n-Nonane		n-Undecane		n-Tridecane	
0.066	0.933	0.069	0.930	0.198	0.798
0.364	0.616	0.431	0.553	0.420	0.570
0.604	0.352	0.663	0.301	0.695	0.280
0.721	0.200	0.787	0.133	0.788	0.167
0.748	0.124	0.785	0.070	0.823	0.109
0.736	0.083	0.703	0.029	0.827	0.074
0.645	0.035	0.544	0.008	0.776	0.034
0.476	0.008	0.463	0.004	0.626	0.008
n-Pentadecane		n-Hexadecane			
0.268	0.728	0.078	0.922		
0.536	0.454	0.449	0.545		
0.741	0.237	0.623	0.368		
0.817	0.147	0.847	0.117		
0.849	0.092	0.866	0.077		
0.852	0.062	0.865	0.049		
0.810	0.029	0.815	0.022		
0.662	0.009	0.664	0.006		

[1]Weight fraction of n-butylcarbitol.
[2]Weight fraction of hydrocarbon.

The phase boundary diagrams for 1-phenylethane and p-xylene were quite similar. At both 6.0 and 2.5 molal aqueous sodium salicylate, the curves were skewed to the right. At 1.0 molal the curves were broad and symmetrical. For mixtures containing no sodium salicylate, the curves were skewed slightly to the left.

The phase boundary diagrams for 1-phenylbutane at both 6.0 and 2.5 molal aqueous sodium salicylate were skewed to the right. At 1.0 molal the curve was skewed somewhat to the right. For the mixture containing no sodium salicylate, the curve was symmetrical.

The phase boundary diagrams for 1-phenylhexane, cyclohexane, 1-phenylheptane, 1-phenyloctane, 1-phenylnonane, and 1-phenyldecane were quite similar. All curves were skewed slightly to the right.

The phase boundary diagrams for n-heptane, n-nonane, n-undecane, n-tridecane, n-pentadecane, and n-hexadecane were all symmetrical.

B. Effect of Increasing the Aqueous Sodium Salicylate Concentration

Tables VI and VII contain the minimum weight fractions of n-butyl-carbitol necessary to produce miscibility in 1:1 weight fraction mixtures of hydrocarbons and aqueous sodium salicylate solutions, and hydrocarbons and water respectively. In the former case the aqueous sodium salicylate was treated as one component in the mixture. In the latter the water in the aqueous salt solutions was treated as one component.

When treating aqueous sodium salicylate as a mixture component, increasing the salt concentration caused salting-in for each hydro-carbon, that is, increasing the salt concentration caused a decrease in

TABLE VI

MINIMUM WEIGHT FRACTIONS[1] OF n-BUTYLCARBITOL NECESSARY TO PRODUCE MISCIBILITY IN 1:1 WEIGHT FRACTION MIXTURES OF HYDROCARBONS AND AQUEOUS SODIUM SALICYLATE

	Molality of Aqueous Sodium Salicylate		
	1	2.5	6
	F_a[2]	F_a	F_a
Benzene	0.365	0.288	0.243
Toluene	0.359	0.310	0.272
1-Phenylethane	0.382	0.341	0.306
p-Xylene	0.380	0.341	0.309
1-Phenylbutane	0.434	0.405	0.362
1-Phenylhexane	0.503	0.472	0.433
Cyclohexane	-	0.487	0.458
1-Phenylheptane	0.533	0.511	0.463
1-Phenyloctane	0.576	0.545	0.495
1-Phenylnonane	0.615	0.593	0.537
1-Phenyldecane	0.649	0.613	0.562
n-Heptane	0.668	0.646	0.615
n-Nonane	-	-	-
n-Undecane	0.775	0.752	0.730
n-Tridecane	0.803	-	-
n-Pentadecane	0.832	0.815	0.806

[1] Estimated from graphs.
[2] Weight fraction of n-butylcarbitol.

TABLE VII

MINIMUM WEIGHT FRACTIONS[1] OF n-BUTYLCARBITOL NECESSARY TO PRODUCE MISCIBILITY IN 1:1 WEIGHT FRACTION MIXTURES OF HYDROCARBONS AND WATER

Hydrocarbon	Molality of Aqueous Sodium Salicylate							
	0		1		2.5		6	
	F_a[2]	± x[3]	F_a	± x	F_a	± x	F_a	± x
Benzene	0.557	0.005	0.380	0.003	0.319	0.003	0.319	0.003
Toluene	0.529	0.003	0.375	0.003	0.350	0.003	0.357	0.004
1-Phenylethane	0.493	0.003	0.400	0.004	0.382	0.003	0.400	0.004
p-Xylene	0.491	0.003	0.405	0.003	0.384	0.003	0.402	0.004
1-Phenylbutane	0.461	0.003	0.458	0.003	0.462	0.003	0.473	0.004
1-Phenylhexane	0.518	0.003	0.522	0.003	0.529	0.003	0.544	0.004
Cyclohexane	0.527	0.004	0.532	0.003	0.531	0.004	0.577	0.005
1-Phenylheptane	0.550	0.003	0.553	0.003	0.564	0.003	0.569	0.004
1-Phenyloctane	0.593	0.003	0.597	0.003	0.598	0.004	0.607	0.005
1-Phenylnonane	0.638	0.003	0.639	0.003	0.640	0.004	0.641	0.004
1-Phenyldecane	0.659	0.003	0.661	0.003	0.663	0.003	0.665	0.003
n-Heptane	0.681	0.003	0.686	0.003	0.688	0.003	0.697	0.004
n-Nonane	0.734	0.003	0.741	0.003	0.743	0.003	0.748	0.003
n-Undecane	0.783	0.003	0.785	0.003	0.786	0.003	0.792	0.003
n-Tridecane	0.814	0.003	0.815	0.003	0.822	0.003	0.828	0.003
n-Pentadecane	0.845	0.002	0.843	0.002	0.844	0.003	0.852	0.003
n-Hexadecane	0.859	0.002	0.861	0.002	0.863	0.002	0.868	0.002

[1]Estimated from graphs.
[2]Weight fraction of n-butylcarbitol.
[3]Total uncertainty.

the amount of n-butylcarbitol necessary to produce miscibility (compared to the amount of n-butylcarbitol required to produce miscibility in pure water). For benzene, toluene, 1-phenylethane, and p-xylene, salting-in was quite dramatic up to 2.5 molal. For the remaining hydrocarbons, gradual salting-in took place upon increasing the salt concentration.

