values were then calculated using the relationship

$$\Delta H^M = x_1 \, \Delta \bar{H}^M + (1 - x_1) \, \Delta \bar{H}_2^M \qquad (2)$$

and the extrapolated ΔH^M values are shown in Figure 6 by the broken line, indicating a set of thermodynamically consistent values, which agree very well with the data obtained in this investigation.

TERNARY DATA

Experimental data obtained for the ternary system ethanol-benzene-*n*-hexane are presented in Table III. In the design of the experiments, all determinations were arranged along constant x_i/x_j lines. This arrangement provides a simple interpolation procedure. Isenthalpic lines in calories per gram mole are presented in Figure 7, in which the compositions are expressed in terms of mole fractions. Attempts to use simple analytical expressions for representing the data have proved unsuccessful. This seems to be due to the presence of ethanol in the mixture.

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NOMENCLATURE

x = liquid mole fraction
ΔH = heat of mixing (enthalpy of mixing) per mole of solution
$\Delta \bar{H}$ = partial molal enthalpy of mixing

Subscripts

i, j = components i and j of mixture
1, 2 = components 1 and 2 of mixture

Superscripts

M = mixing property
E = excess property

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Thermodynamic Stability of the Iodine Complexes of Some *N*-Methyl Lactams

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A spectrophotometric method has been used to obtain thermodynamic data for the iodine complexes of *N*-methyl-2-pyrrolidone and *N*-methyl-2-piperidone. The results indicate that the six-membered ring is more basic than the five-membered ring. This order, along with the decrease in the infrared frequency of the carbonyl group when the complex is formed, shows that oxygen is the basic site.

KATRITZKY and Jones (*6*) have reviewed the literature on the basicity of amides. Many of the data on this subject support the belief that it is oxygen and not nitrogen which acts as the basic site in these molecules. Among these investigations was a study of the ring size effect on the basicity of lactams (*5*) which observed that towards sulfuric acid, the basicity of the six-membered ring was greater than the five-membered ring. Since this is opposite to the order of basicity determined for cyclic imines, the conclusion was drawn that the nitrogen atom is not the basic site in lactams.

Recently, Drago and his coworkers have published the results of some studies on the charge transfer complexes formed between amides and iodine (*2-4, 8*). Infrared data on these complexes indicate that the oxygen again is acting as the electron donor. Information on the effect of ring size on the lactam-iodine complexes would be of interest. The adducts of *N*-methyl-2-pyrrolidone and *N*-methyl-2-piperidone were chosen for this study because it was with the five- and six-membered lactams and cyclic imines that the reversal of basic properties towards hydrogen acids occurs. Both the infrared and visible spectra of iodine-lactam solutions have been studied, and from optical density measurements in the visible region the thermodynamic properties of the adducts were calculated.

EXPERIMENTAL

Purification of Materials. Baker analyzed iodine was resublimed three times and then stored in a desiccator over phosphorus pentoxide.

Fisher spectroanalyzed *n*-heptane and carbon tetrachloride were used without any further purification.

The lactams were obtained from commercial sources and purified by two successive vacuum distillations. They then were stored in a desiccator over calcium chloride until needed.

N-methyl-2-pyrrolidone, b.p. 78° C. at 9 mm.

N-methyl-2-piperidone, b.p. 98° C. at 11 mm.

Preparation of Solutions. Stock solutions of donor and iodine were prepared by weighing out both the solute and solvent. For the measurement in the visible region, *n*-heptane was used as the solvent while carbon tetrachloride was used for the infrared measurements. The solutions to be used in the measurements then were prepared by mixing weighed quantities of stock donor, stock iodine, and pure solvent. By using these weights and assuming that the final dilute solutions had the same density as the pure solvent, the initial molar concentrations were calculated.

Apparatus and Procedure. Infrared spectra of both the free donor and complex were obtained on a Perkin Elmer 112 spectrophotometer.

Spectral data in the visible region were determined with both a Cary 15 and a Beckman DU spectrophotometer. The Beckman DU was equipped with a thermostated cell holder.

As a preliminary step, the spectra of several solutions with various concentrations of donor but the same concentration of iodine were observed on the Cary 15. These spectra indicate the position of the blue shifted iodine peak and the proper range of concentrations to use in determining the equilibrium constants.

