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INV. 63

LABORATORY RECORDS 1954

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MATERIALS CHEMISTRY DIVISION

PROGRESS REPORT

INV 70

ALLOY DEVELOPMENT PROJECT

OREX PROCESS

PROGRESS THROUGH MARCH 31, 1952

INV. 52

DECLASSIFIED

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INV. 67

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
OAK RIDGE, TENNESSEE

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PROGRESS REPORT

ALLOY DEVELOPMENT PROJECT

OREX PROCESS

Progress through March 31, 1952

May 19, 1952

MATERIALS CHEMISTRY DIVISION

G. H. Clewett, Division Director

Edited by K. O. Johnsson

OAK RIDGE NATIONAL LABORATORY
Operated by
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION

Oak Ridge, Tennessee

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FOREWORD

This is the second separate progress report issued on the organic-amalgam system for the separation of the isotopes of lithium. (The first may be found as document ORNL-1238.) As may be noted from the title, the process has now been designated the OREX PROCESS under the Alloy Development Project. The two methods of operating the Orex Process which are being considered are the dual temperature method (designated DT) and the chemical reflux (CR) method.

Beyond the material presented in this report, some fundamental studies are being made on lithium amalgams and are covered in the Elex Process reports.

Arrangements are being made for assistance in further pilot plant design and operation from the Chemical Technology Division of the Laboratory and the Process Design and Analysis Department of the K-25 Plant.

CONTENTS

Foreword 3

PART A: PILOT PLANT STUDIES

Introduction 5

Preparation of Feed Material 6

Solution Stability 6

Temperature Control 8

Flow Control 8

Effect of Tray Openings Size on Throughput 11

Summary of Separation Data 13

Future Work 23

PART B: LABORATORY STUDIES

Temperature Dependancy of Separation Factor 24

Stability of Amalgam-Amine System 29

Reflux Studies 30

Solubilities in EDA 34

Viscosity and Density 37

Amalgamation Study 39

Preparation of Anhydrous EDA 39

Miscellaneous Studies 41
- Instrumentation 41
- Alternate Solvents 42
- Solubilities in EDA 42
- Mixed Salts . . . . .

References 44

[redacted]

PART A: PILOT PLANT STUDIES

A. D. Ryon, J. W. Ramsey, R. R. Wiethaup

INTRODUCTION

The DT pilot plant described in the previous progress report[1] has been operated on a three-shift basis for the past three months. The pilot plant has served the primary purpose of demonstrating the feasibility of the system. It has shown that anhydrous lithium amalgam and ethylenediamine solutions of LiCl can be made and contacted in the pulse columns without serious difficulty. In spite of flow control limitations, it has been possible to obtain reasonable separation of lithium isotopes. With the system run at total reflux, the ratio of tops to bottoms concentration of Li^6 indicates that a stage height of about eight inches may be obtained.

Many of the general characteristics of the system have been studied and the results are described in this report. Screens varying from 10-mesh to 60-mesh have been tested both for maximum throughput and separation. The optimum screen for the cold column appears to be between 10- and 24-mesh, and for the hot column between 20- and 30-mesh. For each screen size there is an optimum pulse stroke and frequency. The maximum range of temperature is limited to 20°C for the cold column and 110°C for the hot column. Below 20°C lithium chloride crystallizes out of the amine and above 110°C there is a mass transfer of lithium from the amalgam to the amine and decomposition of solvent.

The most serious limitation of the pilot plant has been control of flow rates. Minor changes have been made to improve both control of flows and temperature and in the near future new pumps will be installed which should greatly improve operation.

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PREPARATION OF FEED MATERIAL

Amalgam

The amalgam preparation system described in the last progress report has been quite satisfactory. Some solid lithium oxides have formed in the storage tanks after three months service but since they float on the amalgam they are not drawn off the bottom with feed material. Nickel anodes have given cleaner operation than graphite anodes which were first used.

Amine

An amine preparation system has been built adjacent to the pilot plant. The amine is first dried by refluxing over calcium carbide, distilled into storage tanks, and finally passed into a dissolver where lithium chloride is added. This solution is stored as feed material for the columns. The entire system is under an atmosphere of helium.

The amine drying equipment is being modified at present to test an azeotropic distillation using benzene which will produce dry amine directly from the amine monohydrate.

SOLUTION STABILITY

As noted before, complete freedom from moisture is essential for stability in the amalgam EDA system. In spite of many precautions, traces of moisture are apparently present in the feed materials and cause a relatively rapid loss of lithium from the amalgam during the first part of a run. After this moisture has reacted the lithium concentration remains virtually constant as is shown in Figure 1. The average loss in lithium (from the amalgam) after the initial drop has been in the order of 0.0003 moles per hour. Since most of the reaction appears to take place in the hot column a filter is located in the amine effluent from that column (before entering the cold column) to remove any suspended lithium hydroxide which might plug the column plates.

The maximum temperature at which the hot column can be operated is limited by a reaction of the amine with the lithium in the amalgam. The amine becomes a brownish-red in color and analysis of this solution shows an excess of lithium

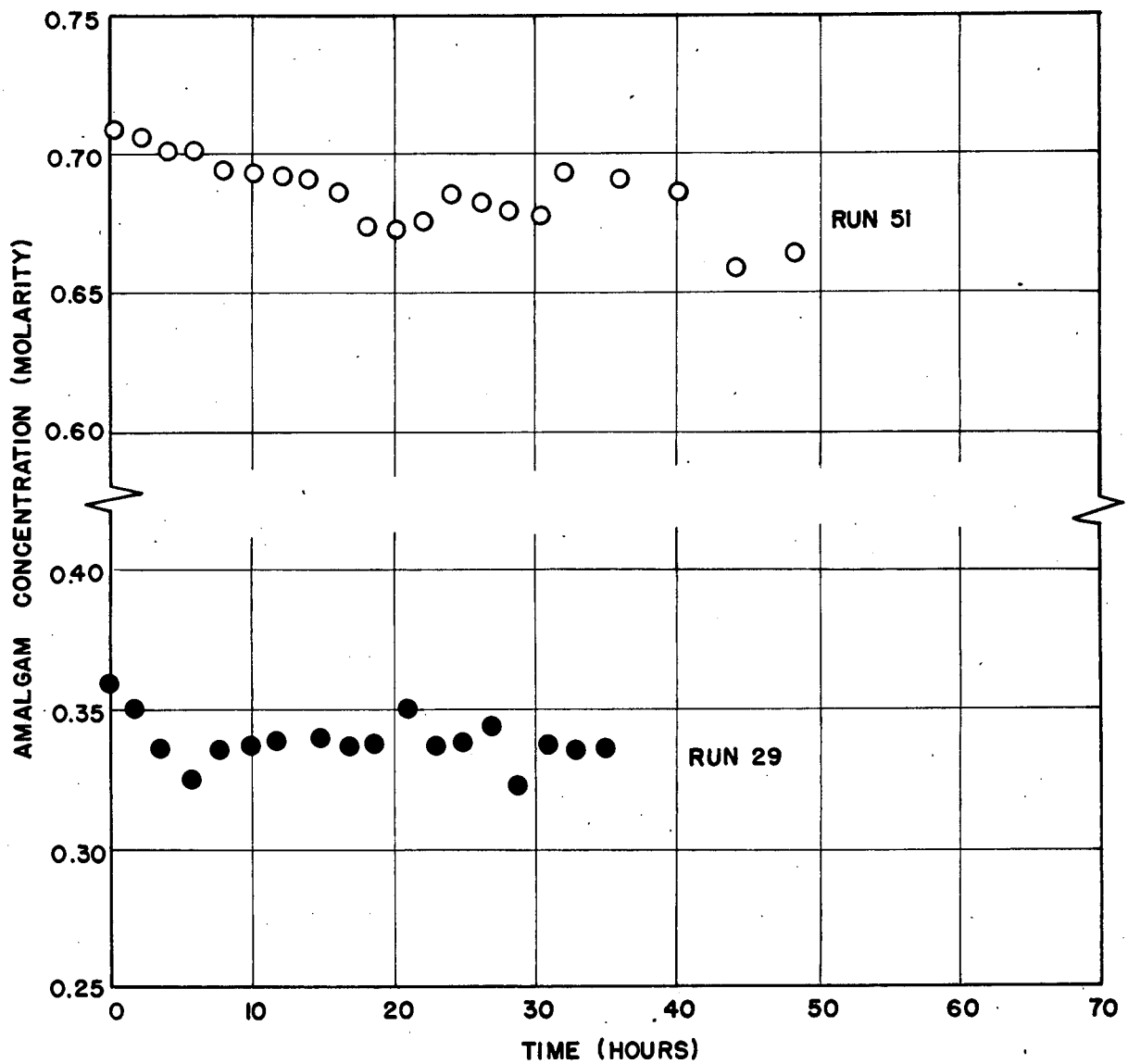

FIGURE 1. LITHIUM CONCENTRATION LOSS DURING RUN

ion over chloride indicating a complex ion such as an alkyl. This reaction occurs at temperatures of 120°C and higher. However at 110°C and lower temperatures the amine solution remains colorless and no excess lithium ion has been detected.

TEMPERATURE CONTROL

Accurate control of temperature of the system is essential for good operation of the pilot plant because of the effect of temperature upon separation and solution stability (as noted above). Control of temperature of the hot column has been improved by dividing the system into three components, each with individual steam pressure regulator stations: (1) the column proper, (2) a preheater for entering amalgam, and (3) a preheater for entering amine. The temperature of each heater is controlled by adjusting the steam pressure on the jacket. With this system it is possible to maintain a uniform temperature throughout the column for a wide range of flows.

In the cold column, where the amine solution is nearly saturated with lithium chloride, the temperature must be maintained above the saturation point to avoid precipitation of solid lithium chloride in the column. The use of tap water for control of the temperatures of the cold column was not satisfactory since tap water temperature has been quite low. A recirculation cooling system has been installed on the amalgam cooler and the cold column. The temperature of the circulated water is controlled by a steam heater and a tap water coil in the head tank.

