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.

LITERATURE CITED

(1) Chun, K. W., PhD Dissertation, Texas A&M University, College Station, Tex., 1970.
(2) Copp, J. L., Everett, D. H., *Discuss. Faraday Soc.*, **15**, 174 (1953).
(3) Cratin, P. D., Gladden, J. K., *J. Phys. Chem.*, **67**, 1665 (1963).
(4) "Glycols," ACS Monograph Series, No. 114, p 49, Crume, G. O., Ed., Reinhold, New York, N.Y. 1952.
(5) Gurney, R. W., "Ionic Processes in Solution," p 187, McGraw-Hill, New York, N.Y. 1953.
(6) Hirata, M., Juda, S., Hakuta, T., *J. Chem. Eng.* (Japan), **2** (2), pp 143–9 (1969).
(7) Lewis, H. H., Schmidt, R. L., Cleaver, H. L., *J. Phys. Chem.*, **74**, (25) 4377 (1970).
(8) "Solute-Solvent Interactions," p 52, Coetzee, J. F., Ritchie, C. D., Eds., Marcel Dekker, New York, N.Y., London (1969).

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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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coefficient of $dn_D/dt = -4.5 \times 10^{-4}$ (°C)$^{-1}$, the literature value corresponded to 1.4121 at 25°C. The reason for the discrepancy is unknown, but the assay indicated a purity satisfactory for the nature of the present study.

The experimental binodal curve data for the caproic acid system are given in Table I, and the smoothed curves are given in Figure 1 for 25°C. The tie lines are given in Table II and in Figure 1 for 25°C. Repeated determinations of the mutual solubilities of the two partially miscible component pairs showed a precision of about ±0.03 wt % for these binary systems. From a plot of the smoothed ternary curves on a large scale, a precision of ±0.1% by weight was indicated there.

As with the lower *n*-alkanoic acid systems (*3–5*, *8*), temperature increase reduced the immiscible region to a small extent. The effect at low furfural concentrations in the aqueous phase was small. Tie-line slopes also showed relatively little temperature dependence, again in agreement with the lower acid systems.

Table I. Binodal Curve

(Weight %)

25°C			35°C		
Water	Caproic acid	Furfural	Water	Caproic acid	Furfural
		Acidic Phase			
4.91	0.00	95.09	5.80	0.00	94.20
6.3	6.9	86.8	7.0	5.6	87.4
7.7	19.4	72.9	8.9	15.0	76.1
9.0	31.5	59.5	10.2	25.9	63.9
10.1	38.5	51.4	12.5	40.0	47.5
11.9	55.0	33.1	13.7	46.8	39.5
12.3	61.3	26.4	14.0	53.3	32.7
11.5	71.0	17.5	14.5	62.0	23.5
11.1	74.5	14.4	13.8	67.2	19.1
7.1	86.4	6.5	11.0	76.1	12.9
2.61	97.39	0.00	7.7	85.6	6.7
			4.9	92.7	2.3
			2.72	97.28	0.00
		Aqueous Phase			
92.00	0.00	8.00	91.12	0.00	8.88
92.0	1.5	6.5	91.1	1.8	7.1
91.9	3.0	5.1	91.1	3.5	5.4
91.4	4.1	4.5	90.7	4.4	4.9
91.7	4.4	3.9	91.9	4.4	3.7
94.7	3.0	2.3	93.1	3.8	3.1
97.2	1.8	1.0	95.1	2.8	2.1
98.99	1.01	0.00	95.9	2.5	1.6
			98.91	1.09	0.00

Table II. Tie-Line Data

(Weight %)

Acidic phase			Aqueous phase		
Water	Caproic acid	Furfural	Water	Caproic acid	Furfural
		25°C			
6.9	14.9	78.2	92.1	1.3	6.6
8.2	24.6	67.2	92.0	2.0	6.0
9.1	31.6	59.3	91.9	2.6	5.5
10.4	42.1	47.5	91.8	3.1	5.1
11.4	49.7	38.9	91.5	4.0	4.5
11.8	69.2	19.0	93.5	3.4	2.8
10.2	77.7	12.1	96.0	2.4	1.6
6.8	87.6	5.7	97.8	1.6	0.6
		35°C			
8.5	13.9	77.6	91.2	1.0	7.9
10.1	23.5	66.4	91.2	2.0	6.9
11.5	32.1	56.4	91.1	3.1	5.8
12.1	35.8	52.1	91.0	3.5	5.5
14.0	51.9	34.1	90.7	4.5	4.8
13.1	70.0	16.9	92.3	4.2	3.5
11.0	76.9	12.1	94.5	3.1	2.4
8.1	85.0	6.9	96.4	2.2	1.4

As a whole, the region of immiscibility on a wt % basis increased continually as the acid chain length increased. That trend was continued with the caproic acid system, but the difference between the valeric and caproic acid systems was largely at higher acid concentrations. This trend eliminated, in the present system, the sharp intersections of the two branches of the acidic phase of the band region found in the valeric acid system. The aqueous phase of the band showed a sharp intersection in both systems, however.

