# Liquid-liquid equilibrium in the system 1-dodecene—1,2-dodecene oxide—methanol

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In order to extract 1,2-dodecene oxide from its mixture with dodecene, the liquid-liquid equilibrium in the ternary system 1-dodecene—1,2-dodecene oxide—methanol was determined analytically at 0.5°C. It was found that this mixture formed a system with one pair of partially miscible liquids. The values found experimentally were correlated by means of the Hand equation, the critical point was determined graphically, and the selectivity values of solvent were calculated.

It follows from the shape of ternary diagram as well as from the slope of conodes that methanol is not a convenient extracting agent for the isolation of pure 1,2-dodecene oxide but it may be used for the separation of a part of pure 1-dodecene from its mixture with 1,2-dodecene oxide.

The higher linear 1,2-alkene oxides are important intermediates for organic syntheses especially in relation to higher 1-alkanols employed in the preparation of tensides. The industrial production of these substances may be carried out by the oxidation of 1-alkenes either with organic peroxy acids [1] or with organic hydroperoxides catalyzed by the compounds of transition metals [2]. The isolation of individual 1,2-alkene oxides may be performed by rectification. However, if a mixture of higher 1-alkenes (*e.g.* the fraction $C_{11}$—$C_{15}$) is oxidized, the boiling points of higher 1-alkenes and those of lower 1,2-alkene oxides overlap. For this reason, this mode of isolation is not convenient.

From other separation methods the liquid-liquid extraction is usually advantageous and technically easily realizable. Among potential extracting agents, methanol seems to be convenient because of its low price, high volatility (it may be easily separated from extract and raffinate by rectification) as well as its immiscibility with 1-dodecene within a wide concentration range owing to its high polarity. This study deals with a quantitative testing of the effect of methanol extraction on the mixture of 1-dodecene and 1,2-dodecene oxide.

## Experimental

A Hewlett—Packard gas chromatograph equipped with a flame ionization detector and a stainless steel column (length 180 cm, internal diameter 3.2 mm) packed with Chromosorb W (80—100 mesh), which was silane-treated with hexamethyldisilazane, was used. A silicone elastomer UCCW 982 (10 wt % with respect to the weight of pack-

ing) was applied as a stationary phase. The flow of nitrogen was 25 $cm^3\ min^{-1}$ and the feed was 0.2 μl.

## *Materials*

The data in brackets are taken from [3].

*1-Dodecene*, obtained from a technical mixture of $C_{11}$—$C_{15}$ alkenes by rectification. B.p. 88.9°C/10 torr (88.83°C/10 torr); $n_D^{20}$ 1.4300 (1.43002); $d_4^{20}$ 0.7600 g $cm^{-3}$ (0.75836 g $cm^{-3}$).

*1,2-Dodecene oxide*, prepared from 1-dodecene by oxidation with *tert*-butyl hydroperoxide according to [4]. B.p. 106—109°C/6 torr (97—98°C/3.5 torr); $n_D^{20}$ 1.4356 (1.4356); $d_4^{20}$ 0.8431 g $cm^{-3}$ (0.844 g $cm^{-3}$).

*Methanol, rectified*. B.p. 65°C/760 torr (64.96°C/760 torr); $n_D^{20}$ 1.3285 (1.3305); $d_4^{20}$ 0.7918 g $cm^{-3}$ (0.7923 g $cm^{-3}$).

## *Method*

The equilibrium diagram of the system 1-dodecene—1,2-dodecene oxide—methanol was determined analytically, *i.e.* the composition of both the extract and the raffinate layers was determined after the equilibrium establishment at 0.5 ± 0.1°C. The mixtures prepared by weighing the pure components were stirred thoroughly several times; the equilibrium was attained after 10 hours at the above-mentioned temperature. The samples were taken by a syringe with a long needle.

The composition of the extract and raffinate layers was determined by gas chromatography using the method of internal standard. For the relative correction factors of individual components (expressed as the ratio of the composition in peak area % read off from chromatogram to the true composition of mixture in weight %) the following values were found:

$$f_{\text{1-dodecene}} = 1.000,$$

$$f_{\text{1,2-dodecene oxide}} = 0.977,$$

$$f_{\text{methanol}} = 0.297.$$

The mutual solubilities of 1-dodecene and methanol were also determined by isothermal titration according to *Othmer* [5].

## Results

The composition of the extract and raffinate layers experimentally found at 0.5°C is given in Table 1. The symbols $x$ and $y$ denote the composition of the raffinate and extract layers, respectively. (All data are given in weight %.)

On the basis of these values, the ternary diagram of the investigated system was plotted.

According to Fig. 1, the mixture forms a system with a pair of partially miscible liquids. For this system, the Hand equation [6] expressing the relationship between the composition of the extract and raffinate layers is valid

$$\log \frac{y_B}{y_C} = k' + n \log \frac{x_B}{x_A}, \qquad (1)$$

*Table 1*

Equilibrium composition of coexisting phases

| Conode | $x_{oxi}$ | | $y_{dod}$ | $y_{oxide}$ | $y_{meth}$ |
|---|---|---|---|---|---|
| *0* | 0.984 | — | 0.016 | 0.066 | — | 0.934 |
| *1* | 0.927 | 0.038 | 0.035 | 0.077 | 0.022 | 0.901 |
| *2* | 0.832 | 0.110 | 0.058 | 0.088 | 0.049 | 0.863 |
| *3* | 0.735 | 0.167 | 0.098 | 0.092 | 0.079 | 0.830 |
| *4* | 0.584 | 0.262 | 0.154 | 0.114 | 0.135 | 0.761 |
| *5* | 0.491 | 0.304 | 0.205 | 0.129 | 0.154 | 0.717 |
| *6* | 0.391 | 0.342 | 0.267 | 0.135 | 0.175 | 0.700 |
| *7* | 0.310 | 0.340 | 0.350 | 0.153 | 0.203 | 0.644 |

where $y_B$ = weight fraction of extracted component in the extract, $y_C$ = weight fraction of extracting agent in the extract, $x_A$ = weight fraction of extracted component in the raffinate, $x$ = weight fraction of solvent in the raffinate, and $k'$ and $n$ are constants.

