

bath maintained at $25.00 \pm 0.02^\circ$. Equilibrium was ascertained by repeated analysis after varying periods of time, and by approach from supersaturation. Alcohol-rich mixtures reached equilibrium more slowly than those which were water-rich. The yellow color of the chromate was visible even in absolute alcohol.

Analyses were made by evaporating weighed samples of the saturated solutions to dryness, and were reproducible to about ± 3 in the last reported digit. Densities were determined with calibrated pipets and with a pycnometer, and are estimated correct to one part per thousand.

Saturated soln.			Saturated soln.		
Solvent	Wt. %	Density	Solvent	Wt. %	Density
Vol. %	K_2CrO_4		Vol. %	K_2CrO_4	
C_2H_5OH			C_2H_5OH		
0	39.67	1.387	60.0	1.238	0.905
10.00	30.69	1.263	75.0	0.160	.863
20.00	21.70	1.152	85.0	.035	.834
30.00	13.50	1.062	95.0	.021	.801
40.00	7.19	0.992	100	.005	.786
50.00	3.214	.942			

NICHOLS LABORATORY
NEW YORK UNIVERSITY
NEW YORK 53, N. Y.

Two Liquid Phases in the Lithium-Ethylamine System at 0° ¹

BY WILLIAM H. HOWLAND AND LEO F. EPSTEIN

RECEIVED SEPTEMBER 25, 1953

Lithium has been reported to be "extremely soluble" in ethylamine.² Investigation of this system at 0° has shown that at equilibrium there are two liquid phases present, similar to the behavior of sodium-ammonia solutions³ at low temperatures, where the system has a critical solution temperature in the neighborhood of -45° .

Eastman "anhydrous" ethylamine was dried by refluxing over lithium until the appearance of the deep blue color, which is observed with solutions of the alkali metals in ammonia and lower primary amines. This anhydrous ethylamine was distilled in a dry helium atmosphere into a glass tube (containing an excess of clean lithium) maintained at 0° with an ice-bath. Almost immediately the deep blue color appeared in the distillate which was vigorously agitated by means of a magnetic stirrer. After the resulting lithium-ethylamine system was equilibrated at 0° , it was observed that two liquid layers separated when the stirring was stopped. The upper layer was deep blue in color and somewhat smaller in volume than the colorless lower layer. Due to slight convection currents, streamers of the blue colored phase slowly circulated through the colorless and slightly denser phase.

In this study great care was observed to keep air and moisture out of the system. Unlubricated ground glass joints sealed with mercury were used throughout, and inert gas atmospheres were employed to eliminate contact of air with the purified ethylamine and lithium.

The apparatus used in this exploratory study was not adapted to the sampling of a two-phase system, so that no information was obtained on the composition of the two layers. Further work on this system has been set aside and therefore, the above observations are being reported at this time.

Seiler has stated⁴ that a trace of ammonia is

(1) The Knolls Atomic Power Laboratory is operated by the General Electric Company for the Atomic Energy Commission. The work reported here was carried out under contract No. W-31-109 Eng-52.

(2) G. N. Lewis and F. G. Keyes, *THIS JOURNAL*, **35**, 340 (1913).

(3) C. A. Kraus and W. W. Lucasse, *ibid.*, **44**, 1949 (1922).

(4) E. F. Seiler, *Astrophysical J.*, **52**, 129 (1920).

needed to catalyze the formation of a lithium-ethylamine solution and that the blue color appeared only after ten hours of stirring. No phase separation was observed in her work. The difference between these earlier observations and those reported here is considered to be entirely due to the relative cleanliness of the two systems with respect to air and moisture.

From this investigation the following preliminary conclusions can be drawn.

1. Ethylamine and lithium form two liquid phases at 0° , one blue, the other colorless.

2. The densities of the two phases are nearly equal, the colorless phase being the denser.

3. No catalyst is needed to initiate the solution of lithium in ethylamine, providing that the solvent is adequately dried and air is kept out of the system. With these precautions, the lithium dissolves rapidly.

GENERAL ELECTRIC COMPANY
KNOLLS ATOMIC POWER LABORATORY
SCHENECTADY, N. Y.

The Catalytic Hydrogenolysis of Proteins and Related Model Compounds¹

BY H. A. LILLEVIK² AND W. M. SANDSTROM

RECEIVED APRIL 2, 1953

Introduction

Adkins³ has shown that the carbon-to-nitrogen linkage in amides is cleaved at high temperatures and pressure by hydrogen in the presence of catalysts such as copper chromite or Raney nickel. Our purpose was to apply this reaction to proteins and to compare the results with those obtained upon some related model compounds. Zein and acetyl zein were examined together with nylon, polyacrylamide, butyl hippurate and acetamide. Since *n*-butyl alcohol employed as solvent could enter into the reaction, studies were included to differentiate the products of butanolysis from those due to hydrogenolysis. The products were examined to determine the extent of the two reactions upon the primary and secondary (peptide) amide linkages.

A survey of the literature reveals that no attempt has been made to apply Adkins' reduction to proteins, their derivatives or split products. Milder reducing agents such as cyanide or sodium-alcohol have been used; however, these are essentially without effect upon the peptide or amide linkages. Alcoholysis, particularly with methanol or ethanol under pressure, results in partial cleavage of proteins with loss of ammonia and volatile amines. Many of these reactions are considered in a survey article.⁴

(1) From part of a thesis submitted by Hans A. Lillevik to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Published with the approval of the Director of the Minnesota Agricultural Experiment Station as Journal Series No. 2730.

(2) Kedzie Chemical Laboratory, Department of Chemistry, Michigan State College, East Lansing, Mich.

(3) H. Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," University of Wisconsin Press, Madison, Wisconsin, 1937, pp. 112-119.

(4) R. M. Herriot, "Advances in Protein Chemistry," Vol. III, The Academic Press, Inc., New York, N. Y., 1947, p. 169.