

VAPOUR-LIQUID EQUILIBRIA OF THE SYSTEMS ACETONE-BENZENE, BENZENE-CYCLOHEXANE AND ACETONE-CYCLOHEXANE AT 25°C

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Abstract—Vapour-liquid equilibrium data for the binary systems acetone-benzene, benzene-cyclohexane and acetone-cyclohexane have been determined experimentally at 25°C. The reduction procedures based on $P-x-y$ as well as on $P-x$ isothermal data sets, which incorporate usual thermodynamically consistent models expressing the dependence of activity coefficients of liquid composition, have been examined for representing the reported results. Nonideal behaviour of the both phases has been taken into account. Thermodynamic consistency of the data has been shown by comparing of the experimentally obtained vapour compositions with those calculated from $P-x$ data using the best of the examined models for activity coefficients.

INTRODUCTION

The use of analytical expressions which relate activity coefficient, composition and temperature is of particular importance in the design and operation of distillation equipment.

Since the existing molecular theories are not always efficient to solve the problems of interest, considerable effort has been lately expended in developing new concepts concerning the reduction of experimental vapour-liquid equilibrium data, in order to obtain reliable expressions which relate activity coefficient and liquid composition [1-4]. Performances of these expressions depend on the choice of the data reduction procedure, and on the specific thermodynamic model for activity coefficients employed [5, 6]. Semiempirical models [7] of Margules, van Laar, Schatchard-Hamer, Wohl and Wilson [8] are traditionally used in the calculational procedures when $P-x-y$ equilibrium data have to be reduced. Some of these models have not been utilized previously to establish the composition dependences of activity coefficients from $P-x$ data sets.

In the systems reported here, specific interactions occur between the constituents [9]. The object of the present work is to compare suitability of the mentioned thermodynamic models and the computational procedures used to reduce the binary vapour-liquid equilibrium data of the investigated systems.

EXPERIMENTAL

Chemicals and their properties Analytical grade acetone (Merck), "Annalar" benzene (BDH), and "RP" cyclohexane (Carlo Erba) were further purified by the methods already described [9].

Physical properties of the chemicals used for experimental work are compared with the selected published values in Table 1. The second virial coefficients, listed in the same table, for acetone and benzene were

estimated, respectively, by graphical interpolation, from the data reported by Bottomley *et al* [10, 11] and [12, 13]. The second virial coefficient for cyclohexane was obtained from the data of Bottomley *et al* [13, 14] by graphical extrapolation. The second virial cross-coefficients for the systems acetone-benzene and benzene-cyclohexane were estimated, by graphical extrapolation, from the data of Knoebel *et al* [15] and Bottomley *et al* [13], respectively. The cross virial coefficient for the system acetone-cyclohexane was predicted by the method of O'Connell and Prausnitz [16]. Partial molar volumes of the components were calculated from the excess volumes of mixing reported by Nigam *et al* [17] for acetone-benzene, Stokes *et al* [18] for benzene-cyclohexane and Radojković *et al* [9] for acetone-cyclohexane system.

Apparatus and procedure Vapour recirculation still as well as the experimental procedure used to obtain the vapour-liquid equilibrium data for the systems acetone-benzene and benzene-cyclohexane were described previously [19]. Isothermal data for the system acetone-cyclohexane were measured by a vapour and liquid recirculation still. This still and the experimental method employed were already described [20].

Equilibrium temperature was measured by a mercury thermometer having 0.1°C divisions. The temperature readings are believed accurate to $\pm 0.02^\circ\text{C}$. Equilibrium pressure was measured by a mercury manometer and read with a precision of 0.05 mm of Hg. The absolute accuracy of these measurements is probably within ± 0.2 mm of Hg. The manometer readings were reduced to millimeters of mercury at 0°C.

Pressure in the still was controlled by a photoelectric amplifying system and by a control manometer [19]. Sampling of the phases at equilibrium was accomplished by the syringes simultaneously. Composition of the samples were determined by measuring their refractive indices at 25°C. A Carl-Zeiss-Abbe refractometer, with an accuracy of 0.0001 was used. This corresponds to the maximum uncertainty in mole fraction of ± 0.002 .

