Extraction of Cyclic Ethers from Mixtures Containing Hydrocarbons

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Vapor phase oxidation of gasoline-range hydrocarbon mixtures produces mixtures of hydrocarbons and oxygenated compounds inseparable by distillation. Studies using *n*-hexane and 2,5-dimethyltetrahydrofuran as representative key components showed that such mixtures could be separated by liquid extraction using γ-butyrolactone, ethylene glycol, or diethylene glycol as solvents.

JONES AND FENSKE (*1*) have demonstrated how cyclic ethers (tetrahydrofurans, oxiranes, and oxetanes) may be produced by the vapor phase oxidation of aliphatic hydrocarbons. Recovery of cyclic ethers from the oxidation of hydrocarbon mixtures such as naphthas, however, cannot be accomplished by conventional distillation because of the overlapping of boiling points of the ethers and hydrocarbons. For example, the cyclic ethers produced from the oxidation of the hexanes boil in the same range as the isomeric heptanes (*1*).

The desired separation of cyclic ethers from aliphatic hydrocarbons is possible by using liquid extraction. The system of interest was the separation of C_6 and C_7 cyclic ethers from oxidized C_6 and C_7 paraffinic hydrocarbons. The most soluble hydrocarbon, *n*-hexane, and the predominant cyclic ether obtained from the oxidation of *n*-hexane, 2,5-dimethyltetrahydrofuran, were chosen as key components. Three solvents, γ-butyrolactone, ethylene glycol, and diethylene glycol were found to be useful for this separation; ethylene glycol permitting recovery of pure components.

MATERIALS

The 2,5-dimethyltetrahydrofuran chosen as a key cyclic ether for this work was obtained by the catalytic hydrogenation of 2,5-dimethylfuran. Purity was 99.2% as found by gas chromatography, the compound existing as 92% of the lower boiling isomer. The *n*-hexane was 98% pure as determined by gas chromatography. The solvents used, their purity, and source were as follows:

Solvent	Purity, %	Source
γ-Butyrolactone	98+	Centura Chemical Co., redistilled
Diethylene Glycol	99+	Dow Chemical Co., redistilled
Ethylene Glycol.	99.9+	Carbide & Carbon Chemicals Co., redistilled

Table I. Purity of 2,5-Dimethyltetrahydrofuran Obtainable with Diethylene Glycol

Temperature, ° F.	Wt., % 2,5-Dimethyltetrahydrofuran
100	84
200	91
280	97

Table II. Cloud Point Data

Solvent, Wt., %	*n*-Hexane, Wt., %	2,5-Dimethyltetrahydrofuran Wt., %	Temp., ° F.
Solvent: γ-Butyrolactone			
96.4	3.6	. . .	68
92.6	3.3	4.1	68
88.7	3.9	7.4	68
94.3	4.0	11.7	68
52.8	12.0	35.2	68
12.2	38.9	48.9	68
4.6	62.1	33.3	68
Solvent: Ethylene Glycol			
86.0	. . .	14.0	68
85.5	. . .	14.5	100
84.4	. . .	15.6	121
82.4	. . .	17.6	175
79.8	. . .	20.2	197
66.9	. . .	33.1	248
57.4	. . .	42.6	259
47.3	. . .	52.7	257
25.2	. . .	74.8	232
13.1	. . .	86.9	162
6.4	. . .	93.6	68
98.8	. . .	1.2	277
99.4	0.45	0.15	95
98.3	0.99	0.31	191
98.2	1.37	0.43	252
97.6	1.82	0.58	322
98.0	0.88	1.12	214
96.8	1.40	1.79	290
7.0	40.9	52.1	277
4.3	42.1	53.6	163
95.9	0.70	3.40	215
94.6	0.92	4.48	266
13.3	6.9	79.8	231
18.6	6.5	74.9	266
15.6	6.0	68.4	306
Solvent: Diethylene Glycol			
98.8	1.2	. . .	176
97.7	2.3	. . .	235
96.6	3.4	. . .	302
57.2	1.3	41.5	109
56.1	3.3	40.6	178
55.0	5.2	39.8	230
Solvent: Diethylene Glycol			
13.8	8.0	78.2	88
12.8	14.7	72.5	151
9.9	33.8	56.1	250
3.3	96.7	. . .	> 261
0.2	43.9	55.9	48
0.5	43.8	55.7	177
0.9	43.6	55.5	257
12.1	7.0	80.9	59
25.6	6.0	68.4	141
37.1	5.0	57.9	167
58.0	3.4	38.6	196
57.5	. . .	42.5	45

