

INVESTIGATIONS ON THE VAPOUR—LIQUID EQUILIBRIUM OF BINARY HOMOAZEOTROPES

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While investigating the vapour—liquid equilibrium of multicomponent homoazeotrop systems, the isobar equilibrium circumstances of some systems, forming binary azeotropes, were thoroughly investigated. From the investigated systems the “heptane-pyridine”, the “heptane-*n*-butanol”, the “toluene-pyridine”, and the “toluene-*n*-butanol” form positive homoazeotropes, while the “pyridine-*n*-butanol” system forms a negative homoazeotrope.

During the course of these investigations the equilibrium and ebullio-metric measurements were completed by calculations; the aim of these calculations was to facilitate the interpolation of the measuring data and to prove the thermodynamic consistency of the values, found in experimental way. Before reviewing the method employed for investigation and the experimental data, the analytics of the individual systems are briefly summarized.

Analysis

The analysis of the systems “heptane-pyridine”, “toluene-butanol”, and “pyridine-butanol” could be the most precisely and the most simply carried out by measuring the refractive index, while in case of the “heptane-butanol” system the quantitative relations of the components, in the investigated mixture, were established by measuring the densities. Both the refractive index and the density proved to be linearly dependent on the composition of the investigated systems.

In the “toluene-pyridine” system the quicker performance of the analysis had to be based on the determination of another physical characteristic.

From the point of view of both accuracy and quickness, the measurement of the surface tension proved to be the most advisable. To measure the surface tension on apparatus modified by the authors[1] and based on the determination of the bubble pressure was employed. This apparatus is shown in Fig. 1.

In certain cases, in the systems containing pyridine, the absolute quantity of the pyridine was determined in an aqueous medium, with the object of

checking, by a titration performed in the presence of the compound-indicator dimethyl yellow—methylene blue [2].

The relative error of the determination was, in every case, lower than 1%, and the time of analysis was less than 15 minutes.

During the experiments C. P. reagents were used.

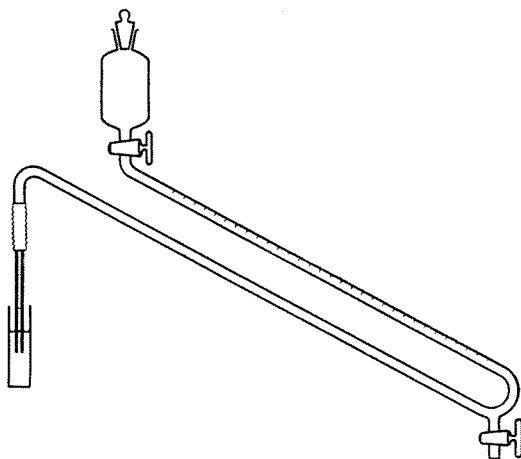


Fig. 1. Apparatus for measuring surface tension

Experimental instruments employed

In order to determine the equilibrium data OTHMER's modified apparatus was employed, the functioning of which was fully described in a previous publication [3]. This apparatus was devised for the investigation of the homogeneous and heterogeneous multicomponent systems, generally being the cause of numerous problems. During these investigations the apparatus functioned in a completely satisfactory way; therefore in the present case its use may be considered fully advisable.

The knowledge of the correct values of the boiling points, in the various mixtures, was necessary for the equilibrium computations employed, while correlating the equilibrium data; therefore the whole diagram giving the correlation between bubble points and compositions was determined by ebulliometric measurements.

In order to determine the correct composition of the azeotrope, in the case of the "heptane—pyridine" system the above mentioned two experimental methods were completed, even by differential-ebulliometric investigations. The principle of these investigations is as follows: while systematically changing the composition the temperature difference (Δt) between the boiling point and the dew point appearing after the establishment of the equilibrium state

is measured. Plotting this difference against the composition, in the case of pure components, as well as of azeotropes, a marked minimum is observed. With the aid of this measurement the boiling point of the azeotrope can be determined with a correctness of about 0,005° C, and the composition with any accuracy, because the components can be fed nearly in infinitesimally small portions.