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Table 1 Physical properties of components and of their binary mixtures at 25°C

Property	Acetone	Benzene	Cyclohexane
Density at 25°C, g/cm ³			
experimental	0.7850	0.8738	0.7738
literature	0.78501 [33]	0.87365 ₀ [18]	0.77387 ₆ [18]
Refractive index at 25°C			
experimental	1.3557	1.4979	1.4231
literature	1.35598 [33]	1.49800 [33]	1.4233 [35]
Vapour pressure at 25°C			
mm Hg			
experimental	230.40	95.05	97.45
literature	229.55 [31] 231.2 [37]	95.15 [34]	97.81 [36]
Liquid molar volume at 25°C, cm ³ /mol	73.987	89.391	108.762
Second virial coefficients for pure components at 25°C, cm ³ /mol	-1981 [10,11]	-1477 [12,13]	-1561 [13,14]
Gross second virial coefficients at 25°C, cm ³ /mol		acetone-benzene -1618 [15] benzene-cyclohexane -1431 [13] acetone-cyclohexane -1356 ⁺	

⁺ Predicted value by the method of ref. [2,3]

CORRELATION OF THE DATA

The experimental vapour-liquid equilibrium data were correlated by two different procedures which take into account the nonideality of both phases. One of them is based on the use of $P-x-y$, and the other on the $P-x$ isothermal data.

The first calculational procedure was carried out through application of eqn (1)

$$\varphi_i y_i P = \gamma_i^{(P0)} x_i f_i^{\alpha(P0)} \exp \frac{\bar{v}_i^L P}{RT} \quad (1)$$

where the fugacity coefficient φ_i of the component i in the vapour phase is given by eqn (2)

$$\ln \varphi_i = \frac{2}{v} \sum_{j=1}^2 y_j B_{ij} - \ln z \quad (2)$$

The molar volume v and the compressibility factor z of the vapour mixture were calculated using eqns (3) and (4)

$$\frac{Pv}{RT} = 1 + \frac{B}{v} \quad (3)$$

$$z = \frac{Pv}{RT} \quad (4)$$

where

$$B = \sum_{i=1}^2 \sum_{j=1}^2 y_i y_j B_{ij}, \quad B_{ij} = B_{ji} \quad (5)$$

The reference fugacity for pure component i in the liquid

phase $f_i^{\alpha(P0)}$ was obtained from eqn (6)

$$f_i^{\alpha(P0)} = P_i^s \varphi_i^s \exp \frac{-\bar{v}_i^L P_i^s}{RT} \quad (6)$$

The fugacity coefficient of pure saturated vapour i was calculated from the virial equation

$$\ln \varphi_i^s = \frac{2}{v_i^s} B_{ii} - \ln z_i^s \quad (7)$$

where

$$z_i^s = \frac{P_i^s v_i^s}{RT} = 1 + \frac{B_{ii}}{v_i^s} \quad (8)$$

The zero pressure activity coefficient $\gamma_i^{(P0)}$ is related to the experimentally obtained activity coefficient $\gamma_i^{(P)}$, for the same liquid composition and temperature, by equation

$$\gamma_i^{(P0)} = \gamma_i^{(P)} \exp \frac{-\bar{v}_i^L P}{RT} \quad (9)$$

Various proposed and well-known integrated forms [7, 8] of the Gibbs-Duhem differential equation

$$\sum_{i=1}^2 x_i d \ln \gamma_i^{(P0)} = 0 \quad (10)$$

were used to obtain the composition dependence of activity coefficients. In order to compute numerical values of the adjustable parameters in these expressions, an optimization technique as well as an objective func-

tion to be minimized were selected. Problems associated with making these choices were considered in the literature [1, 21-23]. In the first calculational procedure the objective function defined as

$$F = \sum_{i=1}^n r_i^2, \quad (n = \text{number of data points}) \quad (11)$$

was used, where

$$r_i = (Q_{\text{exp}} - Q_{\text{cal}})_i \quad (12)$$

The dimensionless excess Gibbs energy Q_{exp} is related to the activity coefficients by equation

$$Q_{\text{exp}} = \frac{g^E}{RT} = \sum_{i=1}^2 x_i \ln \gamma_i^{(P0)} \quad (13)$$

The composition dependence of zero pressure activity coefficients, in the expression for Q_{cal} , was given by equations of Margules, Van Laar, Scatchard-Hamer, Wohl [7] and Wilson [8]. Newton-Raphson nonlinear programming method [24] was used to minimize the objective function F .

