UNCLASSIFIED

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

ORNL-957,
Series A
Chemistry

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES
3 4456 0360848 8

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

RATES OF ION EXCHANGE IN NON-AQUEOUS MEDIA

FRANKLIN S. CHANCE, JR.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS DIVISION
UNION CARBIDE AND CARBON CORPORATION
UCC
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

UNCLASSIFIED

UNCLASSIFIED

ORNL-957

This document consists of 57 pages. This is copy 9 of 188, Series A.

Contract W-7405, eng-26

CHEMISTRY DIVISION

RATES OF ION EXCHANGE IN NON-AQUEOUS MEDIA

Franklin S. Chance, Jr.*

DATE ISSUED: MAR 19 1951

OAK RIDGE NATIONAL LABORATORY
operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A Division of Union Carbide and Carbon Corporation
Post Office Box P
Oak Ridge, Tennessee

*This work was performed while the author was an Oak Ridge Graduate Fellow of the Oak Ridge Institute of Nuclear Studies, and this report is identical with a thesis which was submitted to the Graduate Council of the University of Tennessee in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

UNCLASSIFIED

3 4456 0360848 8

ORNL-957
Chemistry

INTERNAL DISTRIBUTION

1. G. T. Felbeck (C&CCD)
2-3. Chemistry Library
4. Physics Library
5. Biology Library
6. Health Physics Library
7. Metallurgy Library
8-9. Training School Library
10-13. Central Files
14. C. E. Center
15. C. E. Larson
16. W. B. Humes (K-25)
17. W. D. Lavers (Y-12)
18. A. M. Weinberg
19. J. A. Swartout
20. E. D. Shipley
21. E. J. Murphy
22. E. H. Taylor
23. A. H. Snell
24. A. Hollaender
25. F. C. VonderLage
26. K. Z. Morgan
27. M. T. Kelley
28. W. H. Pennington
29. D. W. Cardwell
30. J. A. Wethington
31. F. L. Steahly
32. F. S. Chance, Jr.
33. M. J. Skinner
34-40. Central Files (O.P.)

EXTERNAL DISTRIBUTION

41-48. Argonne National Laboratory
49. Armed Forces Special Weapons Project
50-54. Atomic Energy Commission, Washington
55. Battelle Memorial Institute
56. Brush Beryllium Company
57-60. Brookhaven National Laboratory
61. Bureau of Medicine and Surgery
62-65. Carbide and Carbon Chemicals Division (K-25 Plant)
66. Columbia University (G. Failla)
67. Dow Chemical Company
68-72. E. I. du Pont de Nemours and Company
73-78. General Electric, Richland
79-82. Idaho Operations Office
83-84. Iowa State College
85. Kellex Corporation
86-89. Knolls Atomic Power Laboratory
90-92. Los Alamos Scientific Laboratory
93. Mallinckrodt Chemical Works
94. Massachusetts Institute of Technology (A. Gaudin)
95. Massachusetts Institute of Technology (A. R. Kaufmann)
96-98. Mound Laboratory
99. National Advisory Committee for Aeronautics
100. National Bureau of Standards (R. D. Huntoon)
101. Naval Medical Research Institute
102-103. Naval Radiological Defense Laboratory
104. New Brunswick Laboratory
105-107. New York Operations Office
108. North American Aviation, Inc.
109-112. Carbide and Carbon Chemicals Division (Y-12)
113. Patent Branch, Washington
114. RAND Corporation
115. Sandia Corporation
116. Sylvania Electric Products, Inc.

117-131. Technical Information Service, Oak Ridge
132-133. USAF, NEPA Office
134-135. U. S. Geological Survey (T. B. Nolan)
136-137. U. S. Public Health Service
138. University of California at Los Angeles
139-142. University of California Radiation Laboratory
143-144. University of Rochester
145. University of Washington
146. Savannah River Operations Office, Wilmington
147. Western Reserve University
148-149. Westinghouse Electric Corporation
150-153. Atomic Energy Project, Chalk River
154. Chief of Naval Research
155. H. K. Ferguson Company
156. Harshaw Chemical Corporation
157. Isotopes Division (Mr. McCormick)
158-159. Library of Congress, Acquisition Department (J. W. Cormn)
160. National Bureau of Standards (Library)
161. National Research Council, Ottawa
162. Naval Research Laboratory
163. Nucleonics
164-165. Oak Ridge Institute of Nuclear Studies
166-175. United Kingdom Scientific Mission (M. Greenhill)
176. USAF, Eglin Air Force Base (Technical Library)
177. USAF, Wright-Patterson Air Force Base (Rodney Nudenberg)
178-182. USAF, Wright-Patterson Air Force Base (CADO)
183. U. S. Army, Army Medical Service Graduate School (Col. W. S. Stone)
184. U. S. Army, Atomic Energy Branch (Lt. Col. A. W. Betts)
185-187. U. S. Army, Technical Command (Col. J. H. Rothschild, Attn: Technical Library)
188. UT-AEC Agricultural Research Program (Charles S. Hobbs)

TABLE OF CONTENTS

	PAGE
ABSTRACT	1f
INTRODUCTION	1g
SUMMARY	2
BACKGROUND FOR NON-AQUEOUS EXCHANGE	4
EQUIPMENT AND MATERIALS	9
A. Equipment	9
B. Materials	12
METHOD OF OPERATION	14
RESULTS	19
A. Tables and Graphs	19
B. Effect of Solvents on Resins	22
C. Exchange Characteristics in Various Solvents	23
DISCUSSION	39
CONCLUSIONS	44
SUGGESTIONS FOR FURTHER WORK	45
BIBLIOGRAPHY	47
APPENDIX	49

LIST OF TABLES

TABLE PAGE

I. Typical Data Taken During Run 16

II. Removal of 0.1 M. NaOH with Hydrogen Form Amberlite IRC-50 at Room Temperature 26

III. Removal of 0.1 M. NaOH with -30 + 40 mesh, Hydrogen Form, Dowex 50 at Room temperature. 27

IV. Removal of 0.05 M. HBr with -20 +30 Mesh, Cyanide Form, Amberlite IRA-400 at Room Temperature 28

V. Removal of 0.05 M. HBr with Hydroxyl Form Dowex A-2 at Room Temperature 29

VI. Removal of 0.05 M. HBr with -20 + 30 Mesh, Hydroxyl Form, Amberlite IR-45 at Room Temperature 31

LIST OF FIGURES

FIGURE		PAGE
1.	Sketch of Apparatus for Determining Ion Exchange with Non-aqueous Media, Using Radioisotopes as Tracers for Solute	10
2.	Effect of Flow Rate on Utilization of Amberlite IRC-50 Capacity	33
3.	Effect of Flow Rate on Utilization of Dowex 50 Capacity . .	34
4.	Effect of Flow Rate on Utilization of Amberlite IRA-400 Capacity	35
5.	Effect of Flow Rate on Utilization of Dowex A-2 Capacity . .	36
6.	Effect of Flow Rate on Utilization of Amberlite IR-45 Capacity	37
7.	Relation Between Feed Properties and Exchange Before Leakage at Flow Rate of 0.10 ml. liquid/min./ml. resin . . .	38
8.	Breakthrough Curve Obtained by Measurement of Effluent Radioactivity While Removing Sodium Ions from Methanol in Run 27	50

ABSTRACT

Two cation exchangers, one a weak acid type (Amberlite IRC-50) and one a strong acid type (Dowex 50), have been used in column operation to remove sodium from a solution of 0.1 M. sodium hydroxide in various solvents composed of methanol, benzene, acetone and ethylene glycol singly or in binary combinations. Similarly, three anion exchangers, one a weak base (Amberlite IR-45) and two strong bases (Dowex A-2 and Amberlite IRA-400), have been used to remove the bromine from 0.05 M. hydrobromic acid in various solvents composed of methanol, tertiary-butanol, ethylene glycol, ethyl acetate, dioxane, benzene, acetone and carbon tetrachloride singly or in binary mixtures.

In all cases the resin was regenerated with an aqueous solution and retained much of its water during the exhaustion cycle.

Ion exchange takes place in several non-aqueous solutions almost as rapidly as in aqueous solutions, when the resin is wet with water. If the water wet resin is not swelled or contracted by the solvent, the exchange rate may be almost independent of the physical properties of the solution. Anion removal may take place from solutions that have no measurable electrical conductivity and so presumably only negligible ionization. The rate of cation removal is increased by high electrical conductivity and low fluid viscosity in the solution and by the absence of size change of the water wet resin particle when put into the solute free solvent.

INTRODUCTION

Ion exchange between water and solids is being widely used for water purification and to a lesser extent for the purification of aqueous process solutions. Although organic liquids often require removal of dissolved inorganic impurities, very little work has been done to evaluate the possibility of using ion exchange for this purpose. The present exploratory investigation was undertaken to make a broad semi-quantitative survey of the field of ion exchange between organic solvents and solids, with the intention that discoveries resulting from this work might form a basis for further detailed studies. Strong and weak acidic and basic synthetic exchange resins (for both anions and cations) have been investigated in column operation under steady flow conditions with representatives of various types of organic solvents.

SUMMARY

Two cation exchangers, Amberlite IRC-50 which acts like a weak carboxylic acid and Dowex 50 which acts like a strong sulfonic acid, have been investigated regarding their effectiveness in various solvents composed of methanol, benzene, acetone, and ethylene glycol singly or in binary combinations. Starting with resin which was regenerated in aqueous solution and washed with the solvent to be used, ion exchange took place in several non-aqueous solutions almost as well as in aqueous solutions. For these two cation exchangers the rate of solute exchange appears to vary directly as the cube root of the electrical conductivity of the feed solution and inversely as the viscosity of the solution. Plots are included (Figures 2 and 3) which show the effect of feed liquid flow rate on the percentage utilization of the capacity of the resins, and (Figure 7) the way in which the feed solution properties correlate with capacity utilization at a given flow rate.

Three anion exchangers, Amberlite IRA-400 and Dowex A-2 which act like strong bases, and Amberlite IR-45 which acts like a weak base, have been investigated using 0.05 molar hydrobromic acid in various solvents composed of methanol, tertiary-butanol, ethylene glycol, ethyl acetate, dioxane, benzene, acetone, and carbon tetrachloride singly or in binary mixtures. In most of these systems there also was good removal of the acid but no general correlation with viscosities and electrical conducti-

vities of the feed solutions was obtained. The anion exchange resins which did not give the same type correlations as the cation exchange resins also showed more discoloration within the resin, disintegration, and irregular swelling than the cation exchangers. Tables and plots (Figures 4, 5 and 6) are included which show the effect of flow rate on the utilization of the anion exchange resin capacity.

Column performance was determined by using radioactive isotopes of the solutes in tracer concentrations in the feed liquid, and measuring the radioactivity of the effluent. This method was found to be very convenient for obtaining a continuous precise record of the concentration of the solute leaking through the column.

The results obtained in this work indicate that the best resins for use with organic solvents are those which are <u>not</u> swelled by the solvents and retain their aqueous form when in contact with the non-aqueous solutions. The exchange mechanism in this case may differ from the aqueous one primarily by the additional step of solute transfer from one liquid phase to another at the surface of the particles.

BACKGROUND FOR NON-AQUEOUS EXCHANGE

Only five literature references to ion exchange in non-aqueous media have been found. The most extensive work was reported by Bhatnagar, Kapur, and Puri (1). These investigators studied the absorption of benzoic acid from 50 ml. of 0.01639 N. acid by 0.5 g. of resorcinol-formaldehyde resin in carbon disulfide, benzene, carbon tetrachloride, methanol, ethanol, acetone, and water. One of their conclusions was as follows:

> A solute is apt to be weakly sorbed from solvents in which it is very soluble and from solvents possessing weak dipole moments. If the solubility of a given absorbate is the same in a number of different solvents, greater absorption will occur from solutions, the solvent of which has higher interfacial tension against the absorbent.