When treating the data on a water basis, increasing the salt concentration caused salting-in for some hydrocarbons and salting-out for others. For benzene, toluene, 1-phenylethane, and p-xylene salting-in was observed; maximum salting-in occurred at 2.5, 1.5, 2.0, and 2.5 molal, respectively. For benzene and toluene the amount of n-butylcarbitol necessary to produce miscibility remained constant upon increasing the salt concentration above 2.5 and 1.5 molal, respectively. For 1-phenylethane and p-xylene the amount of n-butylcarbitol increased at salt concentrations greater than 2.0 and 2.5 molal, respectively. For 1-phenylbutane maximum salting-in occurred at 1.5 molal. Then salting-out began to take place. At 2.5 molal the amount of n-butylcarbitol necessary to produce miscibility was the same as that required for the mixture containing no sodium salicylate. Beyond 2.5 molal true salting-out occurred. For the remaining hydrocarbons, slight salting-out took place. The amount of n-butylcarbitol necessary for miscibility increased in a linear fashion as the salt concentration increased.

C. Effect of Increasing the Chain Length of n-Alkanes and Alkylbenzenes

For each aqueous sodium salicylate concentration, plots were made of hydrocarbon chain length versus the amounts of n-butylcarbitol

necessary to produce miscibility in 1:1 weight fraction mixtures of hydrocarbons and aqueous sodium salicylate solutions, and hydrocarbons and water. In the former case the aqueous sodium salicylate was treated as one component; in the latter, the water in the aqueous sodium salicylate. Figures 2 through 9, pages 27 through 34, contain these plots. Because the n-alkanes exhibited distinctly different behavior from the alkylbenzenes, separate plots were made.

Data from Figures 2 and 3 were taken from systems consisting of alkylbenzenes, n-butylcarbitol, and water; and n-alkanes, n-butylcarbitol, and water (no sodium salicylate was present). As the number of side-chain carbons on the benzene ring increased, the weight fractions of n-butylcarbitol necessary to produce miscibility decreased, passed through a minimum at 1-phenylbutane, and began to increase linearly. For 1-phenylethane and p-xylene approximately the same amount of n-butylcarbitol was required to produce miscibility. Apparently miscibility requirements were determined by the number of carbons in the side chains. For the n-alkanes the weight fractions of n-butylcarbitol gradually increased as the chain length increased. Each n-alkane required more alcohol to produce miscibility than the alkylbenzene with the same number of carbons in the side chain.

Figures 4 and 5, pages 29 and 30, contain plots for the 1.0 molal case. By treating the aqueous sodium salicylate as one component, the curves were slightly lower than those obtained by considering only the water in the salt solutions. The same general shape, however, was maintained. Toluene required slightly less n-butylcarbitol than benzene to produce miscibility. After toluene, the amount of alcohol

