# LIQUID–LIQUID EQUILIBRIUM IN THE WATER–ETHANOL–TOLUENE SYSTEM. EXPERIMENTAL RESULTS

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Liquid–liquid equilibrium at 5, 25, and 50°C was measured in the water–ethanol–toluene system. Special attention was paid to the determination of distribution coefficient of ethanol. Besides, the composition and boiling point of azeotropic mixture at normal pressure were determined.

Liquid-liquid equilibrium in the water(1)–ethanol(2)–toluene(3) system was measured at 25°C by Washburn and coworkers[1] who applied both the titration method, and analytically determined the composition of coexisting phases (by means of refractive index). On the basis of these data, Sørensen and Arlt[2] calculated the parameters of the NRTL, UNIQUAC, and UNIFAC (common) equations which, however, cannot be used for calculating the vapour–liquid equilibrium.

Arzhanov and coworkers[3] measured the liquid–liquid and vapour–liquid equilibria at normal boiling point ($\approx$75°C). These authors found out that the heterogeneous region is under these conditions much smaller than that at 25°C, and the tie-lines are nearly parallel to the base-line of the concentration triangle.

The estimate of distribution coefficient of ethanol in this ternary system carried out on the basis of the binary vapour–liquid equilibria (ethanol–toluene and ethanol––water) differed considerably from the value which follows from the paper by Washburn and coworkers[1]. This discrepancy was one of impulses for undertaking this work.

## EXPERIMENTAL

*Substances used.* Toluene (A.R. grade, supplied by Lachema, Neratovice) was shaken five times with concentrated sulphuric acid, then three times with water and finally with NaOH. The main parts of water were removed from toluene by calcined $CaCl_2$, and in the end the substance was dried up with sodium. Toluene treated in this way was rectified on a packed column (40 theoretical plates). The product obtained had the following properties: $\varrho(25°C) = 0.86124$ g/cm$^3$ (0.86231, ref.[4]), $n_D(25°C) = 1.4939$ (1.49413, ref.[4]). Ethanol. Extra fine ethanol was freed from water by azeotropic distillation with benzene. The water content as determined by

the Fischer method[5] was 0·1%. Physical properties of ethanol: $\varrho(25°C) = 0.78498$ g/cm$^3$ (0·78506, ref.[4]), $n_D(25°C) = 1.3605$ (1·35941, ref.[4]). Tetrahydrofuran (A.R. reagent, supplied by Jenapharm-Laborchemie, Apolda) was shaken with FeSO$_4$ first and distilled with sodium on a packed column (40 theoretical plates). Before use it was distilled under vacuum with LiAlH$_4$. Physical properties of the product: $\varrho(25°C) = 0.8819$ g/cm$^3$ (0·88241, ref.[4]), $n_D(25°C) = 1.4046$ (1·40496, ref.[*]). Water. Double redistilled water of specific conductivity $\varkappa = 1.886 \cdot 10^{-4}$ S m$^{-1}$ was used.

Liquid–liquid Phase Equilibrium Determination

*Direct analytical method.* Liquid–liquid equilibrium was measured at constant temperature ($\pm 0.05$ K) in a thermostatted cell[6] in which the initial heterogeneous ternary mixture was intensely stirred for 2—3 hours. After the thorough phase separation, the samples were taken for analysis.

The composition of equilibrium phases in the water–ethanol–toluene ternary system was determined by the chromatographic method of internal standard. Both equilibrium phases were taken into preweighed ampoules to which a small amount of tetrahydrofuran was added (internal standard and simultaneously homogenization agent). Further, the calibration samples were prepared, separately for the aqueous and toluene phases. During the analysis itself, the samples of phases were always injected followed immediately by the injection of calibration samples. Conditions of chromatographic analysis: glass column of 2·5 mm i.d., 1·5 m long, filled with Porapak Q, column temperature 200°C, carrier gas H$_2$, thermal conductivity detector, injection volume $1.1 \cdot 10^{-6}$ dm$^3$, carrier gas flow rate 40 cm$^3$/min. Apparatus used: gas chromatograph Chrom 5 with integrator CI 100 (Laboratorní přístroje, Prague).

*Titration method.* Toluene and ethanol in a chosen ratio were weighed in the differential mode into a thermostatted vessel. To this mixture water was added gradually under continuous stirring by means of a calibrated hypodermic syringe (controlled through micrometer screw) till the appearance of stable turbidity. In this way part of data at 5°C was obtained. The composition of azeotropic mixture was determined so that the mixture which according to the literature corresponded approximately to the composition of azeotropic mixture ($x_1 \doteq 0.33$, $x_2 \doteq 0.43$) was prepared by weighing into a flask. The mixture prepared in this way was distilled on a packed column 1 m long which corresponded approximately to 40 theoretical plates. Already after distilling about 3% the flask charge, the temperature set down at a constant value. After distilling off 30% charge, part of distillate (about 10%) was taken into a known amount of tetrahydrofuran (homogenization agent), and the mixture was analyzed on gas chromatograph.