F. J. Myers (5) found that "a small amount of water will permit acid binding to occur" when using wet solvents and Amberlite IR-4 (made by Rohm and Haas Co.), which reacts like a weak base. He also reported that some strongly ionizing solvent was required to give ion exchange when using resinous cation exchangers. As in the first case, these were static equilibrium experiments. Robinson and Mills (6) tested a porous type anion exchanger, Duolite A-2 (made by Chemical Process Co.), and found that the dry resin removed fatty acids from acetone and Shell solvent, and that it was "also effective in the removal from non-aqueous media of whole salts capable of forming complexes with amines." Their work consisted of equilibrium studies with contact times of twenty-four hours. Kressman and Kitchener (3) reported that cation exchange occurs

readily in mixtures of water and non-aqueous solvents. All the mixtures reported contained at least 30 per cent by weight of water in acetone or ethanol, and the exchange resin was a phenol-sulfonate type. These investigators had found only a single set of previous data (7) in the literature and this was also for aqueous ethanol.

Before the Ion Exchange Division of the Gordon Research Conference held at Hampton, New Hampshire in July, 1950, Dr. Bodamer of the Rohm and Haas Company disclosed (2) that he had found only four references to work done in non-aqueous media (his fourth was a preliminary report of work done for this dissertation). He revealed that his company is now experimenting with non-aqueous media, but here again the work is concerned with the equilibrium capacity and swelling of the resins.

Dr. C. A. Kraus of Brown University, acting in his capacity as consultant for the Oak Ridge National Laboratory, attended one of the preliminary conferences held by the author and his advisors. He recommended that a variety of solvent systems should be investigated before conducting detailed experiments on the behavior of any one system, since there is no information on which to base the choice of a system which would be expected to be best for such studies.

In summary, it may be said that no work has been found or heard about which deals with the rate of exchange between resins and any solutes in non-aqueous media.

Considering the present state of the art of non-aqueous ion exchange, it was decided that the purpose of this investigation should be a quali-

tative survey of the possibilities of ion exchange between a variety of common organic solvents and representatives of the various types of resinous exchangers now commercially available. It was felt that such a survey would give information necessary to encourage industrial research concerning the use of ion exchange from organic process solutions. At the same time the survey would aid in showing the direction of future research for the gathering of more detailed information which would be necessary for postulating and verifying exchange and regeneration mechanisms.

For the primary purpose of determining industrial use, the important part of an exchange cycle is that part which occurs before appreciable leakage of the solute through the resin bed takes place. On the other hand, for determining mechanisms, it is necessary to obtain the entire breakthrough curve as the resin bed becomes saturated. In the present study, primarily with the aim of obtaining a large variety of data in a reasonable length of time, it was arbitrarily decided to end the runs when 5 per cent of the solute was leaking through the resin bed since this would be a useful industrial end point. It was hoped that rough correlations based upon readily measured physical properties of solvent and solute might be obtained without getting into the fine points or deep details of theoretical considerations. In brief, the motivation was toward discovery rather than toward explaining results.

In determining the resins to be investigated, a classification according to reaction characteristics was used. If resins are suspended

in water and titrated with acid or base, the pH changes in the solution depend upon the particular resin present and show the characteristic variations of strong or weak acids or bases when being neutralized. Thus the resins are classified as strong or weak acids or bases, and it was in an attempt to cover the entire resin range that a strong acid type, a weak acid type, a strong base type, and a weak base type resin were selected for investigation. In those cases where there is only one type of active group in the resin it is called monofunctional, and if more than one type of active group it is polyfunctional. Even those resins that are principally monofunctional, however, show some physical absorption and often a minor amount of secondary chemical absorption, especially in the anion exchangers.

The resins used in this investigation were Amberlite IRC-50 which has carboxylic groups and is a weak acid, Dowex 50 which has sulfonic groups and is a strong acid, Amberlite IRA-400 which has strongly basic amine groups, Dowex A-2 which has somewhat weaker basic amine groups, and Amberlite IR-45 which has weakly basic amine groups. The Amberlite IRA-400 is so strongly basic that it requires excessive amounts of regenerant to regenerate it to the hydroxyl form when it is exhausted to the bromide form, since the hydroxyl ions are very lightly bound to the resin matrix.

The resinous exchangers are formed by copolymerization of organic materials which either have active groups already present or into which active groups can be substituted after the polymer is obtained. These

active groups are usually amines or acid groups such as sulfonic, phenolic, or carboxylic. A description of the manufacture of several resins is given in a recent book by Kunin and Myers (4).

EQUIPMENT AND MATERIALS

A. Equipment

Radioisotopes were used as tracers to determine the concentration of ions in the column effluent. The availability of suitable isotopes was a major factor in determining the ions to be studied. Radioactive sodium was prepared by exposing sodium hydroxide or sodium carbonate in the Oak Ridge pile. Radioactive bromide was obtained by a similar treatment of ammonium bromide. The equipment used, other than the general radiation laboratory facilities needed for safe handling of the radioisotopes, is described in the paragraphs that follow.

Two Oak Ridge National Laboratory rate count meters (Model Q-364, serial numbers 106 and 109) were connected to Esterline-Angus strip chart recorders (Model AW, serial numbers 48983 and 77215). One of these meters was connected to an end-window Geiger tube and the other to a thin glass wall Geiger tube as shown in Figure 1. The window of the end-window tube was covered by two inches of lead except for a 1/8 in. x 1 in. slot, which localized the portion of the resin bed that this tube would count. The glass wall tube was surrounded by a helix of small tubing made of glass or plastic through which the effluent was passed, and this assembly was surrounded by lead bricks to give a minimum shielding of about 4 in. of lead.

Determination of solution conductivities required several pieces of equipment. Effluent conductivity was determined by a Leeds and Northrup "Conductivity Micromax" connected to a glass cell containing coils

NOT CLASSIFIED
DWG. 10395

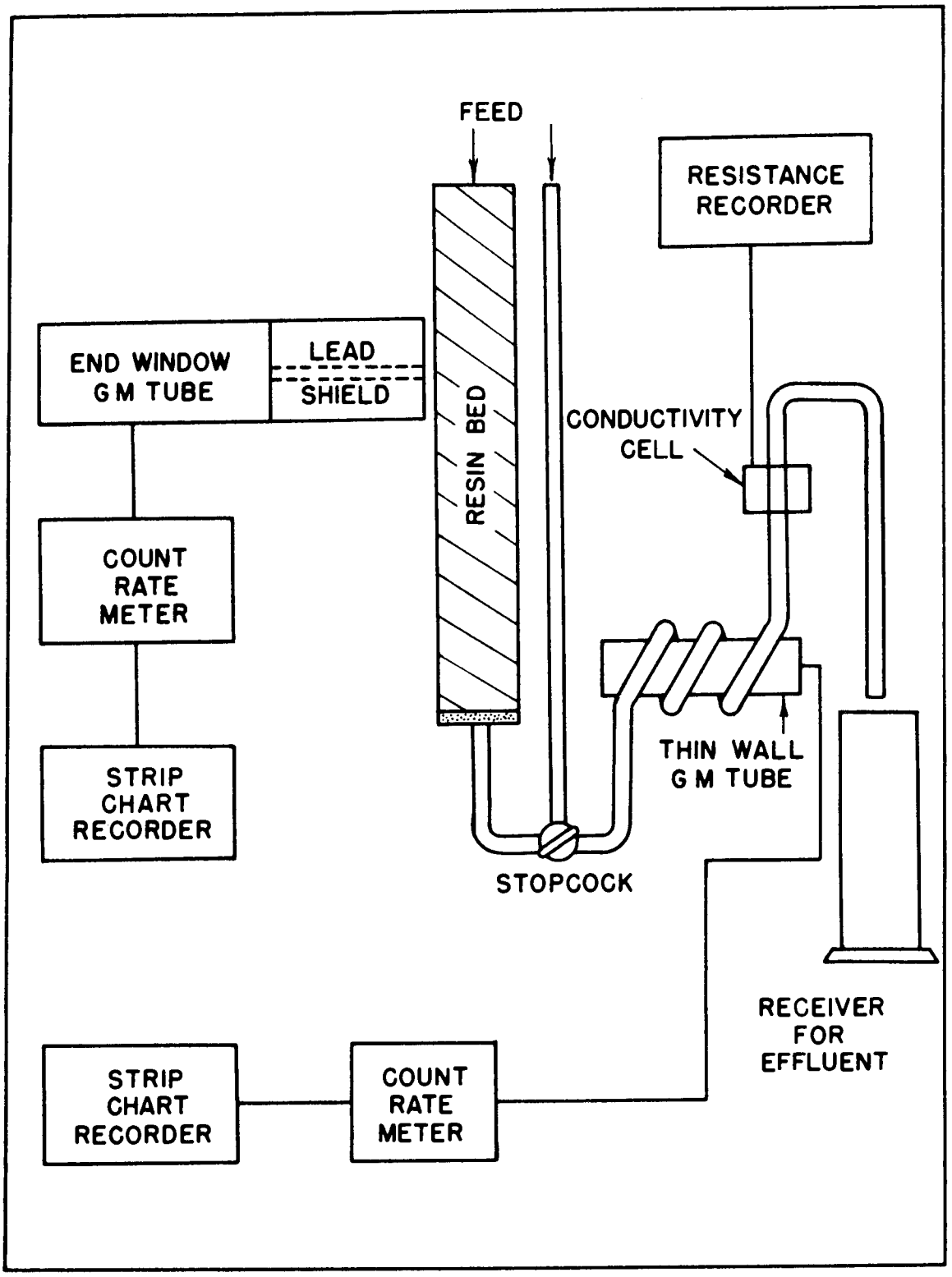

Figure I. Sketch of Apparatus for Determining Ion Exchange with Non—Aqueous Media, using Radioisotopes as Tracers for Solute

of platinum wire about 1/4 in. apart in 8 mm. tubing. With this combination, the minimum scale reading of 5,000 on the recorder corresponded to 0.0003 mhos/cm. conductivity of the effluent, and a scale reading of 100,000 on the recorder corresponded to 0.000015 mhos/cm. for the effluent. The recorder has a logarithmic scale and readings between 100,000 and 200,000 have to be estimated. For conductivities higher than 0.0003 mhos/cm., however, another cell was made with the platinum wires about 1 in. apart in 2 mm. tubing. Conductivities higher than 0.3 mhos/cm. or lower than 0.00001 mhos/cm. were determined with a conductivity bridge by the Analytical Chemistry Division of the Oak Ridge National Laboratory.

Acid, alkali, water and miscellaneous chemical analyses were performed by the Analytical Chemistry Division either by manual titration or by using a modified Precision-Dow Recordomatic Titrator.

The ion exchange was carried out in specially constructed glass columns. These were made with fritted glass filters in the bottom to support the resin bed, and the volume below the support was minimized by connecting the column to a capillary tube just below the filter. The first 10 runs were made in a column about 50 cm. long and 12 mm. in diameter but for all the rest of the runs a column 20 cm. long with a cross section of 1 sq. cm. was used. Each of these columns had an internal volume of about 20 ml. so that the 10 ml. of resin used filled either one about half full and left a space adequate for backwashing.

