

LIQUID-VAPOUR EQUILIBRIUM. LV.* THE SYSTEM METHANOL-BENZENE

K.STRUBL, V.SVOBODA and R.HOLUB

*Department of Physical Chemistry,
Institute of Chemical Technology, Prague 6*

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Vapour-liquid equilibrium has been measured in the binary system methanol-benzene. The aim of this work has been to find whether up to this time a very difficult correlation of the data of this system has been caused by an improper experimental arrangement which then has given inadequate data or by the nature of the system itself, as a consequence of the force interactions of the components. The measurements have been carried out in the isothermal arrangement at 45°C and in the isobaric one at 740 Torr using the modified circulation still of the Gillespie type. Analytical determination of the equilibrium phases has been made refractometrically. The measured data have been correlated by the third order Margules equation, third order van Laar equation, Wilson, and Renon equation. The results of the measurements and the correlation calculations have furnished a proof that when preventing the traces of moisture during the measurements, the data can be obtained whose correlation by the Wilson and the Renon equations has given a good mutual agreement.

From up to now knowledge of the equilibrium behaviour of the system methanol-benzene it follows that this system shows a strong non-ideal behaviour predominant in the region of low methanol concentrations. This fact has so far been shown by considerable difficulties when correlating the dependence of activity coefficients on the composition of liquid by means of usually used relations (the third and fourth order Margules, the Scatchard, the van Laar, and the Redlich-Kister equations), above all for that reason that the high relative volatility in the region of low mol fractions of methanol results in an S-shaped deflection of the calculated dependence $x - y$ at middle concentrations with all consequences (the indication of two-phase region, large deviations of the measured and calculated data, inapplicability of the data for the description of more-component systems and the like). This fact can be faced to a certain extent, though, either by introducing the statistical weight to single points or by leaving out the measurements in the exposed region of low methanol concentration. This way is, however, very formal for it does not solve the substance of the problem. The considerably anomalous behaviour of this system is to be in substance attributed to two main effects: to the force interaction of single particles both in the liquid and gas phase or to the presence of traces of moisture in the measured system. As far as the first cause is concerned, it is known that methanol forms various associated clusters both in the gas and in the liquid phase. While in the gas phase this effect may be, in the main, included into the virial coefficients, there is not a sufficient amount of experimental data in this system for similar corrections in the liquid phase to be made. That is why this effect was neglected for the present.

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In this work, attention was paid to the second possible reason, *i.e.* to the presence of water in the system. It is to be justifiably assumed that water whose solubility in benzene is very low will be strongly influenced the phase behaviour above all in the region of low methanol concentrations. Its presence can cause both the breakdown of the system into two liquid phases and inapplicability of the calculated data owing to the fact that only two components are considered but in reality it is a ternary system.

The system methanol-benzene had been measured several times (Table I). All up to now measured sets of data can be divided roughly into isothermal, isobaric, and high-pressure. The high-pressure ones are out of the range of interest of this work. The sets of remaining two groups were subject to the consistency and physico-chemi-

TABLE I
Survey of Measurements of Vapour-Liquid Equilibrium in the Methanol(1)-Benzene(2) System

Number of set	°C	P Torr	Type of apparatus	Number of points	Ref.	Mean deviation, mole%	
						Wilson	Renon (α_{12} 0.51)
1	35	—	Scatchard	9	1	0.51	0.70
2	40	—	Sameshima	13	2	0.85	—
3	55	—	Scatchard	9	3	0.49	0.47
4	55	—	Scatchard	5	4	0.36	0.38
3 + 4	55	—	Scatchard	14	3.4	0.47	0.49 ^a
5	—	725	Othmer	15	5	4.53	4.38
6	—	730	—	18	6	1.44	1.56
7	—	760	Othmer	45	7	1.38	1.47
8	—	760	distilling	17	8	1.92	2.05
9	—	760	Colburn	18	9	0.67	0.68
10	—	760	Othmer	17	10	—	— ^b
11	—	760	static	14	11	—	— ^b
12	—	760	Colburn	10	12	0.65	0.73
13	90	—	circulating	6	13	0.40	0.36
14	100	—	static	10	14	—	— ^c
15	120	—	static	10	14	—	— ^c
16	140	—	static	10	13	—	— ^c
17	160	—	static	10	13	—	— ^c
18	180	—	static	10	13	—	— ^c
19	200	—	static	10	13	—	— ^c
20	220	—	static	10	13	—	— ^c
21	—	6.8—78.54 atm	alternate data x and y	—	14	—	— ^c

