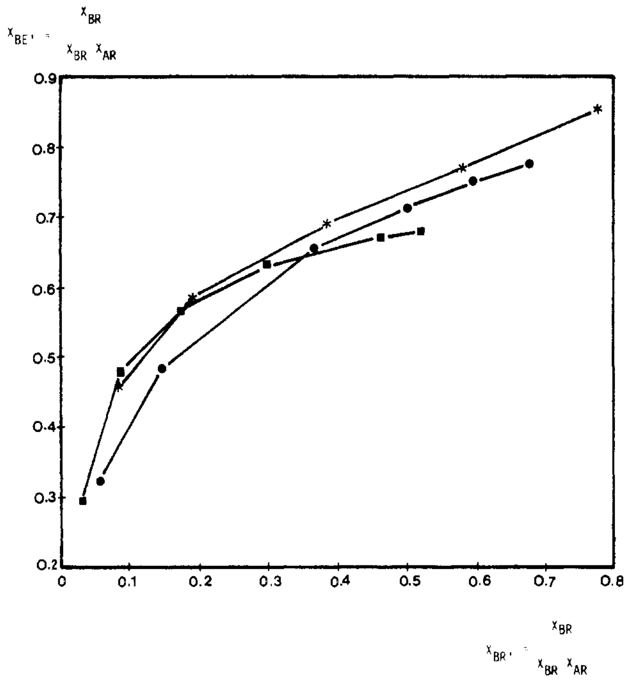

Figure 4. Selectivity diagrams for the ternary system acetonitrile-2-furyloxirane-cyclohexane at *, 20 °C; ●, 30 °C; ◆, 40 °C.

For each tie line, the mixture rule was checked by comparing the data of the segment length ratio MR/ME to the data of the weight ratio weight of extract (E)/weight of raffinate (R).

E and R were the two equilibrium points obtained a prepared heterogeneous mixture M. Experimental results could then be checked.

Figure 4 shows the selectivity curve of 2-furyloxirane extraction by cyclohexane in relation to temperature with

$$X_{BR'} = \frac{X_{BR}}{X_{BR} + X_{AR}}$$

on the abscissa (weight fraction of solute in raffinate on a solvent-free basis) and

$$X_{BE'} = \frac{X_{BE}}{X_{BE} + X_{AE}}$$

on the ordinate (weight fraction of solute in extract on a solvent free basis). In conclusion, the selectivity of 2-furyloxirane extraction by cyclohexane does not dependent on temperature. Therefore the experiment could be carried out at room temperature. This way energy is saved while the asset of a fairly important heterogeneity zone is preserved.

Glossary

X_A	weight precent of acetonitrile in one phase
X_B	weight percent of 2-furyloxirane in one phase
X_S	weight percent of cyclohexane in one phase
X_{BE}	weight percent of 2-furyloxirane in cyclohexane phase
X_{BR}	weight percent of 2-furyloxirane in acetonitrile phase
$X_{BE'}$	weight percent of 2-furyloxirane cyclohexane phase on a cyclohexane-free basis
$X_{BR'}$	weight percent of 2-furyloxirane in acetonitrile phase on a cyclohexane-free basis

Acknowledgment

This study was carried out in collaboration with Mr. Molinier and Mr. Merle (from Agrifurane Ltd) who are gratefully acknowledged.

Registry No. Acetonitrile, 75-05-8; 2-furyloxirane, 2745-17-7; cyclohexane, 110-82-7.

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Liquid-Liquid Equilibrium Diagram for the Ternary System Acetonitrile-2-Furyloxirane-Aliphatic Hydrocarbon

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Problems in the extraction of 2-furyloxirane by cyclohexane (i.e., an extracting solvent) were solved by replacing cyclohexane with an aliphatic hydrocarbon: isopentane, pentane, or hexane. The upper critical temperatures corresponding to the binary system (2-furyloxirane-hydrocarbon) were determined for each of the above solvents. Diagrams of binodal curves for the ternary systems (2-furyloxirane-acetonitrile-hydrocarbon) were of type II and tended toward type I at 30 °C. The extracting capacity of aliphatic hydrocarbons is comparable to that of cyclohexane, although aliphatic hydrocarbons are more selective for the 2-furyloxirane extraction. Pentane seems to be the most suitable extracting solvent.

Introduction

Extraction carried out with a solvent seems to be more adequate when cyclohexane is used as extracting solvent to separate 2-furyloxirane from a reaction medium. However, cyclohexane has a low extracting capacity. The recovery of 2-furyloxirane by evaporating the extract under atmospheric pressure causes an uncontrolled polymerization of 2-furyloxirane.

