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Influence of Temperature on the Liquid–Liquid Equilibrium of the Ternary System Acetonitrile–2-Furyloxirane–Cyclohexane

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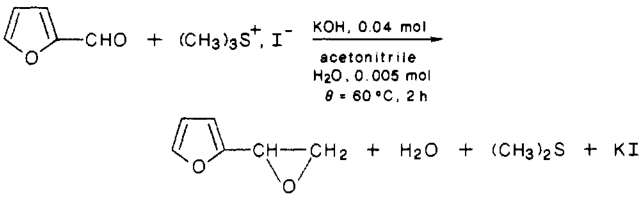
2-Furyloxirane can be obtained by a low hydrated solid–liquid phase transfer process from furfural and a sulfonium salt in basic medium by using acetonitrile as a solvent. It is purified by extraction in a reactive medium with an extracting solvent, cyclohexane. Diagrams on solubility isotherms and tie-line data are given for the ternary system acetonitrile–2-furyloxirane–cyclohexane at 20–30 and 40 °C. Under these conditions 2-furyloxirane extraction by cyclohexane appears not to depend on temperature.

Introduction

2-Furyloxirane was synthesized from furfural in the presence of potassium hydroxide and trimethylsulfonium bromide.

Acetonitrile was used as a solvent and its hydration was rigorously quantified.

This reaction took place according to a solid–liquid transfer process (*1*, *2*). The reactive diagram is as follows:



Purification of 2-furyloxirane could not be achieved by distillation in reactive medium under atmospheric pressure. Indeed, the presence of water induced by the reaction caused an epoxide polymerization (*3*) at temperatures above 120 °C.

Intensive use of vacuum would not be rational for large-scale distillation.

Therefore extraction by solvent was necessary to separate this epoxide in the reaction medium and purify it.

Our work on the efficiency of various solvents led us to choose cyclohexane as the extracting solvent mainly because, at room temperature, it was partly miscible with acetonitrile and totally miscible with 2-furyloxirane.

Experimental Section

Chemicals. Trimethylsulfonium bromide was synthesized from dimethyl sulfide with a purity of 99% and methyl bromide cooled down to −30 °C. The reaction took place in acetonitrile for 10 h at room temperature. The initial concentration of reagents was 2 mol/L. The salt obtained was filtered and then dried under vacuum with a desiccator.

Potassium hydroxide powder was a commercial product with a minimum purity of 85%. Cyclohexane was a commercial product with a minimum purity of 99%. Commercial acetonitrile was dried with a 4 Å molecular sieve before use.

2-Furyloxirane was synthesized from furfural, potassium hydroxide, and trimethylsulfonium bromide in low hydrated acetonitrile according to a new method elaborated in our laboratory (*1*). At the end of the reaction, the reactive medium was filtered, concentrated in a vacuum, and then distilled at 30 °C under 1 Torr in order to obtain pure 2-furyloxirane with the following characteristics: bp = 56 °C (under 14 mmHg), $\alpha^{20}{}_{D}$ = 1.4845, and $D^{20}{}_{4}$ = 1.1411.

Experimental Procedures. The solubility isotherms and the tie-line data for the ternary mixture acetonitrile–2-furyloxirane–cyclohexane were determined at various temperatures. Shaking as well as a constant temperature were maintained with a thermostated magnetic shaker. The mixing temperature was controlled by a mercury thermometer with ±0.5 °C accuracy.

Binaries of known compositions were prepared in order to determine the solubility binodal curves. On the left side of the slope (2-furyloxirane–acetonitrile) cyclohexane was added until the mixture became turbid. On the right side (2-furyloxirane–cyclohexane) acetonitrile was added until the mixture became turbid again. The contents of the three elements could then be determined by analysis.

Heterogeneous mixtures (acetonitrile–2-furyloxirane–cyclohexane) were prepared in order to determine the tie-line data. They were then shaken and left aside for 30 min to separate. Both equilibrium phases were separated and weighted. 2-Furyloxirane and acetonitrile were present in each phase and were measured with a chromatograph in gas phase (DEGS column 20%). Experimental conditions were as follows: length of column, 2.50 m; oven temperature, 180 °C; pressure of gas, 2.4 bar; internal standard, diethylbenzene; diluant solvent, diglyme.

