

VAPOUR-LIQUID EQUILIBRIUM IN THE WATER(1)-MORPHOLINE(2) SYSTEM AT THE PRESSURES OF 50 AND 75 kPa*

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Vapour-liquid equilibrium in the water(1)-morpholine(2) system was determined experimentally at the pressures of 50 and 75 kPa. The data were correlated by the Redlich-Kister equation. The dependence of the excess Gibbs free energy on temperature was expressed by a linear dependence of the first parameter of the two-parameter equation on the reciprocal absolute temperature.

The water-morpholine system represents an industrially interesting binary system. Equilibrium data at the pressure of 101.325 kPa were measured by Palczewska-Tuliniska and coworkers¹. Since the separation under different pressures is considered in industrial practice, the data in a wider pressure (and temperature) range are required. Determination of the data on further pressure levels and finding the relations for the pressure and temperature correlation is a subject of this work.

EXPERIMENTAL

Substances used. Distilled water was redistilled after adding KMnO_4 in an all-quartz still. Morpholine was dried with KOH, distilled, and, on adding sodium, redistilled on a 40 plate bubble-cup column. A middle fraction with $T_{\text{NBP}} = 401.95 \text{ K}$ (401.50, ref.¹; 402.09, ref.²), $n_{\text{D}}^{20} = 1.45445$ (1.4542, ref.³; 1.45478, ref.¹), $d_4^{20} = 1.00055$ (1.00047, ref.³) was used for the measurements.

Apparatus. Vapour-liquid equilibrium was determined in an equilibrium recirculation still of the Dvořák-Bouplík type⁴ which was connected to a pressure unit maintaining the pressure with the accuracy of $\pm 0.05 \text{ kPa}$ in the pressure range of 10–100 kPa. Temperature was measured by calibrated mercury thermometers allowing to determine temperature with the accuracy of $\pm 0.005 \text{ K}$. The pressure in the apparatus was established indirectly from boiling point of water in the ebulliometer also connected to the pressure unit. The equilibrium composition of binary mixtures was determined by means of refractive index measured by an Abbe refractometer with the accuracy of ± 0.0001 . The dependence of refractive index on water mole fraction, x_1 , was expressed by the relation

$$n_{\text{D}}^{20} = 1.3329x_1 + 1.45445(1 - x_1) + x_1(1 - x_1) \cdot [0.04964 - 0.04636(2x_1 - 1) + 0.00607(2x_1 - 1)^2], \quad (1)$$

* Part C in the series Liquid-Vapour Equilibrium; Part XCIX: This Journal 51, 194 (1986).

TABLE I
Vapour-liquid equilibrium in the water(1)-morpholine(2) system at the pressure of 50 kPa.
 $C_0 = 0.118$, $C_1 = -0.270$

x_1	y_1	$t, ^\circ\text{C}$	Δx_1	Δy_1	$\Delta p, \text{kPa}$	$\Delta t, ^\circ\text{C}$
0.0811	0.1740	101.6010	0.0160	-0.0072	-0.0118	0.001
0.1085	0.2939	99.2960	-0.0117	0.0091	-0.1226	0.034
0.1645	0.3427	98.1110	0.0061	0.0005	-0.3030	0.084
0.2455	0.4511	95.1080	-0.0040	-0.0006	0.2655	-0.075
0.3511	0.5681	92.9760	-0.0083	0.0098	-0.0422	0.013
0.3825	0.5815	92.4260	-0.0016	0.0012	0.0342	-0.010
0.5135	0.6856	89.7760	-0.0006	-0.0046	0.3246	-0.097
0.6848	0.8203	87.1160	0.0024	-0.0010	-0.1121	0.036
0.7173	0.8409	86.6660	0.0048	-0.0020	-0.2293	0.070
0.8084	0.9073	84.9660	0.0021	0.0021	-0.2442	0.076
0.8768	0.9495	83.6260	0.0002	0.0041	-0.1680	0.053
0.8954	0.9586	83.2660	0.0002	0.0035	-0.1379	0.044
0.9364	0.9761	82.4110	-0.0006	0.0012	0.0049	-0.002
0.9497	0.9820	82.2510	0.0002	0.0017	-0.0618	0.021
0.9664	0.9865	81.9960	0.0012	-0.0003	-0.0793	0.025