It was pointed out [2-5] that the calculational procedure, described above, makes use of the thermodynamically overspecified set of binary isothermal data. Nevertheless, it is often practically employed. Since the experimental uncertainty is, in most cases, greatest for vapour composition, different methods for the reduction of $P-x$ data have been developed [1-5].

The second calculational procedure, used in this work, requires the experimental $P-x$ data. It is similar to the method proposed by Prausnitz [2]. By minimizing the sum of squares of the differences between experimental total pressure and total pressure calculated by

thermodynamic equation

$$P = \sum_{i=1}^2 \frac{\gamma_i^{(P0)} x_i f_i^{(P0)} \exp(\bar{v}_i^L P/RT)}{\phi_i} \quad (14)$$

this method yields both parameters in the $\gamma_i^{(P0)}$ vs x_i models which satisfy the differential eqn (10) and vapour composition, since partial pressure of the component i can be expressed as product $y_i P$. The same empirical fitting functions for activity coefficients, used in the data reduction procedure described first, were employed in eqn (14) as well.

Throughout the second calculational procedure of data reduction the objective function

$$S = \sum_{i=1}^n (P_{\text{exp}} - P_{\text{cal}})_i^2 \quad (15)$$

and the numerical method [24], already mentioned, was used.

RESULTS AND DISCUSSION

Experimental vapour-liquid equilibrium data for the systems acetone-benzene, benzene-cyclohexane and acetone-cyclohexane at 25°C, obtained in this work, are presented in Table 2.

Vapour-liquid equilibrium data for the system acetone-benzene at 25°C were predicted and reported by Litvinov [25]. It can be seen from Fig. 1 that the data presented here are neither in close agreement with the two control experimental points of Litvinov nor with his predicted values. Brown *et al* [26] reported similar disagreement, comparing their excess Gibbs energies at 45°C, with those corresponding to the data of Litvinov at 25° and 35°C. Kraus *et al* [27] reported the equilibrium data for this system at 30, 40 and 50°C.

Table 2 Experimental vapour-liquid equilibrium data at 25°C

Acetone(1) - Benzene(2)			Benzene(1) - Cyclohexane(2)			Acetone(1) - Cyclohexane(2)		
x_1	y_1	P	x_1	y_1	P	x_1	y_1	P
0.0000	0.0000	95.05	0.0000	0.0000	97.45	0.0000	0.0000	97.45
0.0820	0.2480	116.65	0.1035	0.1375	102.05	0.0115	0.1810	118.05
0.1850	0.4160	137.20	0.1750	0.2170	104.50	0.0160	0.2250	124.95
0.3070	0.5500	156.30	0.2760	0.3130	106.75	0.0250	0.3040	137.90
0.4010	0.6320	169.30	0.3770	0.4015	108.10	0.0300	0.3450	145.00
0.5050	0.7030	182.10	0.4330	0.4460	108.45	0.0440	0.4100	160.30
0.5900	0.7550	191.20	0.5090	0.5050	108.65	0.0575	0.4580	172.90
0.7040	0.8240	203.20	0.5830	0.5620	108.30	0.0890	0.5330	195.70
0.8055	0.8820	213.40	0.6940	0.6505	106.90	0.1125	0.5670	207.70
0.8955	0.9360	220.95	0.7945	0.7410	104.50	0.1775	0.6110	227.70
0.9090	0.9440	222.35	0.9005	0.8565	100.60	0.2330	0.6325	237.85
0.9320	0.9580	225.05	0.9500	0.9220	98.15	0.3090	0.6550	246.35
1.0000	1.0000	230.40	1.0000	1.0000	95.05	0.4235	0.6800	253.90
						0.5105	0.6940	257.45
						0.5760	0.7050	259.40
						0.6250	0.7095	260.50
						0.6605	0.7170	261.10
						0.6920	0.7250	261.50
						0.7390	0.7390	262.00
						0.7575	0.7460	261.90
						0.8605	0.8030	258.70
						0.8930	0.8280	255.70
						0.9250	0.8580	252.00
						0.9625	0.9160	243.80
						1.0000	1.0000	230.40

