LIQUID–VAPOUR EQUILIBRIUM. LVI.*
CORRELATION OF THE BENZENE–METHANOL SYSTEMS

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The isobaric vapour–liquid equilibrium in the benzene–methanol system was measured at 521·2, 340, and 230·5 Torr. Each of the data sets measured was correlated separately by the usually used correlation relations first. In addition to these computations, the simultaneous correlations were carried out of the vapour–liquid equilibria with heats of mixing the data of which were taken over from the literature. Results of the computations proved the possibility of interpolation and extrapolation of equilibrium data with an accuracy comparable with the deviation which corresponds to the correlation of experimental data.

In one of foregoing papers[1], the possibility was discussed of the simultaneous description of the vapour–liquid equilibrium data with heats of mixing of binary systems by means of an empirical equation containing six constants which has, for molar excess enthalpy, the form

$$G^E/RT = \exp\left[(\alpha + \beta T)(x_1 - x_2)\right] x_1 x_2 [A_0 + BT + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2]. \quad (I)$$

The advantage of this equation should be the possibility of the description of the concentration and temperature dependence of molar excess free enthalpy and, in the differentiated relations, in addition, of the logarithm of activity coefficients, molar excess enthalpy and molar excess heat capacity. The relations were applied when correlating the equilibrium and enthalpy data of the binary 1-butanol–cyclohexane system. The results showed good agreement of the measured and calculated values.

For a more general applicability of the relations proposed, it was needed to verify the possibility of interpolation of the equilibrium and enthalpy values for arbitrary temperature and pressure conditions in the region bounded by experimental data and finally also the extrapolation range in which the accuracy would be still warranted which is needed for further use. To this purpose the data on the 1-butanol–cyclohexane system were not suitable. This system exhibits no more such considerable deviations from the ideal behaviour and besides, less data on it are known above all in the region of mixing enthalpies. The benzene–methanol system showed to be much more suitable. Its equilibrium behaviour is extreme and exhibits deviations verging towards separation into two liquid phases. Moreover, there are much more

data available, both the equilibrium and enthalpy ones, for this system. Even when it was found[2] that the sets of equilibrium data which fulfil the conditions necessary for these correlation calculations are not so many it is above all valuable that the data on heats of mixing at more temperatures are known.

The equilibrium data on the benzene–methanol system, obtaining of which does not make difficulties any more, were completed by the sets measured at the pressures 521·2, 340, and 230·5 Torr. After correlating the separate sets, these data were used for the simultaneous correlation.

EXPERIMENTAL

Preparation of pure substances. 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 packed column filled with stainless steel helices. The measured values of its physico-chemical constants (d_4^{25} 0·87350, n_D^{25} 1·4977, n.b.p. 80·10°C and ΔH_v^{25} 103·48 cal.g^{-1}) were in good agreement with the data from the literature[3,4]. 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 measured values of its physico-chemical constants (d_4^{25} 0·78653, n_D^{25} 1·3266, n.b.p. 64·7°C, and ΔH_v^{25} 279·35 cal g^{-1}) were as well in good agreement with published data[3,5,6]. With both components their water content was as well established by the Fischer method, being less than 0·01 weight per cent for methanol and 0·007 weight per cent for benzene.

Determination of components in mixture. The analysis of samples taken was made by measuring their refractive indices at 25°C in a dry box. The samples were taken from the still by a syringe and then set on the prism of refractometer in the dry box. The composition of samples was interpolated using a calibration table calculated by step $x = 0·001$ on the basis of correlation of measured synthetic mixtures whose values are presented in Table II (ref.[2]).

Apparatus. The equilibrium data were obtained by measuring mixtures in the Gillespie-type circulation still as modified by Otsuki and Williams. The whole apparatus including measuring and controlling temperature and pressure are described in detail in the previous paper[2].

