

## PHASE EQUILIBRIA IN THE METHANOL-CYCLOHEXENE SYSTEM

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The liquid-vapour equilibrium in the methanol-cyclohexene system at 740, 521.5, 340.5, and 231.8 Torr, the liquid-liquid solubility equilibrium curve and the temperature dependence of the saturated vapour pressure of cyclohexene were measured. The correlation of equilibrium data was performed for each data set separately by the Wilson and NRTL equations and simultaneously by a six-constant equation which expresses the composition and temperature dependence of the excess Gibbs free energy with satisfactory agreement between experimental and calculated data.

In relation to estimation of the possibility of isolation of nonaromatic compounds from the benzene fraction, the liquid-vapour equilibrium in the methanol-cyclohexene system was measured. Equilibrium data of this system do not also lose theoretical attractiveness as they supplement appropriately measurements in n-alcohols-benzene and n-alcohols-cyclohexane systems, which display such a strong nonideal behaviour that they are on the verge of the thermodynamic stability. As it was found during the experiments that the system exhibits a limited solubility region in the liquid phase, its boundary was established by determining the solubility curve. Finally, the temperature dependence of the saturated vapour pressure of cyclohexene was measured, which is necessary for correlating the equilibrium data and which has not been available with sufficient accuracy in the literature.

## EXPERIMENTAL

## Preparation of Pure Substances

*Methanol.* A mixture of methanol, A. R. grade, and the Grignard reagent was refluxed. The main portion of methanol was added into the boiling mixture and all was further heated for about 5 hours. The dried product was rectified on a 60-plate bubble cap column at the reflux ratio of 1 : 4. Its density and refractive index ( $d_4^{25} = 0.7866$ ;  $n_D^{20} = 1.3287$ ) agreed well with literature data<sup>1</sup>. The Fischer analysis showed the content of water lower than 0.0025 wt.%.

*Cyclohexene.* Cyclohexene was prepared by dehydration of cyclohexanol with concentrated  $H_2SO_4$ . The product was distilled off from the reaction mixture, shaken with a solution of ferric sulphate to remove peroxides, dried with  $CaCl_2$  and rectified on a column packed with stainless helices whose efficiency was about 100 theoretical plates at the reflux ratio of 1 : 2. The distillate,

which contained 0.009 wt.%  $H_2O$ , was mixed with a 20fold excess of  $CaH_2$  with respect to present  $H_2O$ , the mixture was again rectified on the same column and the middle fraction was taken off at an 1 : 5 reflux into ampules sealed with butadiene rubber stoppers. About 1/10 of the ampule content was occupied by the Nalsit A4 molecular sieves which were preliminarily activated for 10 hours at  $360^\circ C$  and simultaneously rinsed with dried nitrogen. The measured values of physico-chemical constants, n.b.p.  $83.01^\circ C$  and  $n_D^{20}$  1.4467, agree well with literature data<sup>1</sup> (n.b.p.  $83.2$ ;  $83.19^\circ C$  and  $n_D^{20}$  1.4467). The Fischer analysis showed 0.0019 wt.%  $H_2O$ .

### Apparatus

The liquid-vapour equilibrium was measured on a Gillespie still as modified by Otsuki and Williams<sup>2,3</sup>. The sampling of the vapour and liquid phases was by syringes from closures sealed with butadiene rubber packings. The pressure was adjusted and stabilized by a vacuum stand, which maintained the pressure in the equilibrium still with a 0.1 Torr accuracy. The temperature was measured by a platinum resistance thermometer, which was calibrated preliminarily at the triple point of water and at 14 values of pressure from the range between  $47^\circ C$  and  $99^\circ C$  in two parallelly connected equilibrium stills filled with redistilled water. The reference temperature was being determined by standard thermometers. Calibrating points obtained in this manner were smoothed by the least squares method using a quadratic interpolation. It may be assumed that this arrangement enables one to measure the temperature in the equilibrium cell of the recirculation still with an accuracy better than  $\pm 0.02^\circ C$ .

The saturated vapour pressure of cyclohexene was measured on a Swietosławski ebulliometer<sup>4</sup> connected to the same vacuum stand and the liquid-liquid equilibrium by the usual turbidity method.