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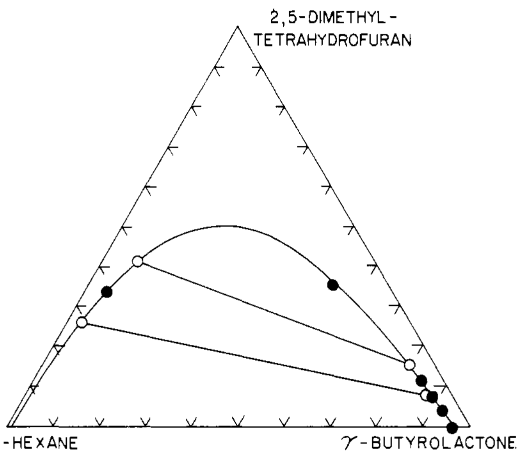

Figure 1. Equilibrium diagram for *n*-hexane, 2,5-dimethyltetrahydrofuran, and γ-butyrolactone at 68° F.

● — From solubility data

○ — From tie line data

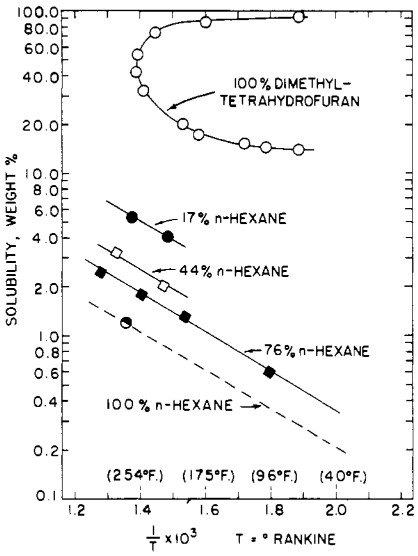

Figure 2. Solubility of *n*-hexane: 2,5-dimethyltetrahydrofuran mixtures in ethylene glycol

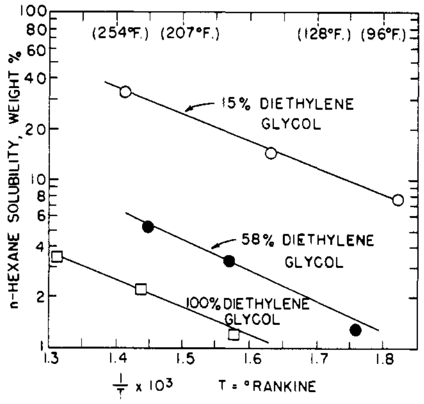

Figure 3. Solubility of *n*-hexane in diethylene glycol: 2,5-dimethyltetrahydrofuran mixtures

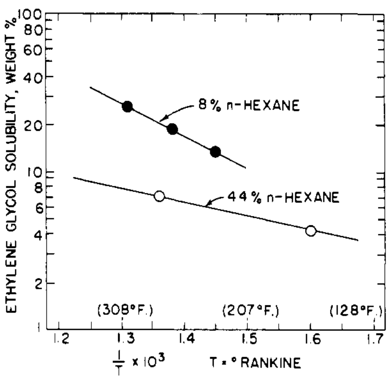

Figure 4. Solubility of ethylene glycol in *n*-hexane: 2,5-dimethyltetrahydrofuran mixtures

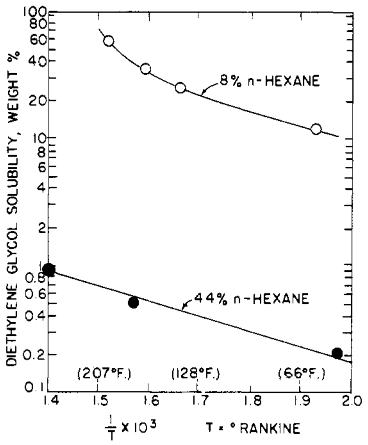

Figure 5. Solubility of diethylene glycol in *n*-hexane: 2,5-dimethyltetrahydrofuran mixtures

