Table III. Enthalpy of Solution of CO_2-DEA Solutions

$-\Delta H_s$, kJ/g-mol CO_2

Normality of DEA solution	α, Mole ratio in liquid, CO_2/DEA 0.2	0.4	0.6	0.8	1.0	1.2	1.4
0.5	57.7^a	53.0^a	44.3^a	37.3^a	31.5^a	27.2^a	23.5^a
2.0	67.2	59.5	47.5	38.8	32.0	27.2	23.5
3.5	76.3	65.4	50.3	40.0	32.4	27.3	23.5
5.0	84.3	70.5	52.6	40.9	32.7	27.4	23.5
6.5	90.7	73.7	54.2	41.5	32.9	27.4	23.5
8.0	96.2	76.3	55.5	41.8	33.0	27.4	23.5

[a] Calculated at 50°C.

smoothed data are presented in Table III. The values for 0.5N are those at 50°C. The enthalpy of solution depends strongly upon the loading of the CO_2 in solution and at low loadings upon the normality of the solution.

Few values of ΔH_s are available for comparison. Kohl and Riesenfeld (*3*) give a value of 653 Btu/lb$_m$ of CO_2 for the enthalpy of solution of CO_2 in DEA solutions. This corresponds to 66.9 kJ/mol of CO_2 which agrees with the present values at low normalities and low loadings of CO_2 in the DEA solutions. Wuithier (*7*) gives a value of 262 kcal per kg which corresponds to 48.3 kJ/mol of CO_2. No information was given as to how this value was obtained. Murzin and Leites (*5*) present the results of the calculation of ΔH_s from their data and indicate that ΔH_s is independent of α in the range 0–0.2. Their results are in good agreement with the first column of Table III at the low normalities, but differ by up to 30% for the 8N solution.

NOMENCLATURE

α = mole ratio, CO_2/DEA
f = fugacity, psia
H = enthalpy, J mol^{-1}
p = partial pressure, y_1P, psia
P = total pressure, psia
R = gas constant
T = temperature, °C
x = mole fraction in liquid phase
y = mole fraction in vapor phase

SUPERSCRIPTS

$\bar{\ }$ = partial molal quantity
$*$ = ideal gas state
l = liquid

SUBSCRIPTS

1 = CO_2
s = solution

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Excess Thermodynamic Properties of Ethylene Diamine–Ethylene Glycol Solutions at 25°C

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The excess Gibbs free energies, enthalpies, entropies, and volumes are reported for mixtures of ethylene diamine–ethylene glycol at 25°C. The refractive indices of these liquid mixtures are also reported for 25°C.

The excess thermodynamic properties have been reported for water–diethylamine solutions at 49.1°C, and ethyl alcohol–diethylamine solutions at 50°C. In both mixtures the excess enthalpies are large and negative over the entire composition range. The same is true for the Ts^E values. However, the Gibbs free energies are much smaller, and are also of opposite sign, being positive for the water–amine and negative for the alcohol–amine solutions (*2*). Investigations have shown that ethylene glycol is a suitable solvent for comparison with water, but without the eccentricities of water (*5*). It appeared to the authors that the excess thermodynamic properties of mixtures of ethylene diamine–ethylene glycol might show some unusual properties and would be worth investigating.

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CHEMICALS

Fisher-certified reagent-grade ethylene glycol was purified by the method previously reported by Cratin and Gladden (*3*). The refractive index of the purified glycol, $n^{25}\text{D}$, was 1.4300, and the density at the same temperature was 1.1100 g ml^{-1}. Reagent-grade ethylene diamine was purified by the method described by Hirata (*6*). The refractive index of the purified diamine, $n^{25}\text{D}$, was 1.4536, and the density at this temperature was 0.8943 g ml^{-1}.

The purified liquids were stored under a dry nitrogen gas atmosphere. The glycol was stored in a glass container, and the basic diamine in a polyethylene container. All solutions were prepared by weighing the components, and all solutions were prepared in a dry box with a dry nitrogen gas atmosphere.

EXPERIMENTAL

The refractive index of each freshly prepared solution was immediately measured with a Bausch and Lomb Abbé 3L refractometer, thermostated to 25 ± 0.02°C. The results of these measurements are given in Table I.

Weld specific gravity bottles of approximately 25-ml capacity were used in all the excess volume determinations. The volume of each specific gravity bottle was determined from the accepted values of the density of water. Duplicate measurements checked to one part in 25,000. Table I also gives the values of the excess volumes V^E for this glycol–diamine system at 25.00 ± 0.01°C.

The vapor pressures of the ethylene glycol–ethylene diamine system were measured by the static method. The bulb which contained the liquid was approximately 50-ml capacity. The apparatus was constructed entirely of pyrex glass.