RESULTS

The measured data are presented in Table I. The consistency of the data was considered using the method proposed by Herington[7] from the values of natural logarithm of the ratio of activity coefficients as they are given, as well, in the corresponding column of Table I. Activity coefficients were calculated according to the equation

$$\ln \gamma_i = \ln \left(\frac{y_i P}{x_i P_i^0} \right) + \frac{(B_{ii} - v_i^L)(P - P_i^0)}{RT} + \frac{P D_{ij} y_j^2}{RT}, \qquad (2)$$

$$D_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (j \neq i).$$

The dependence of the molar volumes of pure liquid components on temperature was considered linear; the calculation of constants was carried out using the data

TABLE I

Vapour–Liquid Equilibrium Data in the Benzene(1)–Methanol(2) System

x	y	°C	$\ln(\gamma_1/\gamma_2)$	x	y	°C	$\ln(\gamma_1/\gamma_2)$
				521·2 Torr			
0·0087	0·0319	54·45	1·745	0·7658	0·4648	49·27	−0·915
0·0163	0·0587	53·86	1·745	0·8189	0·4790	49·82	−1·179
0·0366	0·1202	52·62	1·695	0·8706	0·5039	50·64	−1·472
0·0695	0·1904	51·20	1·558	0·8860	0·5180	51·00	−1·558
0·1317	0·2759	49·62	1·327	0·9177	0·5573	52·95	−1·751
0·2090	0·3330	48·78	1·040	0·9526	0·6363	56·22	−1·993
0·2983	0·3724	48·27	0·736	0·9613	0·6802	57·75	−2·002
0·3598	0·3895	48·22	0·530	0·9683	0·7107	58·86	−2·059
0·4170	0·4016	48·16	0·340	0·9713	0·7299	59·53	−2·063
0·4809	0·4120	48·24	0·125	0·9757	0·7521	60·23	−2·114
0·5403	0·4208	48·33	−0·076	0·9835	0·7966	62·28	−2·244
0·5791	0·4261	48·35	−0·212	0·9867	0·8339	63·24	−2·210
0·6272	0·4367	48·50	−0·369	0·9915	0·8918	65·42	−2·156
0·6928	0·4477	48·71	−0·616	0·9983	0·9639	67·23	−2·587
				340·0 Torr			
0·0041	0·0189	44·87	1·922	0·6272	0·4535	38·39	−0·351
0·0077	0·0310	44·67	1·794	0·6828	0·4627	38·51	−0·560
0·0149	0·0578	44·04	1·775	0·7685	0·4769	38·83	−0·934
0·0357	0·1257	42·80	1·727	0·8053	0·4928	39·20	−1·088
0·0650	0·1969	41·43	1·625	0·8514	0·5024	39·58	−1·373
0·1288	0·2887	39·72	1·368	0·8771	0·5147	40·29	−1·540
0·1993	0·3484	38·85	1·120	0·8873	0·5280	40·81	−1·582
0·2932	0·3865	38·33	0·771	0·9289	0·5760	42·23	−1·886
0·3546	0·4053	38·22	0·569	0·9587	0·6465	45·19	−2·147
0·4114	0·4183	38·13	0·382	0·9713	0·7031	46·92	−2·256
0·4812	0·4324	38·20	0·157	0·9835	0·7853	50·04	−2·371
0·5403	0·4392	38·26	−0·052	0·9932	0·8860	53·27	−2·496
0·5791	0·4478	38·32	−0·174				
				230·5 Torr			
0·0044	0·0195	36·57	1·842	0·5374	0·4522	29·77	−0·033
0·0067	0·0307	36·38	1·884	0·5722	0·4582	29·80	−0·150
0·0153	0·0536	35·93	1·628	0·6248	0·4635	29·84	−0·347
0·0338	0·1278	34·47	1·761	0·6786	0·4740	29·95	−0·542
0·0629	0·2028	33·09	1·655	0·7468	0·4844	30·12	−0·833
0·1222	0·2953	31·44	1·417	0·7995	0·4928	30·46	−1·099
0·1896	0·3546	30·59	1·165	0·8546	0·5173	31·13	−1·385
0·2858	0·4010	30·03	0·823	0·8884	0·5288	31·65	−1·639
0·3490	0·4189	29·86	0·604	0·9340	0·5745	33·03	−2·021
0·4046	0·4328	29·72	0·424	0·9743	0·6954	37·19	−2·457
0·4749	0·4425	29·72	0·117	0·9948	0·9033	43·40	−2·632

given by Timmermans[8]. Their numerical values in $cm^3 mol^{-1}$ are for benzene 56·23 and 0·11150 and for methanol 24·16 and 0·05734. The estimation of the second virial coefficients of the pure components and the mixture was carried out according to O'Connell and Prausnitz[9]. The dependence of vapour pressure on temperature was used in the form of the Antoine equation whose constants were taken over from the paper[10]. The values of critical constants are those from the paper of Zwolinski and coworkers[11].