The feed was supplied from a 2 liter aspirator bottle equipped with an air bleed for maintaining a constant pressure head, and thereby a constant

liquid level over the resin bed. Flow rate was controlled by the elevation of the effluent outlet and the effluent was caught in graduated cylinders.

Viscosities of the solutions were obtained using an Ostwald tube which had previously been calibrated with water. Hydrometers were used for specific gravity determinations.

B. Materials

The solvents and chemicals used were commercially available materials without additional purification. The resins were also commercially available but were screened to give a more narrow particle size range. The range used was either -20 + 30 mesh or -30 + 40 mesh in the wet, as-shipped, form depending upon which of these ranges contained the larger portion of the commercial resin. The materials used and their sources were:

Acetone: B. & A. Reagent (General Chemical Company)

Amberlite IRA-400: Rohm and Haas Company, Lot 2606

Amberlite IRC-50: Rohm and Haas Company, Batch 62

Amberlite IR-45: Rohm and Haas Company, Lot 3631

Ammonium Bromide: B. & A. Reagent (General Chemical Company)

Benzene: Mallinckrodt Purified

Carbon Tetrachloride: B. & A. Reagent or Technical (General Chemical Company), or Mallinckrodt Analytical Reagent

Dioxane: National Aniline CP or J. T. Baker, Lot 102347

Dowex A-2: Commercial grade (Dow Chemical Company)

Dowex 50: Commercial grade (Dow Chemical Company)

Ethyl Acetate: B. & A. USP VIII (General Chemical Company)

Glycol: Eimer and Amend Purified Ethylene Glycol

Hydrobromic Acid: Merck Reagent

Methanol: B. & A. Reagent (General Chemical Company) or Baker's CP

Sodium Hydroxide: Baker's CP

Tertiary Butanol: Eastman Kodak Company

Water: Redistilled steam condensate

METHOD OF OPERATION

The column was first charged with 10 ml. of the resin, measured wet in the form in which it is shipped. The desired solute concentration was obtained by making up the feed solution to 0.1 or 0.05 molar with sodium hydroxide or hydrobromic acid and then adding sodium^{24} ions or bromine^{82} ions in very small amount (less than 0.2 per cent by weight of the total solute). The sodium^{24} was obtained by exposing 30 to 50 milligrams of sodium hydroxide, sodium carbonate or sodium iodide in the Oak Ridge pile for 16 to 62 hours and then dissolving the salt in 10 ml. of water or methanol. Bromine^{82} was obtained by a similar neutron irradiation of 200-400 milligrams of ammonium bromide and this salt was dissolved in 5-10 ml. of water after a two day delay for decay of bromine^{80}. Less than 1 ml. of the radioactive solution was usually sufficient to obtain enough activity in a liter of the feed to give a satisfactory reading on the strip chart.

The operating details may be explained by following a sample run. For this purpose Run 27 has been chosen to illustrate the procedure. The object of the run was the removal of 0.1 M. NaOH from methanol with hydrogen form Dowex 50. The feed was made up of 500 ml. of methanol, 2 g. of NaOH, and 3 ml. of a solution of 50 mg. radioactive NaOH in 10 ml. of water. This radioactive solution was three days old and had become weak since the Na^{24} half-life is only fifteen hours. The resin bed had previously been used, regenerated with a solution of 10 ml. concentrated hydrochloric acid in 100 ml. of water, and rinsed with methanol to remove

acid and excess water.

The data taken during the run are reproduced in Table I and a portion of the chart record of the effluent radioactivity is shown in Figure 8 in the Appendix. This run was chosen for illustration because resin saturation occurred so rapidly that the complete breakthrough curve could be reproduced as Figure 8. In most cases the complete curve (resin saturation) was not obtained because of the time required. In commercial practice ion exchange is seldom continued until the resin is saturated.

At the end of a run the column was by-passed and the feed was conducted directly through the effluent lines. The reading on the chart was then corrected for radioactive decay in the feed during the time interval between the first breakthrough of activity and the determination of the feed activity reading. The endpoint for the run was arbitrarily selected as the time at which the chart reading was 5 per cent of the corrected feed reading.

The effluent was caught in a set of graduated cylinders, cuts being taken at approximately 50 ml. intervals. At various times during the run the cumulative effluent volume was recorded on the strip chart to assist in determining the exact volume which had passed through by the time the endpoint was reached. In most cases an increase in the conductivity of the effluent indicated the imminence of the endpoint.

The electrical conductivity, specific gravity and viscosity were measured on the feed solutions. A sample of the feed and one or more samples of the effluent were submitted to the Analytical Division for

TABLE I

TYPICAL DATA TAKEN DURING RUN

Time	Cut No.	Total Effluent ml.	Flow Rate ml./min.	Counter Reading		Effluent Resistance ohms	Room Temperature	Bed Depth cm.
				Effluent	Column			
11:36	-	0	-	0.02	0.045	200,000	26.4	10.1
11:50	271	14	1.0	0.025	0.09	200,000	26.1	10.1
12:00	271	24.5	1.05	0.03	0.13	>200,000	26.0	10.0
12:15	271	38.5	0.93	0.03	0.18	>200,000	26.0	9.9
1:17	272	101.5	1.0	0.025	0.24	>200,000	27.0	9.6
2:25	273	170.5	1.0	0.025	0.22	>200,000	28.1	9.2
2:47	273	192.5	1.0	0.03	0.225	>200,000	28.0	9.05
3:07	274	212.5	1.0	0.24	0.22	<5,000	28.0	8.95
3:42	274	244.0	0.94	0.68	0.22	-	28.1	8.9
4:11	275	277.0	1.1	0.72	0.20	-	28.2	8.9
	Feed			0.735				

Analyses:	Sample No.	mg. water/ml.	M. NaOH	(ml. x M.) removed
	273	8.8, 8.5	.0006	17.812
	274	8.8, 8.7	.0245	3.651
	275		.0848	.350
	Feed	7.8, 7.9	.0954	

milliequivalents Na on 10 ml. resin = 21.813

water and solute analyses. If the water content of the effluent was the same as that of the feed, it was assumed that the bed was at equilibrium with respect to water in the solvent being used. For the runs which were continued until the radioactivity of the effluent stopped increasing, analysis of all the effluent cuts and the feed permitted calculation of the total ion exchange. This total exchange with aqueous solutions was taken as the equilibrium capacity of the resin bed and these runs are listed in Tables III, IV, and V as having "0" flow rate. For the other two resins tested (Amberlite IRC-50 and Amberlite IR-45) the published equilibrium capacities were used because of the long times required to attain equilibrium for the particular ions being exchanged.

The temperature of the operation was kept approximately constant by maintaining the room temperature at about 25° C. Spot checks of the effluent temperature showed this to be the same as the room temperature. Regeneration usually was accomplished by using 2-10 per cent by volume hydrochloric or sulfuric acid solutions in water for the cation exchangers and 5-10 per cent by weight sodium hydroxide in water for the anion exchangers except in the case of Amberlite IRA-400 where 10 per cent by weight sodium cyanide in water was used. Flow of regenerant at about 2 ml./min. was continued until all radioactivity was removed from the resin. In most cases regeneration was complete in about one hour, but for Dowex A-2 it was very slow and not always completed even after three hours, during which 400 ml. of 10 per cent sodium hydroxide solution was passed through the bed. The bed was then rinsed with distilled water to

remove the regenerant and followed with a rinse and soaking with the solvent mixture (without solute or radioactivity) to be employed in the next run. Swelling or shrinking (if any) of the resin was complete in one or two minutes after being brought into contact with the solvent, so it was assumed that the rate of attainment of equilibrium between the solvent and resin was also rapid.

The resin bed was loosened by backwashing with the solvent to be used next before the start of each run and then allowed to settle freely for the early runs. For later runs the bed was settled while vibrating the column. Although the bed volumes obtained by these methods differ, each should minimize channeling in the bed by giving bed uniformity.

RESULTS

A. Tables and Graphs

The experimental results are summarized in Tables II through VI on the following pages. Table II contains the data for the exchange of sodium, from a 0.1 molar solution of sodium hydroxide in the different solvents, with hydrogen from the hydrogen form of the carboxylic type resin Amberlite IRC-50. The tracer was Na^{24} in sodium hydroxide, carbonate, or iodide. Table III contains the data for a similar exchange with the hydrogen from the hydrogen form of the monofunctional sulfonic acid type resin Dowex 50. In this series the Na^{24} tracer was always from sodium hydroxide.

The data in Tables IV, V, and VI were obtained while using anion exchangers or acid absorbers. Table IV contains the results of the removal of 0.05 molar hydrobromic acid from various solvents by the cyanide form of Amberlite IRA-400. The cyanide form of the resin was used rather than the hydroxide form because of the difficulty of removing bromide ions from the resin with hydroxide. Tables V and VI show similar results for Dowex A-2 and Amberlite IR-45 except that for these the hydroxide or free base form of the resin was used to remove the bromide from solution. The meanings of the various columns in the tables are as follows:

Column 1. The run numbers are in chronological order. Thus the history of the resin bed can be followed by following these numbers. The runs designated with an A were made without

regenerating the resin bed used for the run of the same number without the A. The C designation indicates continuation of the run to resin saturation and calculation of the resin capacity from effluent analyses.

Column 2. Mixed solvents are listed in parts by volume.

Column 3. Water content was determined by the Analytical Chemistry Division Laboratory using Karl Fischer reagent. Where two numbers are given, the first is the water content of the feed and the last is an average water content of the effluent sample.

Column 4. The bed volume recorded is the volume at the "endpoint" of the run. The weak acid or weak base type resins swelled or remained unchanged during the exchange; the strongest base and strong acid type resins contracted or remained unchanged as they were exhausted; but the Dowex A-2 was inconsistent in its behavior.

Column 5. Flow rate was calculated by dividing the average liquid flow in ml./min. by the volume of the resin bed in ml. at the time the endpoint was reached. Where the flow rate is given as 0, the capacity values are equilibrium values calculated from the solute required to saturate the resin.

Column 6. The endpoint was taken as the amount of solute absorbed by the resin before 5 per cent of the influent activity appeared in the effluent. For Dowex 50, Amberlite IRA-400, and Dowex A-2, capacity of the resin was calculated from the amount of solute absorbed by the resin bed from aqueous solution before the

concentration of solute in the effluent became the same as in the influent. With Amberlite IRC-50 and Amberlite IR-45 published equilibrium capacity values were used.

Columns 7, 8, and 9. The properties of the feed solution were obtained at the temperature of the endpoint of the run; viscosity by an Ostwald viscosimeter, conductivity by resistance in cells calibrated with potassium chloride solutions, and specific gravity by hydrometer.

Column 10. This empirical relation gives an interesting correlation with flow rate. These are the values plotted as abscissa in Figure 7.

Figures 2 through 6 are plots of the percentage of maximum resin capacity (in water) utilized before the endpoint was reached, as a function of the flow rate. The figure numbers correspond to the data in the tables of the same numbers. Lines have been drawn through the points to indicate the trends and to serve as short extrapolations of the data.

Figure 7 shows the correlation of rate of exchange with the ratio of the cube root of the electrical conductivity to the viscosity of the feed solutions for Dowex 50, Amberlite IRA-400, and Amberlite IRC-50. There was no such correlation for the other two resins. These points are obtained from the sets of curves in the earlier figures. The correlation also holds for other flow rates as well as for the 0.10 (ml./min./ml.) rate plotted here.

B. Effect of Solvents on Resins

The weak acid cation exchanger, Amberlite IRC-50, swelled more in all the organic solvents than it did in water. On the contrary, the strong acid cation exchanger, Dowex 50, contracted when the surrounding water was displaced with the solvents.