After the charge was placed in the bulb and the apparatus assembled, the bulb was immersed in liquid nitrogen to freeze the contents. The system was then pumped down with a Cenco vacuum pump. Successive freezing-thawing operations were carried out during the evacuation to remove all evidence of dissolved gases from the solution. Usually five to seven freezing-thawing operations were required. The absolute vapor pressures were read with a mercury-sealed manometer with a 100-cm cathetometer calibrated in 0.05-mm units. The reproducibility in the vapor pressure measurements was approximately ±0.06 mm of Hg. The results of the vapor pressure measurements are given in Table II.

Table I. Refractive Indices, Densities, and Molar Excess Volumes of Ethylene Diamine Plus Ethylene Glycol Solutions at 25°C

X_{ED}	$n^{25}\text{D}$	D, g ml^{-1}	v^E, ml mol^{-1}
0.000	1.4300	1.1100	0.000
0.0496	1.4337	1.1028	−0.2816
0.1241	1.4386	1.0914	−0.6653
0.2423	1.4455	1.0719	−1.1850
0.2748	1.4476	1.0663	−1.2973
0.2880	1.4480	1.0637	−1.3376
0.4195	1.4544	1.0376	−1.6099
0.5464	1.4570	1.0100	−1.6784
0.6154	1.4568	0.9932	−1.5699
0.7144	1.4576	0.9684	−1.3109
0.7948	1.4562	0.9482	−1.0491
0.8807	1.4559	0.9256	−0.6408
0.8894	1.4561	0.9228	−0.5633
1.000	1.4536	0.8948	0.0000

A literature search failed to turn up any reported second virial coefficients for ethylene diamine vapor; therefore it was assumed that the diamine vapor behaved as an ideal gas. This assumption should prove to be right inasmuch as the vapor pressures are small. A corrected vapor pressure of ethylene diamine was calculated by means of the following relationship:

$$(P_1')_{\text{mm}} = (P_{\text{meas}})_{\text{mm}} - X_2(0.145)_{\text{mm}}$$

Where $(P_1')_{\text{mm}}$ is the "corrected" vapor pressure of the ethylene diamine, $(P_{\text{meas}})_{\text{mm}}$ is the measured vapor pressure over the mixture, X_2 the mole fraction of glycol in the solution, and $(0.145)_{\text{mm}}$ was the calculated vapor pressure of pure ethylene glycol at 25°C from the data given by Crume (*4*). The activity coefficients of ethylene diamine in the mixture were calculated from the following relationship:

$$\gamma_1 = \frac{(P_1')_{\text{mm}}}{X_1 P_1^{\circ}}$$

Where γ_1 is the activity coefficient of the diamine, X_1 mole fraction of diamine in the solution, and P_1° the vapor pressure of pure diamine at 25°C.

As the vapor pressure of ethylene glycol over these mixtures was too small to measure, the activity coefficients of this component had to be calculated from those of the ethylene diamine by means of the Gibbs-Duhem relationship. The Gibbs-Duhem expression at constant temperature and pressure may be written as

$$d \ln \gamma_2 = -\frac{X_1}{X_2}\, d \ln \gamma_1$$

Where the subscript, 1, refers to the diamine, and 2, to the glycol. When the above equation is integrated by parts, the results are:

$$\ln \gamma_2 = -\frac{X_1}{X_2} \ln \gamma_1 + \int_0^{X_1} \frac{\ln \gamma_1}{X_2^2}\, dX_1$$

Since $\ln \gamma_1$ was known as a function of composition, the above integral was used to calculate the activity coefficients of ethylene glycol in the solutions by the graphical integration of a plot of $\ln \gamma_1 / X_2^2$ vs. X_1.

With the activity coefficients of the two components in the

Table II. Molar Gibbs Energy of Mixing for Ethylene Diamine Plus Ethylene Glycol Solutions at 25°C, and Some Functions Used in Calculations

X_{ED}	P_{ED}, corr, mm Hg	γ_{ED}	μ_{ED}^E, cal mol^{-1}	$\frac{\ln\gamma_{ED}}{(X_{EG})^2}$	γ_{EG}	μ_{EG}^E, cal mol^{-1}	g^E, cal mol^{-1}
0.123	1.17	0.857	−91.2	−0.200	1.014	+8.3	−3.91
0.273	2.23	0.736	−181.7	−0.581	1.056	+32.6	−25.9
0.447	3.82	0.770	−154.5	−0.853	1.173	+94.7	−16.9
0.538	5.03	0.842	−101.8	−0.807	1.179	+97.7	−9.65
0.615	7.24	1.060	+34.8	−0.397	1.100	+56.2	+43.0
0.714	9.40	1.186	+101.2	+2.09	0.981	−11.5	+40.1
0.773	10.05	1.171	+93.5	+3.07	0.731	−185.3	+30.2
0.882	10.62	1.085	+48.3	+5.85	0.636	−268.2	+10.9

mixture known, the excess chemical potentials, per mole of each component in the mixture, were calculated by means of

$$\mu_i^E = RT \ln \gamma_i$$

where, i is either 1 or 2.