The correlations of single systems were carried out by the Wilson and Renon equation whose application for this system had proved, in the previous work[2], to be very suitable. On the contrary, the correlations by the third-order Margules and van Laar equations were abandoned for these equations are little flexible and adjust the high relative volatility in the region of low methanol concentrations by an S-shaped deflection of the middle part of the $x - y$ curve so indicating the existence of two-phase region. The results of the correlation computations in the form of constants of equations used and total deviations of single sets are given in Table II.

For the simultaneous correlations, these sets of data were used: the isothermal equilibrium data at 35°C (9 points, Scatchard[12]), at 45°C (25 points, our measurements[2]) and at 55°C (14 points, Scatchard[13,14]), further the isobaric equilibrium

TABLE II
Results of Correlating Computations

Equation	Constants, deviations $(y_{exp} - y_{calc})$	Measurement at pressure, Torr		
		521·2	340·0	230·5
	$\lambda_{12} - \lambda_{11}$	151·7	159·4	132·3
	$\lambda_{12} - \lambda_{22}$	1 680·7	1 739·0	1 807·0
Wilson	mean absolute	0·0057	0·0029	0·0053
	root mean square	0·0068	0·0031	0·0057
	maximum	0·0140	0·0055	0·0091
	$g_{12} - g_{11}$	686·5	690·7	663·7
	$g_{12} - g_{22}$	1 136·1	1 190·8	1 257·1
Renon	mean absolute	0·0058	0·0052	0·0073
($\alpha = 0·47$)	root mean square	0·0069	0·0064	0·0086
	maximum	0·0136	0·0131	0·0147
	mean absolute	0·0110	0·0097	0·0085
Eq. (1)	root mean square	0·0140	0·0117	0·0103
(selection 2)	maximum	0·0268	0·0226	0·0157

data at 740 Torr (20 points, our measurements[2]) and the above-mentioned data at 521·2, 340, and 230·5 Torr and finally the isothermal heats of mixing at 25, 35, and 45°C (each isotherm 10 points, Mrázek and van Ness[15]). Considering that we endeavoured to judge by calculating how many sets and of which kind were to be used (whether the combination of isothermal equilibrium data with heats of mixing, of isobaric equilibrium data with heats of mixing, and so on), the computation was carried out alternatively in several variants whose description is given in Table III. The result of computations was always the set of six constants which characterize the equations for molar excess free enthalpy and molar heat of mixing. Their values are presented in Table IV. From these equations, the values of mole fraction in the gas phase were then calculated back for such conditions and mole fraction in the liquid which correspond to the experimental values. The results for

TABLE III

Review of Sets Used in Single Variants of Simultaneous Correlation

Selection	Equilibrium data		Isothermal heats of mixing °C
	isothermal, °C	isobaric, Torr	
1	35; 45; 55	740; 521·2; 340; 230·5	—
2	35; 45; 55	—	25; 35; 45
3	—	740; 521·2; 340; 230·5	25; 35; 45
4	45	340	45
5	35	230·5	35
6	—	—	25; 35; 45

TABLE IV

Values of Constants of Eq. (I) for Single Selections

Selection	Constants of Eq. (I)					
	α	β	A_0	B	A_1	A_2
1	0·39 886	−0·00 017	4·05 504	−0·00 672	−0·54 227	0·45 180
2	0·85 114	0·00 017	3·17 704	−0·00 390	−1·70 668	0·90 316
3	0·85 114	0·00 017	3·18 896	−0·00 390	−1·72 099	0·88 446
4	0·80 114	0·00 017	3·31 604	−0·00 425	−1·64 039	0·90 734
5	0·87 614	0·00 017	3·16 628	−0·00 386	−1·73 640	0·96 003
6	−0·24 760	0·00 400	1·60 765	−0·00 372	−0·38 443	−0·53 237

single "selections" and for each set studied are given in the first part of Table V as the mean absolute deviation of the measured and calculated mole fraction in the gas phase. The mean absolute deviations of the mole fraction in the gas phase for correlations of single sets separately, as carried out by means of the Wilson and Renon equations, are presented in the table for comparison[16], too.