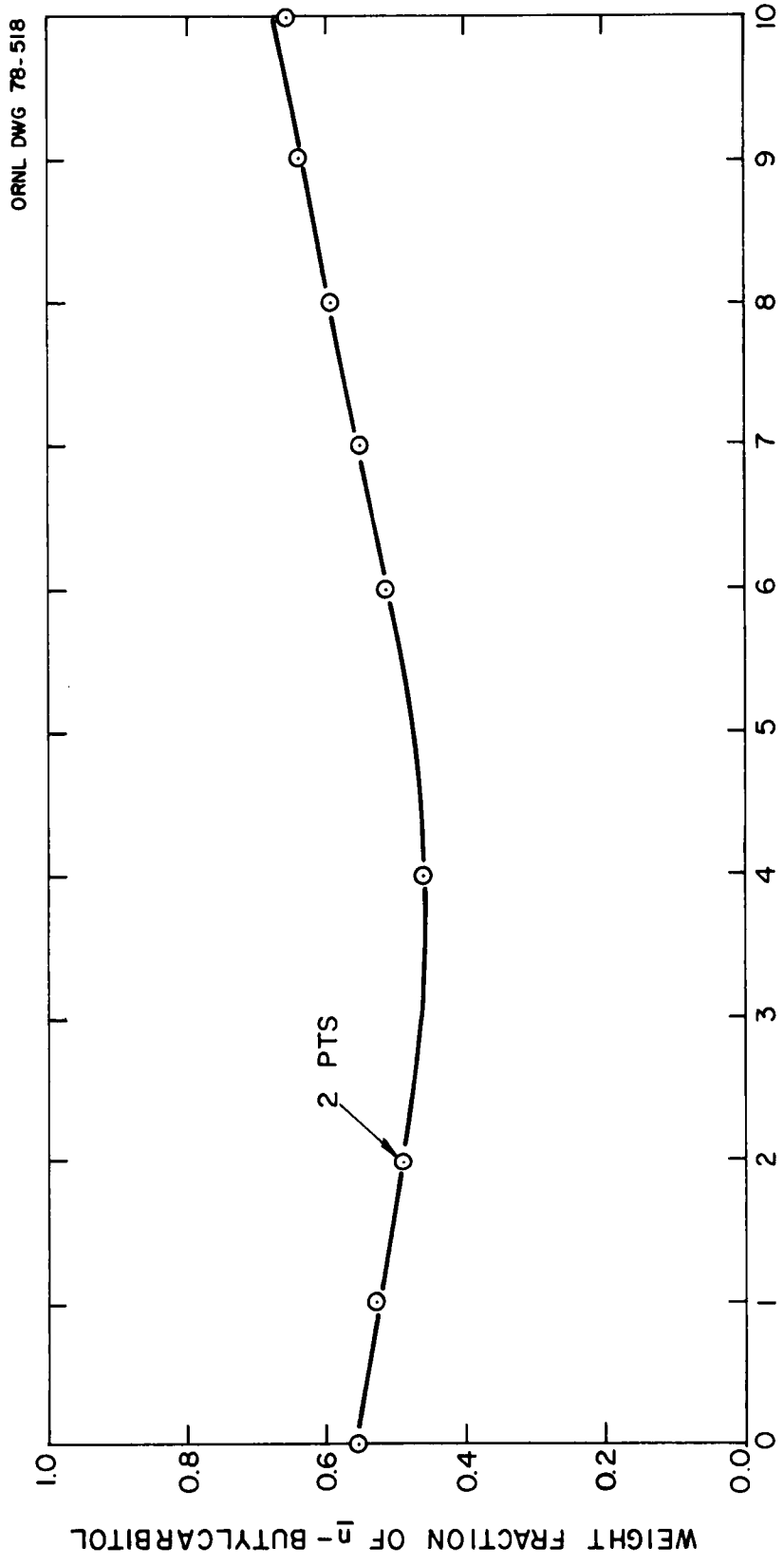


Figure 2. Minimum amount of n-butylcarbitol required to produce miscibility in 1:1 weight fraction mixtures of alkylbenzenes and water.

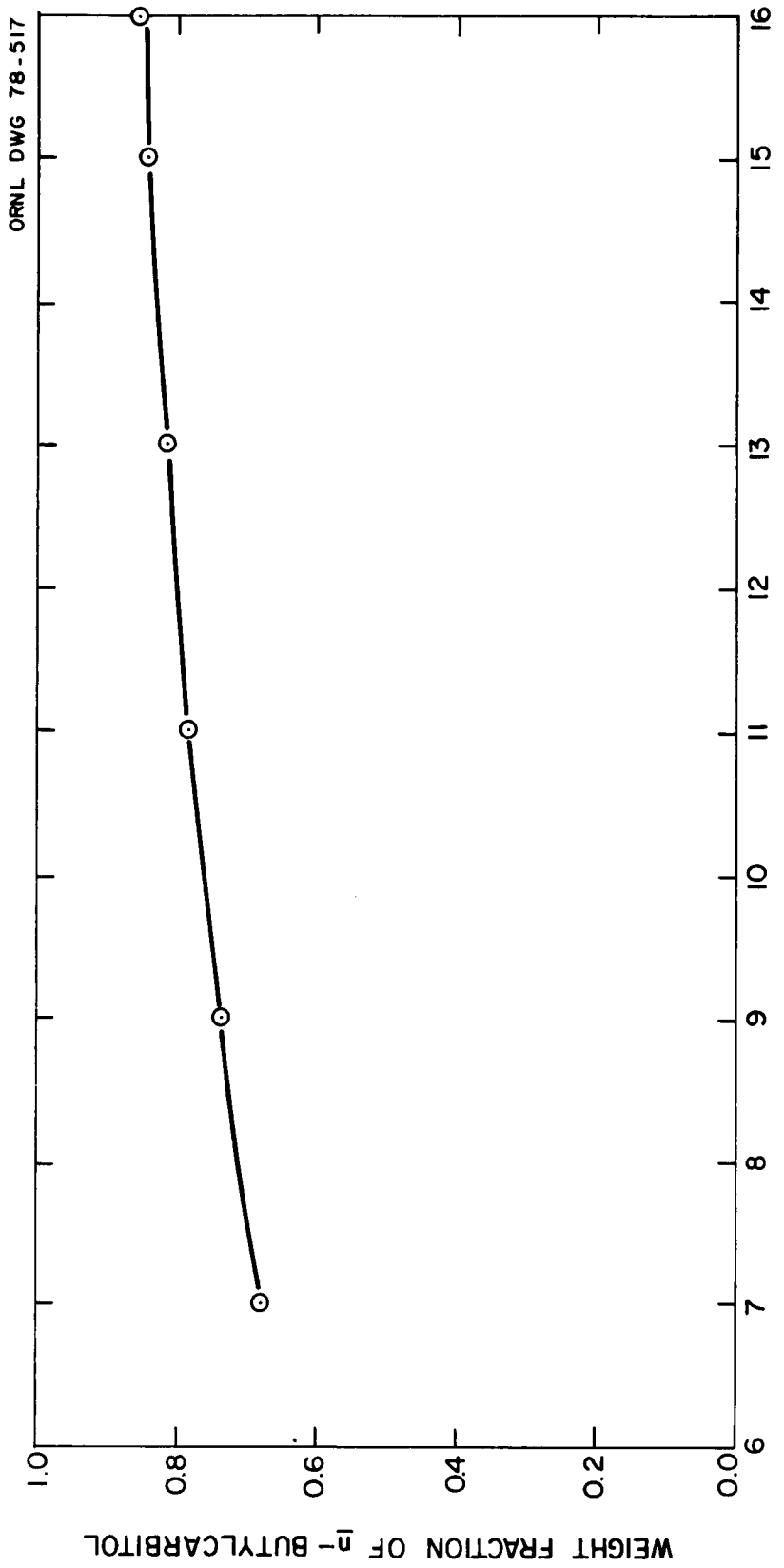


Figure 3. Minimum amount of n-butylcarbitol required to produce miscibility in 1:1 weight fraction mixtures of n-alkanes and water.