FLOW CONTROL

Accuracy requirements in flow rate and concentration of lithium are very great, creating a control problem which is almost unique in chemical production operations. The high accuracy requirement results from the great influence on separation of the ratio of lithium throughputs in the two phases. This may be shown on the McCabe-Thiel diagram by an operating line whose slope is the ratio of lithium throughputs in the two phases and which must lie between the equilibrium curves of the hot and cold systems. These curves are very close together since the coefficients are not far apart

and both very near unity. A slight deviation in slope of the operating line causes "pinching" and consequent ineffectiveness of separation stages. It may be shown mathematically that a fluctuation in the ratio of throughputs of no more than 5% may result in reduced efficiency of a unit by as much as 25 to 50%, depending on the number of stages in that unit. A useful mathematical treatment of this has been made by W. DeMarcus* which leads to the following equations: (these were used to calculate the curves shown in Figure 2)

$$S = 1 + \frac{1}{2}\left(\frac{\epsilon_1 \alpha_2 - \alpha_1 \epsilon_2}{\alpha_1 \alpha_2}\right) \xi$$

where

S = ratio of tops amalgam mole fraction to bottom mole fraction

α_1 = cold separation factor

α_2 = hot separation factor

$\epsilon_1 = \alpha_1 - 1$

$\epsilon_2 = \alpha_2 - 1$

and

$$\xi = \frac{2}{\frac{1}{\alpha_1 A} + \frac{1}{\alpha_2 B}}$$

where

$$A = \frac{e^{N_1(\epsilon_1 + \theta \alpha_1)} - 1}{\epsilon_1 + \theta \alpha_1}$$

and

$$B = \frac{1 - e^{-N_2(\epsilon_2 + \theta \alpha_2)}}{\epsilon_2 + \theta \alpha_2}$$

*Y-B55-5, "Square Dual Temperature Cascade at Total Reflux"

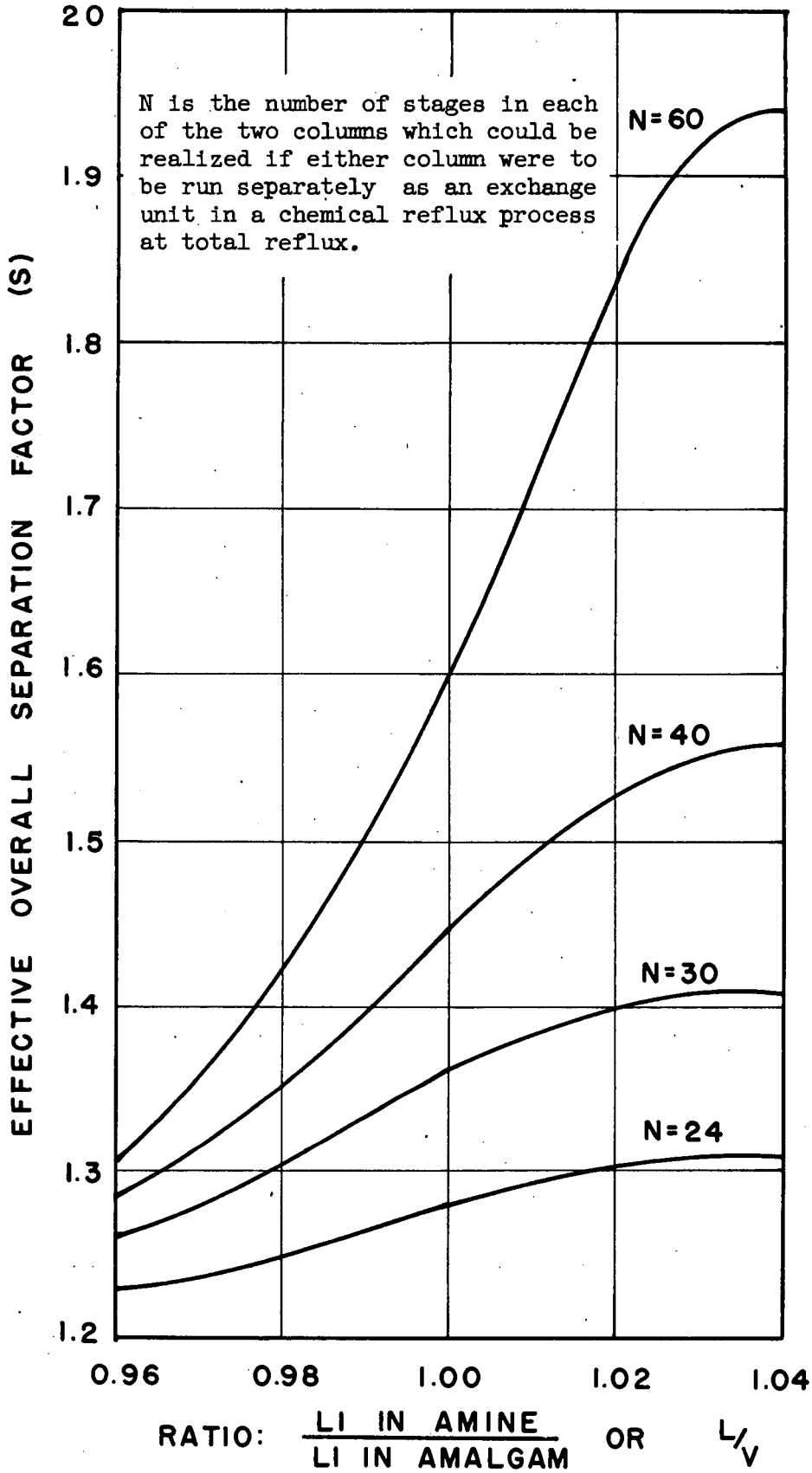

FIGURE 2. EFFECT OF L/V RATIO ON EFFECTIVE SEPARATION FACTOR OF DUAL TEMPERATURE SYSTEM

where:

N_1 = number of stages the cold column would have operated as a single column at total reflux.

N_2 = same as above for hot column.

$$\theta = \frac{L - V}{V}$$

where:

L = lithium flow rate in amine

V = lithium flow rate in amalgam.

Further treatment of this problem is being made by W. N. Johnson and J. Shacter of K-25.

Since Milton Roy pumps were available and had been found satisfactory for other liquid-liquid contacting processes, they were chosen for the initial pilot plant installation. The use of these pumps for the amine has been quite satisfactory. However, for use with amalgam it was necessary to invert the pump cylinder head to permit seating of the gravity operated ball check valves. This permitted occasional gas locking of the pump (since the casting was not designed for inverted operation) and consequently erratic amalgam flows were encountered. Tungsten carbide (Kennametal, sp. gr. 15.7) ball checks were obtained for the amalgam pumps, thus permitting operation with the head in normal position with much better flow control resulting. Diaphragm pumps with spring loaded checks and centrifugal pumps will be tested in the near future.

EFFECT OF SIZE OF TRAY OPENINGS ON THROUGHPUT

Choice of the proper size openings in the trays is important because of the effect on both quantity and quality of the separation. The desired action is alternate dispersion and coalescence of the amalgam as it passes through the successive trays. However, if the dispersion is efficient the degree of coalescence seems to be of secondary importance. To observe the action of various trays, a six inch section of one inch glass pipe was placed in the center of each column.

Temperature has a marked effect upon both dispersion and coalescence of the amalgam. At temperatures less than 50°C very little coalescence occurs except on the finest trays tested, however, the dispersion is good even with 10-mesh screen. At temperatures near 100°C the action is very sensitive to the pulse rate. There is poor dispersion and complete coalescence at pulse rates below 140 cycles per minute and the exact opposite action at pulse rates above 150.

The flooding point was determined for each size tray openings and then the separation factor was measured at several flow rates. Unfortunately, most of the determinations of the separation are subject to error because of erratic flow of the amalgam. In the flooding experiments the cold column flooded at the top with coalesced amalgam accumulating above the top tray. In the hot column, the flow was limited by back flow of dispersed amalgam carried along with the amine stream. The data in Table 1 show the results with various openings and pulse rates at 27°C.

Table 1

Flooding Rates at 27°C

Screen Size	Opening Width (in.)	Open Area (%)	Pulse Stroke Length* (inches)	Pulse Stroke Frequency (cycles/min)	Flooding Rates (cc/min.) Amine	Flooding Rates (cc/min.) Amalg.
60	0.0097	33.9	2	80	100	50
40	0.0155	38.4	2	80	200	100
24	0.0287	47.4	1	60	500	350
24	"	"	1	80	700	300
24	"	"	1	100	950	200
24	"	"	1	150	800	200
20	0.035	49.0	1	65	400	400
20	"	"	1	80	750	300
20	"	"	1	65	920	280
Perforated plates. Each			1	65	400	400
plate 90 holes 0.04" diameter.			1	65	600	300
10	0.075	56.3	1	50	800	400
10	"	"	1	80	900	350
10	"	"	1	55	1000	340
10	"	"	1	65	1100	300

*Maximum column liquid displacement at each stroke.

At 100°C the flooding rate is higher than at 27°C, so that it appears possible to operate with finer screens in the hot column. It has been found that 30-mesh screens in the hot column flood at about the same throughput at which 24-mesh screens flood in the cold column. Also, 20-mesh at 100°C is equivalent to 10-mesh at 27°C.

The throughput is inversely proportional to the pulse frequency, however, at pulse rates below 50 cycles per minute the streams showed a marked tendency to channel, particularly with 10- and 20-mesh screens.

Figure 3 shows the linear relationship between amalgam amine flows at the flooding point for various size screens. Lines representing various ratios of amalgam to amine flow rates are included so that the intersection of any ratio line and flooding curve shows the maximum throughput for that ratio and screen size. For example, if it were desired to operated with 0.8M lithium in amalgam and 0.2M lithium in amine, the ratio of flow rates should be about 1:4. On the graph the intersection of the 1:4 line and the flooding curve for 10-mesh screen shows that the maximum throughput of amalgam is 290 cc/minute and of amine 1150 cc/minute.

SUMMARY OF SEPARATION DATA

Runs 1 through 24 were made before the heavy ball check valves were obtained and were useful only for throughput data and general operating technique for the subsequent runs which are summarized in Tables 2, 3, and 4.

The H.E.T.S.'s were calculated from the equations,

$$\alpha^{N} = S = \frac{R \text{ tops}}{R \text{ bottoms}} \quad \text{and HETS} = \frac{H}{N}$$

where

$\alpha = 1.0115 = 1 + 1/2\ (\alpha \text{ cold} - \alpha \text{ hot})$

N = number of stages (assuming equal number in each column)

S = separation

R = atomic ratio of 6/7

H = height of columns in inches.