### Determination of the Composition of Equilibrium Mixtures

The composition of equilibrium mixtures was determined refractometrically. Since the equilibrium behaviour is extremely sensitive to the water content, the measurements had to be performed in a dry box. The measured values, which covered the whole concentration range, were smoothed by the least squares method using a third-order polynomial. The composition dependence of the refractive index of the mixture is expressed by the relation

$$n_D^{20} = 1.4467 - 0.137970 w_1 + 0.024553 w_1^2 - 0.005065 w_1^3, \quad (1)$$

where  $w_1$  is the weight fraction of methanol in the mixture. The assumed accuracy of the determination is  $\pm 0.2$  wt.%.

## RESULTS

Saturated vapour pressures of cyclohexene are in Table I. Their temperature dependence was correlated by the Antoine equation whose constants were determined by minimizing the sum of squared deviations.

Liquid-vapour equilibrium data are in Table II. They were correlated by minimizing deviations of the logarithm of the ratio of activity coefficients expressed through the van Laar, Margules, and Scatchard third-order equations<sup>5</sup> and Wilson

TABLE I  
The Temperature Dependence of the Saturated Vapour Pressure of Cyclohexene

$t, ^\circ\text{C}$	16.39	19.65	22.31	25.08	27.35	30.90	34.86	39.22
$P, \text{Torr}$	60.0	69.6	78.8	89.6	99.2	115.6	137.1	164.3
$t, ^\circ\text{C}$	42.78	47.91	53.12	58.35	64.66	70.95	77.67	82.10
$P, \text{Torr}$	189.8	231.8	283.8	340.5	423.1	521.5	644.6	739.4

TABLE II  
Experimental Liquid-Vapour Equilibrium Data of the Methanol(1)-Cyclohexene(2) System

$x_1$	$y_1$	$t, ^\circ\text{C}$	$x_1$	$y_1$	$t, ^\circ\text{C}$
$P = 740.0 \text{ Torr}$					
0.0083	0.2677	72.14	0.4205	0.6064	55.52
0.0130	0.3247	69.80	0.4656	0.6098	55.47
0.0238	0.4093	65.84	0.5166	0.6127	55.39
0.0292	0.4488	63.79	0.5782	0.6163	55.36
0.0347	0.4901	61.62	0.6350	0.6188	55.35
0.0488	0.5215	59.97	0.6934	0.6238	55.35
0.0680	0.5454	58.53	0.7497	0.6318	55.36
0.0868	0.5604	57.67	0.7916	0.6414	55.44
0.1248	0.5774	56.78	0.8342	0.6554	55.78
0.1658	0.5868	56.25	0.8804	0.6847	56.36
0.2344	0.5950	55.81	0.9137	0.7216	57.27
0.2859	0.5992	55.63	0.9476	0.7849	58.84
0.3557	0.6022	55.55	0.9656	0.8364	59.96
$P = 521.2 \text{ Torr}$					
0.0184	0.4025	56.04	0.5764	0.5980	46.58
0.0275	0.4708	52.96	0.6245	0.6031	46.59
0.0400	0.5040	51.29	0.6854	0.6064	46.60
0.0576	0.5309	49.73	0.7338	0.6139	46.62
0.0985	0.5622	48.31	0.7638	0.6197	46.73
0.1199	0.5694	47.91	0.7999	0.6262	46.82
0.1886	0.5746	47.18	0.8489	0.6461	47.16
0.2366	0.5791	47.03	0.8854	0.6721	47.75
0.2978	0.5843	46.90	0.9178	0.7119	48.62
0.3335	0.5860	46.85	0.9424	0.7568	49.73
0.4195	0.5903	46.73	0.9660	0.8242	51.31
0.4871	0.5937	46.65	0.9836	0.9024	53.12

TABLE II  
(Continued)