^a Combined set 3 and 4. ^b We were not successful in correlating. ^c Not correlated; the data are out of the region of applicability of vapour pressure equations.

cal analysis as objective as possible. This analysis included besides the judgement of consistency of the data also the appreciation of correlation calculations using the third order Margules equation, the third order van Laar equation, the Wilson and the Renon equations, the comparison of the course of the dependence of molar excess free enthalpy, molar mixing free enthalpy and its first derivative on composition, always between the values calculated directly from the measured data and the values which can be obtained from the single correlation relationships. Using this treatment, it was found that in the region of isothermal equilibria, all conditions were satisfied by the systems 1, 3, 4, and 13 from Table I and in the region of isobaric equilibria, the sets 9 and 12. However, all measurements except the set 9 have too little number of points, both totally and above all in the region of low methanol concentrations. The other sets appear as less suitable either because of their too large experimental error (the sets 6, 7, 10, 11) or the existence of two liquid phases, which with this system was not proved (the sets 2, 5, 8, 10, 11). For these reasons the system methanol-benzene was measured once again. The isothermal measurements at 45°C and the isobaric ones at 740 Torr were made in such arrangement in order that an access of the atmospheric humidity to the measured system might be prevented.

EXPERIMENTAL

Preparation of pure substances. The Grignard reagent was added to methanol predried with anhydrous calcium chloride and the mixture was refluxed for five hours. In this way dried product was distilled on a forty plate bubble-cup column. The main distillation fraction was collected into glass ampoules with a closure made of silicone rubber. The values of its physico-chemical constants (d_4^{25} 0.78653; n_D^{25} 1.3266; b.p. 64.7°C/760 Torr, and ΔH_v^{25} 279.35 cal g⁻¹) were in good agreement with the data from the literature¹⁵⁻¹⁷.

Calcined copper sulphate was added to benzene and the mixture was shaken for three days. Decanted benzene was distilled with sodium on an 150 cm long column packed by stainless steel helices. The values of its physico-chemical constants (d_4^{25} 0.87350; n_D^{25} 1.4977; b.p. 80.10°C/760

TABLE II
Dependence of Refractive Index on Composition in the Methanol(1)-Benzene(2) System

x_1	n_D^{25}	x_1	n_D^{25}	x_1	n_D^{25}
0.0523	1.4945	0.2530	1.4747	0.6643	1.4174
0.0740	1.4922	0.3307	1.4659	0.7590	1.3980
0.0934	1.4908	0.3383	1.4670	0.8363	1.3790
0.1406	1.4868	0.3626	1.4622	0.8922	1.3638
0.1503	1.4859	0.4330	1.4545	0.9482	1.3460
0.1941	1.4825	0.5196	1.4416	—	—
0.2274	1.4772	0.6130	1.4272		

Torr, and ΔH_v^{25} 103.48 cal g⁻¹) were as well in good agreement with published data^{16,18}. With both components their water content was determined by the K. Fischer method which was less than 0.01 weight per cent for methanol and 0.007 weight per cent for benzene.

Determination of components in mixture. To analyse the samples taken the measurement of refractive index at 25°C was used by means of an RL refractometer (product of Poland). The mea-