The Gibbs excess free energy per mole of mixture was then calculated by

$$g^E = X_1\mu_1^E + X_2\mu_2^E$$

Table II gives a tabulation of the quantities associated with the excess Gibbs free energy of mixing ethylene glycol–ethylene diamine at 25°C.

The excess enthalpies of mixing ethylene glycol–ethylene diamine were measured with essentially the same calorimeter which has been adequately described elsewhere (*3*). Two slight modifications were made on the calorimeter: A slight modification was made in the method of mixing the two liquids in the calorimeter, and the General Electric thermistor was replaced with a YSI precision thermistor. The YSI thermistor had a resistance of 3000 Ω at 25°C, and a calibration chart of resistance vs. temperature was supplied by the manufacturer.

Only one change was made in auxiliary equipment used in the calorimetric measurements. A special Wheatstone bridge was used in the present measurements. The new bridge had decade resistances of 1000, 100, 10, 1, 0.1, and 0.01 ohm. With the new bridge and thermistor combination temperature, changes in the calorimeter could be measured to better than $\pm 1 \times 10^{-4}$°C. The method of operating the calorimeter and the techniques used in making the measurements were precisely those which have been previously described (*3*).

The measured heats of mixing ethylene glycol–ethylene diamine at 25°C are given in Table III.

The smoothed values for the excess enthalpies, Gibbs free energies, and entropies of mixing for this binary system at 25°C are given in Table IV and are depicted graphically in Figure 1.

DISCUSSION

The ethylene glycol–ethylene diamine system is rather unusual with respect to the variation of the excess Gibbs free energy with respect to composition. The excess Gibbs free energy is negative at high concentrations of glycol and positive at low concentrations of glycol. This phenomenon, although rare, is not unique with this system. Binary mixtures of benzene and *n*-dodecane (*7*), triethyl amine and *n*-butyl alcohol (*1*), and methanol and triethyl amine (*1*) have been shown to exhibit this excess free energy behavior.

Some of the characteristic features of binary mixtures of alcohols and amines are: The excess enthalpies are large and negative, the values of Ts^E are also large and negative, the excess free energies are much smaller than h^E or Ts^E and may be either positive or negative (*2*).

Table V gives some of the properties of three substituted ethylene compounds. The small value of pK_s for $H_2N(CH_2)_2OH$ indicates that the autoprotolysis reaction for this compound proceeds to the right to a far greater extent than that for the other two compounds. This evidently implies that either (N—H···O) or (O—H···N) or perhaps both are stronger hydrogen bonds than is (O—H···O) or (N—H···N). The net result of mixing ethylene glycol and ethylene diamine, both of which are associated liquids, results in the formation of new types of hydrogen bonds which are also stronger than those in the two pure liquids. This accounts for the highly exothermic nature of the mixing process.

Table III. Molar Excess Enthalpies for Mixing of Ethylene Glycol–Ethylene Diamine at 25°C

Mole fraction of glycol	$-h^E$, cal mol^{-1}
0.0000	0
0.1492	800
0.2351	1170
0.3495	1450
0.4373	1650
0.5193	1670
0.6386	1550
0.7562	1290
0.8277	930
0.8461	700
0.9218	350
0.0000	0

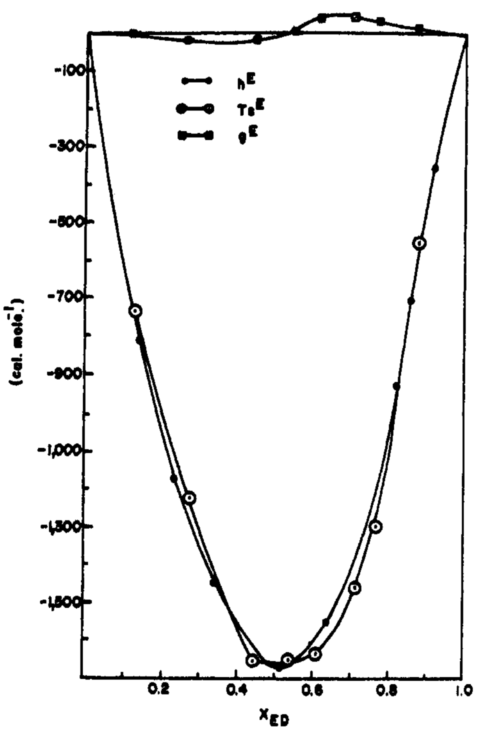

Figure 1. Excess functions for ethylene diamine plus ethylene glycol solution vs. composition at 25°C

