

**LIQUID-LIQUID EQUILIBRIUM IN THE SYSTEM METHANOL -
- WATER - TERT-AMYL METHYL ETHER**

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Liquid-liquid equilibrium was measured in the system methanol (MEOH)-water(W)-tert-amyl methyl ether (TAME) at 20°C. Nine tie-lines and the binary solubilities were correlated by the Rod method. A comparison is presented of the representation of experimental data in terms of the Rod method and the NRTL and UNIQUAC equations.

Similarly to methyl tert-butyl ether, TAME appears to be a very effective antiknock additive to gasoline for lead-free or low-leaded gasoline. TAME is produced by catalytic reaction of MEOH with isoamylenes (2-methyl-2-butene and 2-methyl-1-butene).

The equilibrium data needed for the TAME separation from reaction mixtures are satisfactory as to the vapour-liquid equilibrium. Saturated vapour pressures of TAME as a function of temperature have recently been measured by Palczewska-Tulinska and coworkers¹ and by Červenková and Boublík². Vapour-liquid equilibrium in the system TAME-MEOH at normal pressure was presented by Pavlova and coworkers³ (along with the dependence of azeotrope on pressure within 13 to 100 kPa) and by Červenková and Boublík². VLE data on the systems TAME-2-methyl-2-butene and TAME-2-methyl-1-butene were determined at 40 and 60°C by Pavlova and coworkers³.

As to the liquid-liquid equilibria, no data were found neither on the title ternary system nor on the solubilities in the binary subsystem TAME-W. Therefore we proceeded to the experimental determination of the equilibria mentioned.

EXPERIMENTAL

Preparation of pure substances. TAME was synthesized by the reaction of methanol (A.R. grade, Lachema, Brno) with 2-methylbutan-2-ol (tert-amyl alcohol, BDH product) in diluted sulphuric acid by the method described by Evans and Edlund⁴ for the preparation of ethyl tert-butyl ether. The obtained raw product was twice washed with saturated aqueous CaCl₂ solution to remove alcohols, then repeatedly with water, the ether layer was separated, dried with CaCl₂ and then with sodium. The dry ether was rectified from sodium under reduced pressure (to prevent thermal decomposition of the ether) on a packed column (60 cm long, 3 cm inner diameter) filled with

Pyrex helices (3 mm diameter) at a reflux ratio of 15 : 1. The middle fraction (about 50%) was used for measurements.

Methanol (A.R. grade, Lachema, Brno) was distilled on a sixty-plate bubble-cup column. Then it was freed from water by drying with magnesium⁵ and distilled on a packed column as described above for TAME. Water used for measurements was redistilled, on adding potassium permanganate, in a quartz still and degassed by boiling off immediately before use. Physico-chemical constants of the TAME and MEOH used for measurements are given in Table I. Gas-chromatographic analysis of both the substances showed no impurities.

Apparatus and procedure. To determine the liquid-liquid equilibria, the method of direct measurement of tie-lines was used. A mixture of three substances (for the binary solubilities, of

TABLE I
Physical constants of pure substances

Substance	Density, g cm ⁻³	n_D	NBP, °C	Ref.
MEOH ^a	0.78662	1.3266	64.51	this work
	0.78652—0.78675	1.32652—1.32663	64.501—64.75	5—7
TAME ^b	0.77047	1.3883	—	this work
	0.7703	1.3885	86.3	4, 8
	—	1.38783	86.107	1
	0.77074	1.38848	86.428	2

^a Densities and refractive indices at 25°C; ^b at 20°C.

TABLE II
Liquid-liquid equilibrium in the system MEOH(1)-W(2)-TAME(3) at 20°C (concentrations in mass fractions)

Organic phase			Aqueous phase		
a'_1	a'_2	a'_3	a''_1	a''_2	a''_3
0.0000	0.0068	0.9932	0.0000	0.9870	0.0130
0.0215	0.0102	0.9684	0.2140	0.7715	0.0143
0.0216	0.0170	0.9614	0.2038	0.7808	0.0153
0.0554	0.0246	0.9201	0.3329	0.6364	0.0306
0.0588	0.0306	0.9106	0.3321	0.6428	0.0250
0.1425	0.0583	0.7991	0.4093	0.4876	0.1031
0.1547	0.0732	0.7721	0.4212	0.4594	0.1194
0.2048	0.1028	0.6923	0.4242	0.3783	0.1975
0.2422	0.1164	0.6414	0.4080	0.3244	0.2675
0.2562	0.1312	0.6126	0.3980	0.3113	0.2906

TAME and W only) of suitably chosen ratio of components was sealed into a glass ampoule along with a glass ball to ensure good emulsification of both phases, and a set of such ampoules of different compositions was rotated in a thermostat for about four hours at $20 \pm 0.02^\circ\text{C}$. After separating both phases, the samples were taken carefully by hypodermic syringes.