On a wt % basis, the tendency of caproic acid (as solute) toward greater relative concentration in the organic (acidic) phase near the furfural-water axis was about equal to that of the furfural (as solute) to concentrate preferentially in the acidic phase near the acid-water axis. For the valeric acid system, the former was rather greater than the latter (*4*).

In the valeric acid system the tie-line correlations of Bachman (*1*), Hand (*2*), and Othmer and Tobias (*9*) were considered:

$$A_1 \text{ vs. } A_1/B_2 \quad (1) \qquad (1)$$

$$\log (C_1/A_1) \text{ vs. } \log (C_2/B_2) \quad (2) \qquad (2)$$

$$\log [(B_1 + C_1)/A_1] \text{ vs. } \log [(A_2 + C_2)/B_2] \quad (9) \qquad (3)$$

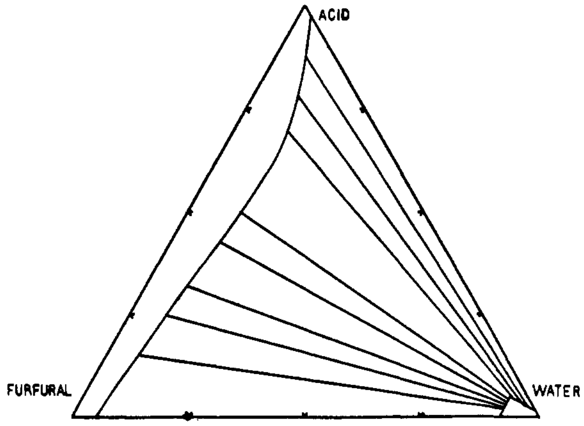

Figure 1. The system furfural–water–caproic acid at 25°C, wt %

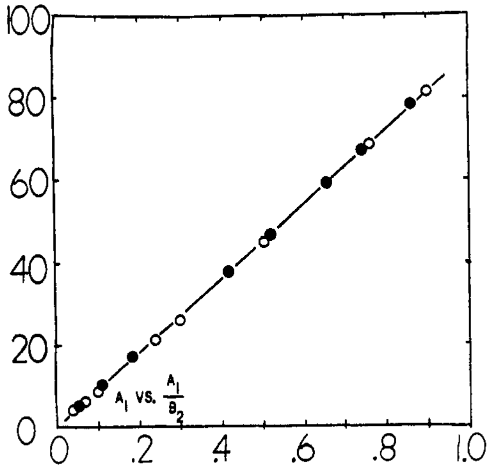

Figure 2. Bachman plot (Equation 1) for furfural–water–acid systems at 25°C

● Caproic acid
○ Valeric acid (*4*)

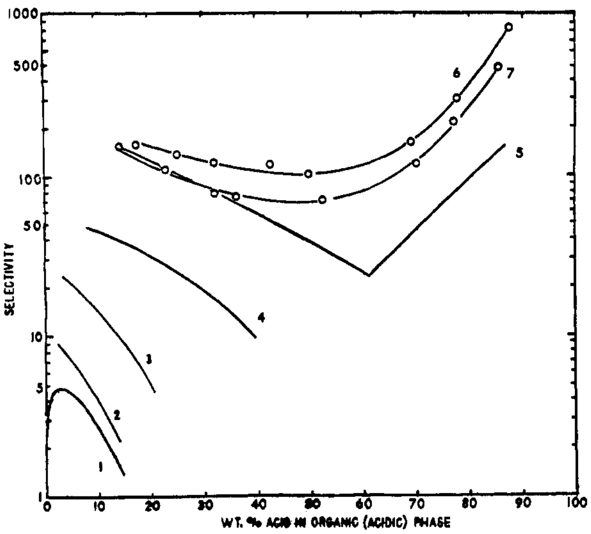

Figure 3. Selectivities in furfural–water–acid systems

1. Formic acid, 25°C (8)
2. Acetic acid, 25°C (5)
3. Propionic acid, 25°C (5)
4. Butyric acid, 25°C (3)
5. Valeric acid, 25°C (4)
6. Caproic acid, 25°C
7. Caproic acid, 35°C