TABLE V

Comparison of Mean Absolute Deviations of Back-Calculated Values of Mole Fraction in the Gas Phase

Set[a]	Wilson Eq.	Renon Eq.	Eq. (I), selection					
			1	2	3	4	5	6
35°C	0·0051	0·0070	0·0110	0·0138	0·0143	0·0172	0·0162	0·1394
45°C	0·0033	0·0046	0·0060	0·0129	0·0122	0·0166	0·0161	0·1312
55°C	0·0047	0·0049	0·0110	0·0161	0·0159	0·0162	0·0155	0·1771
740 Torr	0·0064	0·0072	0·0128	0·0165	0·0152	0·0197	0·0210	0·1352
521·2 Torr	0·0057	0·0058	0·0085	0·0121	0·0114	0·0157	0·0153	0·1107
340·0 Torr	0·0029	0·0052	0·0063	0·0105	0·0096	0·0146	0·0145	0·1224
230·5 Torr	0·0053	0·0073	0·0091	0·0084	0·0085	0·0107	0·0101	0·1183
25°C			77·1	12·6	12·6	19·1	12·4	9·3
35°C			63·4	10·1	10·1	11·9	10·6	2·7
45°C			51·2	13·3	13·3	10·1	14·0	8·4
100°C	0·0055	0·0052	0·0182	0·0255	0·0235	0·0220	0·0227	0·1051
120°C	0·0076	0·0072	0·0191	0·0280	0·0290	0·0277	0·0281	0·0937
140°C	0·0094	0·0095	0·0211	0·0275	0·0271	0·0286	0·0295	0·0873
160°C	0·0141	0·0141	0·0251	0·0276	0·0279	0·0280	0·0284	0·0944
180°C	0·0172	0·0173	0·0291	0·0372	0·0374	0·0368	0·0389	0·0804
200°C	0·0285	0·0286	0·0317	0·0370	0·0376	0·0362	0·0386	0·0896
220°C	0·0343	0·0342	0·0351	—	—	—	—	0·0647

[a] Equilibrium data, $\sigma = \dfrac{1}{N} \sum\limits_{i=1}^{N} |[(y_{exp})_i - (y_{calc})_i]|$, heats of mixing, $\sigma = \dfrac{100}{N} \sum\limits_{i=1}^{N} \left\| \left[\left(\dfrac{\mathscr{H}^E}{RT}\right)_{i,exp} - \left(\dfrac{\mathscr{H}^E}{RT}\right)_{i,calc} \Big/ \left(\dfrac{\mathscr{H}^E}{RT}\right)_{1,exp} \right] \right\|$.

DISCUSSION

Even when only the comparison of mean deviation of each set is given for saving reasons, the results presented in Table V imply that the agreement of the measured and in this way calculated data is satisfactory. Provided that the suitability is to be judged of the application of the proposed Eq. (I) for the description of the dependence

of excess functions in a wide range of conditions (which was one of aims of this work) it is necessary to answer two questions: what is the optimum selection of sets which should be used for the simultaneous correlation and what is the value of deviations between in this manner carried out correlation in comparison with the correlation of a single set.

From alternative selections it followed, as it was possible to assume in advance, that for a good description of the equilibrium and enthalpy values it is necessary to use both types of data. The values of heats of mixing calculated from equilibrium data only show large deviations (selection 1) as well as in the opposite case when calculating the equilibrium data from heats of mixing (selection 6). A fact is interesting with both those alternatives, *viz.* that above all, an increase of deviations occurred with that kind of data which was not considered for calculating the constants of Eq. (*1*) without being compensated by an improvement of the agreement of the values which were used for the calculation. Provided that the equilibrium and enthalpy data are included in the chosen sets the results are roughly the same (selections 2–5).