We were able to check, thanks to data concerning both elements in each phase, that the conjugate points were actually on either side of the solubility isotherm.

Solubility Point Error. The error introduced during the determination of 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 on the tie-line curve induced by several titrations (weighing, GPC) is estimated at about 2%.

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Table I. Acetonitrile (A)-2-Furyloxirane (B)-Cyclohexane (S) at 20 °C

(a) Binodal Curve Data (wt %)

acetonitrile (A)	2-furyloxirane (B)	cyclohexane (S)
89.6	0	10.4
72.4	10.5	15.1
60.1	24.1	15.8
39.6	42.4	18.0
25.0	52.5	22.5
12.6	57.4	30.0
7.2	52.7	40.1
5.0	42.5	52.5
4.4	35.0	60.6
4.0	26.2	69.8
3.8	18.2	78.0
3.0	9.1	37.9
2.4	0	93.6

(b) Tie-Line Data (wt %)

acetonitrile phase (R)			cyclohexane phase (E)		
X_A	X_B	X_S	X_A	X_S	X_S
78.6	7.2	14.2	2.4	2	95.6
69.0	15.9	15.1	2.5	3.4	94.1
50.6	32.4	17.0	2.5	5.0	92.5
32.9	47.1	20.0	3.0	9.1	87.9
15.7	57.1	27.2	3.9	21.2	74.9

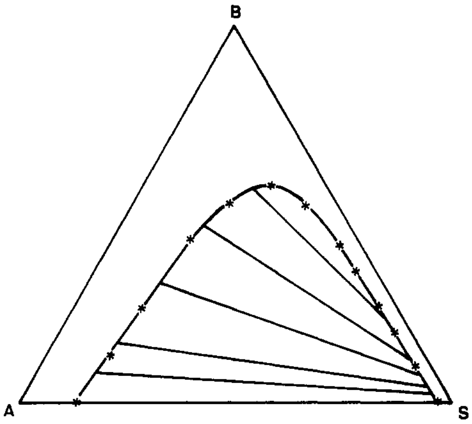

Figure 1. Binodal curve and tie line for the ternary system acetonitrile-2-furyloxirane-cyclohexane at 20 °C.

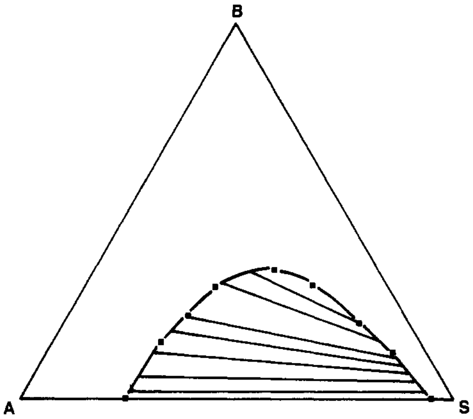

Figure 2. Binodal curve and tie line for the ternary system acetonitrile-2-furyloxirane-cyclohexane at 30 °C.

Presentation and Discussion of the Results

The ternary diagrams and the tie-line data for the system acetonitrile-2-furyloxirane-cyclohexane at 20 and 40 °C are given in weight percentages and are shown in Tables I-III. Figures 1, 2, and 3 show the solubility isotherms and the tie line at 20, 30, and 40 °C, respectively.