TABLE II
Vapour-liquid equilibrium in the water(1)-morpholine(2) system at the pressure of 75 kPa.
 $C_0 = 0.205$, $C_1 = -0.185$

x_1	y_1	t	Δx_1	Δy_1	$\Delta p, \text{kPa}$	$\Delta t, ^\circ\text{C}$
0.0811	0.1758	113.6710	0.0165	-0.0087	0.1285	-0.021
0.1834	0.3427	109.1010	0.0208	-0.0168	0.1905	-0.034
0.2242	0.4458	107.3510	-0.0010	0.0060	-0.4368	0.077
0.2883	0.5115	105.2310	-0.0023	0.0016	0.0549	-0.010
0.3736	0.5928	102.7760	-0.0065	0.0003	0.5954	-0.115
0.4287	0.6370	101.6110	-0.0054	-0.0006	0.6234	-0.113
0.5135	0.6949	100.1910	0.0007	-0.0048	0.3381	-0.065
0.6899	0.8211	97.4060	0.0051	-0.0023	-0.3927	0.076
0.7173	0.8398	96.6710	0.0027	-0.0035	-0.0373	0.008
0.8084	0.9042	95.2660	0.0018	0.0031	-0.4309	0.084
0.8792	0.9457	93.8560	-0.0004	0.0032	-0.1557	0.031
0.8983	0.9554	93.7460	0.0020	0.0041	-0.4628	0.096
0.9385	0.9747	92.9160	0.0006	0.0025	-0.2250	0.045
0.9521	0.9803	92.6870	0.0008	0.0018	-0.2065	0.043
0.9816	0.9923	92.4240	0.0035	0.0017	-0.5263	0.102

whose constants were found by the least-squares method from the values of refractive index of 20 synthetic samples. The standard deviation of the refractive index determination from Eq. (1) has amounted to 0.0004. The form of the index curve causes that the composition determination has not the same accuracy through all the concentration range; it is sufficiently accurate for mixtures with high morpholine concentration, however, less accurate (approximately 1 mole %) for mixtures with high water concentration.

RESULTS AND DISCUSSION

The experimental equilibrium data determined at pressures 50 and 75 kPa are given in Tables I and II, where x_1 and y_1 denote mole fraction of water in the liquid and vapour phases, respectively, and t temperature ($^{\circ}\text{C}$).

The measured data were correlated by the Redlich-Kister two-constant equation. For activity coefficients we then get

$$\begin{aligned}\ln \gamma_1 &= x_2^2 [C_0 + C_1(3x_1 - x_2)], \\ \ln \gamma_2 &= x_1^2 [C_0 + C_1(x_1 - 3x_2)].\end{aligned}\quad (2)$$

The constants C_0 and C_1 were evaluated by the maximum likelihood method; the procedure is described in detail in ref.⁵. The following estimates were used for experimental errors: the error in the liquid and vapour phase composition 0.001, in temperature 0.05 $^{\circ}\text{C}$, and in pressure 0.1 kPa. The saturated vapour pressures of pure substances were calculated from the Antoine equation

$$\log P^0(\text{kPa}) = A - B/[C + t(^{\circ}\text{C})].\quad (3)$$

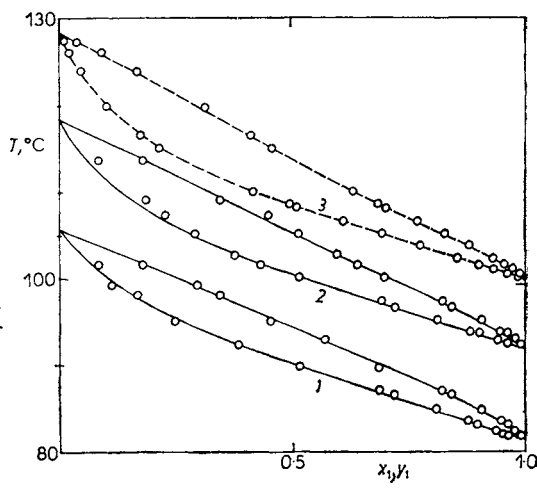


FIG. 1
Vapour-liquid equilibrium in the water(1)-morpholine(2) system at the pressures of 50 kPa (1), 75 kPa (2), and 101.325 kPa (3). The curves calculated from Eq. (2) with constants $C_{00} = -1.480$, $C_{01} = 4.291$, and $C_1 = -0.235$

The used values A , B , C for water, $A = 7.04360$, $B = 1636.909$, $C = 224.920$ and for morpholine, $A = 6.22214$, $B = 1410.227$, $C = 206.117$ were taken from ref.¹. The virial coefficients (for corrections for the vapour phase nonideality) were determined by estimation methods⁶. To represent the dependence of vapour-liquid equilibrium on pressure (and consequently also on temperature), the data at 50 and 75 kPa along with the data from ref.¹ at 101.325 kPa were correlated by the relation with a temperature-dependent constant C_0 ,

$$C_0 = C_{00}/T + C_{01}, \quad (4)$$

where T is the boiling point (K) of pure water at the given pressure. For C_{00} , C_{01} , and C_1 we have

$$C_{00} = -1480, \quad C_{01} = 4.291, \quad \text{and} \quad C_1 = -0.235.$$

The equilibrium curves for 50, 75, and 101.325 kPa, as determined on the basis of relations (2) and (4), are plotted in Fig. 1 and compared with the experimental data. Good agreement of all the sets can be seen with the exception of two concentrations of morpholine at the pressure of 75 kPa when the deviation of calculated and experimental points somewhat increased in comparison with the independent data correlations at single pressures. It follows from dependence (4) and the values C_{00} , C_{01} , and C_1 that the system is relatively little nonideal; the nonideality increases mildly with pressure.

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