The anion exchangers were not consistent in their behavior when the bed was rinsed with solvent. Amberlite IRA-400 contracted in acetone but swelled in methanol and glycol. Dowex A-2 swelled in glycol and the methanol-benzene mixture but in most other cases there was some shrinkage. Discoloration of the Dowex A-2 was apparent to some extent in all solvents used, and some rupturing of the resin particles was heard, and observed by the production of fines in the resin bed.

The polyamine acid absorber, Amberlite IR-45, gave widely varying results depending upon the initial treatment of the resin or its previous exposure to other solvents. A bed of the resin which was treated with a solution of 1 M. hydrochloric acid and then regenerated with a solution of 5 per cent sodium hydroxide in water underwent an irreversible expansion of about 10 per cent and produced a large quantity of fines. After backwashing to remove the fines, the resin was found to be very effective for removing hydrobromic acid from water, dioxane, methanol, acetone or a methanol-acetone mixture. Two other beds with milder treatment did not experience the expansion or disintegration and did not attain the exchange rates of the bed described. The points indicated on Figure 6 are actual experimental values for this fastest resin bed while the lines have been

drawn to follow the patterns obtained with the slower resin beds and they have been elevated to approximate the faster rates expected from the fast bed. All experimental values are given in Table VI.

C. Exchange Characteristics in Various Solvents

Representatives of various classes of common organic solvents were selected for consideration. These representatives were methanol, tertiary-butanol, glycol, ethyl acetate, dioxane, benzene and carbon tetrachloride. The first requirement for the testing of these solvents was that the ions to be exchanged must be soluble in the solvent. This requirement limited the field considerably in the case of sodium and to a lesser extent for the bromide. Specifically, the following qualitative results were obtained with the solvents used.

Methanol supported both cation and anion exchange almost as well as water with all the resins tested. Slow regeneration of Amberlite IRC-50 was possible with 10 per cent by volume concentrated hydrochloric acid or 2 per cent by volume concentrated sulfuric acid in methanol.

Tertiary-Butanol, on the other extreme, was the poorest solvent tried for exchange purposes. Removal of hydrobromic acid from this alcohol was very slow and the sodium which was removed was apparently present as a colloidal suspension which was filtered out rather than exchanged by the resin particles.

Glycol permitted rapid exchange of bromide with Amberlite IRA-400

and Dowex A-2. Sodium exchange with Dowex 50 was also rapid. With the weaker exchangers, Amberlite IRC-50 and IR-45, the exchange was quite slow but definitely measurable.

Ethyl acetate was not tested for cation exchange because of lack of its solvent ability for sodium hydroxide or salts, other than the iodide. Anion exchange from the ester took place quite readily even though hydrolysis of the ester and the resulting production of acetic acid confused the meaning of the quantitative results obtained.

Dioxane permitted rapid removal of hydrobromic acid by Dowex A-2 and Amberlite IR-45 but showed no solvent action for the sodium compounds tried.

Benzene was tested only when mixed with equal parts by volume of methanol to permit the solution of either sodium hydroxide or hydrobromic acid. This mixture was suitable for good cation exchange but gave much slower acid removal. With Dowex A-2 only about half as much of the resin capacity was utilized at a flow rate of 0.1 (ml. liquid/min./ml. bed) in this mixed solvent as in water; and with one of the slower beds of Amberlite IR-45 the results were very poor.

Carbon tetrachloride likewise was used only when mixed with one-third of its volume of methanol to give suitable solubility for hydrobromic acid. The acid was removed from this solvent mixture by Dowex A-2 and Amberlite IR-45 with about half the capacity at a given flow rate as that exhibited by the same resins in aqueous solutions.

Acetone was used alone or with methanol as a solvent for hydrobromic acid and anion exchange took place from this solvent but at an appreciably slower rate than from some other solvents. As a solvent for sodium hydroxide, acetone permitted high exchange rates when mixed with methanol but unexpectedly low rates when mixed with glycol.

TABLE II

REMOVAL OF 0.1 M. NaOH WITH HYDROGEN FORM AMBERLITE IRC-50 AT ROOM TEMPERATURE

COMMERCIAL RESIN USED IN FIRST 10 RUNS; -30 + 40 MESH, WET SCREENED, IN LATER RUNS

Run No.	Solvent	Water(1) Content wt. %	Bed(1) Volume ml.	Flow Rate ml./min. / ml. bed	Endpoint % of Capacity	Feed Liquid Properties(2) Viscosity centipoises	Elect. Cond. mhos/cm.	Sp. Gr.	(Cond.)$^{1/3}$ / Viscosity
3	Water	100	16.3	0.12	57.5	-	-	-	-
2	Water	100	15.6	0.13	51.6	0.90	0.0222	1.004	0.312
13	Water	100	15.1	0.13	52.7	-	-	-	-
10	3 Acetone, 1 Methanol	2.0	14.0	0.14	46.2	0.52	0.0034	0.79	0.289
5	Methanol	0.6	15.8	0.12	39.6	-	-	-	-
4	Methanol	0.6	15.3	0.14	41.2	0.74	0.0052	0.79	0.234
7A	1 Methanol, 1 Benzene	0.8	14.9	0.068	45.0	-	-	-	-
7		0.8	15.2	0.14	29.2	-	-	-	-
6		0.8	15.0	0.14	28.8	0.75	0.00227	0.85	0.175
20	1 Glycol, 1 Acetone	1.4	15.4	0.032	22.7	-	-	-	-
19		1.4	15.3	0.066	10.6	2.4	0.0012	0.98	0.044
18	1 Methanol, 1 Glycol	0.3	14.8	0.070	17.3	-	-	-	-
17		0.3	15.0	0.13	8.5	3.0	0.0023	0.95	0.044
16	9 Glycol, 1 Methanol	0.3	15.5	0.032	18.1	11.2	0.0012	1.08	0.010
15	Glycol	0.5	15.6	0.023	21.7	13.8	0.0010	1.11	0.007

(1) See text for explanation of column headings.

(2) The feed liquid properties in this table were taken from similar feeds made up later.

TABLE III

REMOVAL OF 0.1 M. NaOH WITH -30 + 40 MESH, HYDROGEN FORM, DOWEX-50 AT ROOM TEMPERATURE

Run No.	Solvent	Water Content wt. %	Bed Volume ml.	Flow Rate ml./min. / ml. bed	Endpoint % of Capacity	Feed Liquid Properties: Viscosity centipoises	Feed Liquid Properties: Elect. Cond. mhos/cm.	Feed Liquid Properties: Sp. Gr.	$\frac{(\text{Cond.})^{1/3}}{\text{Viscosity}}$
23C	Water	100	9.6	0	100	0.901	0.0222	1.004	0.312
24C	Water	100	9.5	0	100	-	-	-	-
23	Water	100	9.6	0.104	93	-	-	-	-
39	Water	100	9.4	0.20	92	-	-	-	-
24	Water	100	9.5	0.32	91	-	-	-	-
38	Water	100	9.3	0.31	91	-	-	-	-
27C	Methanol	1.0-1.1	8.3	0	>99	0.767	0.0058	0.792	0.234
27	Methanol	1.0-1.1	8.5	0.12	83	0.767	0.0058	0.792	0.234
26	Methanol	0.5	8.6	0.24	71	0.760	0.0057	0.792	0.235
25	Methanol	0.5	8.7	0.35	64	0.762	0.0057	0.792	0.234
28	1 Methanol	-	8.5	0.12	68	0.771	0.0024	0.836	0.174
29	1 Benzene	-	8.7	0.12	68	0.771	0.0024	0.837	0.174
41		-	8.6	0.12	79	0.753	0.0026	0.835	0.182
31		-	8.6	0.22	72	0.753	0.0024	0.835	0.178
40		-	8.8	0.23	71	0.753	0.0026	0.835	0.182
30		-	8.9	0.33	65	0.778	0.0024	0.837	0.172
35	2 Glycol	1.0-1.3	8.9	0.086	84	2.18	0.0029	0.933	0.065
34	3 Methanol	1.0-1.3	8.8	0.15	74	2.17	0.0029	0.933	0.066
36C	1 Acetone	1.0-1.2	9.2	0	>93	2.27	0.0012	0.979	0.047
37	1 Glycol	1.0-4.3	9.4	0.084	63	2.52	0.0013	0.978	0.043
36		1.0-4.0	9.5	0.14	64	2.27	0.0012	0.979	0.047
32C	Glycol	0.4-0.8	9.4	0	>94	16.2	0.0010	1.115	0.006
33	Glycol	0.4-0.55	9.4	0.050	79	14.25	0.0011	1.111	0.007
32	Glycol	0.4-0.9	9.6	0.090	72	16.2	0.0010	1.115	0.006

TABLE IV

REMOVAL OF 0.05 M. HBr WITH -20 + 30 MESH, CYANIDE FORM, AMBERLITE IRA-400 AT ROOM TEMPERATURE

Run No.	Solvent	Water Content wt. %	Bed Volume ml.	Flow Rate ml./min. / ml. bed	Endpoint % of Capacity	Feed Liquid Properties: Viscosity centipoises	Feed Liquid Properties: Elect. Cond. mhos/cm.	Feed Liquid Properties: Sp. Gr.	$\frac{(\text{Cond.})^{1/3}}{\text{Viscosity}}$
54C	Water	100	9.9	0	99.9	0.854	0.0201	1.003	0.319
55C	Water	100	9.8	0	100.2	0.886	0.0196	1.003	0.304
56C	Water	100	10.2	0	100.0	0.880	0.0197	1.003	0.307
54	Water	100	10.0	0.15	83.5	0.854	0.0201	1.003	0.319
53	Water	100	9.8	0.28	83.5	0.880	0.0197	1.003	0.307
55	Water	100	9.9	0.40	79.0	0.886	0.0196	1.003	0.304
56	Water	100	9.8	0.54	74.9	0.880	0.0197	1.003	0.307
57C	Methanol	1.9	9.8	0	98.5	0.750	0.0047	0.794	0.223
57	Methanol	1.9	10.1	0.31	68.0	0.750	0.0047	0.794	0.223
58	Acetone	-	7.6	0.17	70.5	0.453	0.00052	0.790	0.178
61	Acetone	-	8.4	0.24	54.0	0.459	0.00054	0.794	0.178
60	Acetone	-	8.2	0.40	30.0	0.453	0.00054	0.793	0.180
62	Glycol	0.6-1.1	10.5	0.06	65.5	14.6	0.0010	1.114	0.007
63	Glycol	0.6-0.7	10.6	0.12	61.5	14.1	0.0010	1.113	0.007