The disadvantage of the method is in the fact that the stabilization of the equilibrium circumstances necessitates approximately a day; consequently the investigations should be restricted to as small as possible a range. The principle of these investigations and the developed apparatus are described in an other publication [4].

Experimental

The execution of the equilibrium measurements caused no difficulty, because the differences between the boiling points of the individual components were fairly small. Using compensated heating, during the measurements, the equilibrium was reached in about 50 minutes. In consequence of its dimensions our apparatus rendered the taking of samples even of larger quantities possible; therefore the equilibrium compositions were determined on basis of the results of numerous parallel analyses. Grouped according to the individual systems, the measuring data are shown in Tables I—V; the data of the Tables are summarized in Figs. 2—6.

The dew point diagrams determinable when knowing the bubblepoint diagrams of the mixtures, as well as the equilibrium data, are also shown in the above-mentioned figures.

With the object of controlling the reliability of the experimental data, the relation between the logarithms of the activity coefficients calculable from the measuring results and the corresponding composition are graphically illustrated in the co-ordinate system $\frac{\log \gamma_i}{x_j^2}$ against x_i .

This method of representation is essentially an examination according to the 3 suffix Margules equations which relates to thermodynamic consistency [5]. Transporting the well-known Margules equation

$$\log \gamma_i = x_j^2 [A_{ij} + 2 x_i (A_{ji} - A_{ij})] \quad (1)$$

on the afore-said diagram a straight line is obtained which intersects the ordinate at the point $A_{ij}(x_i = 0)$ and the slope of which amounts to the double of the corresponding Margules constants.

As shown in Fig. 7, the control of the measuring data performed by Margules' above-mentioned method yielded satisfactory results, and at the same time it made possible the quick and exact determination, in graphical way of the binary Margules constants; this method of determination can be essentially more easily carried out than other known methods.

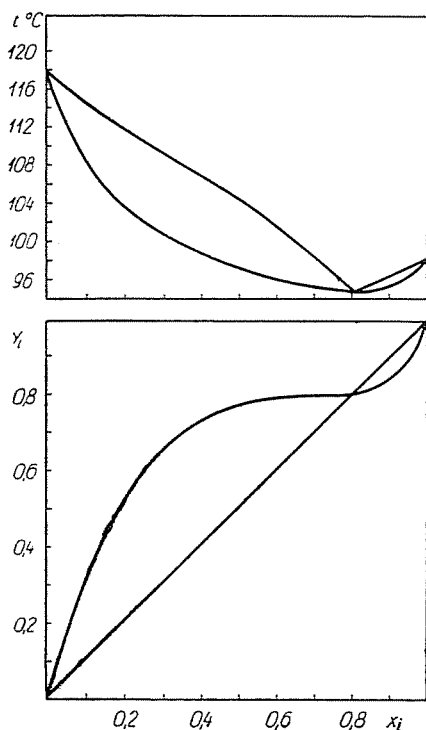


Fig. 2. Vapour—liquid equilibrium of the heptane-butanol system

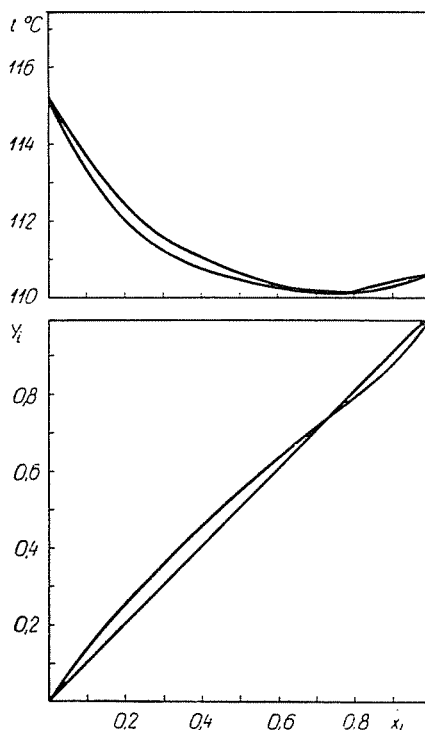


Fig. 3. Vapour—liquid equilibrium of the toluene-pyridine system

While representing the diagrams, in every case the values calculated from the azeotropic composition were considered decisive in regard to the slope of the straight lines and the intersection with the ordinate. Part of the data relating to the azeotrope were available and part of them were obtained as the results of our own measurements [6].