Table II. Acetonitrile (A)-2-Furyloxirane (B)-Cyclohexane (S) at 30 °C

(a) Binodal Curve Data (wt %)

acetonitrile (A)	2-furyloxirane (B)	cyclohexane (S)
83.8	0	16.2
77.9	5	16.6
75.7	16.7	17.6
55.1	25.0	19.9
44.9	32.7	21.4
32.6	41.1	26.3
15.0	42.8	42.2
11.0	37.2	51.8
7.2	22.6	70.2
5.4	12.6	82.0
4.1	0.0	95.9

(b) Tie-Line Phase Data (wt %)

acetonitrile phase			cyclohexane phase		
X_A	X_B	X_S	X_A	X_B	X_S
78.7	4.6	16.7	4.1	2.0	93.9
70.0	12.5	17.5	4.4	4.1	91.5
57.9	22.5	19.6	5.0	5.4	89.6
50.0	28.9	21.1	5.2	10.0	84.9
36.8	38.8	24.4	5.8	14.0	80.2
27.8	43.0	29.2	6.1	18.1	75.8
20.0	45.0	35.0	6.4	21.0	72.6

Table III. Acetonitrile (A)-2-Furyloxirane (B)-Cyclohexane (S) at 40 °C

(a) Binodal Curve Data (wt %)

acetonitrile (A)	2-furyloxirane (B)	cyclohexane (S)
76.2	0	23.8
60.1	14.7	25.2
50.1	22.4	27.5
40.0	30.1	29.9
23.4	34.8	41.8
17.3	30.1	52.6
11.9	26.0	62.1
10.3	20.8	68.9
7.1	12.9	80.0
4.9	0.0	95.1

(b) Tie-Line Data (wt %)

acetonitrile phase			cyclohexane phase		
X_A	X_B	X_S	X_A	X_B	X_S
73.5	2.5	24.0	5.4	2.2	92.2
69.8	5.9	24.3	5.4	4.8	89.8
61.8	13.1	25.1	5.6	7.0	87.4
53.3	19.1	27.6	6.1	8.8	85.1
50.2	21.8	28.1	6.1	10.1	83.8
35.2	32.6	32.2	7.9	15.2	76.9
30.1	34.9	35.0	10.8	20.4	68.8

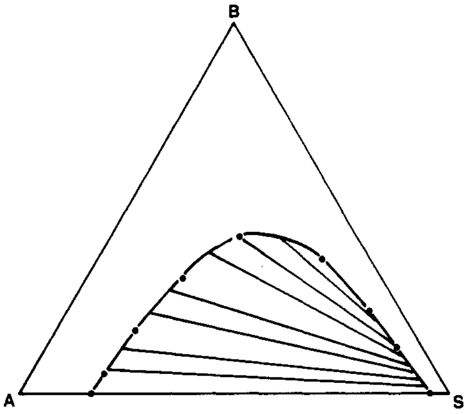

Figure 3. Binodal curve and tie line for the ternary system acetonitrile-2-furyloxirane-cyclohexane at 40 °C.

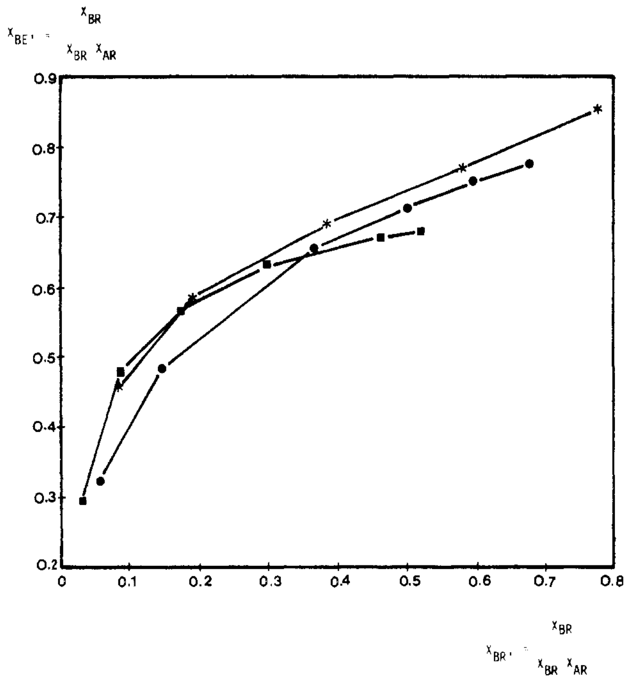

Figure 4. Selectivity diagrams for the ternary system acetonitrile–2-furyloxirane–cyclohexane at *, 20 °C; ●, 30 °C; ◆, 40 °C.

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

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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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