TABLE V

REMOVAL OF 0.05 M. HBr WITH HYDROXYL FORM DOWEX A-2 AT ROOM TEMPERATURE

RESIN WAS -20 + 30 MESH WHEN WET SCREENED IN CHLORIDE FORM

Run No.	Solvent	Water Content wt. %	Bed Volume ml.	Flow Rate ml./min. / ml. bed	Endpoint % of Capacity	Feed Liquid Properties			$\frac{(\text{Cond.})^{1/3}}{\text{Viscosity}}$
						Viscosity centipoises	Elect. Cond. mhos/cm.	Sp. Gr.	
65	Glycol	0.5-0.7	11.7	0.062	72.0	14.1	0.0010	1.113	0.007
64	Glycol	0.5-0.6	12.0	0.12	58.0	14.5	0.0010	1.114	0.007
66C	Methanol	0.8-1.1	11.4	0	101.0	0.728	0.0050	0.793	0.234
68C	Methanol	0.8-1.1	11.7	0	98.0	0.756	0.0048	0.796	0.223
68	Methanol	0.8-1.1	12.0	0.088	84.0	0.756	0.0048	0.796	0.223
66	Methanol	0.8-1.1	12.0	0.17	79.0	0.728	0.0050	0.793	0.234
67	Methanol	0.8-0.9	12.1	0.23	82.5	0.719	0.0051	0.791	0.239
69C	Water	100	10.5	0	99.5	0.938	0.0207	1.005	0.293
71C	Water	100	10.6	0	98.5	0.882	0.0217	1.003	0.316
69	Water	100	10.7	0.091	79.0	0.938	0.0207	1.005	0.293
70	Water	100	10.8	0.15	69.0	0.925	0.0209	1.005	0.298
71	Water	100	10.8	0.24	73.0	0.882	0.0217	1.003	0.316
73A	1 Methanol	1.0	12.6	0.047	52.5	0.735	0.0019	0.836	0.168
73	1 Benzene	1.0	12.8	0.070	34.0	0.731	0.0019	0.835	0.169
72		1.0	13.3	0.14	34.0	0.743	0.0019	0.836	0.167
74	Water	100	11.0	0.17	79.0	0.878	0.0203	1.003	0.311
74C	Water	100	11.0	0	94.0	0.878	0.0203	1.003	0.311

TABLE V

REMOVAL OF 0.05 M.HBr WITH HYDROXYL FORM DOWEX A-2 AT ROOM TEMPERATURE
RESIN WAS -20 + 30 MESH WHEN WET SCREENED IN CHLORIDE FORM (continued)
Second Bed

Run No.	Solvent	Water Content wt. %	Bed Volume ml.	Flow Rate ml./min. / ml. bed	Endpoint % of Capacity	Feed Liquid Properties: Viscosity centipoises	Feed Liquid Properties: Elect. Cond. mhos/cm.	Feed Liquid Properties: Sp. Gr.	$\frac{(\text{Cond.})^{1/3}}{\text{Viscosity}}$
75C	Water	100	10.0	0	100.5	0.840	0.0210	1.002	0.329
76C	Water	100	9.95	0	99.1	0.905	0.0198	1.004	0.299
75	Water	100	10.1	0.21	89.0	0.840	0.0210	1.002	0.329
76	Water	100	10.1	0.37	84.0	0.905	0.0198	1.004	0.299
77C	1 Methanol	0.5-0.6	11.5	0	87.4	0.700	0.000195	1.385	0.083
78C	3 Carbon	0.5	13.1	0	93.5	0.696	0.000195	1.384	0.083
78	Tetrachloride	0.5	11.8	0.075	47.0	0.696	0.000195	1.384	0.083
77		0.5	11.7	0.17	44.3	0.700	0.000195	1.385	0.083
79	t-Butanol	1.6-2.2	10.3	0.13	3.2	5.7	0.000057	0.79	0.007
81A	Ethyl Acetate	0.6-0.8	10.0	0.048	57.2	0.553	0.000022	0.890	0.051
81	Ethyl Acetate	0.6-0.8	10.0	0.097	45.4	0.553	0.000022	0.890	0.051
80	Ethyl Acetate	0.6-0.8	10.7	0.20	42.3	0.548	0.000022	0.890	0.051
82	Dioxane	0.6-0.7	9.85	0.045	41.6	1.15	0.83×10^{-6}	1.037	0.008
83	Dioxane	0.6-0.7	10.35	0.096	46.0	1.13	0.83×10^{-6}	1.036	0.008
85A	Acetone	-	9.75	0.049	41.7	0.459	0.00016	0.796	0.118
86	Acetone	-	9.85	0.051	44.1	0.456	0.00017	0.795	0.121
85	Acetone	-	9.75	0.1	32.2	0.462	0.00016	0.797	0.118
84	Acetone	-	9.35	0.22	20.1	0.454	0.00017	0.794	0.122
87	Water	100	10.05	0.18	58.5	0.885	0.0191	1.000	0.302
87C	Water	100	10.05	0	80.0	0.885	0.0191	1.000	0.302

TABLE VI

REMOVAL OF 0.05 M. HBr WITH -20 + 30 MESH, HYDROXYL FORM, AMBERLITE IR-45 AT ROOM TEMPERATURE

Run No.	Solvent	Water Content wt. %	Bed Volume ml.	Flow Rate ml./min. / ml. bed	Endpoint % of Capacity	Feed Liquid Properties: Viscosity centipoises	Feed Liquid Properties: Elect. Cond. mhos/cm.	Feed Liquid Properties: Sp. Gr.	$\frac{(\text{Cond.})^{1/3}}{\text{Viscosity}}$
90	Water	100	11.8	0.053	85.7	0.892	0.0331	1.006	0.360
89	Water	100	10.95	0.09	44.1	0.892	0.0331	1.006	0.360
88	Water	100	10.35	0.19	20.5	0.890	0.0332	1.006	(0.1 M. HBr)
91	Methanol	1.2-1.4	12.5	0.082	51.0	0.727	0.0044	0.792	0.226
92	Methanol	1.2-1.5	12.55	0.15	31.9	0.736	0.0046	0.794	0.226
96	Glycol	1.5-1.7	12.35	0.022	11.9	14.0	0.00089	1.114	0.007
95	Glycol	1.5-1.8	12.3	0.043	10.3	14.3	0.00088	1.114	0.007
94	Glycol	1.5-1.3	12.35	0.054	9.3	14.6	0.00087	1.115	0.007
93	Glycol	1.5-1.2	12.6	0.068	9.5	13.8	0.00089	1.114	0.007
97	t-Butanol	2.5	12.5	0.017	2.4	5.5	0.00005	0.790	0.007
98	[1 Methanol	0.4	12.25	0.060	38.3	0.680	0.00026	1.38	0.094
99	3 CCl_4]	0.4	12.5	0.11	17.5	0.680	0.00026	1.38	0.094
100	Acetone	-	11.65	0.086	29.8	0.460	0.00055	0.795	0.178
101	Acetone	-	11.7	0.11	20.8	0.459	0.00056	0.794	0.180
102	Water	100	11.0	0.088	57.5	0.882	0.0183	1.00	0.299
103	Water	100	10.8	0.18	31.6	0.896	0.0182	1.00	0.294
105	[1 Methanol	0.9	12.3	0.027	7.2	0.750	0.0019	0.837	0.165
104	1 Benzene]	0.9	12.3	0.076	3.0	0.753	0.0019	0.838	0.164
106A	[1 Methanol	-	11.65	0.031	9.5	0.48	0.0024	0.80	0.279
106	3 Acetone]	-	11.65	0.10	2.0	0.48	0.0024	0.80	0.279
107	[1 Methanol, 3 Acetone} + water]	10	11.7	0.056	7.2	0.70	0.0029	0.83	0.204
109	Ethyl Acetate	-	11.5	0.062	18.8	0.555	0.00004	0.89	0.062
108	Ethyl Acetate	-	11.65	0.095	18.3	0.56	0.00005	0.89	0.066
110	Water	100	10.7	0.10	21	0.95	0.0182	1.00	0.277

TABLE VI

REMOVAL OF 0.05 M. HBr WITH -20 + 30 MESH, HYDROXYL FORM, AMBERLITE IR-45 AT ROOM TEMPERATURE (continued)

Second and Third Beds

Run No.	Solvent	Water Content wt. %	Bed Volume ml.	Flow Rate ml./min. / ml. bed	Endpoint % of Capacity	Feed Liquid Properties: Viscosity centipoises	Feed Liquid Properties: Elect. Cond. mhos/cm.	Feed Liquid Properties: Sp. Gr.	$\frac{(\text{Cond.})^{1/3}}{\text{Viscosity}}$
112	[1 Methanol, 3 Acetone]	-	11.75	0.027	4.5	0.486	0.0024	0.801	0.275
111A		-	11.75	0.029	6.7	0.481	0.0024	0.801	0.278
111		-	11.75	0.085	1.7	0.481	0.0024	0.801	0.278
113	[1 Methanol, 3 Acetone} + water]	10	11.85	0.051	15.4	0.71	0.0030	0.83	0.203
115A	Ethyl Acetate	ca. 1	11.7	0.053	17.8	0.555	0.00005	0.887	0.066
115	Ethyl Acetate	ca. 1	11.7	0.085	13.5	0.555	0.00005	0.887	0.066
114	Ethyl Acetate	ca. 1	11.65	0.12	15.1	0.56	0.00006	0.888	0.070
117	Dioxane	0.8	11.95	0.039	34.6	1.20	$<4 \times 10^{-7}$	1.04	<0.006
116	Dioxane	0.8	11.8	0.068	12.9	1.20	$<4 \times 10^{-7}$	1.04	<0.006
118	Water	100	10.95	0.087	21.8	0.91	0.0187	1.00	0.292
					Third Bed				
119	Water	100	11.45	0.086	91.0	0.92	0.0178	1.00	0.284
124	Water	100	11.35	0.14	74.9	0.94	0.0190	1.00	0.284
121	Water	100	11.5	0.23	64.1	0.90	0.0182	1.00	0.292
120	Dioxane	0.6	12.85	0.078	51.0	1.20	$<4 \times 10^{-7}$	1.04	<0.006
122	Methanol	0.85	12.65	0.10	55.5	0.75	0.0045	0.79	0.220
123	Acetone	1.2	12.2	0.11	47.5	0.455	0.00051	0.80	0.176
125	[1 Methanol, 3 Acetone]	1.6	12.55	0.086	37.4	0.49	0.0025	0.80	0.277