Only in the case of the "heptane-pyridine" system there was found a considerable deviation which also exceeded the experimental limit of error; from the regularity of the deviations, the conclusion can be drawn that a measuring error is out of question and the cause of the deviations is the characteristic asymmetry of the system, proved by the negative sign of the constant A_{ij} , too.

In such cases a better approximation can be reached by employing the equations of a higher index-number; in the present case, however, their use did not seem to be advisable, because the constants of these equations may not be employed in the calculations performed by the 3 index equations relating to the ternary and quaternary systems already mentioned in the prefatory part.

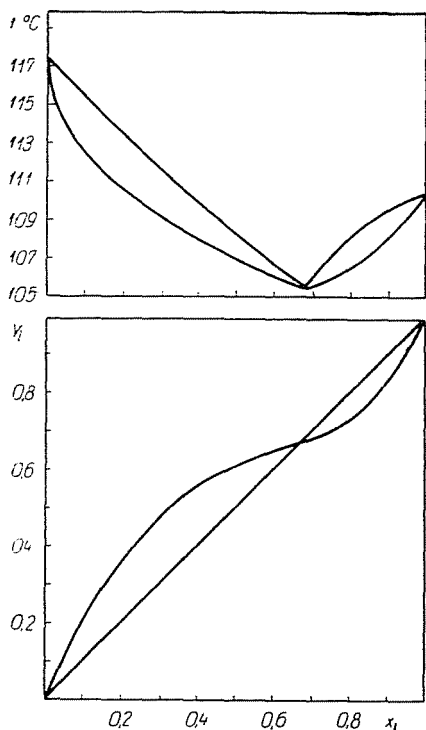


Fig. 4. Vapour—liquid equilibrium of the toluene-butanol system

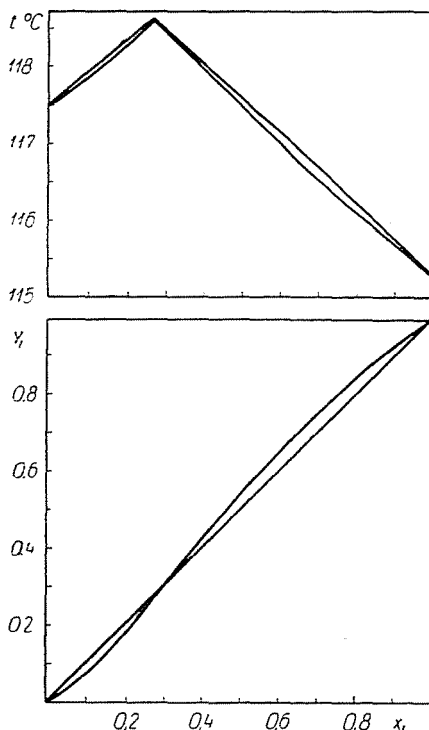


Fig. 5. Vapour—liquid equilibrium of the pyridine-butanol system

Table I

Equilibrium data of the "heptane-butanol" system

x_1	x_2	y_1	y_2	t
0,111	0,889	0,315	0,685	109,2
0,250	0,750	0,594	0,406	102,0
0,435	0,565	0,726	0,274	98,0
0,516	0,484	0,770	0,230	97,1
0,789	0,211	0,789	0,211	94,2
0,915	0,085	0,839	0,161	94,7

The BLACK method suggested to demonstrate the confusions due to the contingent molecule association [7] could not be employed because, in consequence of the negative sign of the logarithms of the activity coefficients, the plotting of the curve $(\log \gamma_i)^{0.5}$ against $(\log \gamma_j)^{0.5}$, was not possible.

