

VAPOR LIQUID EQUILIBRIUM DATA FOR SYSTEMS CONTAINING MORPHOLINE

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ABSTRACT

Results of experimental investigation on the binary mixtures morpholine / methanol (at 74.2 and 30.1 kPa) and morpholine / 2-propanol (at 70.0 and 30.0 kPa) are reported: P, T, x, y data are checked for consistency and then used to calculate parameters of excess Gibbs energy (G^E) models.

INTRODUCTION

Precise determination of excess Gibbs energy as a function of temperature and pressure over the whole composition range are necessary in order to understand the nature of interactions between the molecules in a liquid mixture. In addition, experimental data are of great importance for industrial processes: such data are required for the design of separation processes involving morpholine, which is of particular interest in the petrochemical industry due to its high efficiency in the extraction of monocyclic aromatic hydrocarbons from petroleum products.

Experimental vapor-liquid-equilibrium (VLE) data of morpholine / alcohol systems are reported in the literature only for the system morpholine / ethanol (Palczewska et al., 1980), but no measurements are available for mixtures containing other alcohols.

As about other experimental information, excess volume data for the system morpholine / methanol are reported by Awward et al. (1988). Excess volume data for five systems morpholine / alcohol have recently been measured by Pettenati et al. (1989); viscosities and excess enthalpy for the same systems have been measured by Alessi et al. (1989). This extensive experimental work will provide useful information on morpholine / alcohol systems which should be used in the understanding of some biotechnological processes.

EXPERIMENTAL SECTION

Materials:

The alcohols used in the present study were HPLC grade supplied by Fluka. 2-propanol was used as received with a stated purity > 99.9 mole per cent. Morpholine was dried over fresh sodium after one hour refluxing and fractionated through a 40TP column to collect the main fraction boiling over .005 K range. Methanol was distilled two times over CaH₂ in a 2 m column packed with glass helices (estimated number of stages: 150) by using different reflux ratio. The purity of morpholine and methanol checked after purification via density measurements was better than 99.7 %. Special attention was paid to prevent from water as contamination and oxidation of the chemicals after their purification. Alcohols were stored in bottles over 3A molecular sieves; morpholine in nitrogen atmosphere. Nitrogen and bidistilled water were used for the density-meter calibration. The purity of water was higher than 99.9 mole per cent; that of nitrogen higher than 99.9999 mole per cent. The purity of n-hexane, n-heptane and methyl-cyclohexane used for the refractometer calibration was better than 99.9 mole per cent. Densities and refractive index of the pure components, at 298.15 K and atmospheric pressure, were measured before preparing the mixtures and compared with literature values to check their purity (see Table 1).

Density measurements:

A digital density-meter (Anton Paar DMA 602H - DMA 60) was employed for the density determination of the pure components (Pettenati et al, 1989). The density determination is based on the variation of the natural frequency of a tube oscillator filled with sample liquid with respect to the tube filled with nitrogen.

TABLE 1

Comparison between measured and literature data for pure components: (this work)^a, (extrapolated values from Riddick, 1970)^b, (Riddick, 1970)^c, (Reid, 1977)^d, (Palczewska, 1980)^e, (Mc Garry, 1985)^f.

Component	d (Kg/m ³) (298.15 K)	n _D (288.15 K)	Boiling Temperature (K)	
			70 kPa	30 kPa
morpholine	995.23 ^a	1.45719 ^a	389.13 ^a	364.24 ^a
	995.47 ^c	1.45733 ^c	389.22 ^d	364.23 ^d
			389.14 ^e	364.24 ^e
methanol	786.40 ^a	1.33061 ^a	328.56 ^a	309.61 ^a
	786.64 ^c	1.33057 ^c	328.58 ^f	309.63 ^f
ethanol	785.00 ^a	1.36350 ^a	342.32 ^a	323.55 ^a
	785.04 ^c	1.36345 ^b	342.36 ^f	323.53 ^f
2-propanol	780.82 ^a	1.37940 ^a	346.37 ^a	327.87 ^a
	781.26 ^c	1.37920 ^b	346.38 ^f	327.88 ^f

Refractometry:

The refractive indexes (n_D) of pure components and mixtures were measured with an Abbe type 3 ATAGO refractometer at 288.15 K and atmospheric pressure. The solutions were prepared by using a Mettler balance (Mod. H-31) and air-tight stoppered bottles.