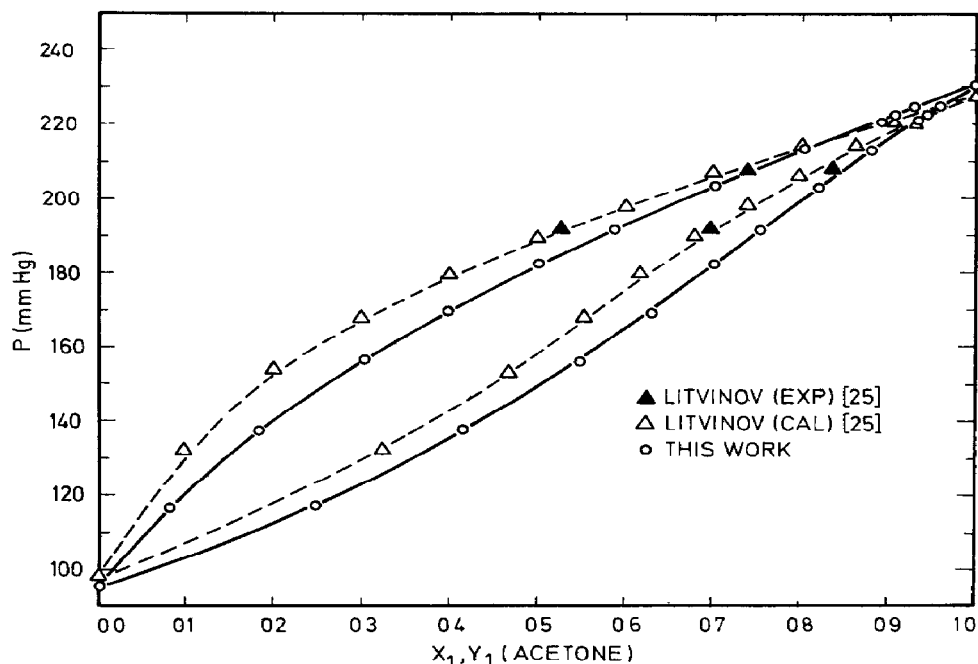


Fig. 1 Equilibrium data for the system acetone(1)-benzene(2) at 25°C

Isothermal data for the system benzene-cyclohexane were reported by Scatchard *et al* [28] at 39.99 and 69.98°C, Boublik [29] at 10 and 60°C and Kortüm and Freier [30] at 119.3°C. No data at 25°C have been found in literature.

Recently, Puri *et al* [31] reported data for the system acetone-cyclohexane at 25°C. Reasonably good agreement of these data with the results obtained in the

present work is shown in Fig. 2. Pronounced steepness of $P-x$ curve below 0.2 mole fraction of acetone caused experimental difficulties, and hence greater uncertainty is associated with the presented data in this region.

The results of two data reduction procedures previously described, which are based on the mentioned fitting models for activity coefficients, are summarized in Table 3. It can be seen from this table that the numerical