$x_1$	$y_1$	$t, ^\circ\text{C}$	$x_1$	$y_1$	$t, ^\circ\text{C}$
$P = 340.0 \text{ Torr}$					
0.0184	0.4049	44.66	0.5808	0.5834	36.68
0.0275	0.4687	41.89	0.6310	0.5860	36.66
0.0400	0.5040	40.28	0.6920	0.5903	36.68
0.0594	0.5272	39.12	0.7378	0.5972	36.73
0.0985	0.5514	37.98	0.7689	0.6039	36.82
0.1117	0.5532	37.80	0.8029	0.6089	36.89
0.1673	0.5595	37.17	0.8526	0.6286	37.26
0.2209	0.5631	37.07	0.8889	0.6554	37.83
0.2859	0.5649	36.97	0.9197	0.6941	38.72
0.3247	0.5694	36.93	0.9450	0.7451	39.88
0.4128	0.5755	36.81	0.9680	0.8151	41.53
0.4871	0.5791	36.68			
$P = 230.5 \text{ Torr}$					
0.0166	0.3991	35.33	0.5860	0.5685	28.33
0.0220	0.4572	32.91	0.6350	0.5711	28.33
0.0382	0.4961	31.35	0.6963	0.5764	28.35
0.0585	0.5176	30.34	0.7411	0.5817	28.40
0.0952	0.5375	29.43	0.7739	0.5886	28.48
0.1085	0.5385	29.34	0.8064	0.5954	28.52
0.1765	0.5487	28.79	0.8553	0.6131	28.88
0.2237	0.5523	28.69	0.8918	0.6406	29.46
0.2819	0.5568	28.60	0.9233	0.6803	30.39
0.3335	0.5613	28.55	0.9476	0.7345	31.80
0.4150	0.5640	28.50	0.9692	0.8111	33.27
0.4951	0.5667	28.40			

and NRTL equations with  $\alpha = 0.47$  (ref.<sup>6</sup>). The natural logarithm of the ratio of activity coefficients of each component was calculated from the equation

$$\log \gamma_i = \ln (y_i P / x_i P_i^0) + [(B_{ii} - v_i^L)(P - P_i^0) + P \delta_{ij} y_j^2] / RT, \quad (2)$$

in which  $\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$  ( $j \neq i$ ), the temperature dependence of molar liquid volumes was considered to be linear, and the second virial coefficients of both pure components as well as the second cross virial coefficient were calculated by the O'Connell and Prausnitz method<sup>7</sup> with critical constants evaluated according to Kud-

chadker and coworkers.<sup>8</sup> All values necessary for the calculation of activity coefficients including the constants in the Antoine equation are given in Table III. The results of the correlations are in Table IV. Since, according to our expectation, the correlations by equations derived from the Wohl third-order expansion yielded inappropriate results, the table contains only values calculated from the Wilson and NRTL equations. Simultaneously, the data sets were correlated by the following six-constant equation

$$G^E/RT = \exp [(\alpha + bT) x_1] x_1 x_2 [A_0 + BT + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2], \quad (3)$$

TABLE III  
Constants Necessary for the Calculation of the Activity Coefficient

	Constants in the Antoine equation				Constants of the temperature dependence of the liquid molar volume		
	<i>A</i>	<i>B</i>	<i>C</i>	Ref.	<i>OA</i>	<i>OB</i>	Ref.
Methanol	7.87863	1 473.11	230	10	24.16	0.05734	1
Cyclohexene	6.91415	1 249.01	226.656	this work	63.94	0.12731	1
	<i>T<sub>k</sub></i>	<i>P<sub>k</sub></i>	<i>v<sub>k</sub></i>	$\omega_H$	$\mu$	$\eta$	Ref.
Methanol	513.2	78.5	118.0	0.105	1.66	1.21	7, 8
Cyclohexene	559.2	41.8	285.0	0.209	0.00	0.00	7, 8

TABLE IV  
The Correlation of Separate Sets of Liquid-Vapour Equilibrium Data

Equation	<i>P</i> , Torr	<i>K</i> <sub>1</sub>	<i>K</i> <sub>2</sub>	<i>y</i> <sup>exp</sup> - <i>y</i> <sup>calc</sup>
Wilson	740	2 315.4	488.6	0.0054
	521.2	2 385.4	476.7	0.0059
	340.0	2 364.1	524.9	0.0070
	230.5	2 397.6	531.1	0.0082
NRTL $\alpha = 0.47$	740	1 637.6	1 183.7	0.0095
	521.2	1 664.5	1 171.5	0.0099
	340.0	1 662.4	1 208.0	0.0108
	230.5	1 692.4	1 212.8	0.0148

which has been described in one of our earlier works<sup>9</sup>. With the following values of constants ( $\alpha = -0.59315$ ,  $\beta = 0.001$ ,  $A_0 = 4.10423$ ,  $B = -0.00567$ ,  $A_1 = 0.49146$ ,  $A_2 = 0.57303$ ), the computations yielded satisfactory agreement between measured and calculated values. (The difference in the mole fraction of methanol in the vapour phase for individual values of pressure (740, 521.5, 340.5, 231.8) was 0.0107, 0.0089, 0.0098, 0.0114, the difference in the calculated pressure in % 0.8, 1.2, 1.3, 0.9, and  $G^E$  calculated from experiments according to Eq. (3) 0.0028, 0.0023, 0.0029, and 0.0031.)

