0.02° C. The percentage change in viscosity for a 0.02° C. change in temperature varies from a high of 0.26 at the lower temperature and higher D.S. values to a low of 0.03 at the higher temperature and lower D.S. values.

The characterization of the sirup is essential for the comparison of data and ultimately for the usefulness of the data. The precision and accuracy of the determination of both the D.S. and the D.E. are estimated to be of the order of 0.1 unit each. The percentage change in viscosity for a 0.1 change in D.E. varies in those cases calculated from a high of 1.1 at the lower D.E., lower temperatures, and higher D.S. values to a low of 0.05 at the higher D.E., lower D.S., and higher temperature values. The percentage change in viscosity for a 0.1% change in D.S. varies from a high of 8.9 at the higher D.S. and lower temperature values to a low of 0.29 at the lower D.S. and higher temperature values. Of the three variables (temperature, D.S., and D.E.) which affect the fourth variable (viscosity), the D.S. determination at the higher values becomes the most significant factor.

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Heats of Mixing of Liquids for the System Ethanol-Benzene–n-Hexane

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Heats of mixing at 25° C. and 1 atm. are reported for the binary and ternary liquid mixtures of ethanol, benzene, and n-hexane.

IN THE COURSE of investigation of the thermodynamic properties of solutions, measurements were made of the heats of mixing of the following liquid mixtures at 25° C. and 1 atm.: ethanol-benzene, ethanol-n-hexane, benzene-n-hexane, and ethanol-benzene-n-hexane. The purpose here is primarily presentation of the data. The data on the binary systems were obtained to test the reliability of the calorimeters employed and to establish new values where discrepancies existed among data in the literature. The ternary data were determined along constant x_i/x_j lines as shown in Figure 1.

Brass calorimeters with thermistors as temperature-sensing elements were employed. Each calorimeter consisted of two compartments of various sizes, separated by a tinfoil diaphragm. Mixing and stirring were achieved with a gold-plated plunger actuated by a solenoid which was energized in a R-C rectified circuit. Fisher Calrod heaters and a Fisher Unitized bath control provided continuous and intermittent heating of the bath. Two Fisher Versatile stirrers and a continuous cooling source facilitated temperature control at 25° ± 0.01° C. The design of the calorimeter was similar to that reported by Lama and Lu (5) and the same experimental procedure was followed. In the determination of ternary data, a premixed binary mixture of known composition was placed in one of the compartments of the calorimeter and the third component was placed in the other before the mixing process. In all the determinations, heats of mixing were observed to be endothermic.

Absolute alcohol (Canadian Industrial Alcohol and Chemicals, Ltd.), spectro grade benzene, and research grade

n-hexane (Matheson, Coleman and Bell) were used without further purification. The refractive indices of these chemicals determined at 25° C. agree with those available in the literature.

BINARY DATA

Experimental data obtained for the three binary systems are presented in Table I, and are compared with available literature values in Figures 2, 3, and 4.

Table I. Heats of Mixing Data for Binary Systems at 25° C.