A, *B*, *C* were, respectively, the wt % of furfural, water, and acid, and 1 and 2 were the organic (acidic) and aqueous phases. Both Equations 2 and 3 were nonlinear there, with the indication of possible discontinuous first derivatives in the plot. The Bachman relationship, Equation 1, was linear. The present system behaved similarly, with a slope and intercept (least-squares procedure) from the ternary tieline data of, respectively, 91.39 and 0.39 for Equation 1. The plot of Equation 1 for both the valeric and caproic acid systems is given in Figure 2, with data for both systems falling nearly on the same line.

The effectiveness of the extraction of a solute by a solvent was given by the selectivity (*12*), which in the present work may be considered as the ability of furfural to separate water and acid. Then the selectivity may be defined here as either B_2C_1/B_1C_2 or the equivalent ratio in wt % units. The selectivities in the caproic acid system at 25° and 35°C, and of the other acid systems at 25°C are given in Figure 3. The selectivity was generally greatest in the caproic acid system, but it became approximately equal for the caproic and valeric acid systems at low acid concentration. The sharply intersecting branches of the selectivity curve for the valeric acid system were replaced by a gradual shift in curvature for the caproic acid system, reflecting a like difference in the shapes of the curves for the acidic phases of the binodal curves.

For *n*-alkanoic acids in water, pK_a values varied only slightly with increasing chain length, excepting formic acid (*7*). Thus the trend is distribution behavior of the *n*-alkanoic acids between furfural and water may be ascribed essentially to variation in acid chain length rather than to variation in acid strength.

LITERATURE CITED

(1) Bachman, I., *Ind. Eng. Chem., Anal. Ed.*, **12**, 38 (1940).
(2) Hand, D. B., *J. Phys. Chem.*, **34**, 1961 (1930).
(3) Heric, E. L., Blackwell, B. H., Gaissert, L. J., III, Grant, S. R., Pierce, J. W., *J. Chem. Eng. Data*, **11**, 38 (1966).
(4) Heric, E. L., Langford, R. E., *ibid.*, **17**, 209 (1972).
(5) Heric, E. L., Rutledge, R. M., *ibid.*, **5**, 272 (1960).
(6) "International Critical Tables," Vol. VII, p 40, McGraw-Hill, New York, NY, 1930.
(7) Kortüm, G., Vogel, W., Andrussow, K., "Dissociation Constants of Organic Acids in Aqueous Solution," pp 240–9, Butterworths, London, 1961.
(8) Langford, R. E., Heric, E. L., *J. Chem. Eng. Data*, **17**, 87 (1972).
(9) Othmer, D. F., Tobias, P. E., *Ind. Eng. Chem.*, **34**, 693 (1942).
(10) Quaker Oats Co., Chicago, IL, *Bull. 203-B*, p 4., (1968).
(11) Skrzec, A. E., Murphy, N. F., *Ind. Eng. Chem.*, **46**, 2245 (1954).
(12) Treybal, R. E., "Liquid Extraction," 2nd ed., p 43, McGraw-Hill, New York, NY, 1963.

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Emf Measurements on Lewis and Sargent Cells with Free Diffusion Boundaries

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Electromotive force (emf) measurements on Lewis and Sargent cells with free diffusion type of static liquid junctions are presented. The cells studied employed Ag, AgCl electrodes and included liquid junctions between 0.100*M* KCl and 0.100*M* NaCl, 0.010*M* KCl and 0.010*M* NaCl, 0.100*M* HCl and 0.100*M* KCl, 0.010*M* HCl and 0.010*M* KCl, and 0.100*M* KCl and 0.100*M* LiCl. The measured emf's are 4.585, 4.496, 28.545, 26.408, and 7.137 mV, respectively, and are reproducible and constant to better than 0.040 mV.

It is well known that accurately reproducible results can be obtained in the measurement of a cell with liquid junction in which solutions of the same electrolyte, at different concentrations, are present on the two sides of the boundary. Measurement of concentration cells with transference is a standard method for determination of activity coefficients of electrolytes (*1*, *7*). On the other hand, the measurement of a cell potential with a heterionic junction involving different ionic species on the two sides of the boundary has generally proved to be unsatisfactory and to depend on the manner in which the junction is formed. For example, the cell potential of the junction, HCl (0.1*M*) : KCl (0.1*M*), at 25°C was reported to