Equilibrium measurements:

Vapor pressure of pure components and of mixtures were measured in a Świątosławski type dynamic ebulliometer (Świątosławski, 1945, Świątosławski et al., 1957, Malanowski et al., 1982) with recycling liquid and vapor phases. The temperature was detected with a digital precision platinum resistance thermometer (Systemtechnik, Model S-1220), calibrated against a platinum resistance thermometer Pt 25 (Rosemount mod. 162 CE) and checked at the water triple point. A quartz Bourdon tube pressure gauge (Battara, model 100) was employed to measure the pressure. The pressure was maintained at its set point by an electronic pressure controller (Battara Model 101).

The composition of the samples withdrawn from the still was determined by precision refractometry at 288.15 K using the calibration based on synthetic mixtures.

Inaccuracy:

Sensitivity and inaccuracy of the instruments used and measurements made are summarized in Table 2. The inaccuracy of the system results from calibration, fluctuations, sample handling etc. Table 1 reports the comparison between the pure component properties measured in this work and the literature data, the agreement is satisfactory.

TABLE 2
Sensitivity (S) and inaccuracy (I) of instruments and systems.

		S	I
vapor liquid equilibrium			
temperature	T, K	0.0005	0.02
pressure	P, kPa	0.0005	0.02
composition, liquid	x	0.0001	0.002
composition, vapor	y	0.0001	0.003
composition, feed	z	0.00005	0.001
refractometry			
temperature	T, K	0.001	0.04
composition	x	0.00005	0.001
density			
temperature	T, K	0.010	0.04
density	d, kg/m ³	0.001	0.1

The initial composition loaded into the still has been determined by weight, using a Mettler balance (Mod. H-31) and air-tight stoppered bottles. The more volatile component was directly poured into the bottle. The charged bottle was closed and weighed. The second component was injected into the bottle through the stopper by means of a syringe. This procedure hindered any vapor loss, contamination and oxidation. The sample was later transferred in the still by means of a syringe.

TABLE 3
Experimental results for the morpholine (1) / methanol (2) system.

P/kPa	T/K	X ₁	Y ₁
74.20	390.79	1.0000	1.0000
74.20	386.96	.9413	.8270
74.20	383.07	.8803	.6755
74.20	378.53	.8192	.5477
74.20	376.33	.7707	.4614
74.20	369.11	.6585	.3003
74.20	357.15	.4599	.1176
74.20	353.38	.3963	.0801
74.20	341.66	.2124	.0159
74.20	339.95	.1798	.0103
74.20	335.35	.1107	.0030
74.20	329.88	.0000	.0000
30.10	364.33	1.0000	1.0000
30.10	359.95	.9338	.7943
30.10	356.74	.8819	.6606
30.10	353.06	.8212	.5293
30.10	348.69	.7447	.3950
30.10	342.21	.6282	.2427
30.10	333.78	.4747	.1122
30.10	329.68	.3922	.0671
30.10	326.37	.3391	.0452
30.10	319.12	.2127	.0130
30.10	316.24	.1548	.0057
30.10	312.68	.0886	.0015
30.10	309.62	.0000	.0000

RESULTS AND CORRELATION

Vapor pressure of pure liquids:

Vapor pressure of pure liquids were measured for the temperature ranging from 300 up to 400 K. The vapor pressure of alcohols were in good agreement (less than 1% deviation from the literature data (Mc Garry, 1983)) while for morpholine a disagreement was found among data reported by different authors, probably due to the purification methods used. Therefore the experimental data were used to determine parameters in the Antoine equation using a maximum

likelihood procedure. The form of the Antoine equation used is:

$$\log_{10} P^{\circ}(\text{mmHg}) = A - B/(t(^{\circ}\text{C}) + C) \quad (1)$$

Antoine's parameters obtained are: $A = 6.949150$; $B = 1320.234$; $C = 196.227$. The data obtained are in very good agreement with those calculated by using the parameters reported in Reid et al., (1977).

