

Liquid—Vapour Equilibrium for the System 1-Heptene—1,2-Heptene Oxide

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The variation of the vapour pressure of 1,2-heptene oxide with temperature as well as the liquid—vapour equilibrium of the system 1-heptene—1,2-heptene oxide at the absolute pressure of 200 Torr were measured.

On the basis of the measured data, the equilibrium $y-x$ and $t-x,y$ diagrams were constructed. It was found that the dependence of vapour phase composition on that of liquid phase did comply with the laws valid for an ideal system.

By treating 1-heptene with peracetic acid, 1,2-heptene oxide arises as the main reaction product [1] which may be isolated from reaction mixture by rectification. It is possible to transform 1,2-heptene oxide by isomerization and subsequent hydrogenation in 1-heptanol [2] which may be used as a higher alcohol for the preparation of surfactants or plasticizers.

The measured vapour pressure data which have not been described in literature yet as well as the equilibrium relationships contained in this paper could be of use for the isolation of this substance.

Experimental

1-Heptene obtained by rectifying a technical mixture of alkenes had the following constants: b.p. 93.6/760 Torr (93.63/760 Torr); n_D^{20} 1.4008 (n_D^{20} 1.3998); d_4^{20} 0.6972 (d_4^{20} 0.6970). The data in parentheses are cited according to [3].

1,2-Heptene oxide was prepared according to [1] with subsequent rectification and had the following constants: b.p. 63.0/50 Torr; n_D^{20} 1.4153 (n_D^{20} 1.4164); d_4^{20} 0.8344 (d_4^{20} 0.8353). The data in parentheses are cited according to [4].

The refractive indexes were measured with a temperature regulated Abbé refractometer while the densities were determined by a pycnometer method.

The vapour pressure of 1,2-heptene oxide was measured by means of the Świątosławski ebulliometer modified according to [5] which was adapted for electric heating. The pressure was measured with the absolute Zimmerli manometer [6], regulated by means of the electric manostat and read by means of a cathetometer. The temperature was measured with the calibrated Anschütz thermometer, accurate to 0.1 deg.

The vapour pressure of 1-heptene necessary for the determination of activity coefficients controlling the liquid—vapour equilibrium in this system was calculated according to the Antoine equation valid for this substance [7]

$$\log P^0 = 6.90069 - \frac{1257.505}{219.179 + t}$$

where P^0 and t denote pressure in Torr and temperature in °C, respectively.

The liquid—vapour equilibrium was measured by means of the Gillespie equipment modified by *Otsuki* [8]. The analysis of the liquid as well as the vapour phase was performed refractometrically using a calibration curve.

The measurement of vapour pressure of 1,2-heptene oxide in dependence on temperature was made over the range from 8.8 to 665.8 Torr. The results were correlated by means of the Antoine equation. The values of constants in the Antoine equation were calculated from the experimental data by means of the least-square method. The measured values are given in Table 1.

Table 1

Variation of the vapour pressure of 1,2-heptene oxide with temperature

Temperature [°C]	$P_{\text{exp.}}$ [Torr]	$P_{\text{calc.}}$ [Torr]	ΔP	$\frac{\Delta P}{P_{\text{calc.}}} 100$
			$P_{\text{exp.}} - P_{\text{calc.}}$ [Torr]	[%]
32.7	8.8	8.6	-0.2	-2.3
42.8	15.4	15.4	0.0	0.0
51.1	23.9	23.9	0.0	0.0
56.7	30.9	31.7	0.8	2.5
66.2	49.4	49.6	0.2	0.4
75.0	72.5	73.1	0.6	0.8
78.0	82.6	82.9	0.3	0.4
80.4	90.7	91.4	0.7	0.8
85.5	112.1	112.1	0.0	0.0
89.3	129.0	129.8	0.8	0.6
96.3	169.9	168.4	-1.5	-0.9
99.7	189.9	190.2	0.3	0.2
108.3	261.7	255.6	-6.1	-2.4
112.7	304.5	295.3	-9.2	-3.1
122.8	403.0	405.2	2.2	0.5
129.3	485.1	491.3	6.2	1.3
140.5	665.8	672.6	6.8	1.0

Table 2

Liquid—vapour equilibrium in the system 1-heptene—1,2-heptene oxide

Temperature [°C]	x_1	y_1	γ_1	γ_2	α
					$\left(\frac{x_2 \cdot y_1}{x_1 \cdot y_2} \right)$
91.0	0.0921	0.3662	1.132	1.008	5.696
84.5	0.1930	0.5516	0.994	1.032	5.148
83.0	0.2203	0.6042	1.000	1.000	5.403
79.3	0.2788	0.6962	1.025	0.964	5.928
72.7	0.3876	0.8034	1.060	0.972	6.456
71.2	0.4085	0.8106	1.068	1.032	6.187
68.2	0.5116	0.8563	0.999	1.083	5.689
61.6	0.6711	0.9375	1.057	0.947	7.351
60.4	0.7305	0.9508	1.029	0.963	7.130
59.3	0.7752	0.9604	1.019	0.980	7.015
57.5	0.8462	0.9747	1.016	0.998	7.002

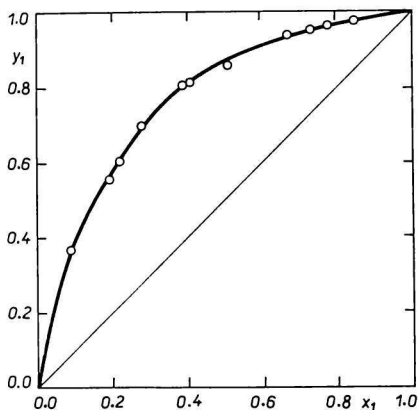


Fig. 1. $y-x$ Diagram for the system 1-heptene-1,2-heptene oxide.

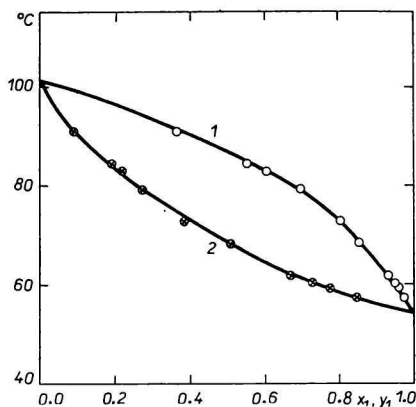


Fig. 2. $t-x,y$ Diagram for the system 1-heptene-1,2-heptene oxide.
1. composition of liquid phase;
2. composition of vapour phase.

The values of constants in the Antoine equation are as follows

$$A = 6.6628, B = 1250.42, C = 185.6.$$

The liquid-vapour equilibrium was measured at the absolute pressure of 200 Torr. The measured equilibrium data are presented in Table 2.

On the basis of equilibrium data the $y-x$ and $t-x,y$ diagrams were constructed (Figs. 1 and 2).

Discussion

The dependence of vapour pressure of 1,2-heptene oxide on temperature can be relatively well expressed over the pressure range from 8.8 to 665.8 Torr by the Antoine equation

$$\log P^0 = 6.6628 - \frac{1250.42}{185.6 + t}.$$

The average deviation of experimental values from the calculated ones is $\pm 1.0\%$.

It is evident from the $y-x$ and $t-x,y$ diagrams, from the values of activity coefficients and from the nearly constant values of relative volatilities that the dependence of the equilibrium composition of vapour phase on that of the liquid phase is controlled by the laws valid for an ideal system what is certainly due to a similar polarity and chemical composition of both investigated components.

Small deviations of activity coefficients from unity as well as deviations of relative volatilities from a constant values may be caused by experimental errors.

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