sides. Figures 2, 3, and 4 illustrate the different etching characteristics of the primary PbTe and Sb. Figure 2 is a photomicrograph of an alloy which contains primary PbTe and eutectic; Figure 3 is of the eutectic composition, and Figure 4 shows primary Sb and eutectic.

The solid solubility of Sb in PbTe is less than 0.1 wt. % and the solubility of PbTe in Sb is less than 0.5%.

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Equilibria and Solubility Data for the Methanol–Water–1-Nitropropane Ternary Liquid System

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The ternary-liquid solubility and equilibria data for the system methanol–water–1-nitropropane are reported at 25° and 30° C. The solubility data were determined by a modification of the "cloud point" method at 25° and 30° C. The equilibria data were determined by the synthetic method and repeated at 25° C.

DURING A STUDY of methods to calculate ternary equilibria data from the salient properties of the binaries, a need for data on a particular liquid system arose. Thus, the ternary-liquid solubility data for the methanol–water–1-nitropropane system were experimentally determined at 25° and 30° C., and the equilibria data for the same system were determined at 25° C. For this liquid system, methanol was the solute, water the solvent, and 1-nitropropane the carrier.

EXPERIMENTAL METHODS

The following standard experimental techniques and apparatus were used:

Reagents. The methanol was distilled and a heart cut with a boiling range of ±0.1° C. was taken. The water was triple distilled. The 1-nitropropane, 99% purity by weight, was obtained from Commercial Solvents Corp.

Specific Gravity. Specific gravity determinations were made with a 25-ml. Weld-type specific gravity bottle.

Refractive Index. A Bausch and Lomb dipping refractometer was used to obtain refractive index readings.

Constant Temperature Control. An Aloe precision circulating temperature control, range 15° to 100° C., ±0.01° C., was used to maintain the constant temperature bath.

Buret. Titrations were performed with a 10-ml. Kimble Micro (Class A) buret. The buret met requirements of Federal Specification DD-V581A.

EXPERIMENTAL DETERMINATION OF SOLUBILITY DATA

The solubility data were determined by a modification of the "cloud point" method which is described in detail by Othmer (*4*) and Hand (*2*). To determine the solvent lean portion of the mutual solubility curve, 20-ml. mixtures of carrier and solute were made at 10 wt. % increments from pure carrier to pure solute. These mixtures were placed in flasks, sealed from the atmosphere, and immersed in a constant temperature bath for approximately four hours. Each container in turn was opened, and the contents titrated from calibrated burets with solvent which had been previously brought to a constant temperature. The end point or "cloud point" of the titration was the formation of turbidity in the mixture. The solvent-rich portion of the solubility curve was obtained by reversing the procedure. That is, prepared samples of solvent and solute were titrated with carrier until the turbidity was observed.

Titration at Constant Temperatures. During the "cloud point" titrations, Hand and Othmer removed their samples from the constant temperature bath. The procedure described herein was modified to eliminate any effects of the ambient temperature and the heat of mixing on the mutual solubility. These possible errors were eliminated, as the vessel containing the mixture being titrated was continually agitated in the constant temperature bath during titration. This was accomplished by using a glass-bottomed, constant temperature bath, thus allowing the end point of the titration to be observed, while keeping the sample in the bath and at a constant temperature.

Agitation Time. A problem arose concerning the proper agitation time after the titration of the two-phase mixture with the third component. An erroneous cloud point results from this type of titration, unless the mixture is agitated in the constant temperature bath for 10 to 15 minutes after each titration. This was accomplished by connecting the capped flask containing the three-component mixture to the shaft of a variable speed laboratory mixer. The flask was then immersed in the constant temperature bath, while the agitation motor was supported by a ring stand.

Titration Near the Plait Point. In the concentration range of 25 to 30 wt. % water, the cloud point was indistinguishable. The situation occurred because this region is near the plait point where one phase cannot be distinguished from another.

The results of these determinations were expressed as wt. % of the three components. Refer to Table I and Figure 1.