Therefore the yield in the extraction is lower. In order to avoid these problems we turned to more volatile solvents.

Aliphatic hydrocarbons can be used as extracting solvents as they either do not mix or mix only partially with our reaction solvent (acetonitrile).

At room temperature these hydrocarbons are only partially miscible with 2-furyloxirane. Their solubility in 2-furyloxirane in relation to temperature was studied in order to determine their

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Table I. Miscibility of 2-Furyloxirane with Hexane in relation to Temperature

	2-furyloxirane phase		hexane phase	
temp, °C	X_B	X_S	X_B	X_S
15	81.5	18.5	24.4	75.6
20	80.0	20.0	25.0	75.0
24	75.1	24.9	27.1	72.9
26	67.4	32.6	32.4	67.6
27	60.0	40.0	37.4	62.4
27.5	53.1	46.9	53.1	46.9

Table II. Miscibility of 2-Furyloxirane with Pentane in relation to Temperature

	2-furyloxirane phase		pentane phase	
temp, °C	X_B	X_S	X_B	X_S
15	83.1	16.9	24.2	75.8
20	81.5	18.5	23.5	76.5
25	76.8	23.2	25.1	74.9
30	64.9	35.1	35.2	64.8
30.5	53.0	47.0	53.0	47.0

critical miscibility temperatures. We also studied the ternary balance (acetonitrile–2-furyloxirane–hydrocarbon) and more particularly the selectivity of these hydrocarbons as regards the extraction of 2-furyloxirane.

Experimental Section

Chemicals. The hydrocarbons used were commercial products with a minimum purity of 99% and with a maximum boiling temperature of 80 °C. The commercial acetonitrile with a minimum purity of 99% was passed through 4 Å molecular sieve before use. 2-Furyloxirane was synthesized from furfural. Solid potassium hydroxide and trimethylsulfonium bromide were mixed in a solid–liquid transfer process in low hydrated medium (*2*,*3*).

Experimental Procedures. Shaking and a constant temperature of mixtures were maintained by a thermostated magnetic shaker. This temperature was measured with a mercury thermometer of ±0.5 °C accuracy.

A certain volume of hydrocarbon was added to known quantity of 2-furyloxirane until an opacity appeared in order to determine the binary solubility curves. Another element (acetonitrile or hydrocarbon) was added to the binary system until the solution became turbid to get ternary solubility isotherms. Analysis was then carried out in order to determine the content of each element.

Several heterogeneous mixtures were prepared (acetonitrile, 2-furyloxirane, hydrocarbon) in order to determine the tie-line data. These mixtures were shaken and then left to set at constant temperature for an hour.

Both equilibrium phases were separated and then weighed. Acetonitrile and 2-furyloxirane were determined in each one by chromatography in the gas phase (*1*).

Solubility Point Error. The error introduced during the determination of the titration end point in combination with the error in weighing permits one to obtain solubility points with relative accuracy of about 2 wt%.

Tie-Line Error. The experimental error in the tie-line curve, induced by several titrations (weighing, GPC), is evaluated at about 2%.

Presentation and Discussion of the Results

Table III. Miscibility of 2-Furyloxirane with Isopentane in relation to Temperature

	2-furyloxirane phase		isopentane phase	
temp, °C	X_B	X_S	X_B	X_S
15	83.1	16.9	24.2	75.8
20	31.5	18.5	22.5	77.5
25	78.8	21.2	23.3	76.7
30	69.1	30.1	32.4	67.6
31	53.1	46.9	53.1	46.9

Table IV. Comparison of Binary Upper Critical Temperature (2-Furyloxirane-Hydrocarbons) and Boiling Point of the Hydrocarbons at 760 mmHg

	isopentane	pentane	hexane
boiling point, °C	28	36	68
upper crit temp, °C	31	30.5	27.5

Table V. Ternary Diagram for the Acetonitrile (A)-2-Furyloxirane (B)-Hexane (S) System

(a) Tie-Line Data (wt %) at 20 °C

acetonitrile phase			hexane phase		
X_A	X_B	X_S	X_A	X_B	X_S
90.1	0.0	9.9	2.9	0.0	97.1
82.6	7.6	9.8	3.1	3.0	93.9
65.9	22.3	12.8	1.4	6.2	92.5
50.8	36.2	13.0	1.2	8.8	90.0
33.2	52.3	14.5	0.9	13.2	85.9
17.0	66.2	16.8	0.4	17.0	82.6
0.0	80.2	19.8	0.0	24.2	75.8