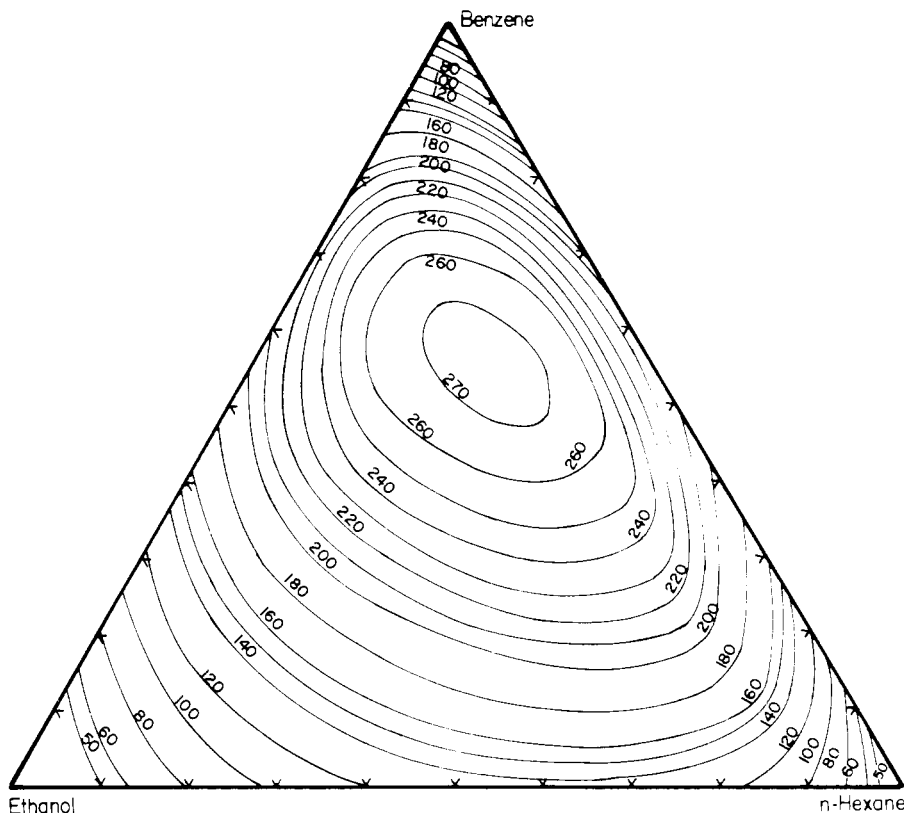| Ethanol-Benzene		Ethanol-n-Hexane		Benzene-n-Hexane	
x_1	ΔH^M, cal./ gram mole	x_1	ΔH^M, cal./ gram mole	x_1	ΔH^M, cal./ gram mole
0.0250	75.2	0.0395	71.9	0.1519	102.9
0.0586	112.0	0.0497	78.5	0.2136	129.8
0.1615	190.0	0.0726	78.3	0.3575	185.5
0.2673	216.5	0.0730	89.1	0.4678	209.7
0.4668	197.0	0.1509	116.7	0.5242	213.5
0.5602	168.4	0.1773	124.6	0.6427	207.5
0.7018	117.0	0.2707	129.5	0.6497	205.2
0.7074	114.8	0.3757	139.6	0.6957	196.1
0.9058	37.8	0.4043	138.6	0.7211	189.3
		0.5680	123.7	0.8075	155.3
		0.6318	116.6	0.9157	82.8
		0.7749	87.0		
		0.8399	69.3		
		0.9526	37.9		
		0.9483	27.3		

Figure 1. Compositions experimentally investigated for heats of mixing at 25° C.

Ethanol–n-Hexane. The experimental values obtained in this investigation agree well with those reported by Brown, Fock and Smith (2) as shown in Figure 2. However, the concentration range covered in this investigation extended into more dilute regions.

n-Hexane–Benzene. Heats of mixing of n-hexane and benzene have been reported by Prigogine and Mathot (7) and Schnaible (8, 9) at 25° C. Figure 3 shows that the data obtained in this investigation agree more or less with those reported by Schnaible. They are slightly lower than those reported by Schnaible at low benzene concentrations.

Ethanol-Benzene. Heats of mixing of ethanol and benzene at 25° C. have been reported by Brown and Fock (1), Goates, Snow, and James (4), Mrazek and Van Ness (6), Prigogine and Mathot (7), and Schnaible (8, 9). The values obtained in this investigation agree well with the literature values, with the exception of Schnaible's data, as shown in Figure 4.