The samples of the ternary equilibrium phases were analysed by gas chromatography using a Chrom 4 chromatograph with a thermal-conductivity detector. The components were separated in a glass column, 120 cm long and 3 mm in diameter, packed with Chromosorb 102-80/100 with hydrogen as a carrier gas (flow rate $20\text{ cm}^3\text{ min}^{-1}$). To achieve a good separation of the mixtures, it was necessary to employ a temperature-programmed control: at 60°C W and MEOH were separated, then temperature was raised by $20^\circ\text{C}/\text{min}$ up to 160°C , and the TAME peak was detected. The accuracy of the mass fraction determination was estimated by repeated measurements of calibration samples, not to be worse than 0.01-0.02 units even at the concentration ends.

To establish the binary solubilities, it was desirable to choose a more accurate analytical method. The solubility of W in TAME was determined by titration by the K. Fischer method⁹. The solubility of TAME in W was measured densimetrically by using a DMA 60+602 densimeter (A. Paar, Austria). The apparatus was calibrated by a number of samples of known composition, and the solubility was determined from the calibration graph.

RESULTS AND DISCUSSION

Experimental data on the liquid-liquid equilibrium in the system MEOH(1)-W(2)-TAME(3) at 20°C are given in Table II along with the data for the binary system W-TAME. Concentrations are expressed as mass per cent. Fig. 1 illustrates the equilibrium behaviour of the system. It is evident that the system exhibits, under the given conditions, a closed binodal curve. The plait point (PP) was constructed by extrapolating the tie-line midpoints, and has the coordinates: 33.70 mass % MEOH, 20.30 mass % W and 46.00 mass % TAME.

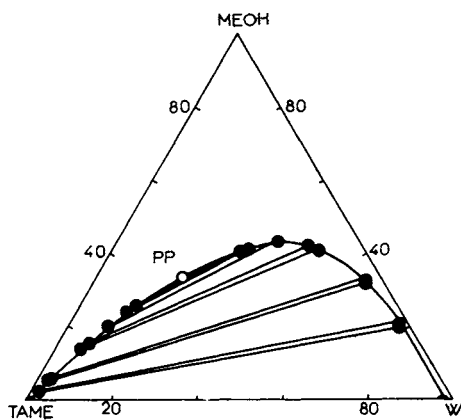


FIG. 1
Liquid-liquid equilibrium in the system MEOH(1)-W(2)-TAME(3) at 20°C (mass concentrations); PP extrapolated plait point

TABLE III

Correlation of the liquid-liquid equilibrium data in the system MEOH(1)-W(2)-TAME(3) by the Rod method¹⁰ (concentrations in mass per cent)^a

Data	MEOH		W		TAME		Mean dev.
	a'_1	a''_1	a'_2	a''_2	a'_3	a''_3	
Exp. tie-line	0.00	0.00	0.68	98.70	99.32	1.30	
Calc. tie-line	0.00	0.00	0.81	98.83	99.19	1.17	
Calc.-exp.	—	0.00	-0.13	-0.13	0.13	0.13	0.10
Exp. tie-line	2.15	21.40	1.02	77.15	96.84	1.43	
Calc. tie-line	2.15	19.96	1.17	78.23	96.68	1.81	
Calc.-exp.	—	1.44	-0.15	-1.08	0.16	-0.38	0.64
Exp. tie-line	2.16	20.38	1.70	78.08	96.14	1.53	
Calc. tie-line	2.16	20.02	1.17	78.16	96.67	1.82	
Calc.-exp.	—	0.36	0.53	-0.08	-0.53	-0.29	0.36
Exp. tie-line	5.54	33.29	2.46	63.64	92.01	3.06	
Calc. tie-line	5.54	33.28	2.10	63.40	92.36	3.32	
Calc.-exp.	—	0.01	0.36	0.24	-0.35	-0.26	0.24
Exp. tie-line	5.88	33.21	3.06	64.28	91.06	2.50	
Calc. tie-line	5.88	34.00	2.22	62.49	91.90	3.51	
Calc.-exp.	—	-0.79	0.84	1.79	-0.84	-1.01	1.05
Exp. tie-line	14.25	40.93	5.83	48.76	79.91	10.31	
Calc. tie-line	14.25	41.03	6.40	48.38	79.35	10.59	
Calc.-exp.	—	-0.10	-0.57	0.38	0.56	-0.28	0.38
Exp. tie-line	15.47	42.12	7.32	45.94	77.21	11.94	
Calc. tie-line	15.47	41.39	7.10	46.57	77.43	12.04	
Calc.-exp.	—	0.73	0.22	-0.63	-0.22	-0.10	0.38
Exp. tie-line	20.48	42.42	10.28	37.83	69.23	19.75	
Calc. tie-line	20.48	42.00	9.93	38.70	69.59	19.30	
Calc.-exp.	—	0.42	0.35	-0.87	-0.36	0.45	0.49
Exp. tie-line	24.22	40.80	11.64	32.44	64.14	26.75	
Calc. tie-line	24.22	41.06	12.11	32.55	63.67	26.39	
Calc.-exp.	—	-0.26	-0.47	-0.11	0.47	0.36	0.33
Exp. tie-line	25.62	39.80	13.12	31.13	61.26	29.06	
Calc. tie-line	25.62	40.25	13.03	30.25	61.35	29.50	
Calc.-exp.	—	-0.45	0.09	0.88	-0.09	-0.44	0.39
Mean		0.46	0.37	0.62	0.37	0.37	