(b) Binodal Data (wt %) at 30 °C

acetonitrile	2-furyloxirane	hexane
85.1	0	14.9
77.6	7.3	15.1
65.2	20.1	15.7
47.5	35.0	17.5
39.8	42.1	18.1
25.0	55.0	20.0
9.9	61.9	28.2
5.0	50.0	45.0
4.2	25.1	70.7
3.8	0	96.2

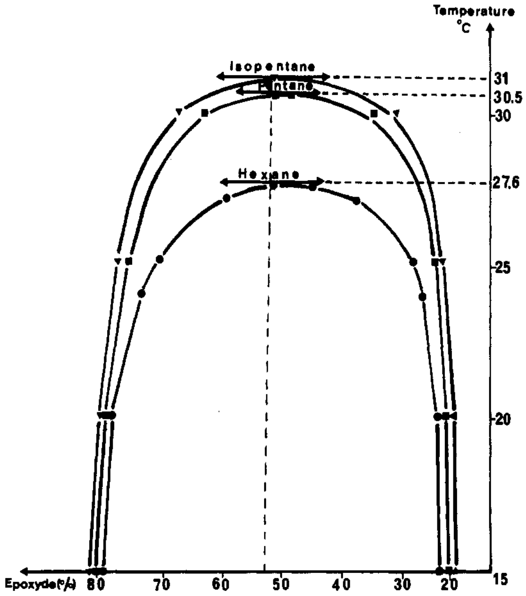

Figure 1. Binary solubility diagram in relation to temperature in weight percentage.

Tables I–III show the data used to determine the binary solubility diagrams (2-furyloxirane, aliphatic hydrocarbons in weight percent). Figure 1 shows the solubility curves of 2-furyloxirane in hexane, pentane, and isopentane at various temperatures. These curves were determined with the data in

Table VI. Ternary Diagram for the Acetonitrile (A)-2-Furyloxirane (B)-Pentane (S) System

(a) Tie-Line Data (wt %) at 20 °C

acetonitrile phase			pentane phase		
X_A	X_B	X_S	X_A	X_B	X_S
85.9	0	14.1	2.7	0	97.3
79.7	6.0	14.3	2.5	4.1	93.4
72.5	13.1	14.4	2.1	6.2	91.7
55.0	30.0	15.0	1.2	9.2	89.6
37.5	47.4	15.1	0.9	12.9	87.2
21.1	63.7	15.2	0.4	19.4	80.2
5.0	77.3	17.7	0.1	23.0	76.9
0	81.9	18.1	0	24.0	76.0

(b) Binodal Data (wt %) at 30 °C

acetonitrile	2-furyloxirane	pentane
88.8	0	11.2
61.3	20.8	17.9
40.3	40.7	19.0
22.1	57.8	20.1
8.1	68.3	23.6
0	54.9	45.1
0	36.0	64.0
2.1	19.2	78.8
3.9	0	96.1

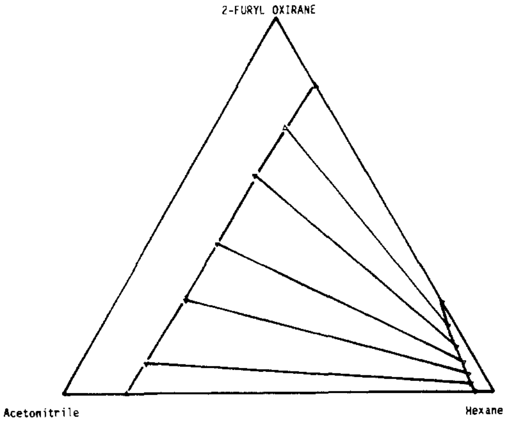

Figure 2. Binodal curve and tie line for the ternary system acetonitrile-2-furyloxirane-hexane at 20 °C.

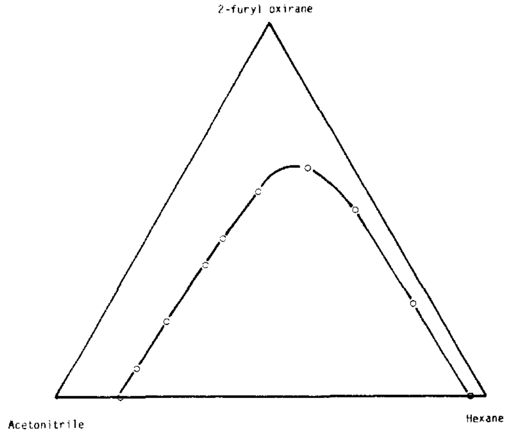

Figure 3. Binodal curve for the ternary system acetonitrile-2-furyloxirane-hexane at 30 °C.