A summary of deviations of literature ΔH^M values from those of this investigation is given in Table II. The

differences are expressed in terms of the maximum and the absolute average deviations. The later was calculated in terms of

$$|\Delta H^M_{Lit.} - \Delta H^M_{Authors}| / \Delta H^M_{Authors}$$

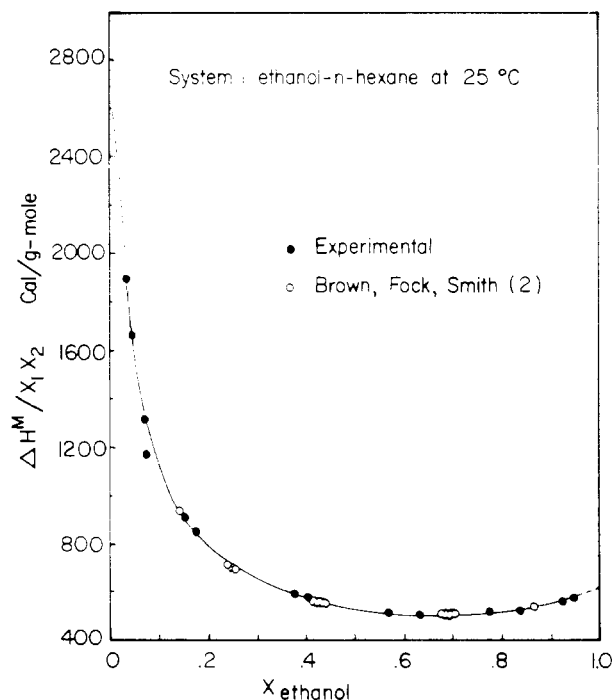from smoothed curves at 0.1 mole fraction intervals of x.

Table II. Summary of Deviations of Literature ΔH^M Values from This Investigation

| System | Ref. | Deviation in ΔH^M, % | |
		Av. abs.	Max.
Ethanol-n-hexane	(2)	1.1	1.8
n-Hexane-benzene	(7)	1.3	3.3
	(8, 9)	1.1	2.6
Ethanol-benzene	(1)	2.5	9.0
	(4)	2.0	9.9
	(6)	3.2	10.3
	(7)	7.2	11.3
	(8, 9)	9.8	22.7

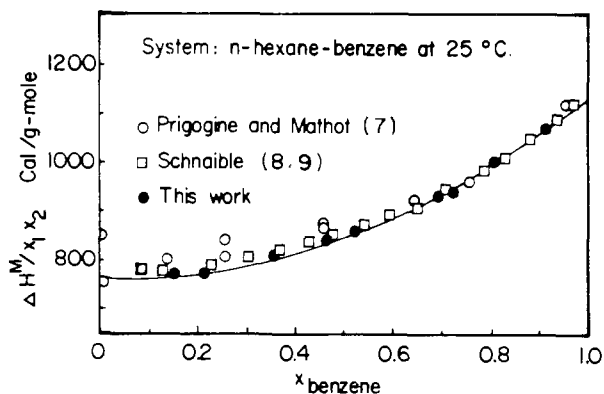Figure 2. Heats of mixing data for the system ethanol–n-hexane at 25° C.

Figure 3. Heats of mixing data for the system
n-hexane–benzene at 25° C.

Figure 4. Heats of mixing data for the system
ethanol-benzene at 25° C.