The special form of the Hand equation for the system 1-dodecene—1,2-dodecene oxide—methanol constructed from experimental data by using the method of least squares is as follows

$$\log \frac{y_{oxide}}{y_{dod}} = -0.5660 + 0.6993 \log \frac{x_{oxide}}{\quad}, \qquad (2)$$

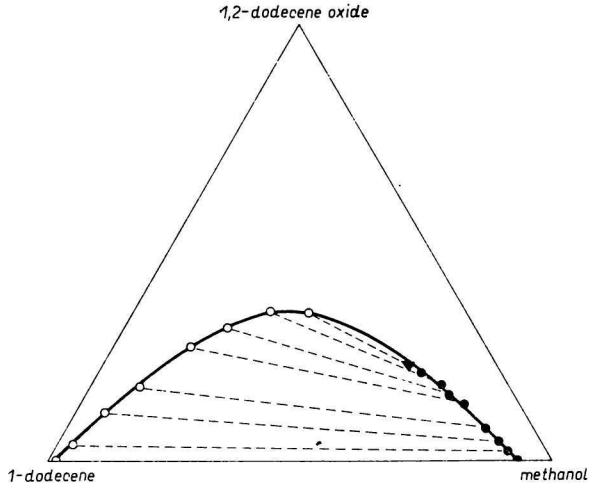


*Fig. 1.* Ternary diagram of the system 1-dodecene—1,2-dodecene oxide—methanol at 0.5°C.

○ the composition of extract layers; ● the composition of raffinate layers; ▲ critical point *K*.

where $y$ and $x$ are weight fractions of the corresponding components in the extract and raffinate, respectively, and the indices "dod", "oxide", and "meth" denote 1-dodecene, 1,2-dodecene oxide, and methanol, respectively.

From the data given in Table 1, the coordinates of the critical point $K$ (in which the composition of extract and raffinate is identical) were determined graphically according to *Treybal* [7]. The composition of the mixture in the critical point is as follows.

$$x_{meth} = y_{meth} = 0.596,$$

$$x_{dod} = y_{dod} = 0.163,$$

$$x_{oxide} = y_{oxide} = 0.241.$$

The data presented in Table 1 were used for the calculation of the selectivity defined for the investigated system according to [8]

$$\beta = \frac{y_{oxide} \cdot x_{dod}}{y_{dod} \cdot x_{oxide}} \qquad (3)$$

and of the separation factor $K_{oxide}$ (as a measure of extraction solvent capacity) defined for the system 1-dodecene—1,2-dodecene oxide—methanol by the formula

$$K_{oxide} = \frac{y_{oxide}}{x_{oxide}}. \qquad (4)$$

The calculated values of the selectivity and capacity of solvent are given for different concentrations of extracted component in the extract in Table 2. The values are reduced to the base without solvent.

*Table 2*

Values of selectivity $\beta$ and separation factor $K_{meth}$ for the equilibrium 1-dodecene—1,2-dodecene oxide—methanol

| Conode | $\frac{y_{oxide}}{y_{oxide} + y_{dod}}$ | $\beta = \frac{y_{oxide} \cdot x_{dod}}{y_{dod} \cdot x_{oxide}}$ | $K_{meth} = \frac{y_{oxide}}{x_{oxide}}$ |
|---|---|---|---|
| *1* | 0.222 | 6.97 | 0.579 |
| *2* | 0.358 | 4.21 | 0.445 |
| *3* | 0.462 | 3.77 | 0.473 |
| *4* | 0.542 | 2.64 | 0.515 |
| *5* | 0.544 | 1.92 | 0.506 |
| *6* | 0.564 | 1.48 | 0.512 |
| *7* | 0.570 | 1.21 | 0.597 |

## Discussion

The mixture 1-dodecene—1,2-dodecene oxide—methanol forms a system with a pair (1-dodecene—methanol) of partially immiscible liquids and thus it shows one region of mutual insolubility.

From Table 2 it is obvious that the selectivity does not reach high values and the extraction solvent capacity of methanol, the mean value of which (0.518) has not changed over the whole range of measurements, is relatively low.

From the value of the selectivity coefficient as well as the slope of conodes (Fig. 1) it is evident that even a multiple extraction does not enable us to obtain pure 1,2-dodecene oxide. It is, however, possible to remove 1,2-dodecene oxide practically entirely from the mixture of 1-dodecene with 1,2-dodecene oxide by multiple extraction.

It follows from these facts that methanol is not a suitable extracting agent for the isolation of pure 1,2-dodecene oxide. It may be rightly assumed [9] that an admixture of small amounts of substances reducing the solubility of hydrocarbons in methanol (*e.g.* water) could raise the selectivity of methanol used as an extracting agent for the given mixture.

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