

weight reported by Maas⁶ requires a content of nine to eleven carbon atoms, and Lederer's suggestion that the eye pigments are pterine derivatives still appears to be a plausible one.⁷

(6) W. Maas, *Genetics*, **33**, 177 (1948).

(7) We are indebted to Mrs. Evelyn Shirck McConnaughey for technical assistance in the culture of flies and in the preparation of the crude extracts.

DEPARTMENT OF CHEMISTRY AND DEPARTMENT OF BIOLOGY
UNIVERSITY OF OREGON RECEIVED MAY 28, 1951

Densities in the Methanol-Water System at 25.00°

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Much work has been done on the methanol-water system but none of the vapor pressure data are sufficiently good to give a consistent check with the Duhem equation. The most convenient way to analyze solutions in this system is by means of density determinations. Since we find no data at 25.00° available (a convenient temperature for our purposes), we have determined the density-mole fraction relations for the system at 25.00° in order to undertake a complete study of the vapor-liquid equilibrium.

Experimental

The water used was distilled from acid dichromate solution and shown to be of conductivity grade. Reagent grade methanol was diluted with an equal volume of water and distilled from a ten-plate fractionating column to give a practically odorless methanol of density d_{25}^4 , 0.78687. "International Critical Tables" lists 0.78683.

Solutions of known composition were made by adding water to weighed ground glass stoppered bottles, weighing, adding methanol and weighing again. Each mole fraction should be accurate to within ± 0.00002 unit.

Density determinations were made at each composition with two pycnometers, one of about 8 ml. volume, the other about 10 ml. calibrated with water as a standard. Every determined value of the density at each composition agreed with the values tabulated below to within ± 0.00004 . Deviations were independent of the pycnometer used.

Weights standardized against a Bureau of Standards calibrated set were used throughout and all values were corrected for the buoyancy of air.

The thermometer was standardized against a thermometer newly calibrated at the Bureau of Standards.

Results

The density of methanol-water solutions at 25.00° as a function of the mole fraction of methanol is given in Table I. No simple equation (third power or less) fits the data because of the high curvature at the ends of the composition range.

Mole fraction methanol (± 0.00002)	d_{25}^4 (± 0.00004)
0.00000	0.99707
.04998	.98225
.13479	.96202
.23820	.93912
.37528	.90852
.51984	.87733
.58901	.86306
.78902	.82386
.86674	.80968
1.00000	.78687

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RECEIVED JULY 6, 1951

Ultraviolet Absorption Spectra of N-Nitrocarbamates, N-Nitroamines and Salts of N-Nitroamines

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Shortly after this study was begun, the ultraviolet absorption spectra of some compounds containing N-nitro and N-nitroso groups were reported by Carmack and Leavitt.² Since our program included the ultraviolet absorption spectra of N-nitrocarbamates and amine salts of N-nitroamines the investigation was continued. Recently, a comprehensive study of the ultraviolet absorption spectra of N-nitroso and N-nitro compounds has been reported by Jones and Thorn.³ They did not include any data on N-nitrocarbamates or amine salts of N-nitroamines.

Seven N-nitrocarbamates have been investigated and found to exhibit absorption maxima in the range 235-240 $m\mu$ whereas the nitroamines and nitroamine salts have maxima in the range 232-235 $m\mu$. The results for the nitroamines are consistent with those of Carmack and Leavitt² who observed maxima for their compounds in the region 228-236 $m\mu$. These investigators used aqueous solutions.

TABLE I

Compound	$\lambda_{max.}, m\mu$	$\epsilon_{max.}$
Ethyl N-nitro-N-isopropyl carbamate	240	4900
Ethyl N-nitro-N-n-propylcarbamate	239	6190
Methyl N-nitro-N-ethylcarbamate	235	6030
Ethyl N-nitro-N-ethylcarbamate	237	5630
n-Butyl N-nitro-N-n-butylcarbamate	238	6710
Ethyl N-nitro-N-t-butylcarbamate	239	2690
N,N'-Dinitro-N,N'-dicarboethoxy-1,6-diaminohexane	238	12070
Isopropyl-N-nitroamine	232	6810
Potassium salt of isopropyl N-nitroamine	234	8210
Isopropylamine salt of isopropyl-N-nitroamine	233	8200
Isobutylamine salt of cyclohexyl-N-nitroamine	235	8080

The results indicate that there is a slight shift toward the visible in the spectra of the N-nitrocarbamates although the shift is not of sufficient magnitude to serve as a means of distinguishing N-nitrocarbamates from N-nitroamines.

The intensities of absorption of the amine salts of N-nitroamines and of the one potassium salt which was measured were found to be consistently greater than the intensities of N-nitrocarbamates and N-nitroamines.

An appreciable decrease in intensity is noted in the N-nitrocarbamate series when the alkyl group attached to the nitrogen atom exhibits branching at the carbon atom adjacent to the nitrogen atom. This is exemplified in Table I for the two isomeric compounds ethyl N-nitro-N-n-propylcarbamate and ethyl N-nitro-N-isopropylcarbamate. Although the absorption maxima for these compounds fall in approximately the same position, the

(1) Abstracted from a portion of the dissertation submitted by Howard M. Curry in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) M. Carmack and J. J. Leavitt, *THIS JOURNAL*, **71**, 1221 (1949).

(3) R. N. Jones and G. D. Thorn, *Can. J. Research*, **27B**, 828 (1949).