^a Constants of correlation relation (2): $P = 0.3227$, $A_{11} = -8.397$, $A_{12} = -29.99$, $A_{13} = -88.55$, $A_{21} = -15.31$, $A_{22} = -49.69$, $A_{23} = -150.0$, $A_{31} = 11.70$, $A_{32} = 14.68$, $A_{33} = 65.29$.

Data Correlation

The experimental data were correlated by the Rod method¹⁰ which is, according to literature¹¹, more flexible than other correlation relations even though apparently based on a better thermodynamic basis.

The distribution coefficient of component i , m_i , is defined by the relation

$$m_i = a''/a', \quad (1)$$

where a denotes a mass concentration and '' and ' the second and first equilibrium phase. The distribution coefficient is, under a constant temperature and pressure, a function of concentration. With regard to the Gibbs–Duhem condition, it is then possible to write for a ternary system

$$\ln m_i = A_{i1}(a'_1 - P) + A_{i2}(a'_1 - P)^2 + A_{i3}(a'_1 - P)^3, \quad (2)$$

where A_{i1} , A_{i2} , A_{i3} are the parameters for individual components, and P is the parameter common to all components (and simultaneously the a_1 coordinate of the plait point) which must be determined from experimental data. The evaluation of the parameters was carried out by the method described in the original work¹⁰. The results of correlation and the comparison with experimental data are given in Table III. It is evident from the deviations that the Rod method represents the given system within the presumed experimental error.

From the point of view of thermodynamics, the equations developed for correlating the vapour–liquid equilibria can be employed as well to correlate the liquid–liquid equilibria. The methods and procedures how to obtain the parameters of the NRTL and UNIQUAC equations from liquid–liquid equilibrium data were described in detail by Sørensen and coworkers¹². Considering that a number of cases is given

TABLE IV

Comparison of the Rod correlation¹⁰ with the NRTL and UNIQUAC correlation¹² for the liquid–liquid equilibrium in the system MEOH(1)–W(2)–TAME(3) at 20°C (concentrations in mole per cent)

Method	$\Delta x'_1$	$\Delta x'_2$	$\Delta x'_3$	$\Delta x''_1$	$\Delta x''_2$	$\Delta x''_3$	Mean
Rod	—	1.41	1.27	0.64	0.73	0.18	0.70
NRTL	0.52	0.98	0.68	0.48	0.79	0.75	0.70
UNIQUAC	0.64	0.90	0.45	0.68	0.60	0.77	0.68

in the literature¹²⁻¹⁴ when the correlations mentioned yield bad results, fail completely or are worse¹¹ than the Rod correlation, it was interesting to carry out a comparison of these three correlations. The basis of the comparison were the data from Table I, with the difference that now the used set of data did not contain the binary solubilities but the extrapolated plait point was included. Besides, the concentrations are converted to molar per cent. The calculation of the NRTL and UNIQUAC parameters followed the procedure proposed by Sørensen¹², the number of evaluated parameters was in both cases six (for NRTL, $\alpha = 0.2$). Even though the principle of the Rod method and the NRTL and UNIQUAC equations is different, and the back calculation differs, too, (especially in that, the Rod correlation assumes x_1 to be a fixed value not subjected to any error) it is evident from Table IV that in the given case, all three methods provide practically the same representation of experimental data.

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