TABLE III
Vapour-Liquid Equilibrium in the Methanol(1)-Benzene(2) System at 45°C

Constants of the Antoine Eq.				Constants of the equation for molar volume			
	<i>A</i>	<i>B</i>	<i>C</i>	<i>a</i>		<i>b</i>	
(1)	7.87863	1 473.11	230.00	24.16		0.05734	
(2)	6.90565	1 211.03	220.79	56.23		0.11150	
<i>x</i> ₁	<i>y</i> ₁	<i>P</i> , Torr	log <i>y</i> ₁ / <i>y</i> ₂	(y _{exp} - y _{calc}) for correlation by relation ^a			
				Wilson	Renon	Laar 3	Margules 3
0.0032	0.0555	237.6	2.530	-0.0021	-0.0009	-0.0051	0.0074
0.0051	0.0869	245.4	2.544	-0.0001	0.0014	0.0098	0.0130
0.0100	0.1527	262.1	2.503	0.0021	0.0037	0.0153	0.0202
0.0227	0.2523	297.6	2.295	-0.0090	-0.0095	0.0005	0.0066
0.0272	0.2909	311.2	2.304	0.0020	0.0008	0.0087	0.0146
0.0317	0.3072	323.6	2.223	-0.0052	-0.0072	-0.0016	0.0039
0.0514	0.3775	350.3	2.030	-0.0069	-0.0112	-0.0166	-0.0134
0.0634	0.4164	373.6	1.969	0.0035	-0.0015	-0.0131	-0.0155
0.0860	0.4412	387.0	1.740	-0.0089	-0.0138	-0.0348	-0.0361
0.1014	0.4683	401.0	1.666	0.0006	-0.0038	-0.0296	-0.0326
0.1272	0.4899	416.1	1.496	0.0009	-0.0020	-0.0335	-0.0389
0.1538	0.5093	428.9	1.351	0.0049	0.0038	-0.0307	-0.0381
0.2250	0.5325	442.1	0.975	0.0030	0.0062	-0.0270	-0.0373
0.2701	0.5438	447.4	0.777	0.0043	0.0091	-0.0185	-0.0292
0.3607	0.5588	453.3	0.415	0.0043	0.0099	-0.0012	-0.0105
0.4721	0.5765	456.1	0.025	0.0060	0.0092	0.0204	0.0157
0.5543	0.5899	458.3	-0.250	0.0060	0.0064	0.0308	0.0304
0.6316	0.6045	456.9	-0.511	0.0047	0.0026	0.0344	0.0378
0.7027	0.6249	454.8	-0.747	0.0053	0.0016	0.0341	0.0405
0.7245	0.6319	454.1	-0.824	0.0047	0.0007	0.0321	0.0391
0.7597	0.6437	452.9	-0.958	0.0021	-0.0021	0.0259	0.0339
0.8680	0.7177	432.9	-1.352	0.0036	0.0010	0.0070	0.0149
0.9173	0.7786	412.0	-1.552	0.0033	0.0023	-0.0054	0.0007
0.9730	0.9002	372.1	-1.792	0.0025	0.0031	-0.0107	-0.0083
0.9853	0.9397	355.3	-1.867	0.0007	0.0012	-0.0088	-0.0075
<i>Mean deviation</i>				0.0039	0.0046	0.0182	0.0217

^a Constants of the correlation equations: Wilson: *A* 1 706.1, *B* 197.7; Renon: *A* 1 203.3, *B* 778.4, α_{12} 0.51; Laar 3: *A* 1.0549, *B* 0.7490; Margules 3: *A* 1.0332, *B* 0.7590.

measurements were made in a dry box. The samples were taken from the still by a syringe and then set on the prism of the refractometer in dry box. The composition of samples was interpolated from a calibration table calculated with a step $x = 0.001$ on the basis of correlation of measured synthetic mixtures (Table II).

Apparatus. The equilibrium data were obtained using the previously described¹⁹ circulation still of the Gillespie type as modified by Otsuki and Williams. For measuring the equilibrium in the methanol-benzene system, the adapters of the receivers of the liquid and gas phase were adapted so that the cocks were replaced by metal nuts with a hole packed with silicone rubber. These nuts connected to the apparatus through Kovar joints prevented the contingent contamination of the systems measured by a lubricating grease and besides, they made possible a simple sampling by syringes.