The comparison of the vapor pressure data measured in this work and the literature data for the components considered is given in table 1 as two boiling temperatures for two pressure measured.

Refractometry:

Refractive index measurements for the binary systems investigated have been correlated by means of the Redlich Kister polynomials and the correlation was used to determine the composition of the withdrawn condensed vapor samples in the VLE measurements.

Vapor - liquid equilibrium data:

Since the assumption that the composition of the liquid phase is identical to the feed composition loaded in the still is acceptable only for close boiling mixtures, a procedure based on the correction factor (f) is applied in this work (Rogalski et al., 1977). In particular, we have determined the f factor by measuring a thermodynamically consistent and well-measured system (benzene / acetonitrile) whose adjustable parameters were known. The actual data were reduced with the simultaneous adjustment of the f factor in order to obtain adjustable parameters as close as possible to the literature values for the same system in the same experimental conditions. The model used in the data reduction was the UNIQUAC equation, and the parameters obtained were ($A_{12} = 249.36$ K and $A_{21} = -53.95$ K). The f factor obtained ($f = 0.110$) agrees fairly well with the value given by Rogalski et al., (1977). In fact, the two ebulliometers are identical, and the systems considered in the two investigations are in the range of relative volatility for which the f factor is considered constant.

The liquid mole fraction calculated through the f factor and those determined by direct sampling agree within the experimental error for the test system considered. The experimental liquid composition data reported in this work are those calculated by using the f factor, while the vapor composition are analyzed after sampling. This method allows the measurement of the complete data set (P , T , x and y) minimizing the perturbation of the equilibrium conditions due to sampling.

Tables 3, and 4 report the measured pressure (P), temperature (T), liquid and vapor composition (x , y in mole fractions) for the systems investigated. Figure 1 shows a comparison between the literature data by Palczewska et al., 1980, (continuous line) and data measured in this work (\odot) for the system morpholine / ethanol: the agreement is good.

Consistency of VLE data:

With the redundant information of T , P , x , y data the consistency of the experimental results can be checked provided vapor phase behavior is known. We

have checked the data for consistency by the direct use of the maximum likelihood (ML) method (Skjold-Jorgensen, 1983) since this test is at least as informative as the simple Barker's method. The experimental uncertainties used in the ML consistency test are those listed in table 1. The root mean square deviations, reported in table 5 and obtained with the UNIQUAC 3 parameter equation, are always of the same order of magnitude of the inaccuracies given in Table 2.

Vapor phase imperfections were taken into account by using the virial equation of state truncated after the second term. Second virial coefficients of the pure components and cross coefficients were calculated according to the correlation of Hayden and O'Connell (1975). The liquid molar volume is calculated by using the Rackett equation and the Poynting correction is calculated by considering the liquid molar volume independent of pressure.