Figure 5. Extrapolated partial molal enthalpies of mixing
for the system ethanol-benzene at 25° C.
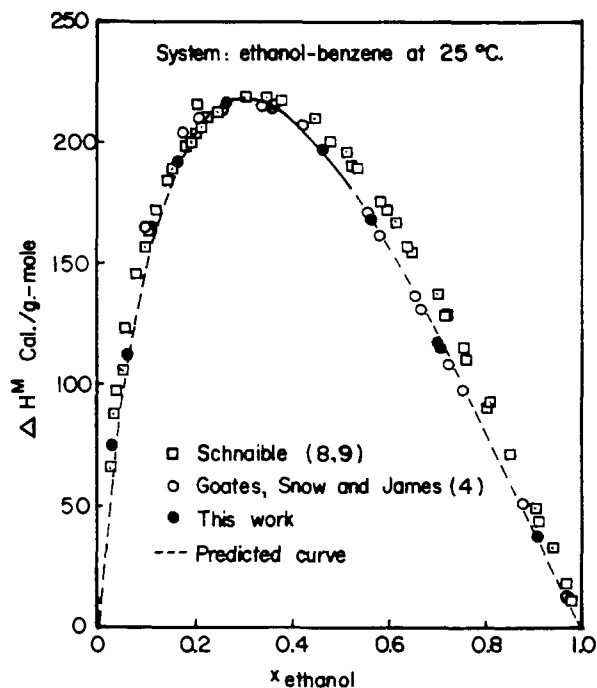
Figure 6. Comparison of predicted heats of mixing values
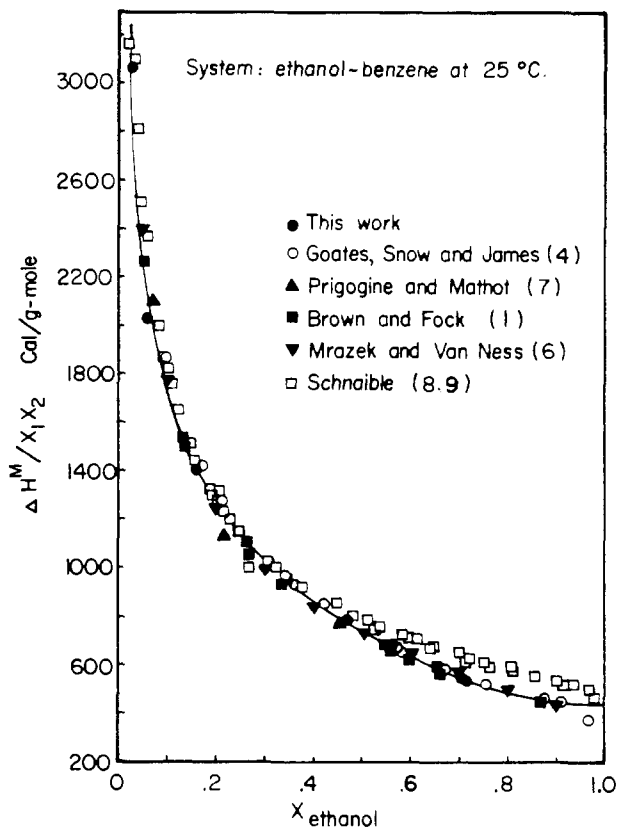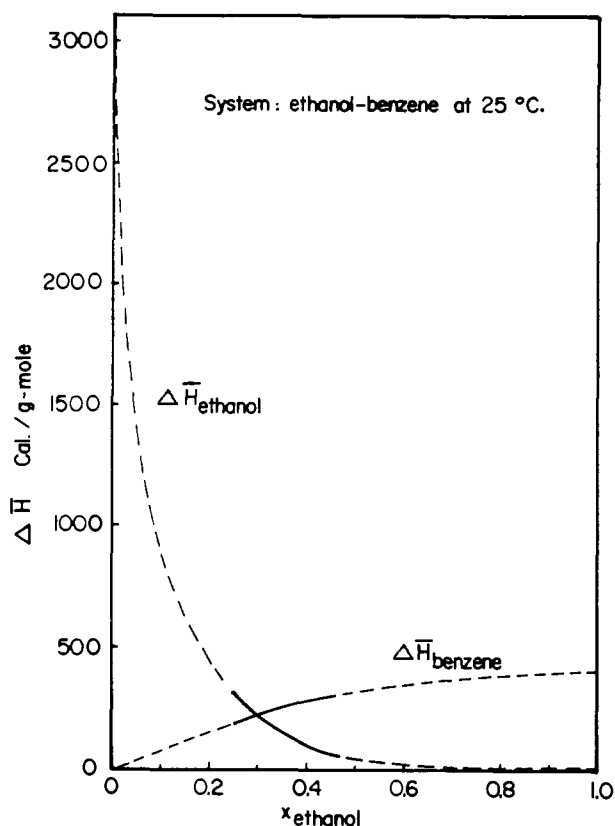with experimental data for the system ethanol-benzene
at 25° C.