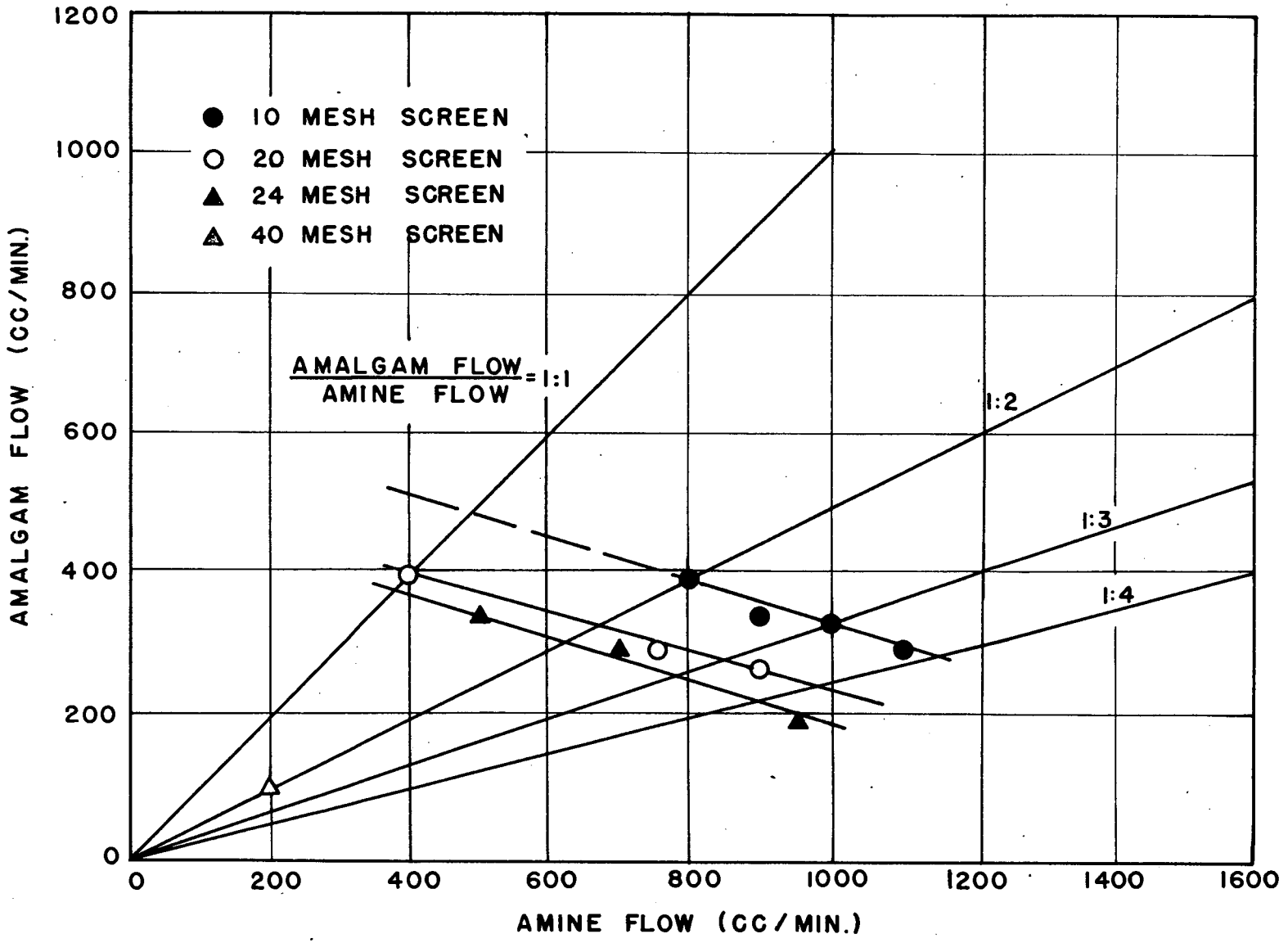

FIGURE 3. FLOODING RATES AT 27°C

Table 2

Hot Column (100°C) : 30-Mesh S.S. Screen

Cold Column (27°C) : 24-Mesh S.S. Screen

Run No.	Run Time (hrs)	Pulse Stroke Hot Column Length* (in.)	Pulse Stroke Hot Column Rate (cycles /min.)	Pulse Stroke Cold Column Length* (in.)	Pulse Stroke Cold Column Rate (cycles /min.)	Flow Rate (cc/min.) Amine	Flow Rate (cc/min.) Amalg.	Lithium Conc. (molarity) Amine	Lithium Conc. (molarity) Amalg.	L/V (Li amine / Li amalg.)	Ratio 6/7 Tops	Ratio 6/7 Bottoms	S	H.E.T.S. (in.)
26	0	1	155	1	65	600	240	0.200	0.38	1.32				
	4					594	260		0.37	1.24				
	8					603	289		0.36	1.16	0.0893	0.0683	1.31	12
	10					600	280		0.35	1.22	0.0894	0.0657	1.36	11
27	0	1	120	1	65	539	321	0.200	0.35	0.96				
	6					540	264		0.35	1.17	0.0852	0.0680	1.25	15
	9					548	253		0.32	1.36	0.0855	0.0681	1.26	15
29	0	1	155	1	55	495	274	0.203	0.360	1.01				
	2					494	274		0.350	1.05				
	4					489	272		0.337	1.08				
	6					489	268		0.325	1.14				
	8					486	270		0.335	1.09	0.0929	0.0642	1.45	9
	10					487	264		0.335	1.12	0.0961	0.0640	1.50	8
	12					486	275		0.338	1.06	0.0948	0.0644	1.47	9
	15					492	266		0.340	1.10	0.0944	0.0630	1.50	8
	17					492	266		0.336	1.12	0.0936	0.0646	1.45	9
	19					492	266		0.337	1.11	0.0954	0.0668	1.43	9
	21					481	266		0.350	1.05	0.0929	0.0672	1.38	10
	23					481	272		0.336	1.07	0.0930	0.0658	1.41	10
	25					495	270		0.338	1.10	0.0964	0.0672	1.43	9
	29					492	267		0.342	1.09	0.0914	0.0695	1.32	12
	35					491	266		0.335	1.12	0.0867	0.0723	1.20	19
34	0	1	155	1	65	489	285	0.203	0.381	0.91				
	4					494	284		0.373	0.94				
	6					486	286		0.369	0.93	0.0857	0.0694	1.23	16
	8					487	282		0.368	0.95	0.0917	0.0717	1.28	14
	10					494	274		0.346	1.05	0.0899	0.0681	1.32	12
	12					494	274		0.351	1.04	0.0938	0.0667	1.41	10
	14					494	269		0.353	1.05	0.0937	0.0642	1.46	9

*Maximum displacement of liquid in column for each stroke.

Table 2 (continued)

Run No.	Run Time (hrs)	Pulse Stroke Hot Column Length* (in.)	Pulse Stroke Hot Column Rate (cycles /min.)	Pulse Stroke Cold Column Length* (in.)	Pulse Stroke Cold Column Rate (cycles /min.)	Flow Rate (cc/min.) Amine	Flow Rate (cc/min.) Amalg.	Lithium Conc. (molarity) Amine	Lithium Conc. (molarity) Amalg.	L/V (Li amine / Li amalg.)	Ratio 6/7 Tops	Ratio 6/7 Bottoms	S	H.E.T.S. (in.)
35	0	1	160	1	65	489	294	0.210	0.339	1.03	0.0918	0.0721	1.27	14
	2					495	294		0.339	1.04	0.0927	0.0689	1.35	11
	4					496	291		0.336	1.07	0.0939	0.0667	1.41	10
	6					489	292		0.325	1.08	0.0933	0.0673	1.39	10
	8					489	278		0.318	1.16	0.0949	0.0672	1.41	10
35B	2					492	286		0.332	1.09	0.0881	0.0756	1.17	21
	4					495	293		0.328	1.08	0.0887	0.0726	1.22	16
	6					489	293		0.325	1.08	0.0961	0.0698	1.38	10
	8					492	291		0.328	1.08	0.0937	0.0694	1.35	11
	10					492	284		0.319	1.14	0.0973	0.0701	1.39	10
	12					494	293		0.300	1.18	0.0944	0.0697	1.35	11
37	0	1	160	1	65	662	314	0.210	0.430	1.03				
	2					667	325		0.425	1.02	0.0893	0.0713	1.25	15
	4					665	315		0.420	1.02	0.0919	0.0669	1.37	11
	6					661	298		0.425	1.10	0.0916	0.0653	1.40	10
	8					660	305		0.420	1.08	0.0961	0.0650	1.48	9
	10					653	330		0.422	0.99	0.0968	0.0614	1.58	7
	12					660	284		0.419	1.16	0.0908	0.0700	1.30	12
	14					674	286		0.424	1.17	0.0834	0.0732	1.14	24
	16					666	302		0.416	1.11	0.0863	0.0733	1.18	20
	18					659	305		0.421	1.08	0.0914	0.0688	1.33	12
	20					671	307		0.420	1.09	0.0915	0.0672	1.36	11

Table 3

Hot Column (100°C) : 20-Mesh S.S. Screen

Cold Column (27°C) : 10-Mesh S.S. Screen

Run No.	Run Time (hrs)	Pulse Stroke Hot Column Length (in.)	Pulse Stroke Hot Column Rate (cycles /min.)	Pulse Stroke Cold Column Length (in.)	Pulse Stroke Cold Column Rate (cycles /min.)	Flow Rate (cc/min.) Amine	Flow Rate (cc/min.) Amalg.	Lithium Conc. (molarity) Amine	Lithium Conc. (molarity) Amalg.	L/V (Li amine / Li amalg.)	Ratio 6/7 Tops	Ratio 6/7 Bottoms	S	H.E.T.S. (in.)
38	0	1-1/2	120	2	40	655	311	0.207	0.411	1.06				
	4					655	306		0.416	1.07	0.0859	0.0723	1.19	19
	6					651	286		0.433	1.09	0.0867	0.0722	1.20	19
	8					658	286		0.435	1.10	0.0852	0.0730	1.17	21
	10					656	296		0.429	1.07	0.0844	0.0724	1.17	21
	12					656	297		0.433	1.07	0.0841	0.0736	1.14	24
40	0	1	155	2	40	735	324	0.197	0.448	1.00				
	2					732	323		0.429	1.04				
	4					742	324		0.431	1.04				
	6					735	319		0.433	1.05				
	8					750	300		0.425	1.15				
	10					737	305		0.424	1.13				
	12					737	333		0.429	1.02	0.0838	0.0717	1.17	21
	14					741	366		0.421	0.95	0.0919	0.0677	1.36	11
	16					749	362		0.429	0.95	0.0900	0.0664	1.36	11
	18					749	354		0.430	0.97	0.0912	0.0665	1.37	11
41	1	1	155	2	40	742	334	0.196	0.493	0.88	0.0915	0.0710	1.29	13
	3					816	334		0.515	0.93	0.0849	0.0720	1.18	20
	5					810	341		0.512	0.91	0.0897	0.0703	1.28	13
	7			1	40	845	335		0.485	1.02	0.0922	0.0686	1.34	11
	9					856	340		0.487	1.01	0.0935	0.0686	1.36	11
	11					865	342		0.490	1.01	0.1049	0.0671	1.56	7
	13					860	340		0.490	1.01	0.0931	0.0672	1.39	10
43	0	3/4	200	1	75	900	351	0.196	0.498	1.01	0.0825	0.0715	1.15	24
	2					910	355		0.500	1.00	0.0867	0.0719	1.21	17
	4					900	355		0.508	0.98	0.0852	0.0696	1.22	17
	6					895	367		0.494	0.97	0.0873	0.0707	1.23	16
	8					885	362		0.479	0.99				
	10					907	370		0.483	0.99	0.0880	0.0653	1.35	11
	12			1	55	865	368		0.492	0.94	0.0901	0.0665	1.35	11
	14					869	368		0.491	0.94	0.0895	0.0668	1.34	11