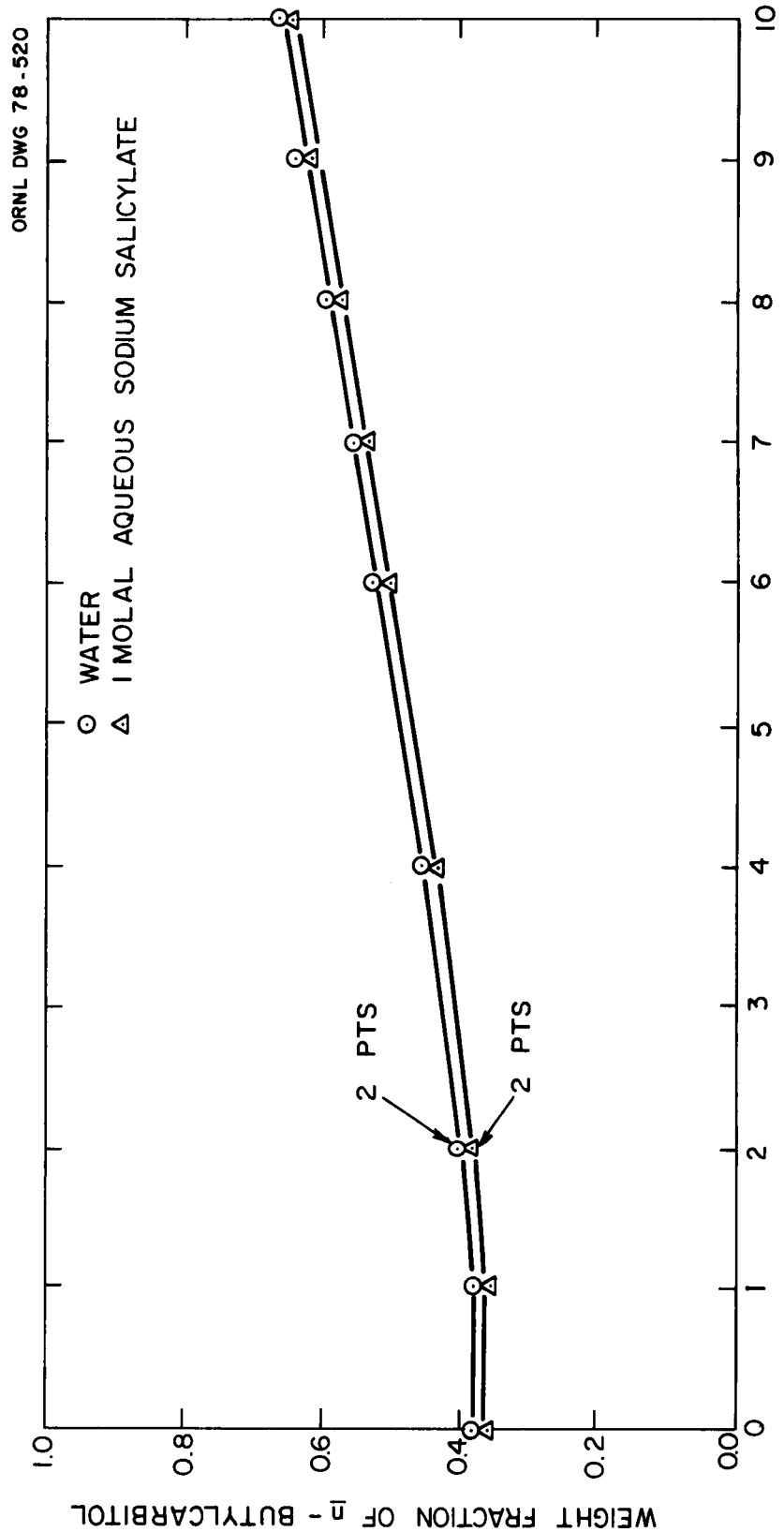


Figure 4. Effect of hydrocarbon chain length on miscibility in the butylcarbitol-1.0 molal aqueous sodium salicylate system (1:1 weight ratio of alkylbenzene and water and 1:1 weight ratio of alkylbenzene and aqueous solution).