Table IV. Molar Excess Functions of Ethylene Diamine Plus Ethylene Glycol Solutions at 25°C

X_{ED}	g^E, cal mol^{-1}	$-h^E$, cal mol^{-1}	$-Ts^E$, cal mol^{-1}
0.123	−3.91	730	726
0.273	−25.9	1260	1234
0.449	−16.9	1670	1653
0.538	−9.65	1660	1650
0.615	+43.0	1590	1633
0.714	+40.1	1420	1460
0.773	+30.2	1270	1300
0.882	+10.9	540	550

Table V. Properties of Ethylene Compounds

Compound	pK_s[a]	Dielectric constant, 20°C
$HO(CH_2)_2OH$ (*5*)	14.3 (19°C)	38.7
$H_2N(CH_2)_2OH$ (*8*)	5.1 (20°C)	37.7
$H_2N(CH_2)_2NH_2$ (*8*)	15.3 (25°C)	14.2

[a] $pK_s = -\log K_s$. K_s is the equilibrium constant for the autoprotolysis reaction, $2SH \rightleftarrows SH_2^+ + S^-$

These binary mixtures are characterized by the fact that $-h^E$ and $-Ts^E$ are almost equal, and this makes the Gibbs free energy of mixing almost equal to that for an ideal solution.

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System Furfural–Water–Caproic Acid at 25° and 35°C

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The binodal curves and tie lines of the system furfural–water–caproic acid have been determined at 25° and 35°C. Behavior is compared with that found in previous studies of lower *n*-alkanoic acids distributed between furfural and water at the same temperatures.

The ternary liquid systems of the *n*-alkanoic acids from formic through valeric and furfural and water at 25° and 35°C have been described previously (*3–5*, *8*). The study is extended here to caproic acid, the second member of the *n*-alkanoic acids which is not completely miscible with water at ambient temperatures. For brevity, in the text below the different furfural–water–acid systems will be indicated by identifying the acid.

MATERIALS AND EQUIPMENT

The furfural used in the present work was the same as that previously described (*4*, *8*). The starting material (Fisher, reagent grade) was distilled at 5 torr pressure, and the middle third was recovered. Distilled furfural was stored in a closed container at −20°C until used. Decomposition under these conditions was negligible (*5*). Decomposition during the time required for the synthesized mixtures to reach equilibrium also had, within the stated uncertainty of the data, negligible effect on the results (*3*).

Purified furfural was prepared in batches, and for the various batches the refractive index at 25°C (sodium-D line) varied by no more than 0.0007 unit from the accepted value of 1.5235 (*10*). There was no measurable effect on solubility from the variation in the batch-to-batch purity of the distilled furfural.

Caproic acid (Eastman practical grade) was purified the same way as furfural. The refractive index of the purified product (25°C, sodium-D line) was 1.4156 [lit, 1.4145 at 19.6°C (*6*)]. Assay of the purified product with standardized NaOH solution indicated a wt % purity of 99.10 ± 0.09 std dev.

The water was singly distilled from an ordinary laboratory still.

All analytical equipment was calibrated against certified standards. Thermostat temperature (constant to ±0.01°C) was monitored with a Beckman thermometer which was set with another thermometer calibrated against an NBS-certified standard.

EXPERIMENTAL PROCEDURE

The methods used in determining the equilibrium data followed established techniques.

Binodal Curve Determination. Homogeneous synthesized samples of known concentration were titrated in thermostated glass-stoppered bottles to the onset of turbidity. The titrant was that component the addition of which effected immiscibility. After the addition of each increment of titrant the mixture was vigorously stirred with a magnetic stirrer to expedite equilibrium. No more than three binodal points were established with a single sample of furfural to keep furfural decomposition negligible.

Tie-Line Determination. Tie lines were determined by titrating the acid in each of the two immiscible phases formed by separation of stirred synthetic mixtures in the two-phase region. Weighed fractions of each phase were removed and titrated with aqueous NaOH. Weighed amounts of ethanol were added to the acid-rich fractions before titration so that the mixture remained homogeneous during titration. The ethanol had negligible effect upon the titration end points (*11*). As a check on the tie-line reliability, each was constructed in the phase diagram, and the closest approaches to the known synthetic mixture concentrations were measured. The agreement indicated no significant decomposition of the furfural in the time required for phase separation.

RESULTS AND DISCUSSION

The refractive index of the caproic acid used in the present work differed significantly from the literature value. When we used the commonly approximated average temperature

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