When, all the heats of mixing data are compared on a plot of ΔH^M vs. x_1, the agreement between the values obtained in this investigation and those reported by Goates, Snow, and James (4) and Schnaible (8, 9) in the maximum region is satisfactory. At high and low alcohol concentrations, discrepancies are observed.

A method was recently proposed by Deshpande and Lu (3) for extrapolating binary vapor-liquid equilibrium data. With slight modification, this method can also be employed for extending other excess thermodynamic functions, such as excess enthalpy of mixing (heat of mixing) and excess volume of mixing.

The two excess partial molal free energies of mixing at a given composition can be obtained directly from a single measurement, and therefore only two experimental points are required for extrapolation (3). When the two excess partial molal properties at a given composition cannot be determined directly from a single measurement, such as enthalpy or volume, a minimum of three experimental points is required.

It can be readily shown that for a binary system at constant T and p, the excess partial molal enthalpies of mixing, ΔH^E, of the two components are related by the equation

$$\left(\frac{\partial \Delta \bar{H}_2^E}{\partial x_1}\right) = -\left(\frac{x_1}{1-x_1}\right)\left(\frac{\partial \Delta \bar{H}_1^E}{\partial x_1}\right) \qquad (1)$$

Figure 7. Heats of mixing values for the system ethanol-benzene–*n*-hexane at 25° C.
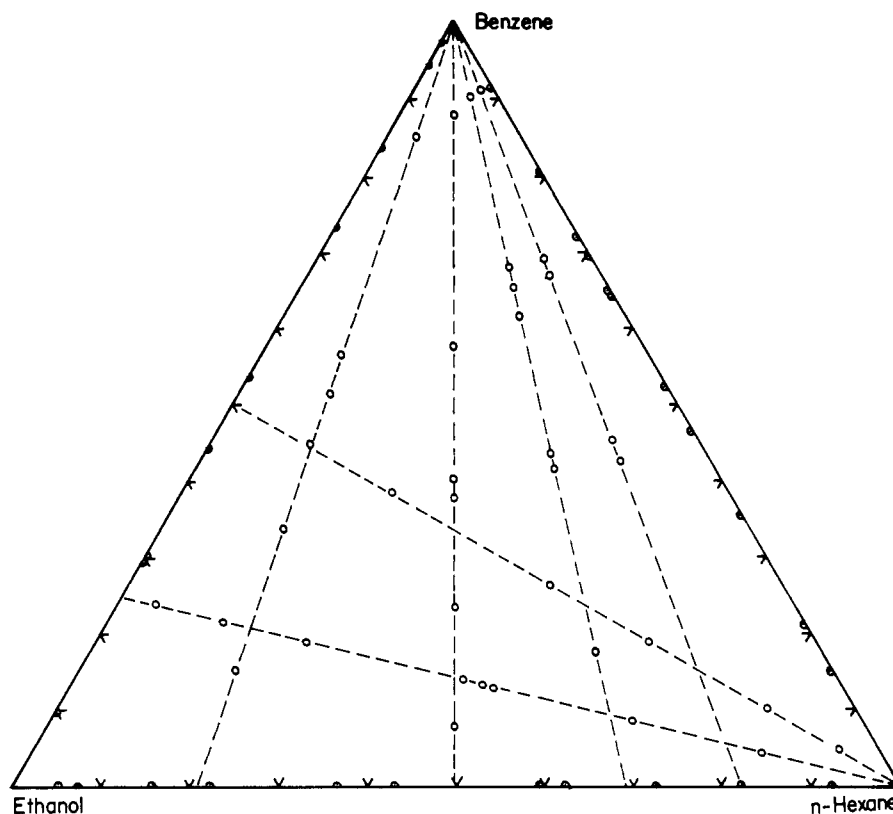
Isenthalpic lines in calories per gram mole, compositions in mole %

It is seen from Equation 1 that at $x_1 = 0$,

$$\left(\frac{\partial \Delta \overline{H}_2^E}{\partial x_1}\right) = 0$$

and similarly, at $x_1 = 1$,

$$\left(\frac{\partial \Delta \overline{H}_2^E}{\partial x_1}\right) = 0$$

Furthermore, at $x_1 = 0$, $\Delta \overline{H}_2^E = 0$ and at $x_1 = 1$, $\Delta \overline{H}_1^E = 0$.