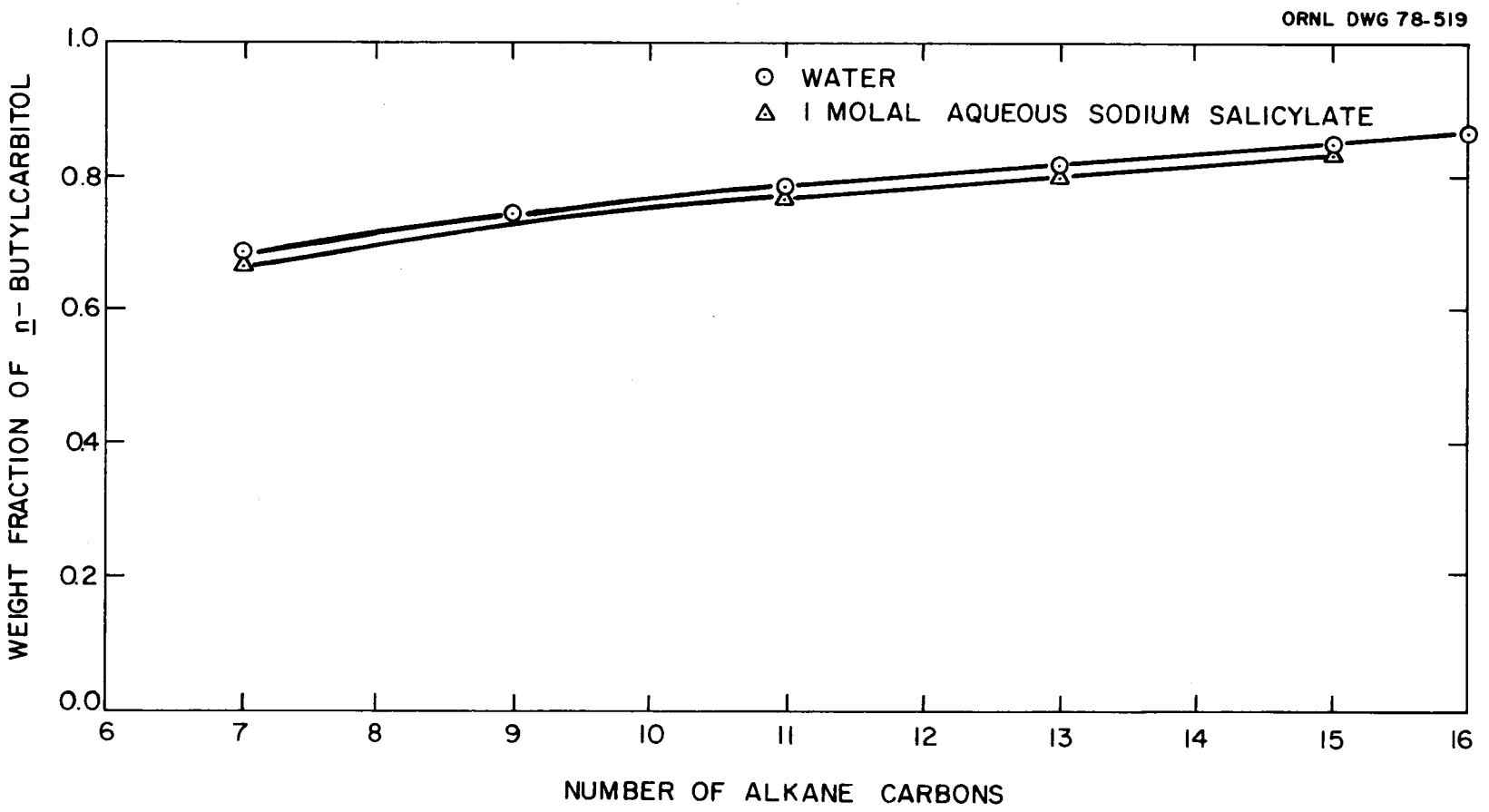


Figure 5. Effect of hydrocarbon chain length on miscibility in the butylcarbitol-1.0 molal aqueous sodium salicylate system (1:1 weight ratio of n-alkanes and water and 1:1 weight ratio of n-alkanes and aqueous solution).