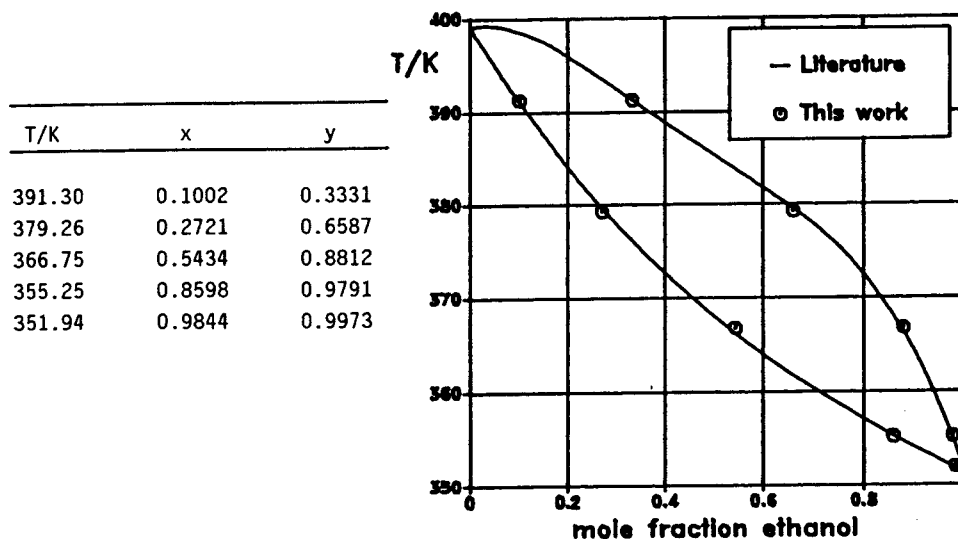


FIGURE 1
Comparison between the literature data of Palczewska et al., 1980 (line) and data measured in this work (○) for the morpholine - ethanol system at 101.32 kPa.

For practical application it is convenient to use excess Gibbs energy models for the representation of the experimental data. Binary parameters of four G^E models (Three-Suffix Margules, Wilson, NRTL and UNIQUAC) (Prausnitz et al., 1980; pag. 211-217) were fitted to the experimental data. The data reduction was performed minimizing the following objective function (Prausnitz

et al., 1980; pag.96-109), based on the ML principle:

$$F = \sum_i \left(\frac{(p^E - p^C)_i^2}{\sigma_{p_i}^2} + \frac{(T^E - T^C)_i^2}{\sigma_{T_i}^2} + \frac{(x_1^E - x_1^C)_i^2}{\sigma_{x_{1i}}^2} + \frac{(y_1^E - y_1^C)_i^2}{\sigma_{y_{1i}}^2} \right) \quad (2)$$

TABLE 4
Experimental results for the morpholine (1) / 2-propanol (2) system.

P/kPa	T/K	X ₁	Y ₁
70.00	389.13	1.0000	1.0000
70.00	384.32	.9236	.7861
70.00	377.75	.8102	.5646
70.00	373.95	.7252	.4409
70.00	369.93	.6298	.3292
70.00	365.95	.5345	.2380
70.00	361.90	.4281	.1549
70.00	357.92	.3241	.0910
70.00	357.92	.2678	.0634
70.00	352.98	.1959	.0356
70.00	350.08	.1204	.0153
70.00	348.32	.0659	.0061
70.00	346.37	.0000	.0000
30.00	364.24	1.0000	1.0000
30.00	360.48	.9225	.7960
30.00	355.46	.8092	.5738
30.00	351.48	.7179	.4365
30.00	348.26	.6299	.3283
30.00	344.73	.5351	.2327
30.00	341.35	.4381	.1543
30.00	337.89	.3342	.0899
30.00	335.81	.2682	.0590
30.00	331.03	.1205	.0149
30.00	329.47	.0659	.0062
30.00	327.87	.0000	.0000

Table 6 reports the results of the fitting in terms of standard deviations in all the measured variables, according to the maximum likelihood principle. The value of $\hat{\sigma}^2$ is also reported because is considered the best overall measure of the goodness of fit in ML method (Cholinski et al., 1981). The definition of $\hat{\sigma}^2$ is:

$$\hat{\sigma}^2 = \frac{F_{\min}}{(n-m)} \quad (3)$$

The F_{\min} is defined as the value of the objective function (eq.2) at the minimum, $(n-m)$ is the number of degree of freedom. The numerical values of the binary interaction parameters for the different G^E models included in table 6 are reported in K for UNIQUAC, NRTL and Wilson models.