Table 3 (continued)

Run No.	Run Time (hrs)	Pulse Stroke Hot Column Length (in.)	Pulse Stroke Hot Column Rate (cycles /min.)	Pulse Stroke Cold Column Length (in.)	Pulse Stroke Cold Column Rate (cycles /min.)	Flow Rate (cc/min.) Amine	Flow Rate (cc/min.) Amalg.	Lithium Conc. (molarity) Amine	Lithium Conc. (molarity) Amalg.	L/V (Li amine / Li amalg.)	Ratio 6/7 Tops	Ratio 6/7 Bottoms	S	H.E.T.S. (in.)
44	2	3/4	205	1	65	1120	274	0.195	0.772	1.03	0.0843	0.0755	1.12	29
	4					1100	274		0.758	1.03	0.0850	0.0714	1.19	19
	6	3/4	260			1070	303		0.740	0.93	0.0843	0.0719	1.17	21
	8					1122	284		0.753	1.02	0.0858	0.0699	1.23	16
	10	1	230			1055	280		0.754	0.98	0.0863	0.0693	1.25	15
	12					1090	282		0.734	1.03	0.0910	0.0688	1.32	12
	14					1090	287		0.749	0.99	0.0920	0.0673	1.37	11
	16					1090	283		0.741	1.01	0.0914	0.0662	1.38	10
	18					1090	280		0.742	1.02	0.0949	0.0661	1.44	9
45	0	1	205	1	90	1103	274	0.197	0.748	1.06	0.0838	0.0745	1.12	29
	2						281		0.753		0.0855	0.0736	1.16	22
	4					1090	278		0.750	1.03	0.0841	0.0737	1.14	24
	6					1030	283		0.737	0.97	0.0844	0.0723	1.17	21
	8					1060	286		0.756	0.97	0.0864	0.0676	1.28	13
	10					1020	284		0.716	0.99	0.0893	0.0679	1.32	12
	12			1	75	1028	284		0.737	0.97	0.0907	0.0663	1.37	11
	14					1053	244		0.734	1.16	0.0835	0.0707	1.18	20
	16					1043	241		0.733	1.16	0.0832	0.0739	1.13	26
	18					1080	257		0.746	1.11	0.0860	0.0707	1.22	17
	20					1050	257		0.738	1.09	0.0857	0.0714	1.20	18
	22					1050	294		0.738	0.95	0.0886	0.0692	1.28	13
	24					1050	281		0.738	1.00	0.0897	0.0679	1.32	12
	26					1050	278		0.738	1.01	0.0931	0.0665	1.40	10
	28					1050	278		0.738	1.01	0.0932	0.0674	1.38	10

Table 3 (continued)

Run No.	Run Time (hrs)	Pulse Stroke: Hot Column Length (in.)	Pulse Stroke: Hot Column Rate (cycles /min.)	Pulse Stroke: Cold Column Length (in.)	Pulse Stroke: Cold Column Rate (cycles /min.)	Flow Rate (cc/min.) Amine	Flow Rate (cc/min.) Amalg.	Lithium Conc. (molarity) Amine	Lithium Conc. (molarity) Amalg.	L/V (Li amine / Li amalg.)	Ratio 6/7 Tops	Ratio 6/7 Bottoms	S	H.E.T.S. (in.)
46	0	1	205	1	75	1130	281	0.197	0.755	1.05				
	4					1094	276		0.769	1.02	0.0897	0.0683	1.31	12
	8					1096	277		0.734	1.06	0.0902	0.0668	1.35	11
	12					1146	275		0.743	1.11	0.0888	0.0676	1.31	12
	16					1168	275		0.744	1.12	0.0879	0.0703	1.25	15
	20					1100	282		0.722	1.06	0.0874	0.0701	1.25	15
	24					1065	279		0.730	1.03	0.0868	0.0688	1.26	15
	28					1065	269		0.733	1.07	0.0889	0.0682	1.30	13
	32					1070	268		0.730	1.08	0.0897	0.0673	1.33	12
	36					1070	275		0.735	1.04	0.0884	0.0678	1.30	13
47	1	1	205	1	75	774	196	0.197	0.732	1.07				
	3					771	196		0.733	1.05				
	5					768	197		0.733	1.05				
	7					762	191		0.713	1.10	0.0929	0.0716	1.30	13
	9					765	193		0.732	1.07	0.0889	0.0705	1.26	15
	11					775	194		0.728	1.08	0.0911	0.0698	1.31	12
48	0	1-1/4	220	1	78	762	200	0.200	0.735	1.04				
	4					774	202		0.731	1.05	0.0884	0.0705	1.25	15
	8					777	205		0.737	1.03	0.0922	0.0688	1.34	11
	12					768	202		0.735	1.04	0.0900	0.0686	1.31	12
	16					762	198		0.734	1.05	0.0906	0.0686	1.32	12
	20			1	155	769	198		0.727	1.07	0.0942	0.0693	1.36	11
	23					762	205		0.730	1.02	0.0964	0.0663	1.45	9
50	1	1-1/4	205	1	130	919	240	0.217	0.734	1.13	0.0887	0.0697	1.27	14
	5					916	235		0.723	1.17	0.0853	0.0736	1.16	22
	9					916	234		0.726	1.17	0.0877	0.0709	1.24	15
	13					920	243		0.723	1.13	0.0863	0.0730	1.18	20
	17					920	245		0.723	1.13	0.0875	0.0720	1.22	16

Table 3 (continued

Run No.	Run Time (hrs)	Pulse Stroke Hot Column Length (in.)	Pulse Stroke Hot Column Rate (cycles /min.)	Pulse Stroke Cold Column Length (in.)	Pulse Stroke Cold Column Rate (cycles /min.)	Flow Rate (cc/min.) Amine	Flow Rate (cc/min.) Amalg.	Lithium Conc. (molarity) Amine	Lithium Conc. (molarity) Amalg.	L/V (Li amine / Li amalg.)	Ratio 6/7 Tops	Ratio 6/7 Bottoms	S	H.E.T.S. (in.)
51	0	1-1/4	205	1	150	234	62.5	0.228	0.709	1.20				
	4					236	63.5		0.700	1.21	0.0816	0.0737	1.11	32
	8					236	70.7		0.692	1.10	0.0852	0.0722	1.18	20
	12					234	68.9		0.690	1.12	0.0836	0.0726	1.15	24
	16					214	67.4		0.685	1.06	0.0841	0.0716	1.17	21
	20					213	68.6		0.670	1.06	0.0827	0.0696	1.19	19
	24					216	68.1		0.685	1.06	0.0874	0.0702	1.25	15
	28					213	69.6		0.679	1.03	0.0871	0.0692	1.26	15
	32					215	73.0		0.692	0.97	0.0877	0.0692	1.27	14
	36					214	70.3		0.691	1.00	0.0901	0.0682	1.32	12
	40					212	69.0		0.686	1.02	0.0869	0.0660	1.32	12
	44					212	70.7		0.655	1.04	0.0926	0.0662	1.40	10
	48					215	72.2		0.661	1.03	0.0886	0.0698	1.27	14
	52					214	72.2		0.660	1.02	0.0954	0.0696	1.37	11

Table 4

Hot Column (100°C) : 20-Mesh S.S. Screen

Cold Column (27°C) : 20-Mesh S.S. Screen

Run No.	Run Time (hrs)	Pulse Stroke: Hot Column Length (in.)	Pulse Stroke: Hot Column Rate (cycles /min.)	Pulse Stroke: Cold Column Length (in.)	Pulse Stroke: Cold Column Rate (cycles /min.)	Flow Rate (cc/min.) Amine	Flow Rate (cc/min.) Amalg.	Lithium Conc. (molarity) Amine	Lithium Conc. (molarity) Amalg.	L/V (Li amine / Li amalg.)	Ratio 6/7 Tops	Ratio 6/7 Bottoms	S	H.E.T.S. (in.)
52	0	1-1/4	200	1	78	731	304	0.221	0.657	0.81				
	2					725	237		0.649	1.04				
	4					743	242		0.670	1.01				
	6					719	238		0.655	1.02	0.0883	0.0666	1.33	12
	8					719	239		0.651	1.02	0.1003	0.0665	1.51	8
	10					728	242		0.650	1.02	0.0943	0.0637	1.48	8
	12					737	238		0.660	1.04	0.0954	0.0635	1.50	8
	14					738	242		0.644	1.05	0.0972	0.0638	1.52	8
	16					730	240		0.640	1.05	0.1078	0.0635	1.70	6.5
	18					720	244		0.650	1.00	0.0931	0.0620	1.50	8

All of the runs were made at total reflux and the equilibrium time was about 8 to 10 hours. Comparison of runs 26 and 27, which were identical with the exception of the pulse rate on the hot column, shows the improvement in separation due to finer dispersion of the amalgam at the higher pulse rate.

Runs 29 through 35 were all made with 30-mesh screen in the hot column and 24-mesh in the cold column under nearly identical conditions to obtain checks on separation factors.

In run 37 the throughput was about 50% greater than the previous runs with no appreciable effect upon the separation.

The series of runs from 38 through 50 were made with 20-mesh screen in the hot column and 10-mesh in the cold column. In general, the separation was lower than that obtained with finer screens, however, a larger throughput was possible. In this series the throughput was varied to determine the effect upon separation. In runs 50 and 51 the throughput was 0.05 mole lithium per minute, which was about one-fourth of flooding rates. Runs 38, 40, 47, and 48 were made at about two-thirds flooding rate. In runs 44, 45, and 46 the throughput was greater than 0.2 mole lithium per minute, which is very near the flooding rate in both columns. Comparison of the runs shows practically no effect of throughput on separation.

Run 52 was made under column conditions similar to those for runs 40, 47, and 48 with 20-mesh screen in the cold column instead of 10-mesh. The improvement in separation is marked and compares with separation obtained from runs made with 24-mesh screen in the cold column and 30-mesh in the hot.

A concise summary of the separation results has been made by averaging all results obtained where the L/V ratio was in the range 1.00 to 1.08. These averages for various size screens are given in Table 5.

Table 5

Effect of Screen Size on Separation

(L/V = 1.00 to 1.08)

Screen Size (mesh)		Number of Runs	Average "S" (95% C.I.)
Cold Column	Hot Column		
10	20	4	1.30 ± .03
20	20	1	1.50 ± .02
24	30	4	1.40 ± .05

FUTURE WORK

A chemical reflux pilot plant based on a 0.43-inch diameter by twenty feet long column is being constructed. The column will be first operated with an "infinite" reservoir at the lithium seven end (enriching the six end). Reflux at the six end will be accomplished by means of a sodium-lithium inversion using either sodium bromide in solution or a sodium chloride slurry.