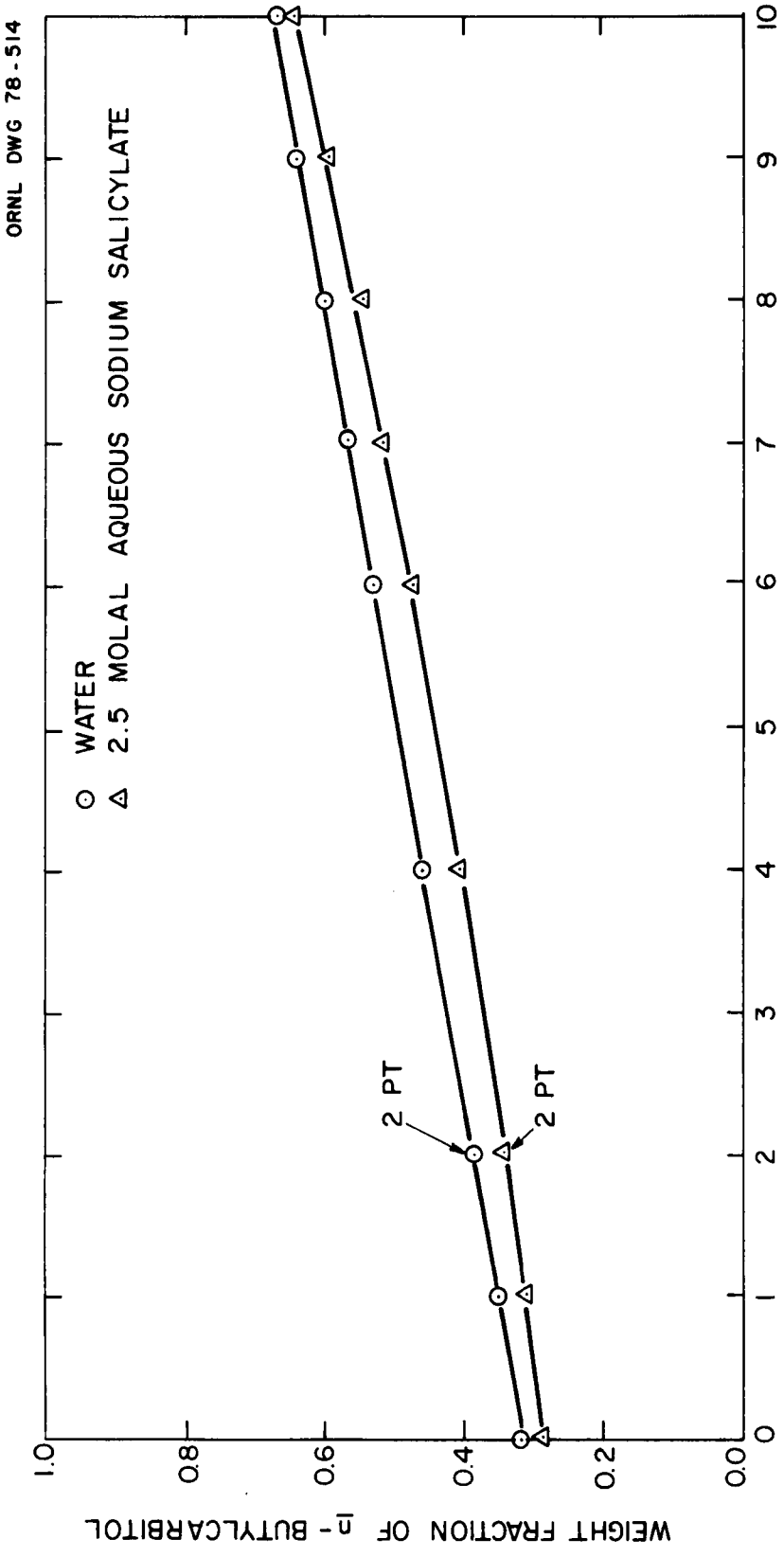


Figure 6. Effect of hydrocarbon chain length on miscibility in the butylcarbitol–2.5 molal aqueous sodium salicylate system (1:1 weight ratio of alkylbenzenes and water and 1:1 weight ratio of alkylbenzenes and aqueous solution).

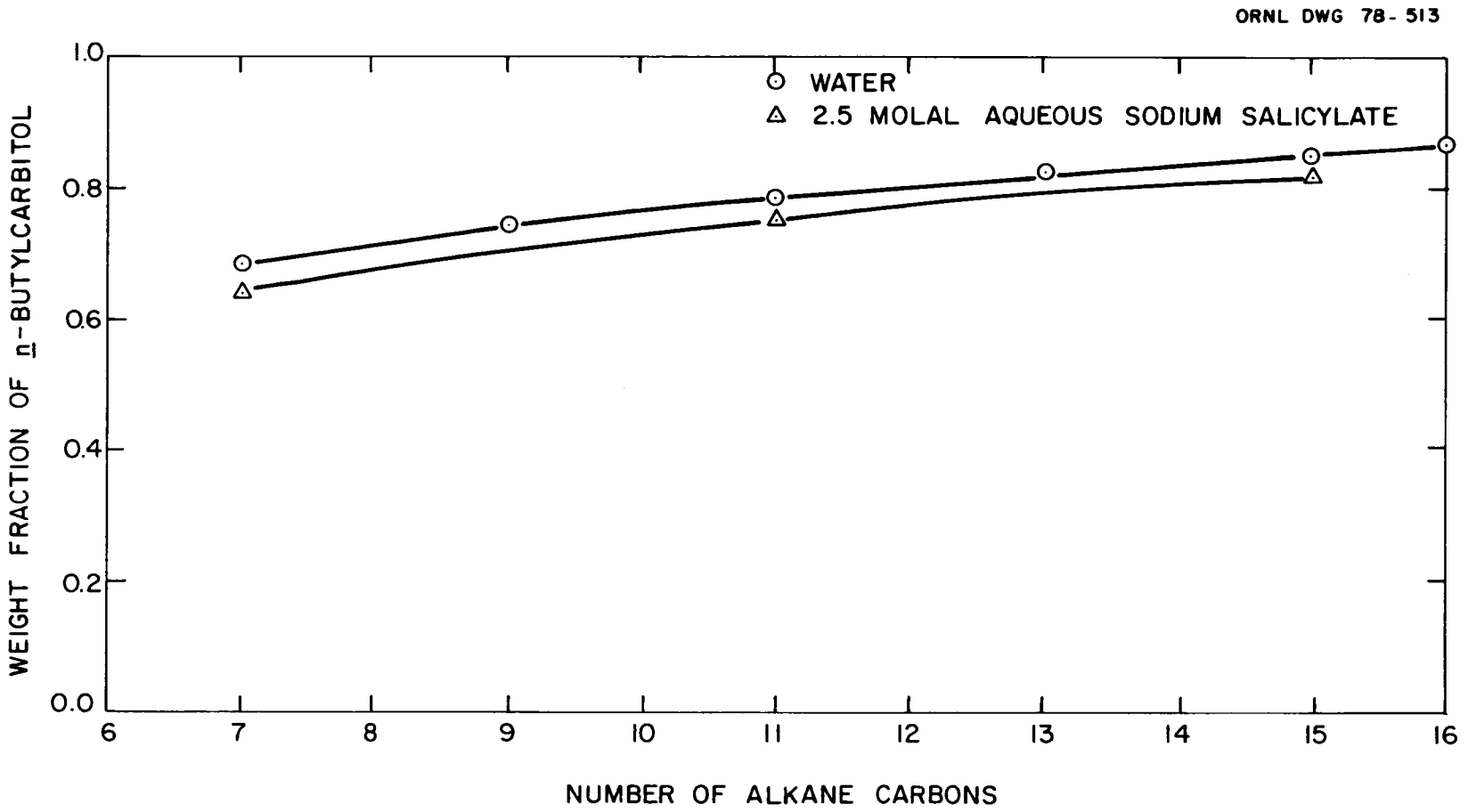


Figure 7. Effect of hydrocarbon chain length on miscibility in the butylcarbitol-2.5 molal aqueous sodium salicylate system (1:1 weight ratio of n-alkanes and water and 1:1 weight ratio of n-alkanes and aqueous solution).