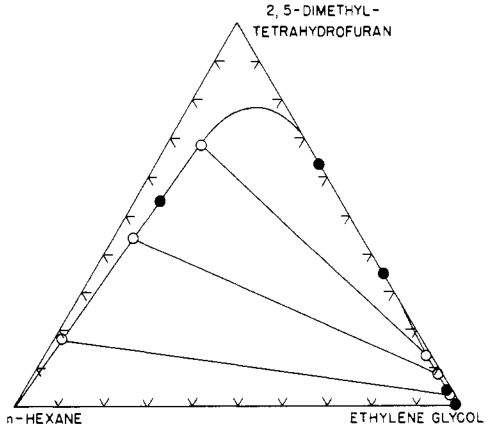

Figure 6. Equilibrium data for *n*-hexane, 2,5-dimethyltetrahydrofuran, and ethylene glycol at 248° F.

● — From solubility data

○ — From tie line data

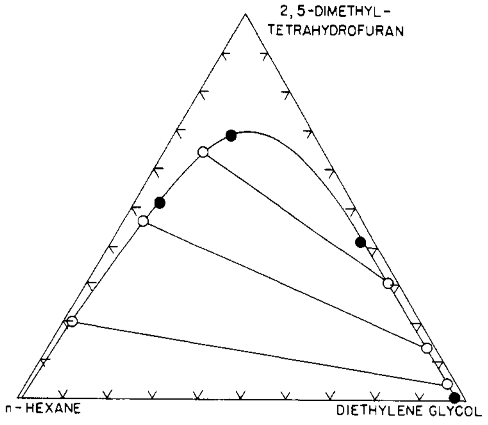

Figure 7. Equilibrium data for *n*-hexane, 2,5-dimethyltetrahydrofuran, and diethylene glycol at 176° F.

● — From solubility data

○ — From tie line data

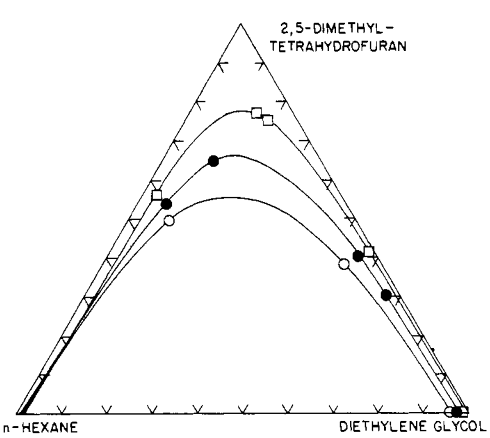

Figure 8. Equilibrium data for *n*-hexane, 2,5-dimethyltetrahydrofuran, and diethylene glycol at various temperatures

□ — 100° F.
● — 200° F.
○ — 280° F.

EXPERIMENTAL PROCEDURES

Ternary phase diagrams for the γ-butyrolactone system at 68° F. were obtained by a titration procedure (*2*). Pure compounds or mixtures were titrated into known volumes of other pure compounds or mixtures until cloud points were reached. Temperature control was maintained by means of a water bath. Equilibrium tie lines were obtained by equilibrating known mixtures of *n*-hexane, 2,5-dimethyltetrahydrofuran, and γ-butyrolactone at 68° F. The *n*-hexane in each phase was determined by solubility in 85% phosphoric acid; both the 2,5-dimethyltetrahydrofuran and γ-butyrolactone being soluble. A titration procedure based on the reaction of γ-butyrolactone with aqueous NaOH was used for determining the γ-butyrolactone content of each phase. Weighed amounts of sample were added to a flask containing 10.0ml. of known strength NaOH solution and the excess NaOH was back titrated with standardized H_2SO_4 solution. Best results were obtained when about 0.3*N* NaOH was used for the raffinate phase, and about 2.6*N* NaOH was used for the extract phase.