The result of such computations carried out in the case of the "toluene-pyridine" system analogous to the "heptane-pyridine" system proved that the curvature of the curve obtained, referring to the degree of association,

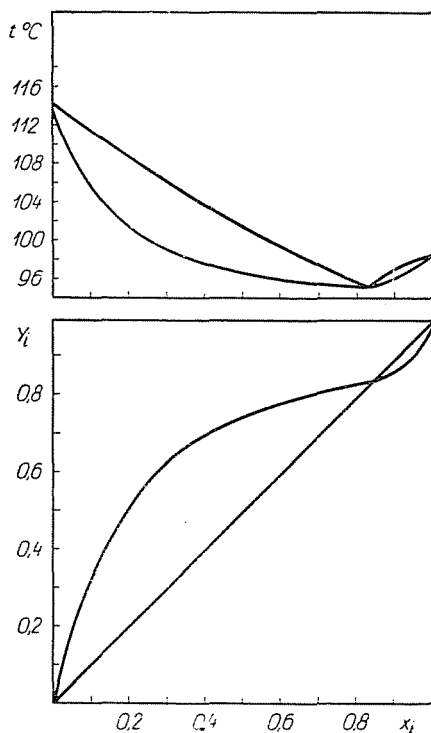


Fig. 6. Vapour—liquid equilibrium of the heptane-pyridine system

Table II
Equilibrium data of the "toluene-pyridine" system

x_i	x_j	y_i	y_j	t
0,084	0,916	0,111	0,889	113,7
0,240	0,760	0,290	0,710	111,8
0,412	0,588	0,468	0,532	110,8
0,626	0,374	0,652	0,348	110,3
0,808	0,192	0,808	0,192	110,2
0,932	0,068	0,928	0,072	110,4

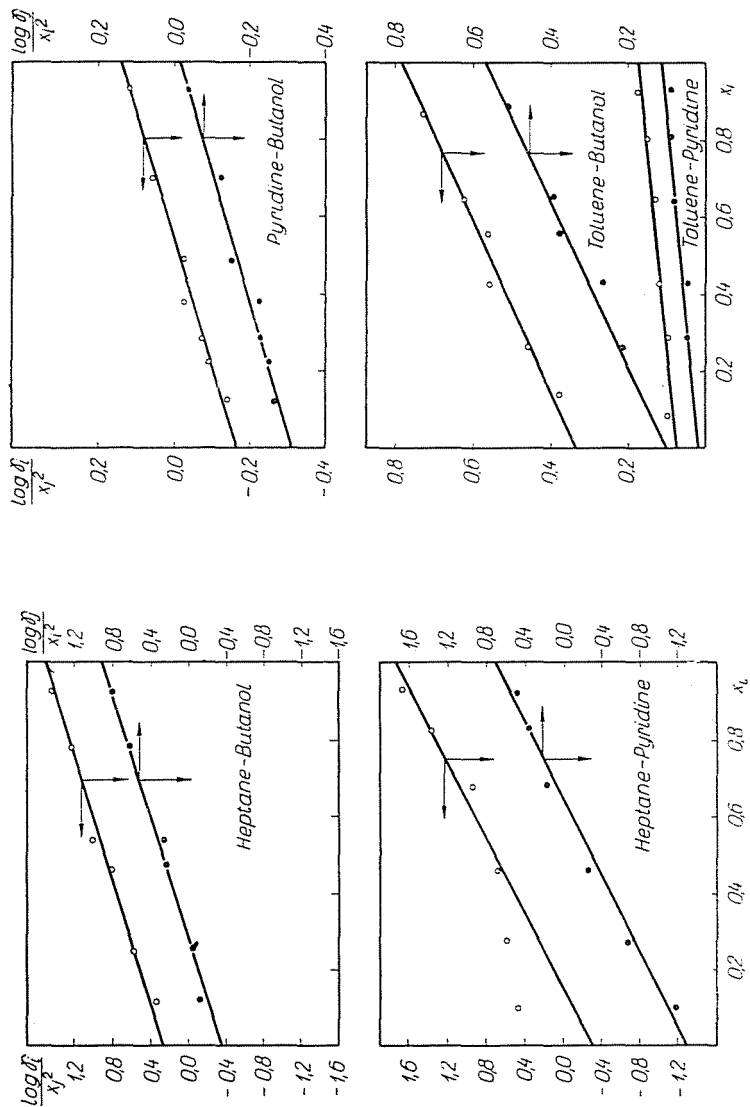


Fig. 7. Checking equilibrium data for thermodynamic consistency

is very insignificant (see Fig. 8). Consequently, also in case of the system "heptane-pyridine" system the deviations could presumably be explained, rather by the anomalous decrease of the hetero-molecular attractive forces, than by association.