Data and their treatment. The data measured at 45°C are presented in Tables III and IV. The consistency of the isothermal data was verified using the relation

$$\int_0^1 \log (\gamma_1/\gamma_2) dx_1 = 0, \quad (1)$$

for the isobaric data the method was used proposed by Herington²⁰. Activity coefficients were calculated from the equation

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + \frac{PD_{ij}y_j^2}{RT}. \quad (2)$$

The dependence of the molar volumes on temperature was considered linear, the calculation of constants was carried out using the data given by Timmermans²¹. The estimation of the second virial coefficients of pure components and the mixture was carried out according to Prausnitz and O'Connell²². The dependence of the vapour pressure on temperature was used in the form of the Antoine equation and its constants were taken over from²³. The values of critical constants needed are from the paper of Zwolinski and coworkers²⁴.

For correlation, the following equations were used first of all: the Margules equations of the third and fourth order, the Scatchard equation, the van Laar equation of the third order, the Wilson equation²⁵ (the use of which is fully justified with respect to the homogeneity of the liquid phase) and the Renon equation²⁶ with a chosen constant α_{12} . In all cases the difference of the experimentally found and calculated logarithm of the ratio of activity coefficients was minimized by the method of least squares. The Redlich-Kister equation was not used. It was namely assumed that with regard to the expected asymmetrical course of the dependence of G^E on x , the correlation would have been successful only on using more-constant types. However, a form of this sort would have distorted, for a change, the course of dependences which can be derived by differentiating (H^E , C_p^E , $\partial^2 \Delta G^M/\partial x^2$, S^E , and so on), where then extremes and points of inflection occur in the places where they cannot be on these curves. For the same reason it was also expected the unsuitability of the use of the fourth order Margules equation, which was proved by calculations. Less understandable was a very bad agreement with the Scatchard equation.

The resulting correlations were carried out by the Margules and van Laar equations of the third order and by the Wilson and the Renon equations. With the last equation the method of optimization of two constants for several values of the constant α_{12} chosen in advance was used and graphic determination of such constant α_{12} for the resulting correlation whose choice would have ensured the least mean deviation. This method appears (till the time than it is proved that the same course cannot be expressed by more than one triad of constants) more suitable than

TABLE IV
Vapour-Liquid Equilibrium in the Methanol(1)-Benzene(2) System at the Pressure of 740 Torr

x_1	y_1	$t, ^\circ\text{C}$	$\log \gamma_1/\gamma_2$	$(y_{\text{exp}} - y_{\text{calc}})$ for correlation by relation ^a			
				Wilson	Renon	Laar 3	Margules 3
0.0085	0.1207	75.73	2.267	-0.0021	-0.0010	0.0063	0.0089
0.0100	0.1600	74.52	2.434	0.0197	0.0210	0.0295	0.0323
0.0197	0.2057	72.75	2.058	-0.0241	-0.0231	-0.0134	-0.0098
0.0374	0.3012	68.85	1.919	-0.0311	-0.0314	-0.0245	-0.0212
0.0569	0.3808	65.68	1.844	-0.0175	-0.0191	-0.0185	-0.0163
0.0931	0.4611	62.22	1.652	-0.0033	-0.0058	-0.0175	-0.0175
0.1240	0.4948	60.68	1.471	-0.0004	-0.0025	-0.0224	-0.0240
0.1507	0.5148	59.78	1.327	0.0020	0.0006	-0.0240	-0.0267
0.2100	0.5411	58.78	1.031	0.0033	0.0041	-0.0250	-0.0291
0.2259	0.5471	58.60	0.962	0.0046	0.0058	-0.0232	-0.0276
0.2780	0.5620	58.05	0.747	0.0071	0.0096	-0.0167	-0.0215
0.4002	0.5843	57.53	0.289	0.0084	0.0110	0.0008	-0.0030
0.5052	0.5985	57.28	-0.078	0.0060	0.0067	0.0131	0.0114
0.5953	0.6170	57.10	-0.366	0.0075	0.0061	0.0240	0.0245
0.6409	0.6265	57.25	-0.520	0.0060	0.0036	0.0255	0.0269
0.7838	0.6762	57.60	-1.014	0.0022	-0.0008	0.0194	0.0229
0.8787	0.7482	58.62	-1.363	0.0016	0.0004	0.0059	0.0091
0.9467	0.8504	60.45	-1.625	-0.0025	0.0028	-0.0038	-0.0021
0.9738	0.9167	61.82	-1.713	0.0038	0.0042	-0.0029	-0.0021
0.9872	0.9539	62.75	-1.817	0.0001	0.0004	-0.0044	-0.0040
<i>Mean deviation</i>				0.0077	0.0080	0.0160	0.0170