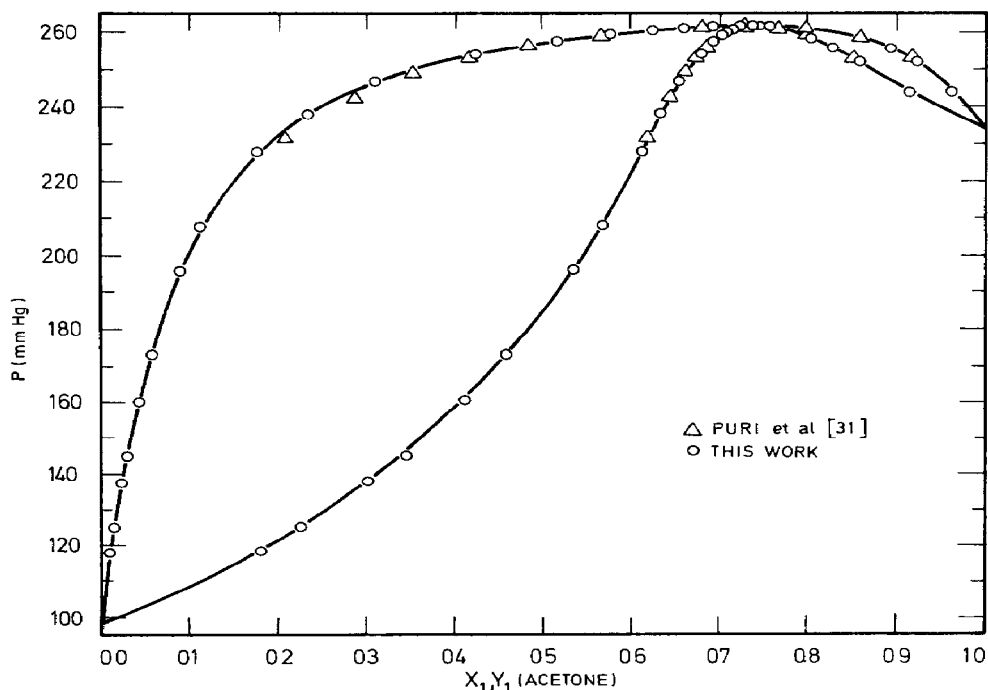


Fig. 2 Equilibrium data for the system acetone(1)-cyclohexane (2) at 25°C

Table 3 Parameters of the fitting models for systems investigated at 25°C

Parameters from experimental P-x-y data														Parameters from experimental P-x data					
Model ^a	Number of parameters	A	B	D	q ₂ /q ₁	Λ ₁₂	Λ ₂₁	A	B	D	q ₂ /q ₁	Λ ₁₂	Λ ₂₁						
ACETONE(1)-BENZENE(2)																			
Margules	2	0.5073	0.4400					0.5069	0.4259										
	3	0.5566	0.4782	0.2067				0.5569	0.4568	0.1726									
van Laar	2	0.5117	0.4402					0.5149	0.4267										
	3	0.5652	0.4712	0.2126				0.5735	0.4497	0.1852									
Scatchard-Hamer	2	0.4955	0.4337					0.4908	0.4206										
	3	0.5457	0.4877	0.2253				0.5440	0.4678	0.1981									
Wohl	3	0.5117	0.4402		0.8575			-	-	-									
	4	0.5509	0.4830	0.2138	1.1110			0.5664	0.4527	0.1737	0.8705								
Wilson	2					0.6562	0.9064					0.6297	0.9437						
BENZENE(1)-CYCLOHEXANE(2)																			
Margules	2	0.4498	0.4952					0.4561	0.5108										
	3	0.4424	0.4880	-0.0335				0.4610	0.5159	0.0225									
van Laar	2	0.4509	0.4960					0.4572	0.5126										
	3	0.4427	0.4867	-0.0386				0.4649	0.5187	0.0294									
Scatchard-Hamer	2	0.4502	0.4945					0.4566	0.5115										
	3	0.4430	0.4847	-0.0350				0.4601	0.5167	0.0171									
Wohl	3	0.4423	0.4894		0.8403			-	-	-									
	4	0.4722	0.5107	0.7045	0.1566			-	-	-									
Wilson	2					0.8578	0.7003					0.8690	0.6810						
ACETONE(1)-CYCLOHEXANE(2)																			
Margules	2	2.0176	1.7398					2.0207	1.6829										
	3	2.2052	1.9565	0.9777				2.1572	1.9470	0.9494									
van Laar	2	2.0348	1.7423					-	-										
	3	2.2325	1.9227	0.9984				2.1761	1.9025	0.9105									
Scatchard-Hamer	2	1.9171	1.6360					-	-										
	3	2.1205	2.0798	1.1798				2.0940	2.1411	1.3074									
Wohl	3	2.0269	1.7170		0.8476			-	-	-									
	4	2.1860	1.9810	1.0981	0.9970			2.1864	1.8818	0.8098	0.9183								
Wilson	2					0.2067	0.3206					0.2164	0.3220						

^a $\ln \frac{f_i}{f_i^0}$ form, ^b Convergence was not achieved

values of parameters depend on the choice of the calculational procedure used for their determination. Both treatments have to produce the same values of parameters if the perfect set of $P-x-y$ data is reduced using a suitable model for activity coefficients. In addition, lack-of-convergence was encountered for some of the models used in the reduction procedure of $P-x$ data. This fact is due to the behaviour of the objective function in the parameter space and to the nature of the minimization method employed.

Standard errors of estimate for vapour composition R_{y_1} and for total pressure R_P are presented in Table 4, indicating both the adequacy of two data reduction procedures and the flexibility of thermodynamic models employed.