Operation of the dual temperature system will continue with modifications made in the piping to permit use of only part of the hot or cold column length in separate experiments. From data obtained with various column lengths it will be possible to determine the effective number of stages in each column. Lapp Pulsafeeder diaphragm pumps will also be installed, in place of the Milton Roy pumps, to aid in maintaining precise flow control. Studies of the effect of various types of column plates will also be continued.

LABORATORY STUDIES

TEMPERATURE DEPENDANCY OF SEPARATION FACTOR

J. S. Drury

Additional laboratory batch runs have been made to determine further the temperature dependancy of the separation factor. Using the method described in the last report,[1] individual four-stage batch runs were made at 60° and 99°C. The isotopic assay of samples resulting from these runs are given in Tables 6 and 7. These data are plotted in Figures 4 and 5. The separation factor corresponding to 60°C was found to be 1.044, ± 0.004 (95% C.I.) and for 99°C, 1.027, ± 0.006 (95% C.I.). Two additional determinations of the separation factor were made at 74 and 87°C. These runs differed from previous ones in that they were single-stage determinations. The following procedure was followed:

Reagent grade Eastman Kodak Company ethylenediamine dihydrochloride was dried at 100°C in vacuo and 0.8454 grams were weighed out and placed in a 100 ml graduate fitted with a ground glass joint. The graduate was flushed with dried helium and 40 mls of EDA, freshly distilled over sodium, was added to the graduate. After the EDA.2HCl dissolved, 40 mls of 0.675N lithium amalgam was added and the contents of the graduate was transferred to a 100 ml double-walled flask fitted with a stopcock drain, an opening for a mercury sealed stirrer and an inlet and outlet for sweeping the system with helium. Water from a constant temperature bath was circulated in the outer jacket of the flask so that the contents were maintained at 74 ± 1°C during four hours of agitation. At the end of this time the two phases were separated and the lithium from each phase converted to lithium sulphate. The lithium sulphate from each phase was divided into six identical samples which were submitted to the Mass Spectrographic Laboratory for isotopic assay. Results of these assays are shown in Table 8. The single-stage separation factor, α, was found to be 1.031 ± 0.007 (95% C.I.) at this temperature.

A similar run was made at 87 ± 1°C. The results from this run are shown in Table 9. From these data α was calculated to be 1.034 ± 0.007 (95% C.I.).

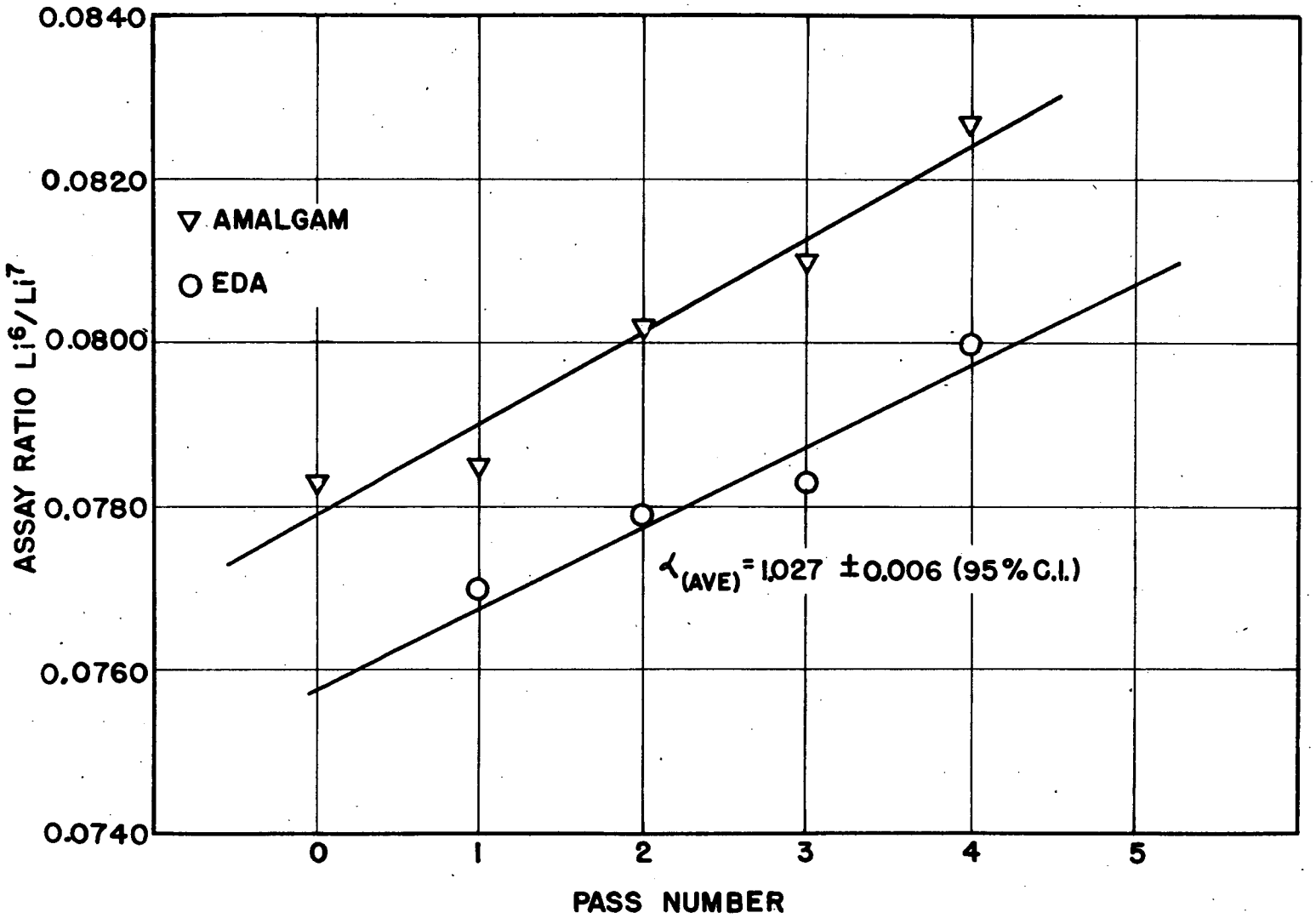

FIGURE 4. Li AMALGAM–EDA–LiCl BATCH RUN #3 TEMPERATURE 99 ± 1°C

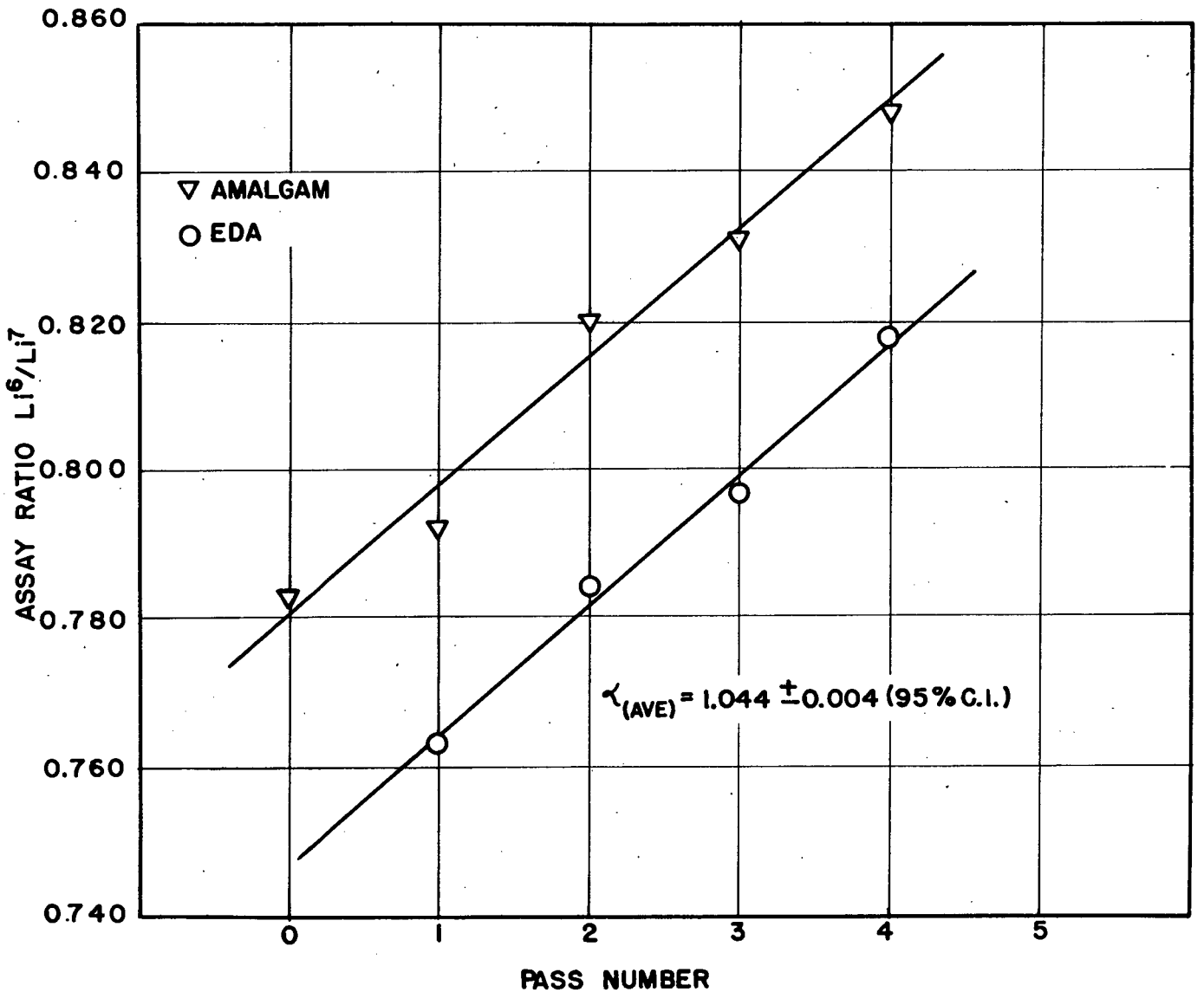

FIGURE 5. Li AMALGAM-EDA-LiCl BATCH RUN #4 TEMPERATURE 60 ± 1°C

Table 6

Batch Run No. 3, 99 ± 1°C

After Pass No.	Equilibration Time per Pass (min.)	Ratio Li^6/Li^7 ± 0.001	
		Amalgam	EDA
0		0.0783	
1	240	0.0785	0.0770
2	270	0.0802	0.0779
3	300	0.0810	0.0783
4	300	0.0827	0.0800

Table 7

Batch Run No. 4, 60 ± 1°C

After Pass No.	Equilibration Time per Pass (min.)	Ratio Li^6/Li^7 ± 0.001	
		Amalgam	EDA
0		0.0783	
1	240	0.0792	0.0763
2	240	0.0820	0.0784
3	240	0.0831	0.0797
4	240	0.0848	0.0818

Table 8

Batch Run No. 5, 74 ± 1°C

(Single Stage Determination)

Sample No.	Ratio Li^6/Li^7 ± 0.001 Amalgam	EDA
1	0.0795	0.0765
2	0.0778	0.0766
3	0.0794	0.0765
4	0.0787	0.0762
5	0.0792	0.0768
6	0.0786	0.0765

$\alpha = 1.031 \pm 0.007$ (95% C.I.)