Tables I-III. They show an upper critical temperature corresponding to a binary with 53% of 2-furyloxirane and varying in relation to the nature of the hydrocarbon (Table IV).

Tables V-VII show the ternary solubility isotherms and the tie-line data at 20 and 30 °C determined for 2-furyloxirane-acetonitrile-pentane and for 2-furyloxirane-acetonitrile-isopentane (Figures 2-6).

Table VII. Ternary Diagram for the Acetonitrile (A)-2-Furyloxirane (B)-Isopentane (S) System: Tie-Line Data (wt %) at 20 °C

acetonitrile phase			isopentane phase		
X_A	X_B	X_S	X_A	X_B	X_S
85.9	00.0	17.1	3.5	00.0	96.5
78.0	7.2	14.8	3.1	3.2	93.8
60.0	24.6	15.4	2.4	4.4	93.2
44.6	39.9	15.5	2.0	7.9	90.1
26.8	57.4	15.8	1.4	11.8	86.8
12.6	71.2	16.2	0.9	19.3	80.3
00.0	82.0	18.0	0.0	24.1	75.9

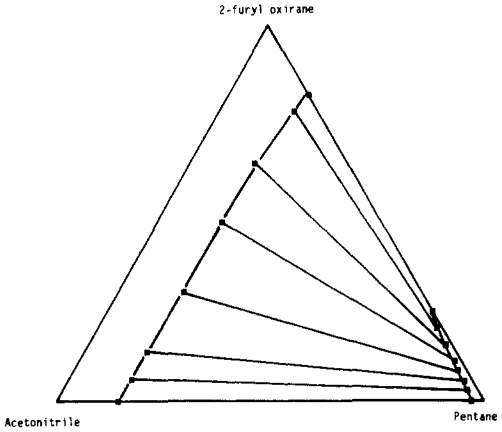

Figure 4. Binodal curve and tie line for the ternary system acetonitrile-2-furyloxirane-pentane at 20 °C.

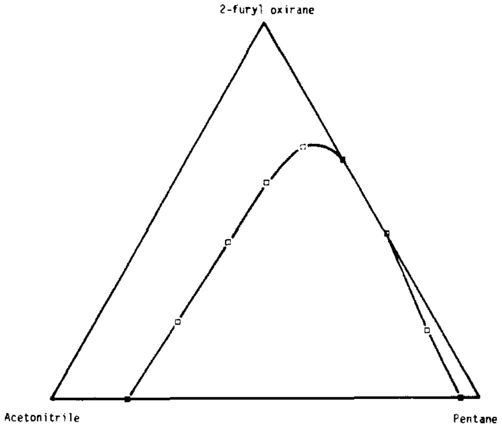

Figure 5. Binodal curve for the ternary system acetonitrile-2-furyloxirane-pentane at 30 °C.

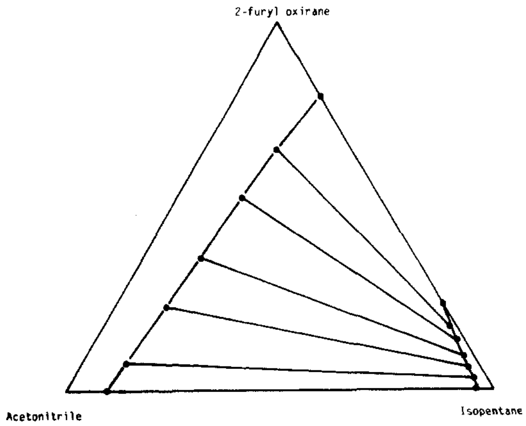

Figure 6. Binodal curve and tie line for the tenary system acetonitrile-2-furyloxirane-isopentane at 20 °C.