Values of the liquid-liquid solubility curve are in Table V.

TABLE V

The Solubility Curve of the Methanol(1)-Cyclohexene(2) System

$x_1$	0.10	0.17	0.205	0.26	0.315	0.315	0.36	0.40	0.42
$t, ^\circ\text{C}$	-13.15	-5.30	0.85	3.15	4.90	5.15	5.10	5.45	5.50
$x_2$	0.44	0.50	0.56	0.60	0.64	0.68	0.73	0.81	0.92
$t, ^\circ\text{C}$	5.60	5.40	5.05	4.25	3.05	1.30	-5.15	-16.15	-41.85

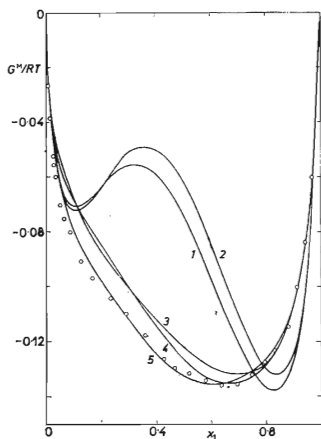


FIG. 1

The Dependence of  $G^M/RT$  on the Liquid Phase Composition at 740 Torr

○ Experimental points, 1 van Laar, 2 Margules, 3 Wilson, 4 NRTL, 5 the six-constant equation.

## DISCUSSION

The methanol-cyclohexene system is a highly nonideal one, which imposes extreme demands both on experimental technique and on the analytic evaluation of data. Above all, the equilibrium behaviour is extremely sensitive to the presence of water whose traces bring about the separation into two liquid phases up to the normal boiling point. Besides this, in the region of mole fractions of methanol of 0.1–0.7 the mixture possesses an extremely low surface tension and, consequently, necessary precautions had to be taken to avoid foaming of the mixture in the equilibrium cell.

Analogously, the correlation of the data is extremely difficult due to the exceptional course of the equilibrium curve. Correlation relations derived from the Wohl's third-order expansion exhibit an insufficient flexibility and can express this course only by an S-shaped curve which indicates a two-phase region and is of no physical meaning. Only the Wilson and NRTL equations are sufficiently flexible. For the latter equation it would still be possible to improve slightly the agreement by optimizing the constant  $\alpha$ . Since, for more general purposes, it is more advantageous to compare correlation calculations using the same value of the constant  $\alpha$ , we retained the value which was recommended by the author of the equation<sup>6</sup> and which has been employed earlier for correlations in benzene-alcohol and cyclohexane-alcohol systems. The six-constant equation can then with good results express simultaneously both the temperature and concentration dependence. The situation is well illustrated on Fig. 1 which contains plots of the dependences of  $G^M/RT$  as they were calculated from individual correlation equations and experimental points and which may simultaneously serve as a document that the investigated system can become — due to its exceptional equilibrium behaviour — a good standard for testing the adequacy of employed correlation relations.

## REFERENCES

1. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*. Elsevier, Amsterdam 1950.
2. Otsuki H., Williams C. F.: *Chem. Eng. Progr. Symp. Ser.* 49 (6) 55 (1953).
3. Strubl K., Svoboda V., Holub R., Pick J.: *This Journal* 35, 3004 (1970).
4. Swietoslawski W.: *Rocz. Chem.* 9, 608 (1929).
5. Hála E., Pick J., Fried V., Vilím O.: *Vapour-Liquid Equilibrium*, 2nd Ed., p. 51. Pergamon Press, London 1967.
6. Renon H.: *Thesis*. University of California, Berkeley 1966.
7. O'Connell J. P., Prausnitz J. M.: *Ind. Eng. Chem. Proc. Des. Dev.* 6, 245 (1967).
8. Kudchadker A. P., Alani G. H., Zwolinski B. J.: *Chem. Rev.* 68, 659 (1968).
9. Voňka P., Svoboda V., Strubl K., Holub R.: *This Journal* 37, 18 (1971).
10. Holmes M. J., van Winkle M.: *Ind. Eng. Chem.* 62, 21 (1970).

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