Table 9

Batch Run No. 6, 87 ± 1°C

(Single Stage Determination)

Sample No.	Ratio Li^6/Li^7 ± 0.001 Amalgam	EDA
1	0.0800	0.0772
2	0.0790	0.0768
3	0.0793	0.0772
4	0.0796	0.0775
5	0.0794	0.0762
6	0.0804	0.0773

$\alpha = 1.034 \pm 0.007$ (95% C.I.)

STABILITY OF AMALGAM-AMINE SYSTEM

J. S. Drury

The following experiments were performed to determine the highest temperature at which the amalgam-amine system might be expected to operate in the dual temperature process.

About five mls each of 0.5M dry lithium amalgam and 0.25M LiCl in EDA were sealed in a tube of heavy gage glass. This Carius tube was wrapped in glass wool and placed in a length of iron pipe fitted with screw caps on either end. This assembly was placed in an oven and heated to 180°C. After 21 hours it was removed, cooled, and inspected. The EDA phase was strongly colored a deep blood-red.

Similar results were obtained with a system utilizing LiBr instead of LiCl.

Repeating this experiment with EDA alone did not produce this coloration.

EDA containing LiCl did not produce any color under these conditions even after 40 hours exposure.

Although the identity of the color forming agent is not known at this time, pilot plant data indicates that a mass transfer of lithium from the amalgam to the EDA phase is associated with its formation. If it is desirable to avoid this mass transfer of lithium in the system, then an operating temperature less than 180°C is indicated by these experiments.

Subsequent to these 180°C experiments, a similar coloration of the EDA phase was observed under pilot plant conditions at 135°C. Since this reaction had not been observed in pilot plant runs at 110°C, the following laboratory experiments were made to check the system stability between 110° and 135°C. Small Carius tubes were prepared, each containing about one ml each of 0.5M lithium amalgam and 0.25M LiCl in EDA. Wire from stainless steel screens used in the pilot plant pulse columns was included in half of these tubes so that possible catalytic effects from this source might be qualitatively evaluated. Two of these tubes, one with stainless steel wire, one without wire, were placed in each of four flasks fitted with reflux condensers and containing solvents whose respective boiling points were 113, 116, 124, and 128°C. These solvents were continuously refluxed for 29 days. At the end of this time the EDA phase in each Carius tube had become colored a deep blood-red. The time required for each system to become colored is recorded in Table 10.

Table 10

Relative Stability of Amalgam-Amine Systems

System	Temperature	Time Required to Form Color (days)
$Li(Hg)_x$-LiCl-EDA	113	29
"	116	19
"	124	15
"	128	17
$Li(Hg)_x$-LiCl-EDA + S.S. Wire	113	15
"	116	9
"	124	4
"	128	5

From Figure 6 it is apparent that the stability of the system, as measured by the formation of colored reaction products in the EDA phase, is both temperature dependent and is catalyzed by the presence of stainless steel.

In order to compare the catalytic effects of black iron and stainless steel, two additional Carius tubes were filled as described before. Into one of these tubes was placed small pieces of stainless steel wire as before and into the other tube a small piece of greaseless black iron cut from a piece of pipe similar to the kind which might be used for column construction. These tubes were placed in the same constant temperature bath which was held at 115.5°C until the EDA phase of both tubes became colored. The tube containing black iron required three days while that containing the stainless steel wire required nine days. It would seem from this evidence that the catalytic effect of black iron is greater than stainless steel.

REFLUX STUDIES

A. C. Rutenberg, G. M. Begun

Six End

In the previous report[1] work was reported on the NaCl method of reflux. This method of reflux converts the lithium in the lithium amalgam into lithium chloride dissolved in EDA. This was accomplished by batchwise stirring of the lithium amalgam with EDA and excess solid NaCl. A possible method of accomplishing this reflux in a continuous manner is to pass dry EDA upward

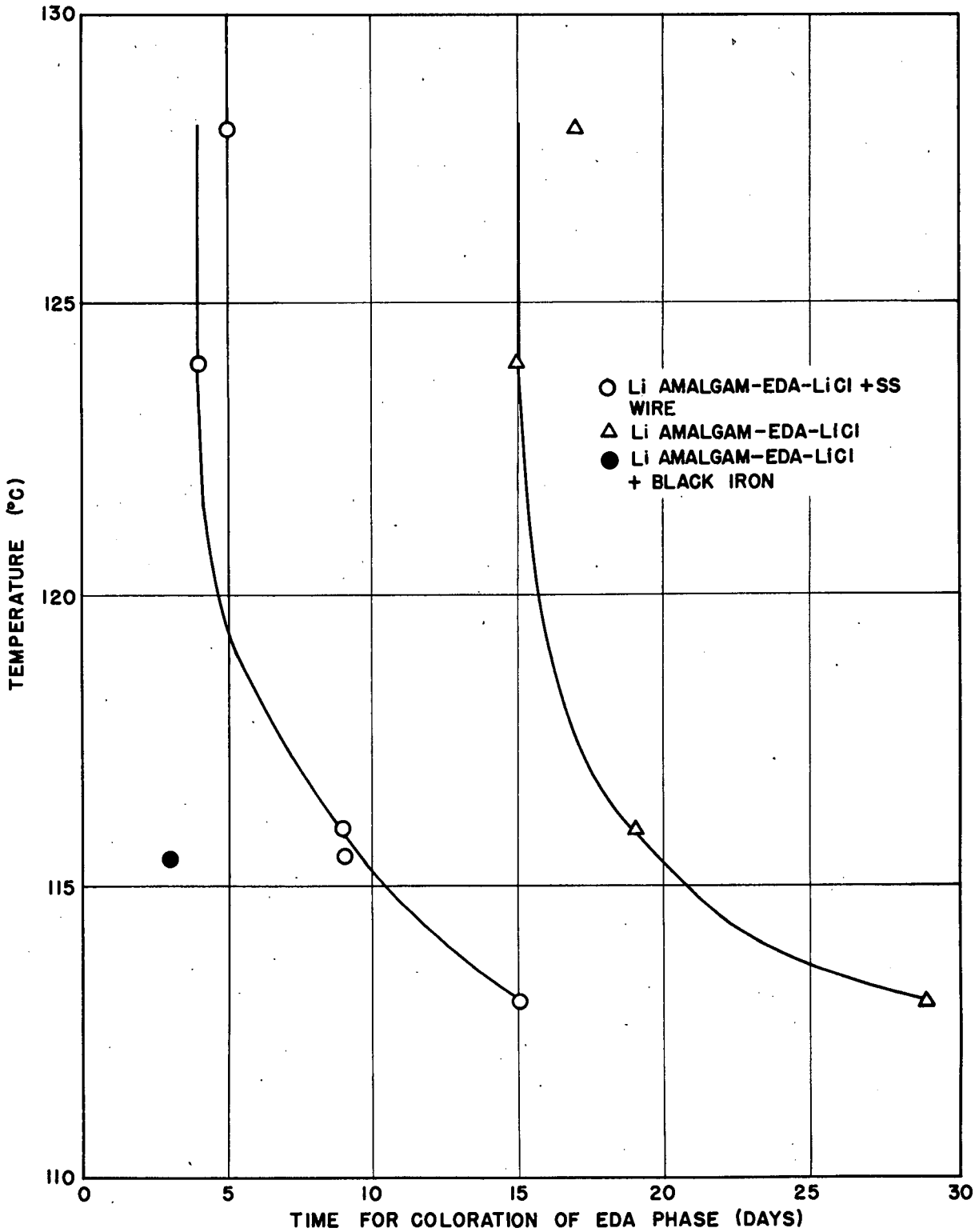

FIGURE 6. RELATIVE THERMAL STABILITY OF AMINE-AMALGAM SYSTEM

through a column packed with rock salt, while the amalgam is allowed to flow downward through the salt. This system was studied using a one-inch column constructed of pyrex pipe. The EDA was allowed to flow through the pipe at a rate two or three times that of the amalgam flow and the removal of lithium from the amalgam was studied as a function of the rate of flow of the amalgam and the length of the column. The rock salt used in the column was of a size large enough to be retained by a 8-mesh screen. The amalgam at the top of the column was dispersed by several stainless screens and flowed down the column dispersing through the rock salt quite evenly. The results are shown in Table 11.

Table 11

Rock Salt Column

No.	Column Length (in.)	Amalgam Flow (ml/min)	Effluent Amalgam Conc. mol./liter Na	Effluent Amalgam Conc. mol./liter Li	% Li Removed
1	10.5	0.5	0.521	0.105	83
2	"	2.8	.605	.1665	78
3	"	6.9	.542	.190	74
4	"	34.5	.335	.361	48
5	29	1.2	.680	.125	84
6	"	2.8	.616	.097	86
7	"	16.7	.634	.100	86
8	"	25.4	.507	.247	67
9	"	56	.456	.260	64

The column was not flooded even at the most rapid amalgam flow rate (56 ml/min), although this was close to the maximum flow possible.

The percent of lithium removed increases with column length and decreases with increasing flow rate. However, succeeding lengths of column do not appear to remove as large a percentage of the remaining lithium. This may be due to the slow solubility

of the rock salt in EDA, or to a lack of agitation of the amalgam droplets descending through the column. The experiments indicate that a very long column would be necessary to remove nearly all of the lithium from the amalgam unless more efficient means of intermixing are developed.

A proposed alternate means of reflux at the six end of the system involves the use of EDA·2HCl. EDA·2HCl is a relatively stable white solid which is quite soluble in EDA. When a solution of EDA·2HCl in EDA (containing an excess EDA·2HCl) was shaken vigorously with lithium amalgam, gas was evolved and the amalgam was depleted of its lithium within a few minutes. Presumably hydrogen gas is given off and LiCl is formed. In making equilibrium studies for separation factor determination EDA·2HCl was dissolved in EDA to remove one-half of the lithium from 40 ml of amalgam. It was found that the reaction took several hours at room temperature but proceeded rapidly at 87°C. At lower temperatures there was considerable frothing and some formation of a semi-solid lumpy amalgam. (Possibly ethylenediammonium amalgam was formed which then decomposed evolving hydrogen). In order to use this reaction as a method of reflux it would be necessary to carry out the exchange at an elevated temperature and provide a means of escape for the hydrogen gas.