TABLE 5
Result of the consistency test for system containing morpholine: σ_i are the standard deviations.

Component 2	N	P/kPa	σ_p /kPa	σ_T /K	σ_x	σ_y
methanol	10	74.20	.0249	.0134	.0029	.0042
	11	30.10	.0044	.0063	.0033	.0012
2-propanol	11	70.00	.0211	.0184	.0039	.0045
	10	30.00	.0148	.0191	.0019	.0021

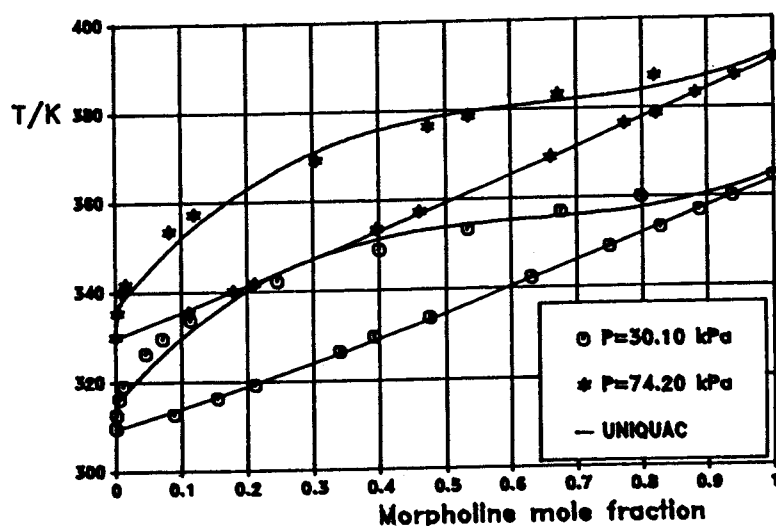


FIGURE 2
Experimental and calculated (UNIQUAC) data for the morpholine (1) - methanol system.

CONCLUSIONS

The systems measured show large deviations from ideality which can be directly deduced from figures 2 and 3. The systems can be classified as asymmetric with strong tendency to exhibit liquid phase association phenomena. This fact is evidenced by the calculated activity coefficients which are always less than one.

TABLE 6

Values of the coefficients of the correlation equations and standard deviations: component 1 is morpholine.

Component 2:	methanol		2-propanol	
	P=74.20 kPa	P=30.10 kPa	P=70.00 kPa	P=30.00 kPa
UNIQUAC - 2 parameters				
A_{12}/K	-209.05	-156.35	+20.325	+172.14
A_{21}/K	-62.9513	-106.47	-235.18	-318.578
$\bar{\sigma}$	3.161	1.902	4.7220	3.122
σ_p	0.0051	0.0044	0.0071	0.0139
σ_T	0.0134	0.0063	0.0184	0.0182
σ_x	0.0038	0.0033	0.0074	0.0036
σ_y	0.0060	0.0012	0.0057	0.0054
NRTL ($\alpha=0.20$) - 2 parameters				
A_{12}/K	+2151.6	+2044.2.	+1551.1	+1366.4
A_{21}/K	-1175.3	-1114.5	-933.95	-882.80
$\bar{\sigma}$	24.6	22.7	13.7	9.71
σ_p	0.0259	0.0011	0.0212	0.0350
σ_T	0.0789	0.0792	0.0607	0.0497
σ_x	0.0422	0.0387	0.0228	0.0143
σ_y	0.0138	0.0144	0.0114	0.0097
Wilson - 2 parameters				
A_{12}/K	+935.56	+116.321	-465.86	+412.80
A_{21}/K	-484.84	-338.15	+1394.4	-442.52
$\bar{\sigma}$	2.98	1.97	24.3	2.31
σ_p	0.0047	0.0046	0.036	0.0104
σ_T	0.0127	0.0066	0.1055	0.0134
σ_x	0.0033	0.0034	0.0380	0.0022
σ_y	0.0059	0.0011	0.0152	0.0047
Three-Suffix Margules - 2 parameters				
B_{12}	-1.6175	-1.7049	-0.6634	-0.7208
B_{21}	-0.4354	-0.5344	-0.1119	-0.3960
$\bar{\sigma}$	21.8	19.4	13.9	10.7
σ_p	0.0201	0.0425	0.0191	0.0320
σ_T	0.0582	0.0569	0.0531	0.0454
σ_x	0.0298	0.0254	0.0186	0.0132
σ_y	0.0368	0.0358	0.0241	0.0191