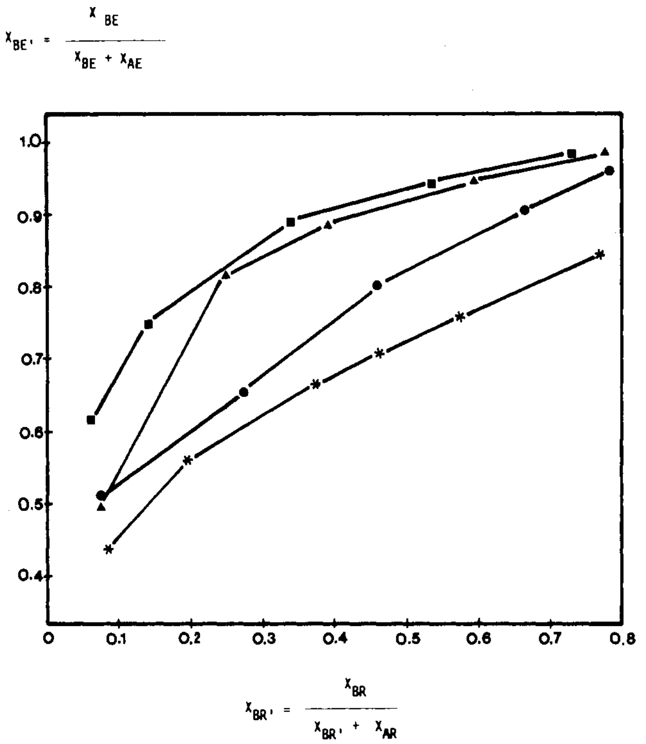

Figure 7. Selectivity diagrams at 20 °C for the system (*) acetonitrile–2-furyloxirane–cyclohexane, (●) acetonitrile–2-furyloxirane–hexane, (▼) acetonitrile–2-furyloxirane–pentane, (■) acetonitrile–2-furyloxirane–isopentane.

These figures show that at room temperature the diagrams are from type II and tend toward type I when the temperature increases.

In Figure 7 one can compare the selectivity diagrams of hexane, isopentane, and pentane relevant to the 2-furyloxirane in acetonitrile at 20 °C. The curve corresponding to cyclohexane is given as a reference.

Results from Figure VII show that the extracting capacity of aliphatic hydrocarbons is practically identical with that of cyclohexane, although they are more selective toward the 2-furyloxirane extraction.

Isopentane is more volatile than pentane but it is also less selective. Therefore pentane seems to be the best hydrocarbon for the 2-furyloxirane extraction in its reactive medium.

Glossary

X_A	weight percent of acetonitrile in one phase
X_B	weight percent of 2-furyloxirane in one phase
X_S	weight percent of a hydrocarbon in one phase
X_{BR}	weight percent of 2-furyloxirane in acetonitrile phase
X_{BE}	weight percent of 2-furyloxirane in hydrocarbon phase
$X_{BR'}$	weight percent of 2-furyloxirane in acetonitrile phase on a hydrocarbon free basis
$X_{BE'}$	weight percent of 2-furyloxirane in hydrocarbon phase on a hydrocarbon free basis

Registry No. 2-Furyloxirane, 2745-17-7; acetonitrile, 75-05-8; isopentane, 78-78-4; pentane, 109-66-0; hexane, 110-54-3.

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Compressed Liquid Propene Densities between 5 and 73 °C at Pressures to 9.6 MPa

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Compressed liquid densities of propene were measured at 11 temperatures between 5 and 73 °C at pressures from near saturation to 9.65 MPa with a vibrating tube densitometer. Comparisons with densities computed using a liquid density correlation, COSTALD, and an existing empirical fit to a BWR equation show that both methods are accurate to better than 0.2% at typical custody-transfer conditions.

Introduction

Since large quantities of propene are bought and sold daily, it is important to know the fluid's density as a function of temperature and pressure for accurate custody transfer. Compressed liquid densities, known to ±0.2% or better, are needed since metering operations occur in the compressed liquid region. Four sets of compressed liquid density data exist in the open literature (*1*–*4*). Also, there are two correlations (*5*, *6*) for calculating liquid densities of propene. To resolve discrepancies between the sets of data and to evaluate the accuracy of the correlations, we measured the compressed liquid density of propene at 11 temperatures between 5 and 73 °C. Pressures extended from near the vapor pressure to 9.65 MPa.

Experimental Section

Materials. Matheson Research Grade propene with a stated purity of 99.6 mol % minimum purity was used. Gas chromatographic analysis indicated 99.5 mol % with the balance being mostly propane. The propene was frozen with liquid nitrogen and evacuated to remove residual air. To calibrate the densitometer, Phillips Research Grade propane and Linde pure argon, with stated purities of 99.6 and 99.998%, respectively, were used. The propane was evacuated at low temperature to remove any possible air; the argon was used without further purification.

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