^a Constants of the correlation equations: Wilson: A 1.698.8, B 177.1; Renon: A 1.160.2, B 773.0, α_{12} 0.51; Laar 3: A 0.9598, B 0.7530; Margules 3: A 0.9475, B 0.7567.

the optimization of all three constants. The results of the computations are presented in Tables III and IV. The fourth column in both tables expresses the logarithm of the ratio of activity coefficients. These data were used when investigating the consistency of the experimental data.

DISCUSSION

Even the visual comparison of the $x - y$ curve in the region of low methanol concentrations with curves constructed using the data from the literature (Table I) suggested that the presence of water had an essential effect on the equilibrium behaviour. The measurement described in this work which was carried out very carefully as far as the prevention of air humidity was concerned showed the smoothest course in the representation $x - y$ from the up to now known sets in the region from the methanol

mole fraction $x_1 = 0$ to the azeotropic point (at first the minimum steepness and after reaching the bending of the curve, on the contrary, the maximum one), with an expressive shift of the azeotropic point towards the higher concentrations of methanol. This qualitative result was supported by the results of the correlation computations whose mean deviation from the measurements kept about two per cent of mol fraction in the vapour phase, which with systems of this type is still reasonable at the present time. However, it was possible to observe a conspicuous difference between the results obtained when using the Wilson and the Renon equations on the one hand and the van Laar and the Margules equations of the third order on the other hand. Whereas with the first two equations very good agreement was reached, the deviations with the van Laar and the Margules equations confirmed that the both equations were little flexible and were not able to adjust the high relative volatility in the region of low methanol concentrations (without suppressing the significance of the points) otherwise than by an S-shaped deflection of the middle part of the $x - y$ curve. Considering that this fact results in the indication of the existence of two-phase region, both equations appear as unsuitable for the correlation of the system. The situation is demonstrated well in Figs 1–3. From different course of the curves for the Margules and the van Laar equations then follow very different courses of the dependences of $\log \gamma_1$, $\log \gamma_2$, and $\log (\gamma_1/\gamma_2)$ on x_1 for both equations, too

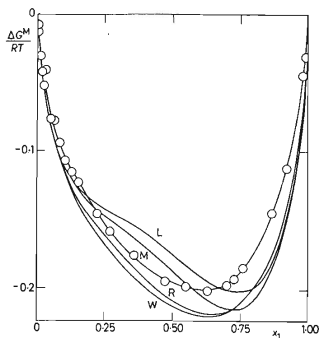


FIG. 1

Dependence of $\Delta G^M/RT$ on x_1 at 45°C

Circles values calculated from experimental data, W Wilson equation, R Renon equation, L van Laar third order equation, M Margules third order equation.

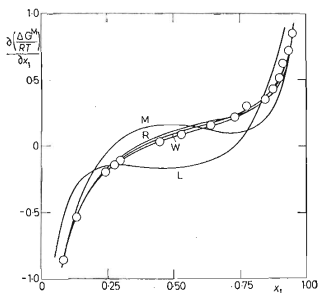


FIG. 2

Dependence of $\partial(\Delta G^M/RT)/\partial x_1$ on x_1 at 45°C

(Figs 4–6). In case of the isobaric measurement at 740 Torr, very similar dependences were obtained.

The comparison of the curves of molar excess free enthalpy was least conclusive in this case (Fig. 7). In the region of low methanol concentrations, the deviations for the van Laar and the Margules equations from the values obtained from the experimental data are relatively low and on the contrary they increase

FIG. 3

Dependence of $\partial^2(\Delta G^M/RT)/\partial x_1^2$ on x_1

1 The Renon equation for 45°C and α_{12} 0.51, 2 the van Laar third order equation for 45°C, 3 the Margules third order equation for 45°C, 4 the Renon equation for 740 Torr, 75.73°C and α_{12} 0.51, 5 the Renon equation for 740 Torr, 57.10°C and α_{12} 0.51, 6 the van Laar third order equation for 740 Torr, 7 the Margules third order equation for 740 Torr.