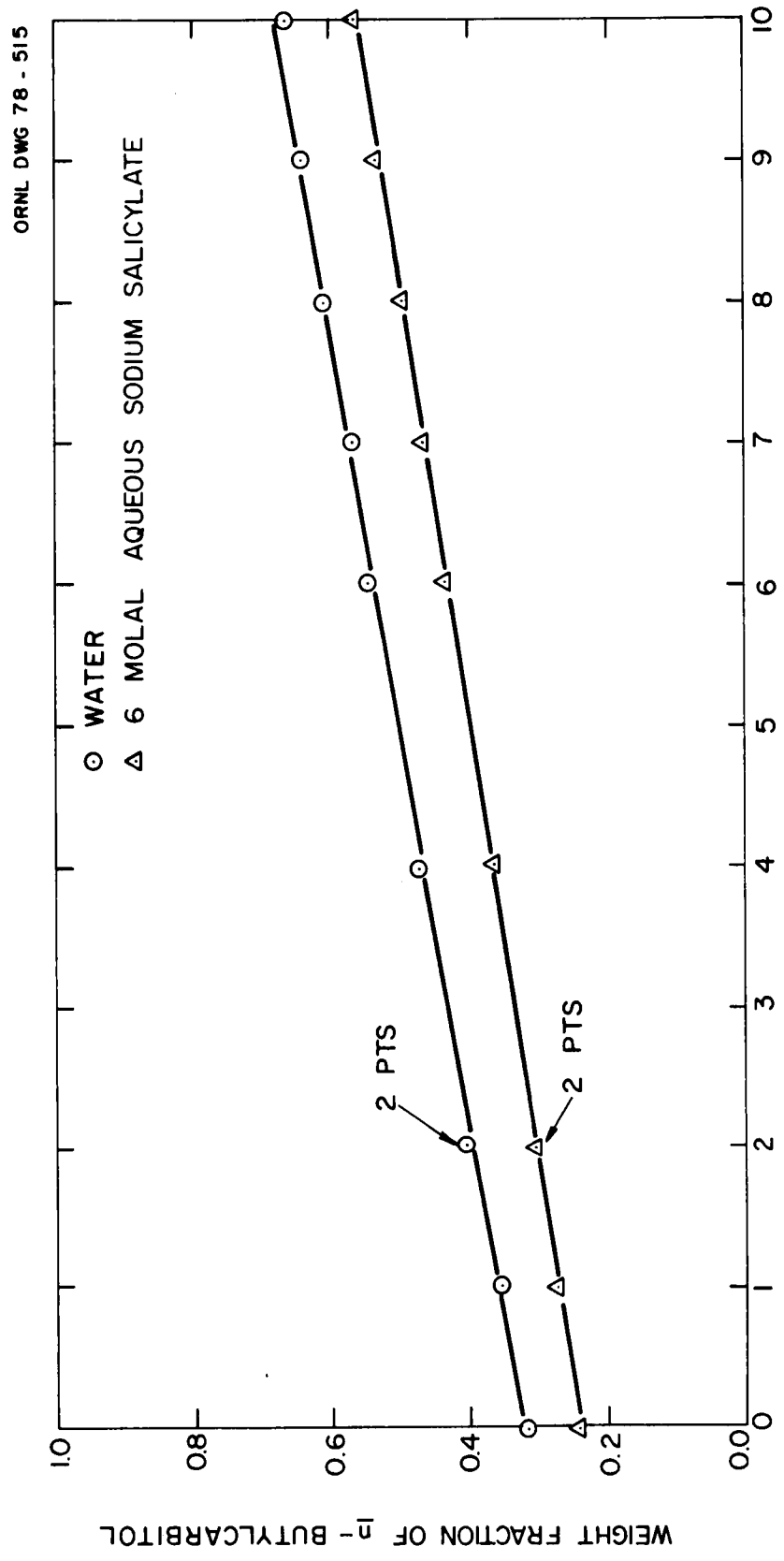


Figure 8. Effect of hydrocarbon chain length on miscibility in the butylcarbitol-6 molal aqueous sodium salicylate system (1:1 weight ratio of alkylbenzenes and water and 1:1 weight ratio of alkylbenzenes and aqueous solution).