Seven End

The problem at this end of the column is to remove the LiCl from the EDA and convert the lithium to lithium amalgam. The EDA must also be saved for further use. A method of achieving this reflux is to precipitate the lithium by means of an ethylenediammonium salt which reacts to form an insoluble non-solvated lithium salt. The other product of the precipitation would be EDA·2HCl which would stay dissolved in the EDA and could be used for the amalgam reflux. The EDA·$2H^+$ salt should preferably be fairly soluble but even a low solubility might be utilized by adding excess solid.

EDA·H_2SO_4 was prepared and dried, and its solubility in EDA was found to be less than 0.001 molar at room temperature. The salt formed by the addition of solid CO_2 to aqueous EDA (probably EDA·H_2CO_3 or EDA·$2H_2CO_3$) was difficult to crystallize and dry. It decomposed at temperatures of 200°C or lower leaving no residue. This salt was found to be quite soluble in EDA and to form a cloudy precipitate when added to EDA containing LiCl. Further work is being done on this substance. If Li_2CO_3 could be quantitatively precipitated from the EDA-LiCl solution, this could be converted easily to LiCl or LiOH.

Another possible method of removing LiCl from EDA solution is to employ a salting out agent. This substance should be subsequently easily separated from the EDA. Diethyl ether was tried for this purpose. The ether was dried over potassium hydroxide and then with lithium amalgam. Addition of ether to a saturated LiCl solution in EDA produced a precipitate which was analyzed and found to be LiCl·2EDA. A mixture of 4 parts saturated LiCl in EDA and 1 part diethyl ether removed only part of the LiCl, the final EDA still contained 0.05M LiCl. An equal volume mixture of LiCl in EDA and diethyl ether gave a resulting EDA solution 0.02M in LiCl. The addition of diethyl ether does not salt out sufficient LiCl from the EDA to be useful as a reflux method.

SOLUBILITIES IN EDA

A. A. Palko

The solubilities of sodium and lithium chlorides and bromides in anhydrous ethylene diamine were determined. The salts were vacuum dried; and the ethylene diamine was dried by refluxing for several hours first with CaC_2 and then with BaO. A constant temperature bath with a temperature control of $\pm$ 1/2°C was used to equilibrate the anhydrous amine and the salt. Solid salt was kept in contact with the liquid phase at all times by agitation. All solubilities were determined by a modified Volhard method for bromide and chloride. Results are shown in moles per liter at the temperature recorded in Table 12 and Figure 7.

Table 12

Solubility of Various Salts in EDA

Temp. (°C)	Salt Concentration (Moles per liter) NaCl	NaBr	LiCl[1]	LiBr
12.5	-	-	0.1486	-
15	-	-	-	0.1506
20	-	-	0.2020	-
25	0.045	4.03	-	0.2296
29	-	-	0.3113	-
36	-	-	-	0.3633
45	-	-	0.6570	-
49	-	-	-	0.6149
57	0.0275	-	-	-
60	-	-	1.369	-
63	-	3.83	-	-
66	-	-	-	1.1633
74.5	0.0215	-	-	-
77	-	-	2.585	-
96	-	-	4.741	-
98	0.0163	3.39	-	2.713

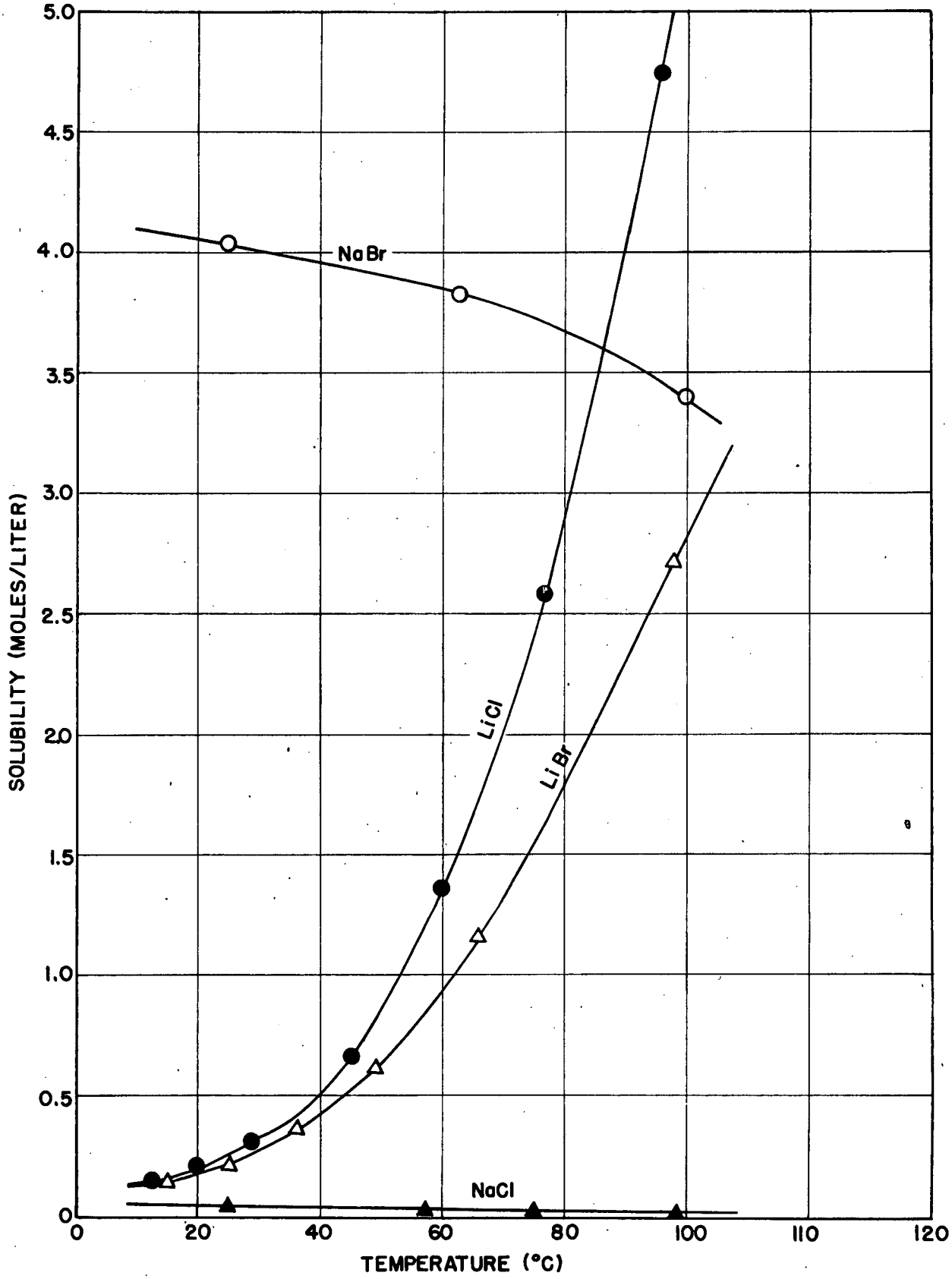

FIGURE 7. SOLUBILITY CURVES FOR VARIOUS SALTS IN ANHYDROUS EDA

VISCOSITY AND DENSITY

A. A. Palko

The viscosity of anhydrous ethylene diamine and of ethylene diamine-lithium chloride solutions was determined using an Ostwald-Fenske viscometer. The density was determined with a 10 and 25 cc pycnometer. In both cases distilled water was used as a standard. The diamine was dried as before with CaC_2 and BaO. The results for viscosity are tabulated in millepoises. The viscosity of water is given as a reference and was taken from Lange's Handbook, Seventh Edition. The results presented are an average of several readings. They are shown in Table 13 and Figure 8.

Table 13

Viscosity and Density

	Ethylene diamine		0.234N LiCl in EDA		Water	
T	Density (gm/ml)	Viscosity (m.poise)	Density (gm/ml)	Viscosity (m.poise)	Density (gm/ml)	Viscosity (m.poise)
12	0.898	18.018	-	-	0.9995	12.363
23.5	.894	13.665	0.904	16.838	.9974	9.250
59	.863	6.669	.875	7.565	.9837	4.759
75	.845	5.102	.854	5.668	.9749	3.799