## RESULTS AND DISCUSSION

The measured values of composition of coexisting phases are given in Tables I and II and in Fig. 1. It is apparent from the figure that the heterogeneous region is reduced with increasing temperature, and simultaneously the inclination of tie-lines decreases with temperature. This finding agrees with the conclusions of Arzhanov and co-workers[3].

The dependence of distribution coefficient of ethanol, $K_2$, determined by the relation

$$K_2 = \frac{(x_2)_{\text{aqueous phase}}}{(x_2)_{\text{toluene phase}}},$$

as a function of mole fraction of ethanol $x_2$ in the aqueous phase for the temperature of 5, 25, and 50°C is depicted in Fig. 2. The values of the distribution coefficient determined by Washburn and coworkers[1] and Arzhanov and coworkers[3] are also presented in the figure. For a comparison, the dependence of distribution coefficient of ethanol in the water–ethanol–benzene system at 25°C (ref.[7]) is plotted as well. The dependence reported by Washburn and coworkers[1] is probably erroneous and

TABLE I

Equilibrium compositions in the water(1)–ethanol(2)–toluene(3) system determined by the titration method at the temperature of 5°C

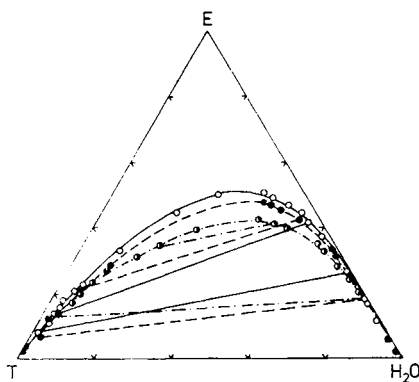| $x_1$ | 0·0356 | 0·0587 | 0·1045 | 0·1978 | 0·2780 | 0·4151 | 0·4251 |
|-------|--------|--------|--------|--------|--------|--------|--------|
| $x_2$ | 0·1024 | 0·2341 | 0·3230 | 0·4425 | 0·5000 | 0·4921 | 0·5536 |
| $x_3$ | 0·8620 | 0·7072 | 0·5724 | 0·3516 | 0·2220 | 0·0937 | 0·0213 |



FIG. 1

Equilibrium compositions in the water(1)––ethanol(2)–toluene(3) system at various temperatures. ○ ——— 5°C, ● — — — 25°C, ◑ –·—·— 50°C
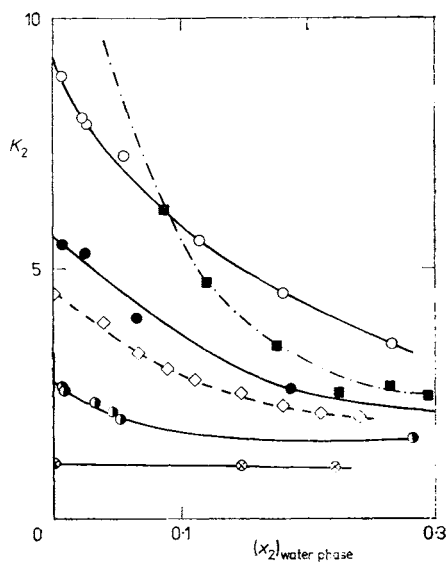


FIG. 2

Dependence of $K_2$ on $x_2$ in the aqueous phase at various temperatures. ○ 5°C, ● 25°C, ◑ 50°C, ⊗ 75°C Arzhanov and coworkers[3], ■ 25°C Washburn and coworkers[1], $\dot{v}$ values of $K_{ethanol}$ in the water––ethanol–benzene system at 25°C

TABLE II

Equilibrium compositions in the water(1)–ethanol(2)–toluene(3) system determined by the direct analytical method at various temperatures