Further measurements were carried out on the Beckman DU. Absorbance readings were taken at the maximum of the blue shifted iodine peak for all of the solutions at several temperatures. Iodine solutions of the same concentration as the samples were used as the reference.

Calculations. The procedure used to calculate the equilibrium constants, absorption coefficients, and ΔH's are those developed by Drago and his group (*2–4, 7, 8*). When only 1 to 1 complexes are formed, the following is valid:

$$K^{-1} = \frac{A - A^0}{a_C - a_I} - C_I - C_D + \frac{C_D C_I (a_C - a_I)}{A - A^0}$$

where K is the association constant, and a_C and a_I are the absorption coefficients for the complex and free iodine, C_D and C_I are the initial concentrations of donor and iodine, and $A - A^0$ is the optical density of the solution with an iodine blank. The above equation was solved for the two unknowns, K and $a_C - a_I$, by a graphical procedure. For each solution, values of K^{-1} were calculated for several arbitrary values of $a_C - a_I$ and then plotted as a function of $a_C - a_I$. A series of lines was obtained; the crossing points of each pair of lines gave a set of values for K^{-1} and $a_C - a_I$ which are solutions for the above equation. The average value of $a_C - a_I$ obtained from the crossings at 25° C. was then used in the equation to calculate K for each solution and at each temperature. Applying the van't Hoff equation to the variation of K with T gave the value of ΔH^0 for each solution. Error limits for the reported values were calculated by standard procedures and are reported for the 90% confidence level.

RESULTS AND DISCUSSION

The preliminary runs on the Cary 15 showed that at the concentration ranges studied there exists an isobestic point at 494 mμ for *N*-methyl-2-pyrrolidone and 490 mμ for the *N*-methyl-2-piperidone. The blue shifted iodine peak appears at 446 mμ and 438 mμ for the five- and six-membered rings, respectively. The concentrations and optical densities at these wavelengths are given for 25° C. in Table I. The average values of $a_C - a_I$ and K obtained from these data are also given in this table. Both sets of plots have most of their crossing points in a small area, which indicates a fairly good precision for the data. The precision is also shown by the error limits calculated for 90% confidence level. Table II gives values of ΔH^0 and ΔF^0_{25} calculated for each solution.

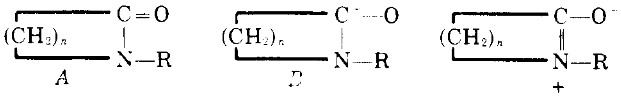
Table I. Data Employed to Calculate Equilibrium Constants at t = 25° C.

Solution	$C_D \times 10^2$	$C_I \times 10^3$	$A - A^0$
N-methyl-2-pyrrolidone at = 446 mμ			
1	8.8652	0.93939	0.658
2	4.7106	0.98003	0.512
3	5.3433	0.92576	0.551
4	1.2407	0.69830	0.147
5	0.47171	0.70271	0.062
6	1.7225	0.93740	0.265
7	1.1245	0.93232	0.184
8	7.6326	0.52252	0.355
9	0.48576	4.2171	0.382
Av. $K = 18.7 \pm 0.4$		Av. $a_C - a_I = 1148 \pm 30$	
N-methyl-2-piperidone at = 438 mμ			
1	3.32676	0.46736	0.242
2	1.5493	0.46527	0.161
3	5.42774	0.29493	0.198
4	3.35452	0.28500	0.158
5	2.98628	0.78170	0.408
6	2.05383	0.76879	0.308
7	1.34912	0.75975	0.219
8	6.06729	0.60006	0.389
Av. $K = 31.1 \pm 1.2$		Av. $a_C - a_I = 1096 \pm 45$	

A comparison of these thermodynamic data shows that the six-membered lactam forms the more stable complex. The values of ΔH^0 are very close, within experimental error; however, the trend is quite clear when the values of ΔF^0_{25} are examined.

The variation in the strength of the interaction of lactams with iodine as a function of ring size is six- > five-membered ring, the same order that was found by Huisgen *et al.* for the interaction of lactams and hydrogen acids. Since this trend in basicity is the opposite of that found for cyclic imines, oxygen must be the basic site in lactams both for hydrogen acids and for iodine. This order is also in agreement with data on phenol lactam complexes (*9*) and nickel lactam complexes (*1*).