The nature of these results is a consequence of relatively large differences in nonideal behaviour of the investigated systems. It can be seen from Table 4 that for the system acetone-benzene the reduction method, based on $P-x$ data, provides better agreement of the experimental and calculated vapour compositions than the other method used. Significant improvements in the same sense can be observed especially for the system acetone-cyclohexane. These observations are in agreement with the conclusions of Mackay and Salvador[32] who stated that the $P-x$ method should be used in the cases of high relative volatility and where $P-x$ gradient is high. The results of Table 4, corresponding to the system benzene-cyclohexane, show that both methods of data reduction provide practically

Table 4 Comparison of experimental and calculated equilibrium data at 25°C

		Standard errors of estimates and maximal deviations corresponding to the use of P-x-y data				Standard errors of estimates and maximal deviations corresponding to the use of P-x data			
Model ^a	Number of parameters	y ₁		P		y ₁		P	
		R _{y₁} ^b	Δy _{1max}	R _P ^c	P _{max}	R _{y₁} ^b	Δy _{1max}	R _P ^c	P _{max}
ACETONE(1)-BENZENE(2)									
Margules	2	0.0031	-0.0058	0.5613	1.08	0.0029	-0.0065	0.3807	0.66
	3	0.0018	-0.0031	0.2950	0.76	0.0018	-0.0046	0.2680	-0.59
van Laar	2	0.0030	-0.0060	0.5431	1.08	0.0029	-0.0061	0.3881	-0.65
	3	0.0018	0.0030	0.3194	0.82	0.0017	-0.0036	0.2818	-0.52
Scatchard- Hamer	2	0.0036	-0.0074	0.6340	1.02	0.0035	-0.0076	0.4153	-0.69
	3	0.0020	-0.0039	0.2794	0.71	0.0023	-0.0053	0.3273	-0.69
Wohl	3	0.0030	0.0060	0.5424	1.08	-	-	-	-
	4	0.0023	0.0045	0.5366	1.17	0.0018	-0.0040	0.2884	-0.55
Wilson	2	0.0029	-0.0055	0.5254	1.06	0.0026	-0.0060	0.3436	-0.62
BENZENE(1)-CYCLOHEXANE(2)									
Margules	2	0.0014	0.0040	0.0609	0.13	0.0018	0.0040	0.0654	-0.13
	3	0.0016	-0.0036	0.0470	0.11	0.0017	-0.0036	0.0646	-0.11
van Laar	2	0.0014	-0.0039	0.0632	0.13	0.0019	-0.0039	0.0704	-0.12
	3	0.0017	0.0535	0.0539	-0.09	0.0018	-0.0034	0.0785	0.12
Scatchard- Hamer	2	0.0014	-0.0040	0.0613	0.13	0.0020	-0.0040	0.0710	-0.13
	3	0.0016	-0.0037	0.0442	0.12	0.0019	-0.0037	0.0702	-0.11
Wohl	3	0.0016	0.0037	0.0490	0.12	-	-	-	-
	4	0.0010	-0.0022	0.2614	-0.45	-	-	-	-
Wilson	2	0.0014	-0.0026	0.0700	0.16	0.0017	-0.0037	0.0639	-0.12
ACETONE(1)-CYCLOHEXANE(2)									
Margules	2	0.0142	0.0254	4.1184	-9.76	0.0129	0.0246	3.6039	-7.84
	3	0.0058	-0.0113	1.8749	-3.80	0.0038	-0.0065	0.6719	-1.47
van Laar	2	0.0133	-0.0235	3.9341	-9.57	-	-	-	-
	3	0.0060	-0.0127	1.6782	-3.34	0.0032	-0.0050	0.4542	-0.86
Scatchard- Hamer	2	0.0219	0.0424	5.8432	-11.52	-	-	-	-
	3	0.0076	-0.0170	2.7316	-7.83	0.0081	-0.0139	1.9407	-4.07
Wohl	3	0.0128	0.0236	3.6278	-8.17	-	-	-	-
	4	0.0102	0.0193	2.5521	-4.78	0.0031	-0.0049	0.4074	-0.69
Wilson	2	0.0059	-0.0143	0.4846	-2.55	0.0032	-0.0078	0.3654	-0.61

$$^a \ln \gamma_1^{(PO)} \text{ form, } ^b R_{y_1} = \left[\sum_1^n (y_{1\text{exp}} - y_{1\text{cal}})^2 / n \right]^{1/2}, \quad ^c R_P = \left[\sum_1^n (P_{\text{exp}} - P_{\text{cal}})^2 / n \right]^{1/2}$$

the same accuracy. Minor advantage of the method based on $P-x-y$ data is also in agreement with the findings of Mackay and Salvador. This is due to the fact that the system benzene-cyclohexane has the lowest relative volatility.