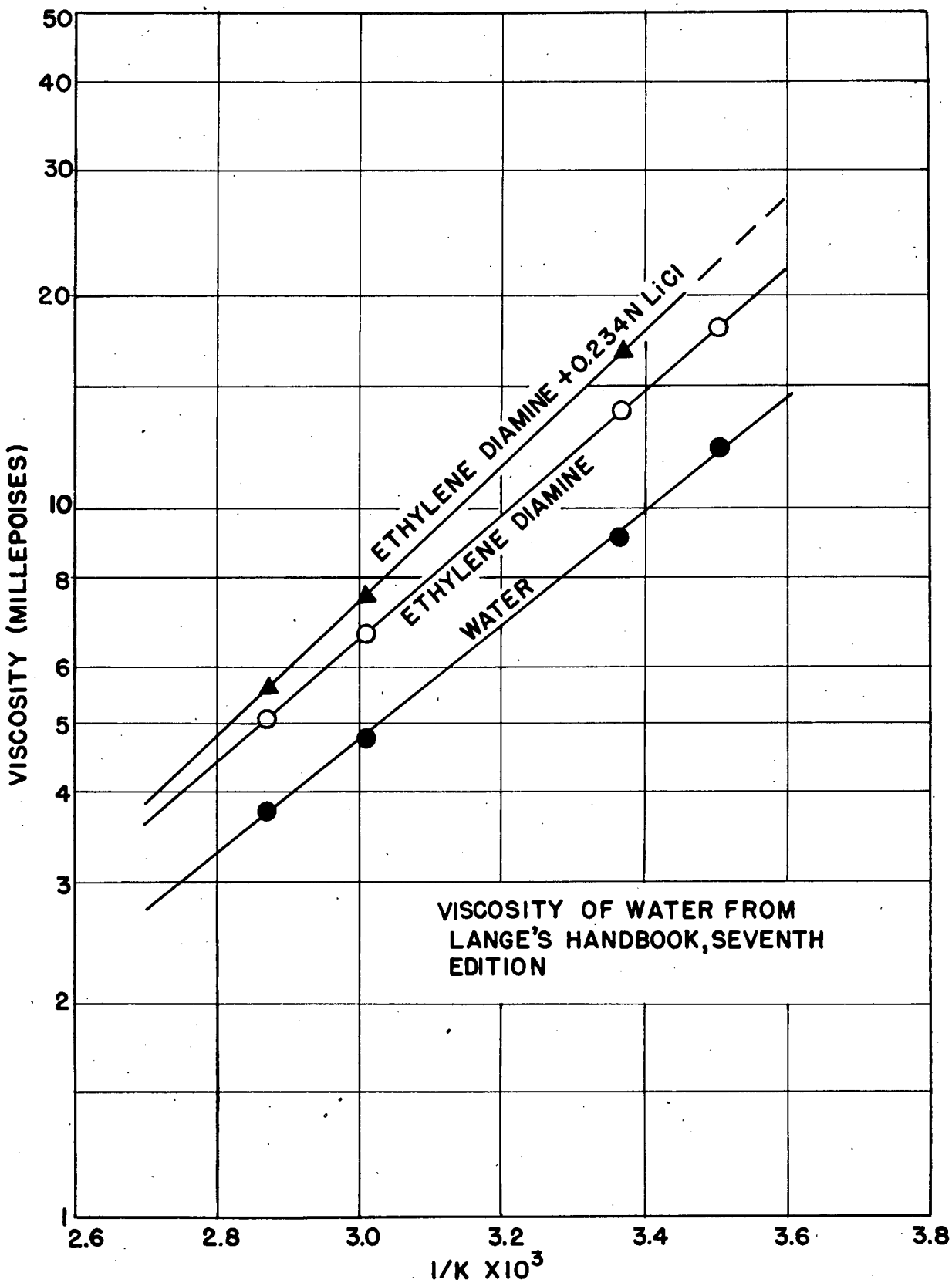

FIGURE 8. VISCOSITY OF ANHYDROUS ETHYLENE DIAMINE AND ETHYLENE DIAMINE-LiCl SOLUTIONS

AMALGAMATION STUDY

A. A. Palko

A study was made to test the possibility of amalgamating various metals in an anhydrous system containing lithium amalgam, ethylene diamine and lithium chloride. Tests were also made to determine whether metals amalgamated before being placed into the system would retain their wettability. Dynamic and static tests of approximately 100 hours duration were made on 20-mesh screens of brass, nickel, black iron, and 18-8 stainless steel. The brass and nickel were found to amalgamate very slowly in the anhydrous system; black iron and stainless did not amalgamate at all. If amalgamated before being placed into the system, brass and nickel retained their amalgamation for the duration of the test. However, brass dissolves rather quickly in the diamine system giving a deep prussian blue color. It was found that the test samples of brass had been about one-half dissolved during the 100 hour tests. Nickel dissolves only slightly giving a yellow color. Black iron, amalgamated before being placed in the system, showed a tendency to lose its wettability.

PREPARATION OF ANHYDROUS ETHYLENEDIAMINE

D. A. Lee

During this period anhydrous ethylenediamine has been prepared in this laboratory to supply the needs of the pilot plant. The two-step process was used consisting of salting out 95% ethylenediamine from 77% ethylenediamine with sodium hydroxide and reacting the water in the 95% ethylenediamine with calcium carbide at 116°C. A product of 99.9+% ethylenediamine with essentially a 100% theoretical yield was obtained.

Experiments to determine the effect of sodium hydroxide concentration in the "salting out" step were made. Two hundred fifty mls of 77% ethylenediamine were placed in a 500 ml flask equipped with a reflux condenser, stirrer, and thermometer. The amine was heated and various amounts of solid NaOH pellets were added. The system was heated to the boiling point with stirring and after approximately an hour of refluxing a sample of the ethylenediamine phase was taken and analyzed for water. The results are listed in Table 14.

Table 14

Effect of Sodium Hydroxide Concentration

Grams NaOH/100 ml 77% EDA	% H_2O in EDA Phase
10	17.2
20	12.2
30	9.9
40	4.5
50	4.7
60	2.9

Sixty grams of NaOH per 100 ml ethylenediamine monohydrate was chosen as the upper limit because of the solubility of NaOH. The last three results in Table 14 were determined by the Karl Fisher method. The precision of this method does not appear to be satisfactory in this application.

Experiments have been in progress on the azeotropic drying of ethylenediamine. The literature[2] reports that 2-methyl furan forms an azeotrope with water which boils at 58.2°C. This compound received from Du Pont was distilled with 77% ethylenediamine in a 90-inch column packed with glass helices. The 2-methyl furan in the azeotrope was separated from the water and returned to the top of the column. The azeotrope collected at 58 to 63°C. A very small amount of ethylenediamine was found in the collected water ($\sim$ 0.05N). This differs from benzene and toluene as determined by D. W. Kuhn.[3] Benzene and toluene remove ethylenediamine in the azeotrope. The amount of removal is a function of the benzene concentration. The greater the benzene concentration the less ethylenediamine is removed. The ethylenediamine collected contained 0.29% water by the Karl Fisher method, but sodium metal added to this ethylenediamine indicated that it had less water than shown by the Karl Fisher analysis.

With the addition of a continuous separator and entrainer refluxer at the top of the column and extra column height, benzene was found to be more efficient than previously indicated. Several runs were made in the 90-inch column and ethylenediamine was collected containing as little as 0.16% water. The problem of ethylenediamine coming over in the azeotrope is being investigated. This work is not complete but indications are that as the benzene concentration is increased the amine in the azeotrope is decreased. Also as the benzene concentration is increased the rate of water removal is increased. This work will be reported more completely at a later date.

A continuous stripping apparatus (which should be more efficient than the azeotropic distillation process) is being considered. This consists of allowing heated 77% ethylenediamine to flow down a packed column while super heated benzene is passed up the column. The benzene and water are separated at the top of the column and the benzene recycled. The anhydrous ethylenediamine is collected at the bottom of the column. This apparatus has not been tested.

MISCELLANEOUS STUDIES

A. C. Rutenberg, G. M. Begun

Instrumentation

Conductance of LiCl-EDA Phase. In a continuous operating separation system it is desirable to know the concentration of LiCl in the amine phase at all times. A continuous recording method would be much more convenient than the sampling and subsequent chloride titration now in use. One means suggested is to continuously record the conductance of the EDA phase. Conductivity measurements are rather sensitive to temperature variations so that a temperature compensating device would have to be incorporated into the instrument. This can be accomplished either by a dummy cell placed inside the system or by a calibrated variable resistance built into the bridge. Platinum black electrodes which are ordinarily used for low frequency conductance measurements would be unsatisfactory in this system since the porous surface would adsorb organic decomposition products.

The available commercial conductivity apparatus uses a 60 cycle frequency across the electrodes. This apparatus failed to give reproducible conductivity readings on solutions of LiCl in EDA when used with bright platinum electrodes. An Industrial Instruments Inc. RC-1B conductivity bridge (1000 cycle) gave quite stable readings with bright platinum electrodes when an appropriate capacitor was used in the circuit.

The effect of impurities in the system on the conductivity will have to be determined empirically. The conductance of a 0.227M LiCl solution in EDA at 25.2°C using platinum black electrodes determined with a 60 cycle bridge is 1.73×10^{-4} mho.

Another instance in which conductivity measurements might prove useful is to moniter the recycling EDA after reflux to

detect any carry-over of LiCl. Such a recycle of LiCl would cause isotopic dilution of the product.

Concentration Cell $Li(Hg)-Li^{+}(EDA)-Li^{*}(Hg)$. It was suggested that a concentration cell could be used to measure the concentration of lithium in the amalgam phase. This cell would consist of an amalgam of known concentration and another amalgam of unknown concentration both immersed in the EDA-LiCl phase. The concentration of the unknown amalgam could then be calculated from the observed e.m.f. using the equation

$$E = \frac{-RT}{n} \ln \frac{\gamma_1 C_1}{\gamma_2 C_2}$$

where C_1 and C_2 are the concentrations of lithium in the two amalgams and γ_1 and γ_2 are their respective activity coefficients. If the two amalgams are at about the same Li concentration, the activity coefficients should cancel each other. In order to use this system over a concentration range, the activity coefficients would have to be determined or the e.m.f. readings calibrated vs. the concentration of the two amalgams.

A cell was designed with two stainless steel cups to hold the amalgam electrodes, one electrode caught samples of the descending amalgam, and the other held standard amalgam. The cell was very sturdy but the stainless steel did not polarize rapidly or reproducibly enough to give accurate e.m.f. values. A cell having one electrode held in a stainless steel cup and the other in glass was also tried and found to be unstable. A redesigned cell using all glass electrodes gave quite stable performance.

Alternate Solvents

LiCl is fairly soluble ($\sim$3.0M) in pyridine, but pyridine has been found to react slowly with lithium amalgam. It was hoped that other compounds of the pyridine type might be found which would dissolve LiCl and be inert toward the amalgam. Piperidine was dried over sodium and distilled into a container containing dry LiCl. The solubility of LiCl was found to be 0.04 molar. γ-Collidine (2-4-6-tri methyl pyridine) was dried by refluxing over CaC_2 and then distilled. LiCl solubility in dry γ-collidine was found to be $<$0.001M. Propylene Diamine is believed to have promise and has been ordered.

Solubilities in EDA

Lithium Salts. Since the last report the following salts have been investigated.

LiOMe - prepared by the reaction of lithium metal with methyl alcohol. The excess MeOH was pumped off with a water pump vacuum and the product gently dried under reduced pressure. Solubility in EDA - $<0.001\underline{M}$.

LiOEt - prepared in the same manner as LiOMe except substituting ethyl alcohol for methyl alcohol. This salt dissolved to some extent in EDA but immediately began to react giving off a gas with an ammoniacal odor.

$LiNH_2$ - Metalloy Corporation $LiNH_2$ was used without further treatment. A purple color appeared on shaking with dry EDA which was discharged when moist air was admitted. The amide solution in EDA was $\sim 0.05\underline{M}$.

LiOH - Metalloy Corporation $LiOH \cdot H_2O$ was dried by heating to 150°C on a vacuum system. The solubility of LiOH in EDA was $0.0067\underline{M}$.

Mixed Salts. Since such salts as $LiAlCl_4$ are known to exist, the solubility of a mixture of $AlCl_3$ and LiCl in EDA was determined. The high aluminum content of the solution (Ca. $2\underline{M}$) indicates that there is some sort of interaction between the $AlCl_3$ and LiCl, since $AlCl_3$ alone dissolves only to the extent of $\sim 0.01\underline{M}$. The total Li concentration, however, was only of the order of 5-10% above that of LiCl in EDA. The method of analysis was not accurate enough to quote an exact figure but the increase was small.

In order to test the possibility of double salt formation of the type $LiCl \cdot LiBr$ in EDA which might enhance the lithium solubility, a mixture of the two salts was dried and the lithium molarity in EDA found to be 0.30. This indicates no enhancement of the solubility.

[redacted]

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1. "Progress Report of Materials Chemistry Division for Period Ending December 31, 1951, ORNL-1238.

2. J. Applied Chem. USSR 13, 140-1 (1940) C.A. 34, 7682.

3. Laboratory Notebook Y-NB-1654, C&CCC - Y-12, issued to D. W. Kuhn.

[redacted]