Table III. Betas for Single Stage Extraction Data

Solvent, Wt., %	*n*-Hexane, Wt., %	2,5-Dimethyl-tetrahydrofuran, Wt., %	Temp., ° F.	Beta
		Solvent: γ-Butyrolactone		
87.1	5.0	7.9	68	4.3
3.2	70.6	26.2	68	
79.4	5.4	15.2	68	3.5
7.4	51.4	41.2	68	
		Solvent: Ethylene Glycol		
96.8	0.80	2.40	248	15.0
2.3	81.2	16.5	248	
91.6	0.76	7.64	248	12.1
4.6	51.9	43.5	248	
86.0	0.56	13.44	248	9.3
7.3	25.3	67.4	248	
		Solvent: Diethylene Glycol		
95.8	1.58	2.62	176	6.5
2.1	77.9	20.0	176	
84.4	2.19	13.41	176	6.2
4.9	48.5	46.6	176	
66.1	3.05	30.85	176	4.2
8.6	26.6	64.8	176	

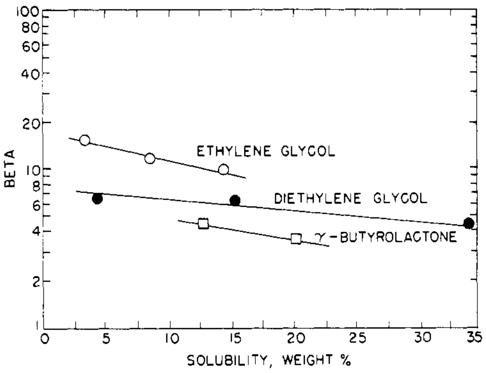

Figure 9. Variation of "Beta" *vs.* solubility for *n*-hexane: 2,5-dimethyltetrahydrofuran in butyrolactone, in ethylene glycol and in diethylene glycol solvents

The high temperature phase diagrams for ethylene glycol and diethylene glycol were obtained by a cloud point method using a heavy walled 15m. test tube in a sealed apparatus containing a thermocouple. Known mixtures were added, the apparatus sealed, and the contents heated with mixing until one phase was reached. Then the contents were slowly cooled until a cloud point was observed, at which time the temperature was recorded. Tie lines were obtained by equilibrating known mixtures at the desired temperature, separating the two phases, and analyzing each. Samples were collected in chilled 30% NaOH solution to prevent loss of sample. Mixing of the sample with 30% NaOH solution was found to remove all of the glycol solvents so that the remaining two components could be analyzed by refractive index.

DISCUSSION OF RESULTS

Figure 1 shows the equilibrium diagram for *n*-hexane, 2,5-dimethyltetrahydrofuran, and γ-butyrolactone at 68° F. The maximum purity of 2,5-dimethyltetrahydrofuran obtainable was found to be 77 weight %. Even as low as minus 70° F. this phase diagram is closed.

Figures 2 and 3 are plots of log solubility *vs.* reciprocal temperature for various mixtures of *n*-hexane and 2,5-dimethyltetrahydrofuran in ethylene glycol and in diethylene glycol. Figures 4 and 5 are similar plots for the solubility of ethylene glycol and diethylene glycol in *n*-hexane-2,5-dimethyltetrahydrofuran mixtures. Complete ternary phase diagrams, Figures 6 and 7, were obtained by plotting the solubilities of known mixtures obtained at the desired temperature from Figures 4–7. Additional data for the tie lines were then added. As can be seen in Figure 6, liquid extraction with ethylene glycol will permit recovery of both pure *n*-hexane and 2,5-dimethyltetrahydrofuran from mixtures of the two. The maximum purity of 2,5-dimethyltetrahydrofuran obtainable using diethylene glycol as a solvent varies with temperature as shown in Table I. These data were obtained by drawing tangents to the binodal curves of Figure 8.