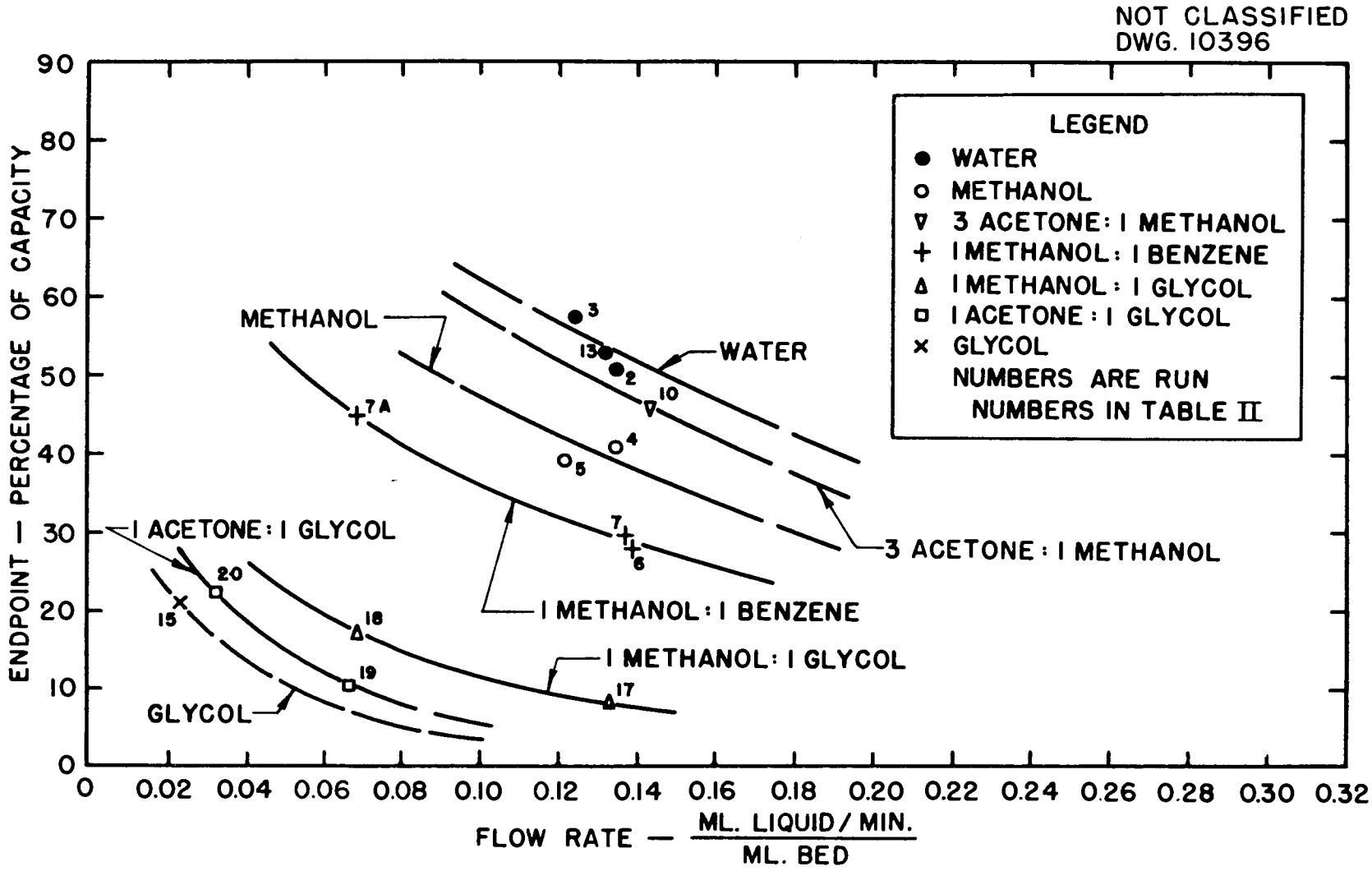

Figure 2. Effect of Flow Rate on Utilization of Amberlite IRC-50 Capacity
Removal of 0.1 *M*. NaOH at room temperature

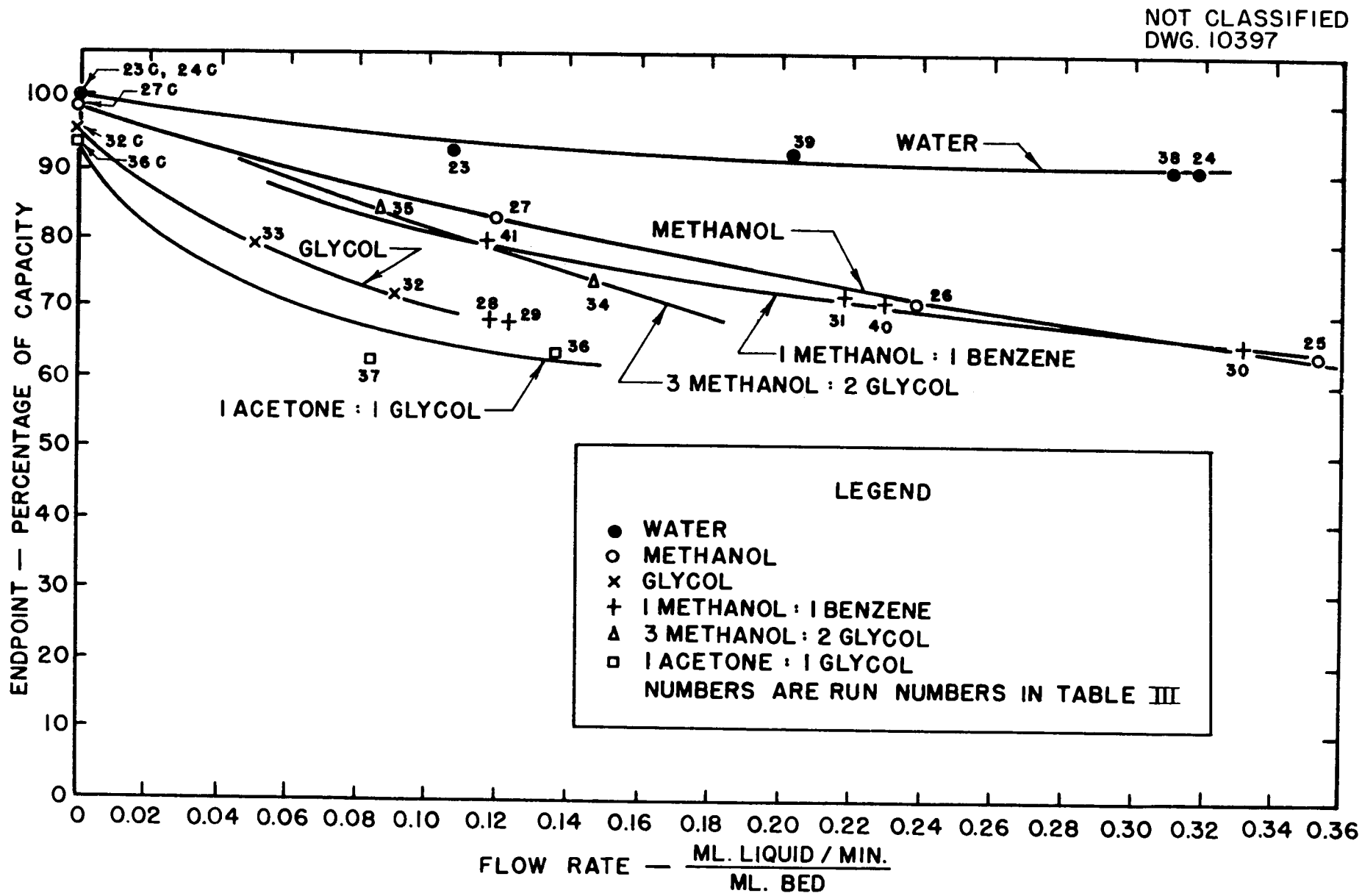

Figure 3. Effect of Flow Rate on Utilization of Dowex 50 Capacity
Removal of 0.1 *M.* NaOH with −30 + 40 mesh, hydrogen form, resin at room temperature

NOT CLASSIFIED
DWG. 10398

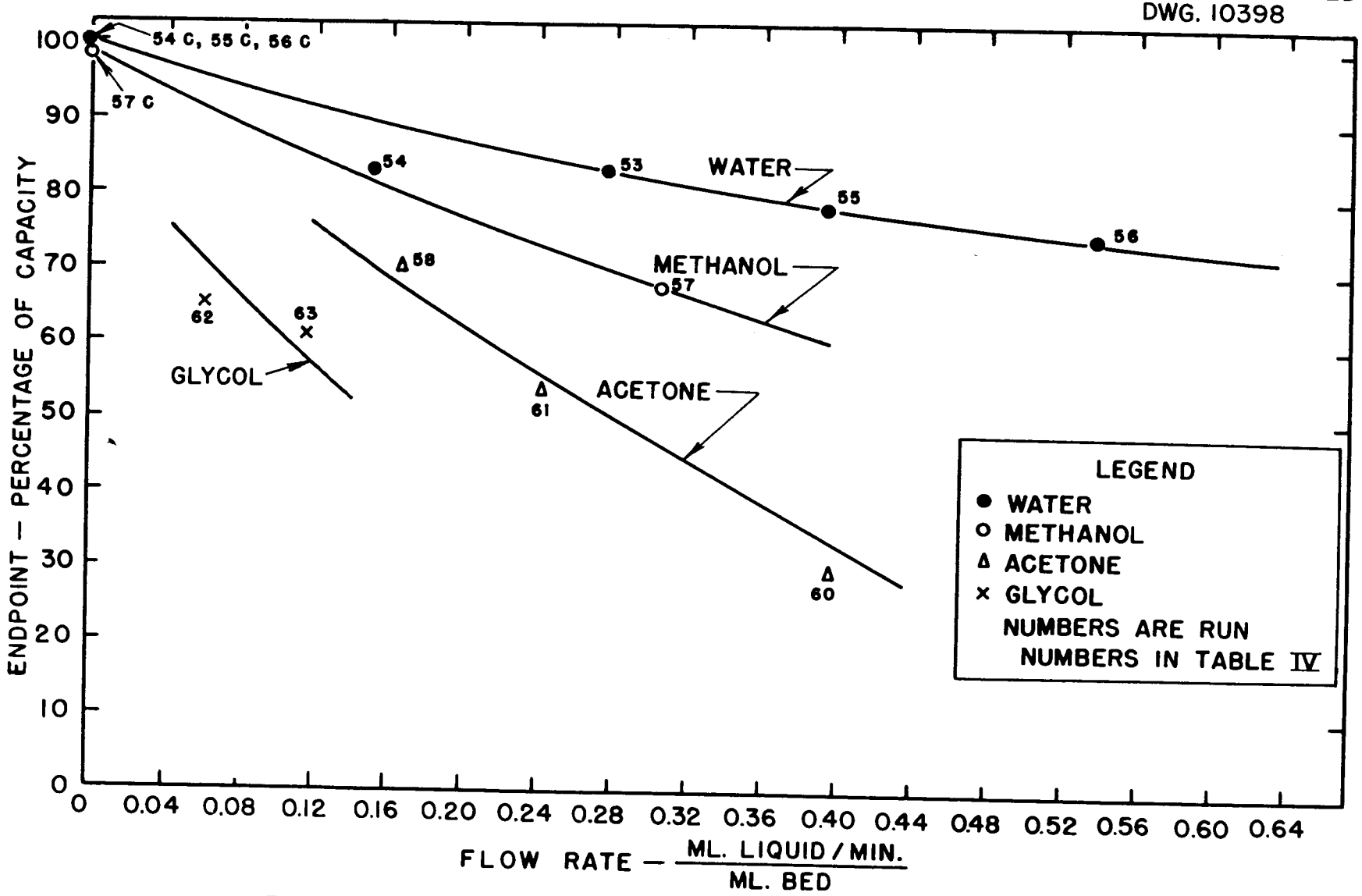

Figure 4. Effect of Flow Rate on Utilization of Amberlite IRA-400 Capacity
Removal of 0.05 *M*. HBr with −20+30 mesh, hydrogen form, resin at room temperature