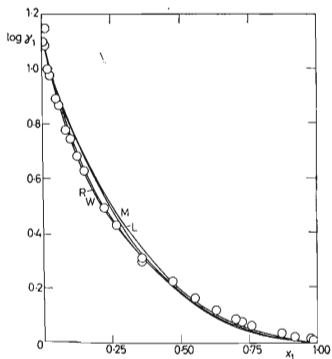
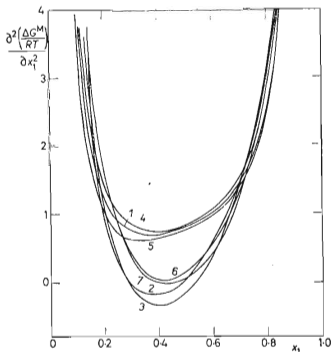


FIG. 4

Dependence of $\log \gamma_1$ on x_1 at 45°C

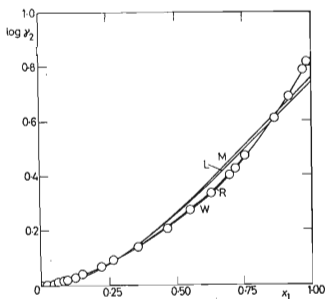


FIG. 5

Dependence of $\log \gamma_2$ on x_1 at 45°C

with higher methanol concentrations where the correlation has not done any difficulties up to now. From the figures it follows the over-all good agreement of the Wilson and the Renon equations (for the optimum $\alpha_{12} = 0.51$) in all dependences. It is evident that both equations are practically equivalent and at the same time that the preference of the Wilson equation is a good agreement on keeping only two constants and of the Renon one the fulfilment of the condition of homogeneity of the liquid phase. It is to be assumed that these circumstances will be shown when correlating more-component systems without adding further constants.

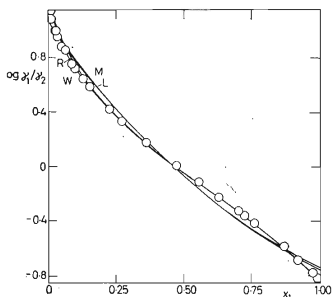


FIG. 6
Dependence of $\log(\gamma_1/\gamma_2)$ on x_1 at 45°C

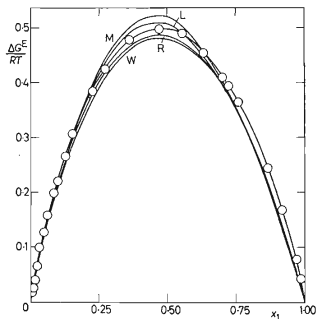


FIG. 7
Dependence of $\Delta G^E/RT$ on x_1 at 45°C

LIST OF SYMBOLS

A	constant in correlation equations; constant of the Antoine equation
B	constant in correlation equations; constant of the Antoine equation
B_{ii}	second virial coefficient of the i -th component (ml mol^{-1})
C	constant of the Antoine equation
C_P^E	molar excess heat capacity at constant pressure (cal K mol^{-1})
D_{ij}	$= 2B_{ij} - B_{ii} - B_{jj}$
G^E	molar excess free enthalpy (cal mol^{-1})
ΔG^M	molar mixing free enthalpy (cal mol^{-1})
H^E	molar excess enthalpy (cal mol^{-1})
P	total pressure (Torr)
P_k	critical pressure (Torr)
P_i^0	vapour pressure of the pure i -th component (Torr)
R	gas constant
T	temperature (K)

T_k	critical temperature (K)
V_i^G, V_i^L	molar volume of the i -th component in the gas and liquid phase, resp.
x_i	mole fraction of the i -th component in liquid
y_i	mole fraction of the i -th component in vapour
α_{12}	constant of the Renon equation
γ_i	activity coefficient
τ	association constant
μ	dipole moment
ω	acentric factor

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