A comparison of the efficiency of γ-butyrolactone, ethylene glycol, and diethylene glycol for extracting 2,5-dimethyltetrahydrofuran from *n*-hexane is shown in Figure 9 where log β is plotted *vs.* solubility. β is defined by the following equation:

$$\beta = \frac{\left(\frac{\%\text{ of the more soluble component}}{\%\text{ of the less soluble component}}\right)\text{extract}}{\left(\frac{\%\text{ of the more soluble component}}{\%\text{ of the less soluble component}}\right)\text{raffinate}}$$

Ethylene glycol is seen to be the most selective solvent at the temperature studied. It also is the only solvent of the three that will permit recovery of both components pure. Its low solubility characteristics, however, require high solvent to feed ratios.

Experimental data collected for each of the three solvents studied are tabulated in Tables II and III.

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LITERATURE CITED

(1) Jones, J.H., Fenske, M.R., *Ind. Eng. Chem.* **51**, 262 (1959).
(2) Treybal, R.E., Liquid Extraction, 2nd Ed., McGraw-Hill, New York, 1963.

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Effect of Contaminants on the Thermal Stability of Maleic Anhydride

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Heat and gas evolution data are presented for molten maleic anhydride which has been contaminated with Na^+, Li^+, K^+, Rb^+, NH_4^+, Ca^{++}, Ba^{++}, Mg^{++}, H_2O, diethylamine and triethylamine. The alkali metal ions and the alkylamines showed the largest catalytic effect. CO_2 was the principle gaseous decomposition product. The sulfate anion diminished the effect of Na^+ contamination. Na^+ had no effect on the stability of phthalic anhydride.

CONTAMINATION with sodium salts can drastically decrease the stability of maleic anhydride at elevated temperatures. Serious accidents on an industrial scale have resulted from sodium salt contamination (*7*), and the patent literature makes reference to additives designed to mitigate the effects of sodium ion contamination of maleic anhydride. Quantitative data on heat and gas evolution were needed to define more exactly the maximum sodium ion contamination that might be tolerated in the safe manufacture and use of maleic anhydride. These same data could be used to design suitable venting systems for vessels which are employed in maleic anhydride service. This paper presents quantitative data on the relationship between sodium salt concentration in maleic anhydride and heat and gas evolution rates. The influence of various anions associated with the sodium ion was studied, and the effect of other alkali metal and alkaline earth ions on the thermal stability of maleic anhydride was surveyed.

EXPERIMENTAL DETAILS

Heat and gas evolution rates were measured with a previously described differential thermal stability (DTA) apparatus with which gas evolution rates could be measured simultaneously (*1*, *2*). After the sample vessel had cooled to room temperature at the end of the experiment, samples of the decomposition gases could be transferred to an infrared absorption cell for analysis.

Salt contaminated samples were prepared by pulverizing commercial maleic anhydride briquets and then dispersing the contaminant salt by careful trituration. The amine and water contaminated samples were prepared by adding the contaminant directly to the powdered maleic anhydride sample in the DTA cell.

The sodium and potassium salts of maleic acid were prepared by adding the appropriate alkali hydroxide to an aqueous solution of maleic acid to a pH of 8-9. The resultant solutions were concentrated by evaporation and cooled to crystallize the salts. The crystals were filtered and dried overnight at 130° C. and finally under vacuum. The salts prepared in this manner were assumed to be anhydrous.

The alkaline earth maleates were prepared by adding the alkaline earth chloride to an aqueous solution of maleic acid and precipitating the salt by addition of ammonium hydroxide. The resultant slurries were boiled for 10 minutes to improve the crystal form and after cooling were filtered. The crystals were washed with dilute NH_4OH and dried overnight at 130° C. and finally under vacuum. This procedure was assumed to give an anhydrous and ammonia-free product. The magnesium maleate used was already available and was not further purified for this work. Its preparation involved precipitation using NaOH and was subsequently found to contain 2.4% Na^+ as sodium maleate.

Anhydrous ammonium maleate was prepared following the procedure of Keiser and McMaster (*3*) which involved dissolving dry maleic acid in ether and bubbling dry NH_3 through the solution until no more of the diammonium salt separated. The precipitate was air dried and finally vacuum dried at room temperature to remove the remainder of the ether. The salt prepared in this manner was thermally

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