NOT CLASSIFIED
DWG. 10399

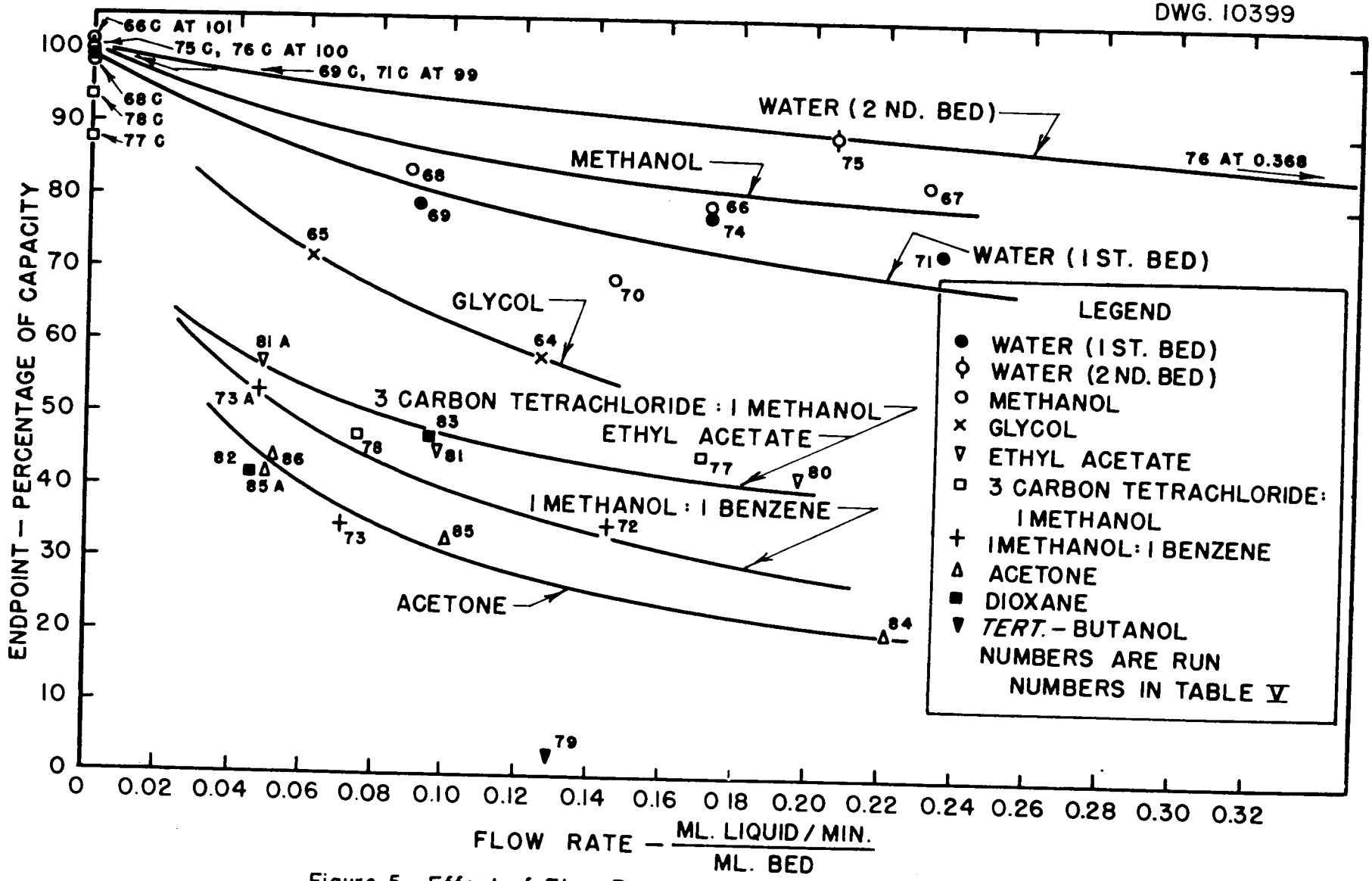

Figure 5. Effect of Flow Rate on Utilization of Dowex A-2 Capacity
Removal of 0.05 *M.* HBr with −20+30 mesh, hydrogen form, resin at room temperature

NOT CLASSIFIED
DWG. 10400

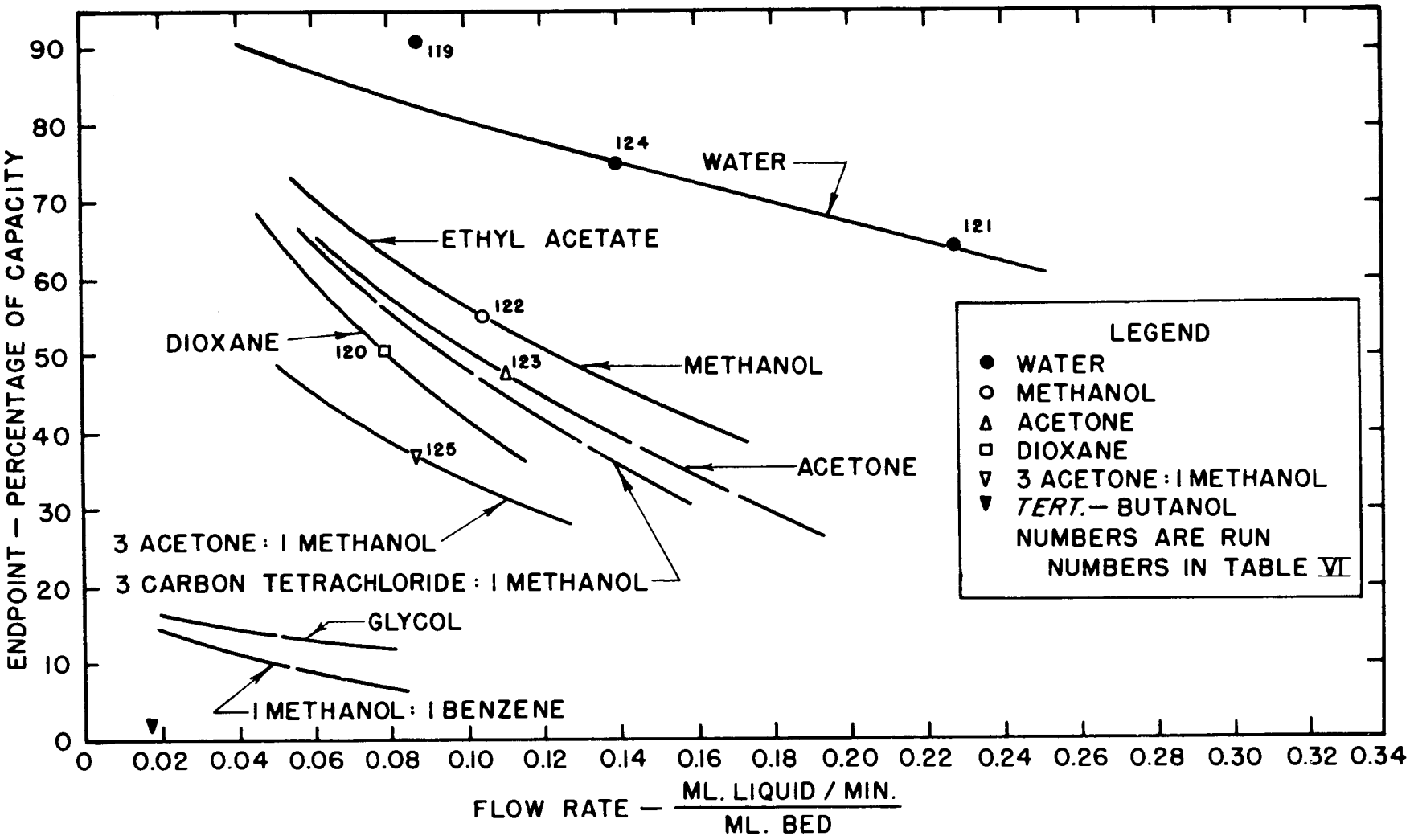

Figure 6. Effect of Flow Rate on Utilization of Amberlite IR—45 Capacity
Removal of 0.05 *M*. HBr with −20 +30 mesh resin at room temperature
Most experimental points have been omitted. See the text for explanation.

NOT CLASSIFIED
DWG. 10401

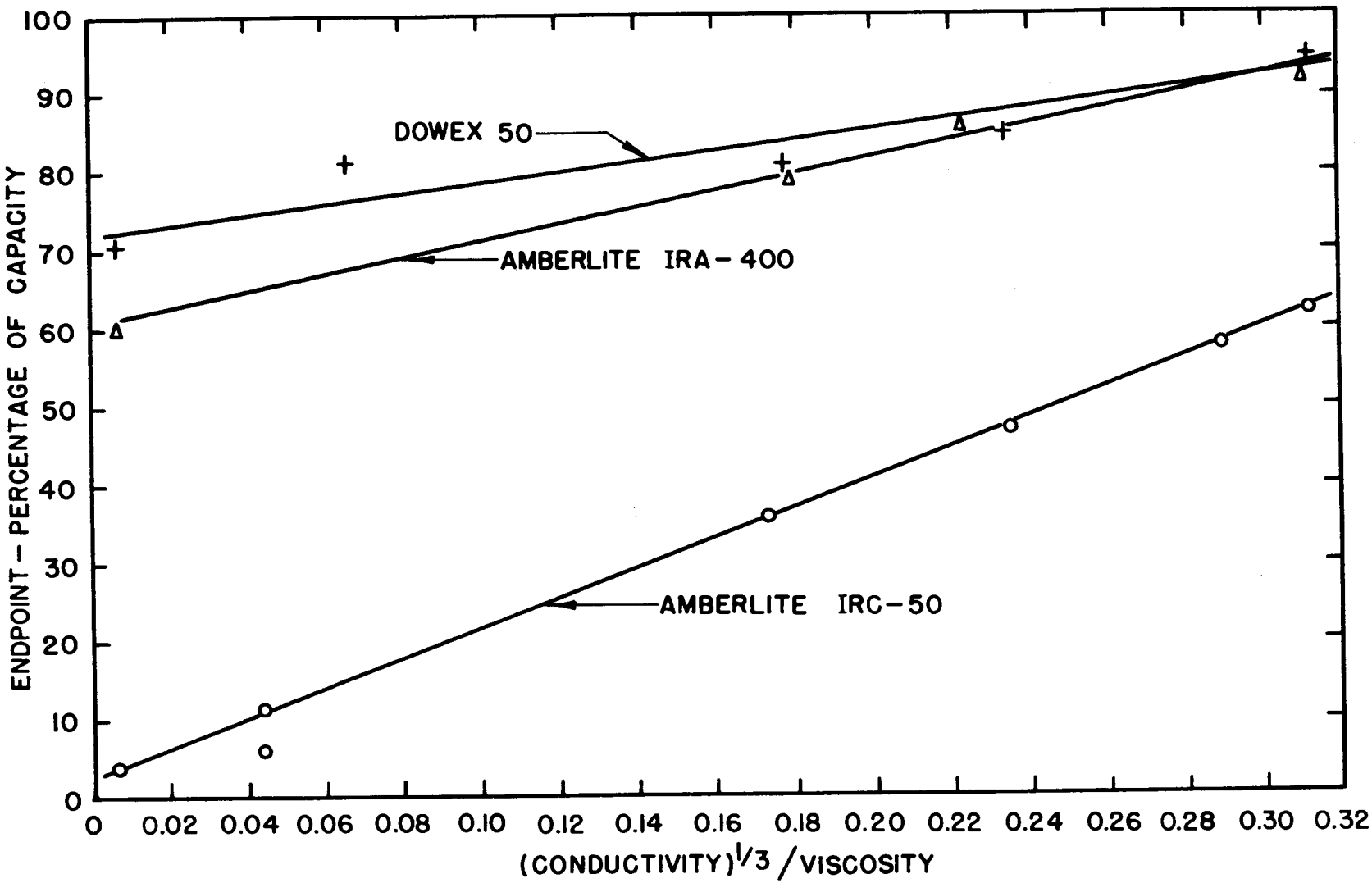

Figure 7. Relation Between Feed Properties and Exchange Before Leakage at Flow Rate of 0.10 ml. Liquid / Min. / ml. Resin Bed

Each point represents a different solvent. Data from Figures 2,3,& 4

DISCUSSION

Sodium was chosen as the cation to study because of its prevalence and the existence of a suitable and easily secured isotope for use of the tracer technique. It seemed that a desirable anion to study would be the chloride ion but since bromine has a much more satisfactory isotope it was considered to be a more suitable material for this survey project. The use of the sodium in the hydroxide form and bromine as the hydrobromic acid caused the effluent to contain only solvent and water. This permitted a check of leakage in the effluent by a conductivity measurement since the solvents have very low conductivities. This procedure was not always satisfactory since some of the feed solutions, notably dioxane, had a conductivity too small to measure (less than 4×10^{-7} mhos/cm.) even with 0.05 M. HBr present. A simple acid or alkali determination was also unsatisfactory in some cases because of acid impurity present in some solvents, such as dioxane, or acid resulting from the hydrolysis of ethyl acetate. In these cases an electrometric titration with silver nitrate solution was used. These difficulties emphasized the value of the radioisotope technique as a means for analysis when dealing with non-aqueous solvents.