By using the same reasoning that Drago and coworkers have applied to amide : iodine complexes (*7*), the infrared data also support this conclusion. This argument is based on the three resonance structures of the amides, or in this case, the similar structures for lactams:



If oxygen is the basic site, then one would expect that in the complex the resonance structures *B* and *C* would have an increased contribution. This would have the effect of

Table II. Thermodynamic Data for I_2-Lactam Complexes

Solution	$-\Delta H^0$ Kcal./Mole	$-\Delta F^0_{25}$ Kcal./Mole
1	5.0	1.75
2	5.2	1.71
3	5.3	1.78
4	5.9	1.73
5	7.0	1.70
6	6.0	1.75
7	6.0	1.73
8	5.2	1.74
9	5.9	1.75
Av.	5.6 ± 0.3	1.74 ± 0.04
N-methyl-2-piperidone		
1	6.5	1.98
2	5.7	2.06
3	6.4	1.99
4	5.7	2.04
5	5.8	1.95
6	5.7	2.02
7	6.2	2.03
8	5.8	1.99
Av.	6.0 ± 0.3	2.01 ± 0.04

Table III. Carbonyl Stretching Frequencies

Compound	ν, Cm.$^{-1}$
N-Methyl-2-pyrrolidone	1697
N-Methyl-2-pyrrolidone–I_2	1655
N-Methyl-2-piperidone	1667
N-Methyl-2-piperidone–I_2	1623

decreasing the bond order for the carbonyl group and thus its frequency. As reference to Table III will show, this is indeed the case. The frequencies of the carbonyl group in both donors are lowered when the iodine complex is formed.

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Solubility and Refractive Index of Ammonium Perchlorate in Water

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The solubility of ammonium perchlorate in water has been determined for the temperature range 10° to 80° C. The data are represented with an accuracy of 0.1% by

$$\log x = \frac{-1531}{T} - 0.006846\,T + 5.733$$

where x is the mole fraction of ammonium perchlorate at absolute temperature T. The presence of a small quantity of potassium perchlorate decreases the solubility of ammonium perchlorate. Two sets of data are presented on high grade commercial and recrystallized ammonium perchlorate and the results are compared with published work which shows inconsistency. Refractive index values for a solution in water at a known temperature and concentration are given by the equation

R.I. $= 1.3325 + 0.00079c - 0.00016\,(t - 20)$
where c = **concentration in grams per 100 grams of solution**
t = **temperature, ° C.**

The equation is valid over the range 20° to 50° C., and a significant feature is the linearity of the relation whether the solution is saturated, undersaturated, or supersaturated.

THREE ORIGINAL PUBLICATIONS (*1, 2, 3*) give solubility figures for ammonium perchlorate but there is an inconsistency between them, arising perhaps from impurities or analytical difficulties. Solubility and refractive index measurements have been made and the former are compared with existing data.

In this work the solutions were prepared either from high grade commercial Swedish ammonium perchlorate or from material from the same source recrystallized from distilled water to give a product with the analysis shown in Table I. The analysis shows a typical high potassium content which is reduced only by many recrystallizations or by special methods. Specially prepared material with low potassium content can be prepared by reacting ammonia and perchloric acid. The solubility was determined only at 25° C. on a special preparation of this kind as shown below. In all cases the crystals in contact with the liquor at or below saturation point were in the size range 200 to 400 microns.

EXPERIMENTAL PROCEDURE FOR SOLUBILITY

Gravimetric analysis was used for the determination of concentration by evaporation to dryness at 110° C. There is some decomposition of ammonium perchlorate at this temperature which introduces an error not exceeding 0.1%, as shown by preliminary experiments.

A stainless steel container, with a tightly fitting polytetrafluoroethylene bung equipped with a stirrer, was immersed in a constant temperature bath, the temperature

Table I. Analysis of Ammonium Perchlorate

Volatile matter, wt.%	0.015
Sulfated ash, wt.%	0.022
Ammonium chloride, wt.%	<0.0002
Chlorate as sodium chlorate, p.p.m.	144
Potassium ion, p.p.m.	700
Lead, sodium, iron, aluminum, p.p.m.	<10
Copper, chromium, p.p.m.	<1