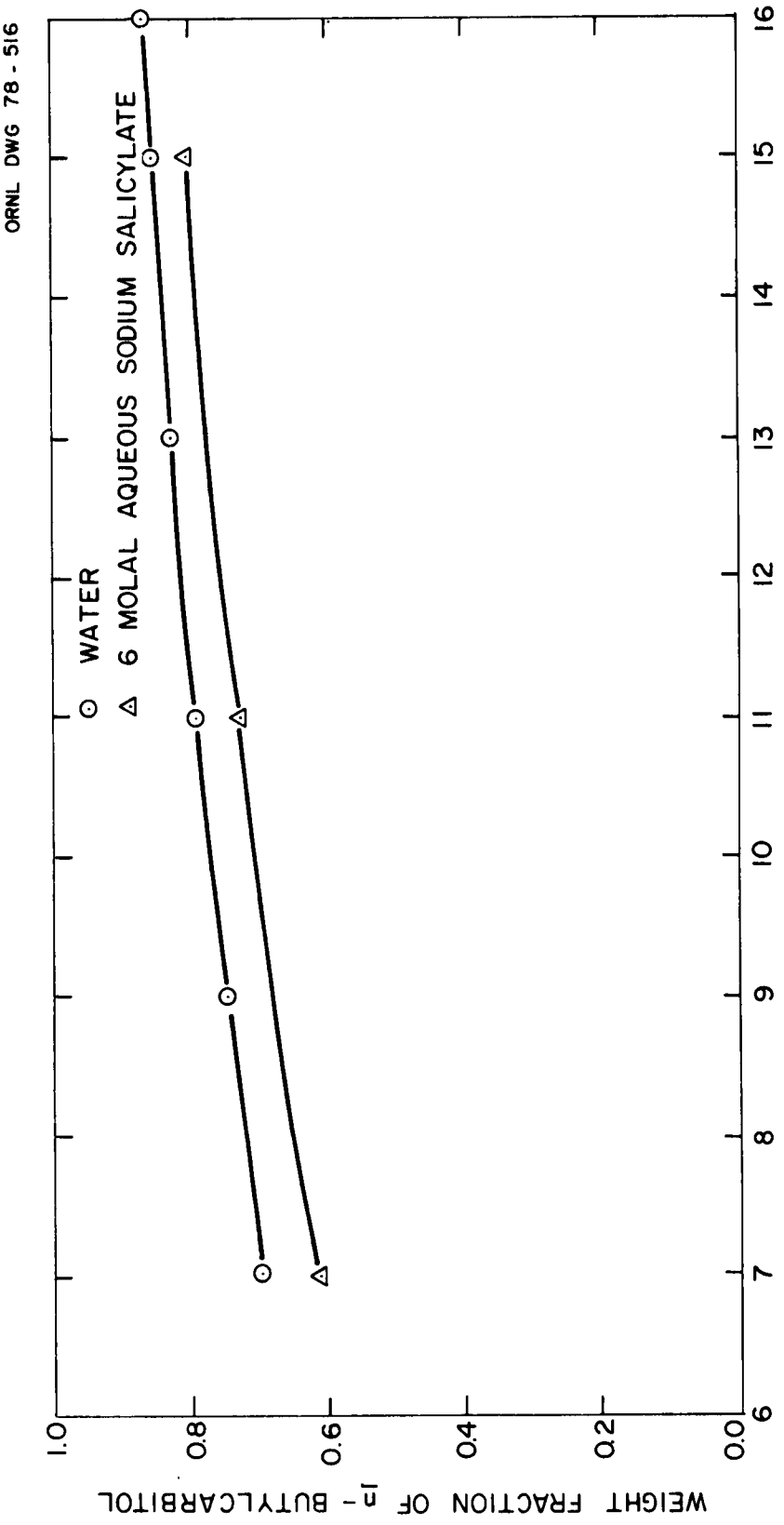


Figure 9. Effect of hydrocarbon chain length on miscibility in the butylcarbitol-6 molal aqueous sodium salicylate system (1:1 weight ratio of n-alkanes and water and 1:1 weight ratio of n-alkanes and aqueous solution).

required for miscibility increased linearly as the number of side-chain carbons increased. Almost the same amount of alcohol was required for 1-phenylethane as for p-xylene. For the n-alkanes the weight fractions of n-butylcarbitol gradually increased as the chain length increased. Each n-alkane required more alcohol to produce miscibility than the alkylbenzene with the corresponding carbon number.

Figures 6 and 7, pages 31 and 32, contain plots for the 2.5 molal case. As before, treating the salt solution as one component resulted in lower curves. For the n-alkanes the same general shape was maintained. The weight fractions of n-butylcarbitol required for miscibility gradually increased as the number of alkane carbons increase. For the alkylbenzenes, however, a straight line was obtained when considering only the water in the aqueous salt solutions as a component. When considering the aqueous sodium salicylate as a component, a slightly nonlinear increase in the weight fractions of n-butylcarbitol was observed up to 1-phenylethane (and p-xylene). Beyond this point the amount of alcohol increased linearly. Almost the same amounts of alcohol were required for 1-phenylethane and p-xylene to produce miscibility. For systems consisting of alkylbenzenes, 1-butanol, and 2.5 molal aqueous sodium p-cymenesulfonate, similar results were obtained.[14] For 1-phenylbutane and p-isopropyltoluene, almost the same amounts of 1-butanol were required to produce miscibility; hence for alkylbenzenes the number of side-chain carbons, not the position, determines the miscibility characteristics. In systems consisting of n-alkanes, 1-butanol, and 2.5 molal aqueous sodium p-cymenesulfonate, with 1-phenylhexane and n-hexane the same amounts of 1-butanol were

required to produce miscibility.[14] At greater alkyl chain lengths the n-alkanes required less. These results are opposite from those obtained with n-butylcarbitol and aqueous sodium salicylate.

Figures 8 and 9, pages 33 and 34, contain plots for the 6.0 molal case. As before, treating the aqueous salt solution as one component resulted in lowered curves. The same general shape was maintained with both the n-alkanes and the alkylbenzenes. For the alkylbenzenes, the amount of n-butylcarbitol required for miscibility increased in a linear fashion as the chain length increased. As has been the case previously, 1-phenylethane and p-xylene required almost the same amounts of alcohol. For the n-alkanes, the weight fractions of of n-butylcarbitol required to produce miscibility gradually increased as the chain length of the alkane increased.

LIST OF REFERENCES

LIST OF REFERENCES

1. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold Publishing Co., New York, N. Y., 1958, p. 531.

2. W. D. Bancroft, Science, 82, 388 (1935).

3. P. A. Winsor, Trans. Faraday Soc., 44, 376 (1948).

4. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold Publishing Co., New York, N. Y., 1958, pp. 80-83.

5. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold Publishing Co., New York, N. Y., 1958, pp. 83-88.

6. B. E. Conway, J. E. Desnoyers, and A. S. Smith, Philos. Trans. R. Soc. London A256, 389 (1964).

7. W. F. McDevit and F. A. Long, J. Am. Chem. Soc., 74, 1773 (1952).

8. F. A. Long and W. F. McDevit, Chem. Rev., 51, 119 (1952).

9. S. K. Shoor and K. E. Gubbins, J. Phys. Chem., 73, 498 (1969).

10. H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys., 31, 369 (1959).

11. H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, J. Chem. Phys., 32, 119 (1960).

12. R. Aveyard and R. Heselden, J. Chem. Soc., Faraday Trans. 1, 71 312 (1975).

13. D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry," 2nd ed., Holt, Rinehart, and Winston, Inc., Atlanta, GA, 1969, pp. 750-751.

14. P. C. Ho, unpublished results, Oak Ridge National Laboratory, Oak Ridge, TN.

VITA

Richard George Burnette was born in Knoxville, Tennessee, on October 18, 1950. He graduated from East High School of Knoxville, Tennessee, in June 1968. After four years at The University of Tennessee he graduated with a B.S. in Chemistry.

In September, 1972 the author was drafted into the Army.

In January, 1975 the author entered the Graduate School of The University of Tennessee, where he held a teaching assistantship.

The author is a member of the American Chemical Society.