Therefore, on a plot of $\Delta \overline{H}^E$ vs. x, both $\Delta \overline{H}^E$ curves approach their zero values with a horizontal tangency. This condition together with the modified Equation 1

$$(1 - x_1) \left(\frac{\partial \Delta \overline{H}_2^E}{\partial x_1}\right) \Delta x_1 = - x_1 \left(\frac{\partial \Delta \overline{H}_1^E}{\partial x_1}\right) \Delta x_1 \qquad (1a)$$

provides the basis for the extension method. To follow the previously proposed procedure (3), the extension method is limited to the situation where the excess partial molal enthalpy in question does not change sign over the complete concentration range.

The extension method is particularly useful for obtaining consistent data when, for a system at a given condition, several sets of data are available but do not agree with each other over the complete concentration range. The heat of mixing of ethanol with benzene at 25° C., as discussed above, is a typical example of this situation. Since the agreement is good in the maximum region, it is useful to apply the extrapolation method to extend the data from this region to cover the complete concentration range. A small curve was drawn in this region from ethanol mole fraction $x_1 = 0.25$ to $x_1 = 0.46$ as shown in Figure 6 with emphasis given to the values obtained in this investigation and those reported by Goates *et al.* (4). The partial molal enthalpies of mixing for the two components were obtained by using the procedure suggested by Van Ness and Mrazek (10) on a plot of $\Delta H^M / x_1 x_2$ vs. x_1. The excess molal enthalpy of mixing, ΔH^E, is equal to the integral enthalpy of mixing per mole of solution, ΔH^M, as the enthalpy of mixing is zero for an ideal solution. Therefore the excess partial molal enthalpy of mixing, $\Delta \overline{H}^E$, is equal to the partial molal enthalpy of mixing, $\Delta \overline{H}^M$. The obtained values of partial molal enthalpy of mixing were then plotted on a large graph paper and extrapolated over the complete concentration range, using the technique reported previously. The extrapolated curves are shown in Figure 5. The ΔH^M

. Table III. Heats of Mixing Data for Ternary System
Ethanol (1)-Benzene (2)–*n*-Hexane (3)

x_1	x_2	ΔH^M, Cal./ Gram Mole	x_1	x_2	ΔH^M, Cal./ Gram Mole
0.4449	0.4449	226.2	0.6709	0.1501	133.0
0.3814	0.3814	241.2	0.5237	0.3383	198.2
0.2630	0.2630	233.5	0.3846	0.5141	242.9
0.2620	0.2620	233.5	0.3444	0.5648	249.5
0.8850	0.8850	210.2	0.1165	0.8528	183.6
0.0994	0.0994	149.5	0.7172	0.2389	117.7
0.0450	0.0450	82.0	0.6513	0.2170	145.0
0.2557	0.1742	208.4	0.5722	0.1906	167.7
0.1822	0.4123	274.5	0.4203	0.1401	186.4
0.1750	0.4353	277.7	0.4017	0.1338	186.9
0.1073	0.6536	273.4	0.3914	0.1305	186.7
0.1195	0.6143	280.4	0.2586	0.0862	175.0·
0.0991	0.6802	265.9	0.1312	0.0437	132.4
0.0296	0.9045	120.7	0.1011	0.4255	256.9
0.4614	0.0757	161.5	0.0964	0.4520	259.9
0.3841	0.2352	215.7	0.0581	0.6699	239.5
0.3129	0.3770	250.2	0.0543	0.6916	232.8
0.3009	0.4009	254.6	0.0154	0.9122	102.7
0.2122	0.5774	272.2			
0.0601	0.8804	153.4			

values were then calculated using the relationship

$$\Delta H^M = x_1 \Delta \bar{H}_1^M + (1 - x_1) \Delta \bar{H}_2^M \qquad (2)$$

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.

ACKNOWLEDGMENT

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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.