| $x_1'$ | $x_2'$ | $x_3'$ | $x_1''$ | $x_2''$ | $x_3''$ | $K_2$ |
|--------|--------|--------|---------|---------|---------|-------|
| | | | Temperature 5°C | | | |
| 0·9938 | 0·0062 | 0·0000 | 0·0013 | 0·0007 | 0·9979 | 8·86 |
| 0·9783 | 0·0217 | 0·0000 | 0·0052 | 0·0027 | 0·9921 | 8·01 |
| 0·9763 | 0·0237 | 0·0000 | 0·0051 | 0·0030 | 0·9919 | 7·90 |
| 0·9447 | 0·0553 | 0·0000 | 0·0036 | 0·0076 | 0·9888 | 7·28 |
| 0·8855 | 0·1145 | 0·0000 | 0·0050 | 0·0206 | 0·9830 | 5·56 |
| 0·8197 | 0·1803 | 0·0000 | 0·0053 | 0·0401 | 0·9546 | 4·50 |
| 0·7283 | 0·2656 | 0·0061 | 0·0168 | 0·0752 | 0·9079 | 3·53 |
| 0·6037 | 0·3708 | 0·0255 | 0·0235 | 0·1249 | 0·8515 | 2·97 |
| 0·5554 | 0·4085 | 0·0361 | 0·0310 | 0·1359 | 0·8332 | 3·01 |
| 0·5171 | 0·4387 | 0·0442 | 0·0418 | 0·1491 | 0·8091 | 2·94 |
| 0·4727 | 0·4618 | 0·0655 | 0·0369 | 0·1736 | 0·7895 | 2·66 |
| 0·3951 | 0·5053 | 0·0996 | 0·0512 | 0·2053 | 0·7435 | 2·46 |
| | | | Temperature 25°C | | | |
| 0·9930 | 0·0070 | 0·0000 | 0·0014 | 0·0013 | 0·9973 | 5·46 |
| 0·9745 | 0·0255 | 0·0000 | 0·0020 | 0·0048 | 0·9932 | 5·31 |
| 0·9364 | 0·0636 | 0·0000 | 0·0072 | 0·0158 | 0·9770 | 4·03 |
| 0·8082 | 0·1846 | 0·0072 | 0·0232 | 0·0706 | 0·9062 | 2·61 |
| 0·8710 | 0·3114 | 0·0176 | 0·0332 | 0·1432 | 0·8237 | 2·17 |
| 0·6530 | 0·3300 | 0·0170 | 0·0295 | 0·1356 | 0·8167 | 2·15 |
| 0·6093 | 0·3602 | 0·0305 | 0·0460 | 0·1683 | 0·7857 | 2·14 |
| 0·5171 | 0·4258 | 0·0571 | 0·0586 | 0·2040 | 0·7374 | 2·09 |
| 0·4518 | 0·4535 | 0·0948 | 0·0963 | 0·2688 | 0·6349 | 1·69 |
| 0·4227 | 0·4601 | 0·1172 | 0·1000 | 0·2800 | 0·6200 | 1·64 |
| 0·4009 | 0·4726 | 0·1265 | 0·0998 | 0·2808 | 0·6194 | 1·68 |
| | | | Temperature 50°C | | | |
| 0·9928 | 0·0072 | 0·0000 | 0·0013 | 0·0027 | 0·9960 | 2·67 |
| 0·9908 | 0·0092 | 0·0000 | 0·0038 | 0·0035 | 0·9927 | 2·63 |
| 0·9674 | 0·0326 | 0·0000 | 0·0058 | 0·0139 | 0·9855 | 2·35 |
| 0·9534 | 0·0466 | 0·0000 | 0·0027 | 0·0216 | 0·9757 | 2·16 |
| 0·9447 | 0·0523 | 0·0000 | 0·0073 | 0·0255 | 0·9672 | 2·05 |
| 0·8252 | 0·1701 | 0·0047 | 0·0275 | 0·1056 | 0·8669 | 1·61 |
| 0·7929 | 0·2003 | 0·0068 | 0·0439 | 0·1228 | 0·8273 | 1·55 |
| 0·7481 | 0·2438 | 0·0081 | 0·0488 | 0·1551 | 0·7961 | 1·57 |
| 0·6856 | 0·2813 | 0·0331 | 0·0552 | 0·1729 | 0·8216 | 1·63 |
| 0·6403 | 0·3291 | 0·0306 | 0·0655 | 0·2051 | 0·7294 | 1·60 |
| 0·6082 | 0·3490 | 0·0428 | 0·0764 | 0·2348 | 0·6888 | 1·49 |
| 0·5045 | 0·3934 | 0·1021 | 0·1570 | 0·3040 | 0·5390 | 1·29 |
| 0·4592 | 0·4152 | 0·1256 | 0·2033 | 0·3414 | 0·4553 | 1·22 |
| 0·4146 | 0·4251 | 0·1603 | 0·2726 | 0·3954 | 0·3320 | 1·08 |

caused by an unsufficiently precise determination of the ethanol content in the toluene-rich phase. This conclusion is also confirmed by the estimate of the distribution coefficient on the basis of vapour–liquid equilibrium data which, including its temperature dependence, will be discussed in detail in the second part of this work[8].

On determining the boiling point and composition of the azeotropic mixture, these values were found:

$$t_{bp} = 74\cdot40°C, \quad x_1 = 0\cdot304, \quad x_2 = 0\cdot436, \quad x_3 = 0\cdot260.$$

The agreement with the literature values

$$t_{bp} = 74\cdot40°C, \quad x_1 = 0\cdot326, \quad x_2 = 0\cdot432, \quad x_3 = 0\cdot242 \ \left(\text{ref.}[9]\right)$$

$$t_{bp} = 74\cdot40°C, \quad x_1 = 0\cdot335, \quad x_2 = 0\cdot404, \quad x_3 = 0\cdot261 \ \left(\text{ref.}[1]\right)$$

may be considered satisfactory.

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