It is well known that the deviations between measured and predicted equilibrium variables come from both the systematic errors of the measurements and from inadequacy of the thermodynamic model employed in the reduction procedure. If a specific vapour-liquid equilibrium data set is represented by different models, their relative suitability can be indicated by comparing the corresponding deviations,† R_{y1} and R_p values for the system benzene-cyclohexane, where deviations from ideality are not large, indicate that all the models have similar suitability. Nevertheless, Margules's equation

with three parameters ($P-x-y$ method) is proposed. For the system acetone-benzene some differences exist in the applicability of the models. It seems that three-parameter van Laar's equation ($P-x$ method) gives the best representation of the data. The results of Table 4, for the system acetone-cyclohexane, lead to the conclusion that significant variations in flexibility of the models are present. Wilson's equation ($P-x$ method) and four-parameter Wohl's equation ($P-x$ method) gave similar results for this system. Wilson's equation, which uses only two adjustable parameters, seems to be slightly better.

Plots Δy_1 and ΔP vs x_1 for all investigated systems and for both data reduction procedures, in which above recommended correlating models were incorporated, are shown in Fig. 3. Deviations presented in Δy_1 vs x_1 plots can be compared with the experimental uncertainty in order to check the validity of vapour-liquid equilibrium data. One sees from Fig. 3 that the individual deviations Δy_1 for most of the data points, corresponding to the