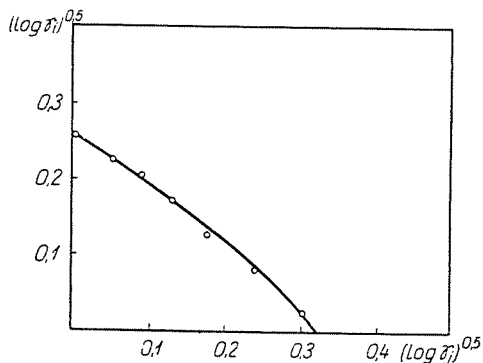


Fig. 8. Checking the vapour—liquid equilibrium in the toluene-pyridine system

The MARGULES constants suitable for describing the vapour—liquid equilibrium of the individual systems and determined in the above-mentioned manner are shown in Table VI.

Table III
Equilibrium data of the "toluene-butanol" system

x_i	x_j	y_i	y_j	t
0,125	0,875	0,262	0,738	112,3
0,258	0,742	0,440	0,560	109,6
0,425	0,575	0,572	0,428	107,5
0,576	0,424	0,631	0,369	206,0
0,679	0,321	0,679	0,321	105,5
0,869	0,131	0,790	0,210	108,0

Table IV
Equilibrium data of the "pyridine-butanol" system

x_i	x_j	y_i	y_j	t
0,113	0,887	0,096	0,904	117,9
0,208	0,792	0,198	0,802	118,4
0,276	0,724	0,276	0,724	118,7
0,490	0,510	0,522	0,478	117,7
0,702	0,298	0,742	0,258	116,7
0,922	0,078	0,931	0,069	115,6

Table V
Equilibrium data of the "heptane-pyridine" system

x_i	x_j	y_i	y_j	t
0,110	0,890	0,360	0,640	106,0
0,275	0,725	0,606	0,394	100,0
0,431	0,569	0,713	0,287	97,6
0,680	0,320	0,795	0,205	96,0
0,831	0,169	0,831	0,169	95,6
0,929	0,071	0,890	0,110	96,9

Table VI
Margules constants of the binary systems

System	A_{ij}	A_{ji}
Heptanol-butanol	0,292	0,912
Toluene-pyridine	0,071	0,123
Toluene-butanol	0,338	0,571
Pyridine-butanol	—0,158	—0,003
Heptane-pyridine	—0,290	0,757

For the sake of completeness it may be mentioned that in the case of the "heptane-pyridine" system an appropriate approximation is given by the equations only in the vicinity of the azeotropic point.

Signs employed

- t bubble point
- Δt difference between boiling point and dew point
- x_i molar fraction of the more volatile component in the liquid phase
- x_j molar fraction of the less volatile component in the liquid phase
- y_i molar fraction of the more volatile component in the vapour phase
- y_j molar fraction of the less volatile component in the vapour phase
- A_{ij} and A_{ji} constants of the binary 3 index Margules equation
- γ_i activity coefficient of the more volatile component
- γ_j activity coefficient of the less volatile component.

Summary

The vapour—liquid equilibria of five binary homoazeotropes were experimentally determined and the experimental data checked by computations.

During the computations, with the object of determining the binary Margules constants a graphical method which was easy to perform has been employed, thus ensured due precision, and directly yielding results from single measuring data. It has been established that the equilibria of the "heptane-butanol", "toluene-butanol", "toluene-pyridine", and "pyridine-butanol" systems can be satisfactorily described by the 3 suffix Margules equation, while in the case of the "heptane-pyridine" system the method of computation is not suitable for reproducing the experimental data.

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