The deviations of equilibrium data are on the average about twice worse than those calculated by means of the Wilson or Renon equations. To judge better the location of deviations as a function of concentration the deviations between the measured and calculated mole fraction in the gas phase are given in the seventh column of Tables I–III. The calculation of constants of Eq. (*1*) was made for the selection 2, that is for such alternative which does not contain the compared isobars. Heats of mixing could be compared only with experimental values. The deviations between measured and calculated values are rather higher. With respect to the considerably asymmetrical course of the concentration dependence, some difficulties are, however, to be expected which can become evident as a worse agreement of the measured and calculated data even when trying to correlate each set separately. The suitability of using the equation for the interpolation of equilibrium data is illustrated in Fig. 1, too, in which the dependence of free enthalpy of mixing on composition for the isobaric data at 340 Torr is plotted.
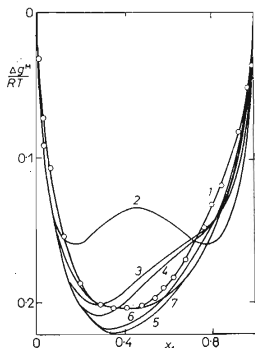

Fig. 1

Back-Calculated Dependence of $\Delta G^M/RT$ on Composition for Equilibrium Data at 340 Torr

1 Measured data, *2* Scatchard, *3* the third-order Margules, *4* the third-order van Laar, *5* Renon, *6* Wilson, *7* Eq. (*1*) of this work for selection 2.

The second aim, which was pursued by this procedure, was to judge the possibility of extrapolating the values of excess quantities into regions where experimental data are missing or where their obtaining is considerably more difficult. Considering that for the benzene–methanol system the isothermal equilibrium data were measured up to a temperature of 220°C it was possible to make very well the comparison of such extrapolation. The results, again for single sets, up to the temperature of 220°C are included in the second part of Table V even though the temperature 220°C is

TABLE VI

Comparison of Deviations of Mole Fraction in the Gas Phase between Correlation of Sets by the Wilson and Renon Eqs and Extrapolation according to Eq. (1)

x	y	P, atm	$\log(\gamma_1/\gamma_2)$	$(y_{exp} - y_{calc})$ of equation used		
				Wilson	Renon	this work (selection 1)
				200° C		
0·0480	0·0566	40·05	0·647	0·0198	0·0198	−0·0307
0·1010	0·1055	40·28	0·543	0·0316	0·0316	−0·0381
0·1722	0·1451	40·11	0·294	0·0263	0·0260	−0·0440
0·3350	0·2398	38·34	0·071	0·0327	0·0322	−0·0160
0·4734	0·3098	36·13	−0·119	0·0359	0·0357	−0·0080
0·5944	0·3561	33·38	−0·367	0·0226	0·0231	−0·0341
0·7534	0·4689	27·93	−0·571	0·0364	0·0379	−0·0488
0·8685	0·5965	23·20	−0·775	0·0395	0·0405	−0·0456
0·9251	0·7007	20·28	−0·909	0·0317	0·0314	−0·0324
0·9728	0·8446	16·81	−1·096	0·0088	0·0075	−0·0189
Mean deviation				*0·0285*	*0·0286*	*0·0317*
				220° C		
0·0479	0·0523	56·82	0·482	0·0232	0·0232	−0·0345
0·1067	0·1001	56·89	0·333	0·0369	0·0368	−0·0489
0·1765	0·1431	55·87	0·177	0·0413	0·0411	−0·0505
0·2526	0·1882	54·47	0·075	0·0460	0·0458	−0·0398
0·3489	0·2394	51·61	−0·043	0·0473	0·0472	−0·0277
0·5004	0·3136	47·16	−0·242	0·0415	0·0419	−0·0272
0·6383	0·3956	42·15	−0·393	0·0401	0·0410	−0·0390
0·8222	0·5515	33·85	−0·640	0·0283	0·0290	−0·0589
0·9252	0·7374	26·84	−0·728	0·0272	0·0267	−0·0226
0·9767	0·8932	22·32	−0·816	0·0106	0·0098	−0·0025
Mean deviation				*0·0343*	*0·0342*	*0·0351*

already obviously so high that most calculations (as well as the correlation of a single system) already fails. To judge the location of deviations in dependence on concentration of the liquid the results of computations at the temperature of 220°C are presented in Table VI. The computations were carried out for comparison both by means of the single usually used correlation relations and by Eq. (1) using the constants corresponding to the first selection in Table III.

From the results it is to be concluded that the method described, expressing the values of excess functions of the benzene–methanol system by the equation with six constants, enables to make the interpolating determination of the equilibrium and enthalpy data with good agreement and at the same time a considerably wide temperature extrapolation which is sufficient to characterize the dependence of activity coefficients on composition.

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