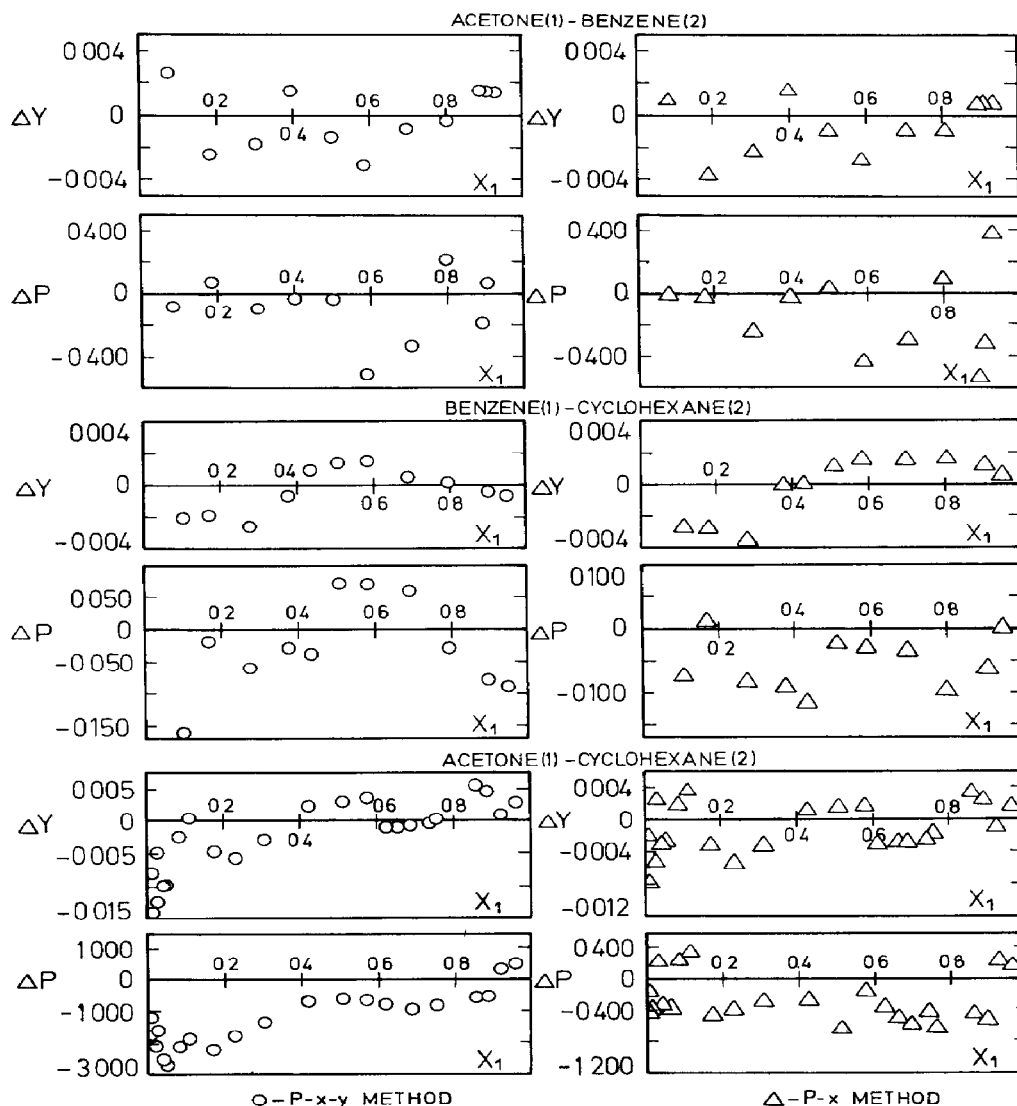


Fig. 3 Δy_1 and ΔP vs x_1 for the systems investigated at 25°C

acetone–benzene and benzene–cyclohexane systems, are within the range of experimental error. Proposed models for these systems gave standard errors $R_{y,i}$ which do not exceed the range of experimental uncertainty as well, indicating that the data are thermodynamically consistent and that the reduction procedure is correct [4].

Although the Wilson's equation for the system acetone–cyclohexane gave standard error $R_{y,i}$ not much outside the range of the experimental error, individual deviations Δy_i in the acetone dilute region are more pronounced. These higher uncertainties of the data are due to the previously mentioned experimental difficulties experienced for these compositions.

Although plots ΔP vs x_1 do not check the consistency, they indicate the ability of proposed analytical expressions for activity coefficients to fit the experimental $P-x$ data. It should be noticed from the ΔP vs x_1 plot of Fig. 3, for the system acetone–cyclohexane, that pressure measurements are not represented within the limits of experimental uncertainty by Wilson's equation. Moreover, distribution of individual ΔP points in this plot is, to some extent, characterized by nonrandom behaviour. Consequently two possibilities can occur: either the lack-of-flexibility of the Wilson's equation for acetone–cyclohexane system, or some degree of inconsistency of the equilibrium data. It is known that these two cases cannot be strictly distinguished.

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NOTATION

$A, B, D, q/q_n, \Lambda_n, \Lambda_n$	parameters of the thermodynamic models relating activity coefficients and liquid composition
B	second virial coefficient defined by eqn (5), cm^3/mole
B_{ii}, B_{jj}	second virial coefficient of pure i and pure j , cm^3/mole
B_{ij}	second virial cross-coefficient of a binary mixture ($B_{ij} = B_{ji}$), cm^3/mole
F	objective function defined by eqn (11)
f_i^L	liquid phase fugacity of i , mm Hg
$f_i^{(PO)}$	reference fugacity of pure liquid i at system temperature and zero pressure, mm Hg
g^E	molar excess Gibbs energy, cal/mole
n	number of data points
P	total pressure, mm Hg
P_i^S	saturation (vapour) pressure of pure liquid i at temperature T , mm Hg

Q	dimensionless excess Gibbs energy defined by eqn (13)
R	universal gas constant, cal/(mole °K)
R_P	standard error of estimate in pressure, mm Hg
$R_{y,i}$	standard error of estimate in vapour-phase mole fraction of i
r_i	difference defined by eqn (12)
S	sum defined by eqn (15)
T	absolute temperature, °K
V^E	excess molar volume of mixing, cm^3/mole
v	molar vapour volume of a binary mixture, cm^3/mole
v_i^L	molar liquid volume of pure i at temperature T , cm^3/mole
\bar{v}_i^L	partial molar liquid volume of i in the binary mixture of temperature T , cm^3/mole
v_i^S	saturated molar volume of pure vapour i , cm^3/mole
x_i	liquid-phase mole fraction of i
y_i	vapour-phase mole fraction of i
z	compressibility factor
z_i^S	compressibility factor of i at temperature T and saturation pressure P_i^S

Greek symbols

γ_i^P	experimental isothermal liquid-phase activity coefficient of i
$\gamma_i^{(PO)}$	activity coefficient of i at temperature T adjusted to zero pressure
Δ	difference between experimental and calculated values
ϕ_i	vapour-phase fugacity coefficient of i
ϕ_i^S	fugacity coefficient of pure saturated vapour i at temperature T and saturation pressure P_i^S

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