Commercial or laboratory grade solvents were used directly without an additional purification. Water content was measured but not adjusted since the resins tend to absorb water and quickly reach an equilibrium with the solvents when either contains moisture. In all cases the wet

form of the resins was used because it was expected that this would be the more active form. This is in line with the principal object of the survey, which was to determine the possibility of removing foreign materials from the solvents rather than to determine exchange mechanisms and details in anhydrous media. Such more quantitative investigations were considered in planning this experimentation, but were assigned a lower priority, as work to be done subsequently by other investigators.

In order to determine a possible dependence of rate of ion exchange upon some simple physical properties of the solvent, the electrical conductivity, viscosity and specific gravity of the feed solutions were measured. It is thought that these, among others, should be related to the concentration of ions and their mobility in the solutions. Therefore, if the solvent plays a major role in governing the rate of exchange, there should be some correlation with these properties. At the outset it was hoped to discover an empirical correlation, independent of any theoretical considerations, which would give semi-quantitative estimations of the feasibility of ion exchange with a known process liquid. Such a procedure, irrespective of the reasons for its success, would be quite useful. Further speculations, after more data are accumulated to test theories, were left for future investigators.

A reasonably good correlation was obtained with both cation exchangers and with Amberlite IRA-400. This relationship is shown in Figure 7, where the endpoints at a flow rate of 0.10 ml. liquid/min./ml. of resin bed are cross plotted from Figures 2, 3, and 4 against the cube

root of the specific conductivity divided by the absolute viscosity. If the kinematic viscosity is used in this relationship instead of the absolute viscosity, the points fit curves instead of straight lines. This empirical correlation is not followed by the other two anion exchangers, however. In the case of the Amberlite IR-45 this discrepancy is to be partially anticipated since this resin is supposed to be an acid absorber, i.e., picks up whole acid molecules from liquids, hence ionization would not be expected to be a factor in its rate of exchange. The deviations of the Dowex A-2 may be partially explained by the instability of this resin with respect to the solvents. However, much more data should be obtained before any of these correlations are assumed to be more than coincidental. The present usefulness of this work is to indicate that ion exchange occurs at appreciable rates in almost all organic solvents encountered in process solutions and can be considered as a possible tool in working with these solutions. This supplies the answer to the question originally raised concerning ion transfer from non-aqueous organic media to exchange resins.

The swelling of resins by the solvents is another factor which should be expected to nullify the chance of obtaining a simple correlation between arbitrarily computed exchange rate and solvent properties. For example, Amberlite IRC-50 was swelled considerably by some of the solvents. Therefore, considerable amounts of the solvent must have become incorporated into the particles. Consequently, the solvent becomes involved in the exchange mechanism both inside and outside the resin

particle. On the other hand, the sulfonic type resin (Dowex 50) did not change in volume when in contact with the organic solvents and so may have remained in essentially an aqueous condition inside the particles. In any event, there is no basis for expecting that a simple correlation will be universal. That it happens to work in some cases may be considered fortuitous. In the last analysis, the question of the added swelling action produced by the solvents emphasizes the fact that an explanation of the transfer mechanism must include not only the anions, cations, and molecular exchange waves, but also the water and solvent exchange waves and the transfer across the water-solvent interface. It is therefore anticipated that the mathematical formulas that describe this process will be quite complicated.

The fact that the rate of exchange depends upon the resin used as well as upon the solvent indicates that the exchange rate inside the particles is of importance, and that there is no so called "rate controlling step" that holds for all the conditions studied. Moreover, if the overall transfer rate is significantly dependent upon the mass motion within the resin particles, factors that alter the interior configuration of the resin should play a major role in determining the overall exchange rate. Therefore, entrance of the solvent into the particle would greatly accentuate the effect of the solvent on the exchange rate of the resin. This suggests the possibility that better results in a non-aqueous medium will be obtained if the resin is <u>not</u> affected by the solvent and is used in the wet condition, and regenerated in aqueous medium. This is

contrary to the usual assumption that to be effective in anhydrous media the dry resin must be attacked and swelled by the solvent.

CONCLUSIONS

The results obtained in this work indicate the following conclusions:

(1) Ion exchange will take place at an appreciable rate between most non-aqueous solvents and the water-wet form of exchange resins.

(2) If the wet resin is not modified by the solvent, the exchange rate may be almost independent of the properties of the solution. This may be a very significant discovery in that it shows the very durable, solvent resistant, commercial resins to be suitable for use in many organic solvents.

(3) The influence of the solvent on the resin may be specific, so extrapolation of results to other solvents may lead to only rough approximations.

(4) An estimation of the feasibility of the use of cation exchange for a process solution may be made by considering (a) the volume change of the resin in solution and (b) the viscosity and electrical conductivity of the solution. High electrical conductivity, low fluid viscosity, and lack of volume change of the water-wet resin when equilibrated with solvent are conducive to fast rates of ion exchange.

(5) Anion removal may take place from solutions that have no measurable electrical conductivity and so, presumably, only negligible ionization.

SUGGESTIONS FOR FURTHER WORK

Since the object of this work was to survey the possibilities of non-aqueous ion exchange, it is hoped that the results will suggest much further experimentation, both to expand the scope of the present report and to check theories indicated by these data. Some of the experiments which would be very helpful are enumerated.

(1) Continuation of this work with other ions and with other solvents would determine whether the results are general for the types of ions and solvents.

(2) The effect of water of hydration in changing the ions sizes might be indicated by studies of the effects of addition of small quantities of water in the solvents.

(3) Surface active agents may affect the interface between the wet resin and the solvent and modify that step in the transfer path enough to indicate its importance.

(4) In some cases mixed solvents give the maximum swelling of the resin particles and thus might be more effective in exchange of large ions. In any case, precise data on swelling are needed to determine how these fit into empirical correlations.

(5) Water may be slowly removed from the resins by some solvents. A study of the water-solvent exchange wave would give information which might later be superimposed on the ion exchange wave.

(6) Actual anhydrous operations, including regeneration, can now

be conducted using new, porous forms of resinous exchangers.

(7) A careful determination of the aqueous regenerative wave after non-aqueous exchange might indicate the nature of changes which take place within the resin during the non-aqueous exhaustion step.

(8) Eventually enough data may be obtained to permit determination of a mathematical design equation for ion exchangers. At the present time such an equation would have to consider transfer of absorbing ions through (a) the body of the liquid, (b) the liquid film around the particle, (c) the solvent-water interface, and (d) the interior of the particle; then the ion replaces another ion and the replaced ion has the same path to traverse in the reverse order. With the present state of the art, none of these steps can be ignored for all conditions.

Much of the work suggested here could be done without using tracers since conductivity measurements would be suitable for many of the solvents. This fact would make it practical to continue such studies as academic theses without requiring a radiation laboratory.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Bhatnagar, S. S., Kapur, A. N., and Puri, M. L., J. Indian Chem. Soc., 13, 679 (1936).

2. Bodamer, G., as reported by Dr. B. A. Soldano.

3. Kressman, T. R. E., and Kitchener, J. A., J. Chem. Soc. (London), 1211 (1949).

4. Kunin, Robert, and Myers, R. J., "Ion Exchange Resins," John Wiley and Sons, Inc., New York, N.Y., 1950, Chapter 5.

5. Myers, F. J., Ind. Eng. Chem., 35, 858 (1943).

6. Robinson, D.A., and Mills, G. F., Ibid., 41, 2221 (1949).

7. Wiegner, G., and Jenny, H., Kolloid - Z., 42, 268 (1927).

APPENDIX

NOT CLASSIFIED
DWG. 10402

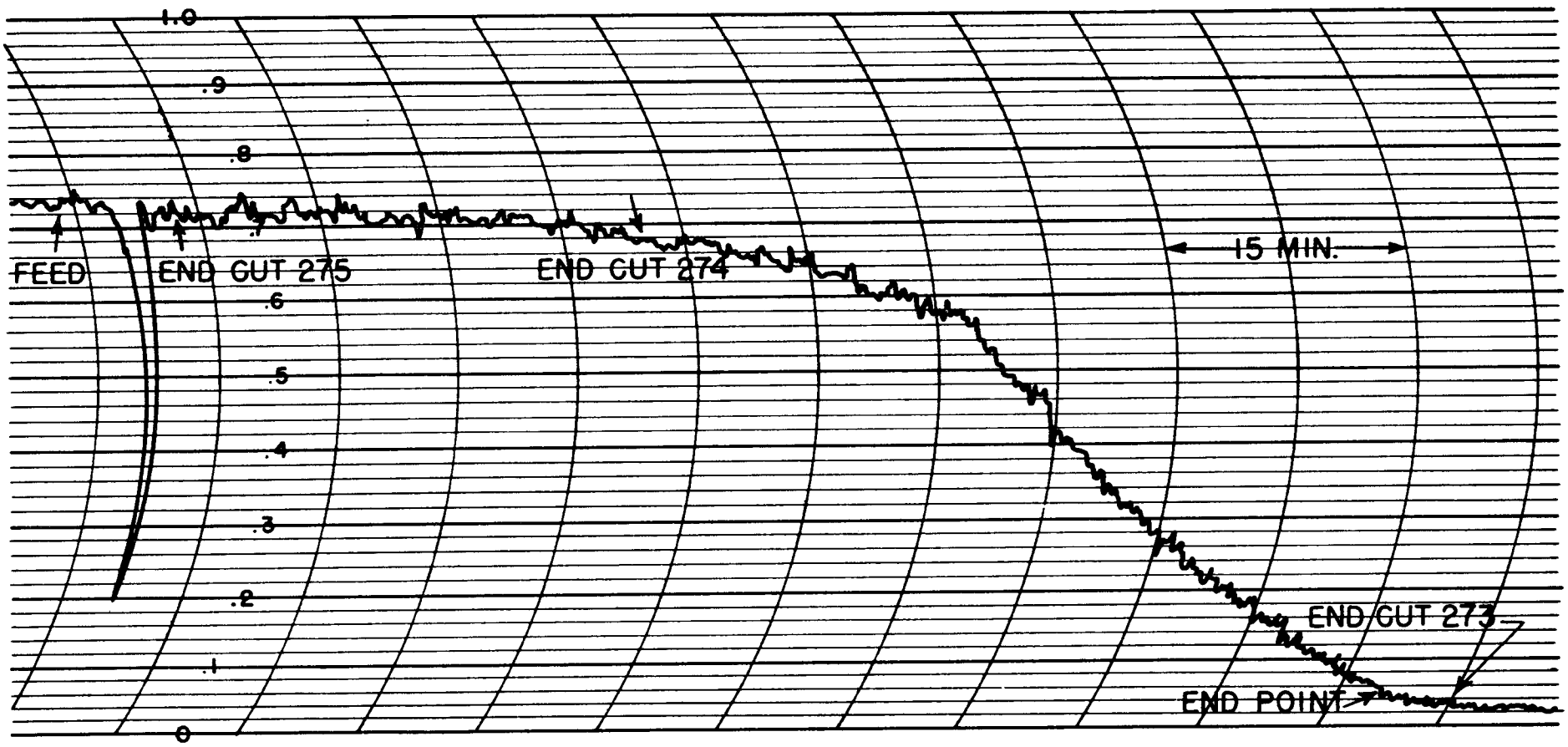

Figure 8. Breakthrough Curve Obtained by Measurement of Effluent Radioactivity While Removing Sodium Ions From Methanol in Run 27