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Table I. Ternary-Liquid Solubility Data

Composition 1-Nitropropane, Wt. %	Composition Water, Wt. %	Composition Methanol, Wt. %
	At 30° C.	
1.8	98.1	0.0
2.4	84.2	13.3
3.2	73.4	23.2
4.1	68.5	27.2
4.5	64.7	30.7
6.4	57.2	36.3
8.6	50.9	40.3
10.8	45.6	43.4
13.8	40.9	45.4
16.0	38.3	45.6
19.1	34.4	46.4
22.8	30.7	46.3
27.3	27.2	45.3
21.7	26.4	51.8
28.3	26.4	45.1
41.0	19.7	39.2
52.3	14.2	33.3
61.3	10.7	27.9
70.0	7.5	22.3
82.9	3.8	13.2
99.7	0.2	0.0
	At 25° C.	
0.9	99.0	0.0
2.1	84.4	13.3
2.7	73.8	23.3
3.1	65.6	31.1
5.2	58.0	36.7
7.3	51.7	40.9
9.2	46.5	44.1
12.0	41.7	46.1
13.8	38.0	48.1
28.8	25.3	45.7
34.2	22.2	43.5
41.8	18.1	39.9
52.9	13.4	33.6
61.6	10.4	27.9
71.7	5.5	22.7
83.4	3.3	13.2

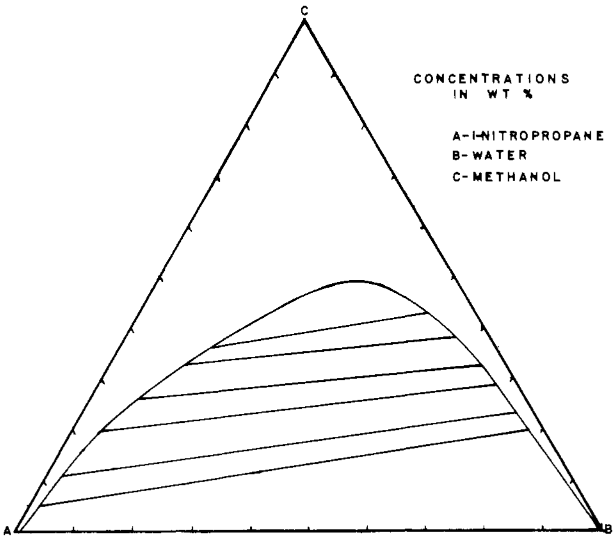

Figure 1. Equilibria data for the system water–methanol–1-nitropropane at 25° C.

Table II. Equilibria Distribution in Conjugate Phases at 25° C.

Water Phase, Wt. %			1-Nitropropane Phase, Wt. %		
A	B	C	A	B	C
3.0	77.1	19.9	93.9	1.4	4.7
3.2	73.9	22.9	86.9	2.9	10.2
3.6	68.0	28.4	75.2	5.3	19.5
4.5	63.2	32.3	65.2	8.7	26.1
6.1	56.0	37.9	54.2	12.9	32.9
8.4	49.3	42.3	48.1	16.1	35.9

A, 1-nitropropane; B, water; and C, methanol.

DETERMINATION OF EXPERIMENTAL EQUILIBRIA DATA

The equilibria data were determined experimentally by the synthetic method described by Othmer (*4*). This method involved the recording of the refractive index at various points on the solubility curve. This established a curve of refractive index on the solubility curve as a function of solute concentration. The next step was to make solutions consisting of all three components. These solutions were of such composition that they would be in the two-phase region. Six such mixtures were prepared at different compositions. These two-phase mixtures were then sealed in polyethylene containers and placed in the constant temperature bath. The containers were vigorously shaken each day for 2 weeks to ensure that the mixtures would reach equilibrium. At the end of this two-week period, each container was removed from the constant temperature bath, the two-phases were separated, and the refractive index of each phase was determined. As the end of each equilibrium tie-line must fall on the mutual solubility curve, a comparison of the refractive indices of the split phases with the curve of refractive index as a function of solute concentration on the solubility curve established the tie-lines. The equilibria data were expressed as wt. % of the components (Table II and Figure 1).

DISCUSSION

A study of the mutual solubility data, Table I, shows that the solubility relationships for this system do not change appreciably with temperature. Although no replicate points were experimentally determined, the sizeable number of points obtained around the curve are consistent.

The validity of the ternary equilibria data were checked by the Othmer Plot (*3*). This method, which was derived from an empirical investigation of published ternary-liquid systems, will result in a straight line plot if the data are consistent. The Othmer Plot indicates that the tie-line which intersects the solubility curve at 42.31 wt. % methanol in the water phase is in error.

The tie-lines on the triangular diagram do not have a consistent slope; however, other systems of this type have been noted in the literature (*1*). At the higher concentration of methanol, that is, above 30 wt. %, in the combined phase mixture, the two phases separated very slowly. At lower concentrations of methanol, the phase split was much more rapid. This situation may be accounted for by a study of the tie-line slopes. At the lower concentrations of methanol, a larger per cent of the methanol goes to the water phase than to the 1-nitropropane phase, thus increasing the inherent density difference between water and 1-nitropropane. However, as the concentration of methanol in the original mixture increases, the ratio of the quantity going to each phase decreases. Thus, the density difference between the two phases decreases.

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