Furthermore, the activity coefficients at infinite dilution of morpholine are always less than those of the alcohols. Activity coefficients less than one and same relative trend were also observed by Palczewska et al. for the system ethanol - morpholine.

Correlations with G^E models are generally satisfactory as far as the use in chemical process design is concerned. The NRTL model gives the worse correlation, according to the results reported in table 6 in terms of overall standard deviations and deviations in x and y . This is due to the fixed value of the α parameter (0.20) used in the parameter estimation. Better results are obtained by considering α as adjustable parameters, but unreasonable values of such parameters are obtained. Satisfactory results are obtained by using UNIQUAC model. This is probably due to the modified q values used for the alcohols (Prausnitz et al., 1980). Some difficulties are also encountered during the parameter estimation procedure using Wilson equation and for the system morpholine - 2-propanol. The Margules equation shows large overall standard deviations and unrealistic standard deviation in T (0.05 K) and in mole fraction (1-4%).

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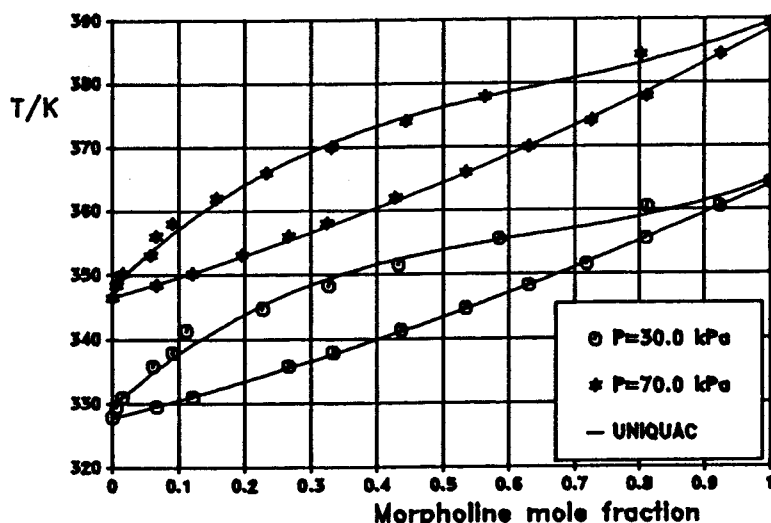


FIGURE 3
Experimental and calculated (UNIQUAC) data for the morpholine (1) - 2-propanol system.

GLOSSARY

A,B,C	Antoine constants (eq. 1)
A_{ij}	Model parameters (UNIQUAC, NRTL, Wilson), K
B_{ij}	Model parameters (Margules)
f	ebullimeter correction factor f
F	objective function (eq. 2)
m	number of model parameters
n	number of experimental data
T	Temperature, K
P	Pressure, kPa
p^0	Vapor Pressure of pure substances, kPa
x	liquid mole fraction
y	vapor mole fraction
$\hat{\sigma}$	overall standard deviation, (eq 3)
σ_T	temperature standard deviation, K
σ_p	pressure standard deviation, kPa
σ_x	liquid mole fraction standard deviation
σ_y	vapor mole fraction standard deviation

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