

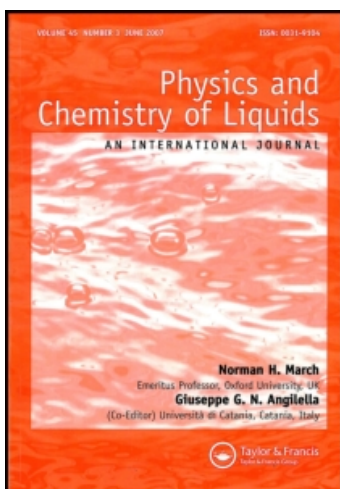
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## Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

### Vapour-liquid equilibria of butyl acetate with aromatic hydrocarbons at 298.15 K

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**To cite this Article** Maken, S. , Deshwal, B. R. , Singh, K. C. , Park, S. -J. and Park, J. W.(2005) 'Vapour-liquid equilibria of butyl acetate with aromatic hydrocarbons at 298.15 K', *Physics and Chemistry of Liquids*, 43: 2, 149 – 156

**To link to this Article:** DOI: 10.1080/00319100512331330799

**URL:** <http://dx.doi.org/10.1080/00319100512331330799>

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## Vapour–liquid equilibria of butyl acetate with aromatic hydrocarbons at 298.15 K

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(Received 30 August 2004)

Vapour pressures of butyl acetate + benzene or toluene or *o*- or *m*- or *p*-xylene were measured by static method at 298.15 ± 0.01 K over the entire composition range. The activity coefficients and excess molar Gibbs's free energies of mixing ( $G^E$ ) for these binary mixtures were calculated by fitting vapour pressure data to the Redlich–Kister equation using Barker's method of minimizing the residual pressure. The  $G^E$  values for the binary mixtures containing benzene are positive; while these are negative for toluene, *ortho*, *meta* and *para* xylene system over the whole composition range. The  $G^E$  values of an equimolar mixture for these systems vary in the order: benzene > *m*-xylene > *o*-xylene > *p*-xylene > toluene

**Keywords:** Vapour–liquid equilibrium; Gibbs free energy; Butyl acetate; Aromatic hydrocarbon.

### 1. Introduction

The chemical industries have recognized the importance of the thermodynamic and physical properties in design calculations involving chemical separations, heat transfer, mass transfer and fluid flow. The design of separation processes in industry requires a great knowledge of the behaviour of different systems in the phase's equilibria. Accurate vapour–liquid equilibrium (VLE) data are essential for chemical engineers to design distillation tower, which is the most important part of petroleum refining and also important to chemists to understand the nature of molecular interactions. A number of experimental as well as theoretical studies on thermodynamic properties for alkyl ester with alkanes [1–9], aromatic hydrocarbon [8–17], alcohols [18,19], chloroalkane [20], and acetonitrile [16,21] have been reported in literature. Among them,

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systematic data for alkyl ester + aromatic polar solvent are relatively rare [10–17]. Alkyl esters are characterized by dipole–dipole interactions in the pure state [1–3]. The degree and strength of dipole–dipole interactions decreases with the increasing size of alkyl group in the esters. The additions of inert solvents like alkane generally break the orientation order of pure alkyl esters to give the positive value of excess thermodynamic functions like excess molar volume ( $V^E$ ), excess molar enthalpy ( $H^E$ ), and excess molar Gibb's free energy ( $G^E$ ) [4,5]. However, these values become very less and even negative in the mixtures of alkyl esters + aromatic hydrocarbons [10,11,14,15]. Specific interactions of dipole-induced dipole type are postulated to account for such behaviour [14,15].

These considerations prompted us to carry out a systematic study on the thermodynamic properties of alkyl esters with aromatic hydrocarbons. In our earlier paper [22], the measured  $V^E$  and  $H^E$  data for *n*-butyl acetate + cyclohexane or benzene or toluene or *o*- or *m*- or *p*-xylene were interpreted in terms of graph theoretical approach [23,24]. In this article, the measured VLE data for *n*-butyl acetate + benzene or toluene or *o*- or *m*- or *p*-xylene at  $298.15 \pm 0.01$  K are reported along with excess molar Gibbs free energies of mixing ( $G^E$ ) calculated from Bakers' method [25]. To the best of our knowledge, no VLE data have been previously reported in the literature for the present systems at 298.15 K.

## 2. Experimental section

Butyl acetate (Merck) was dried over anhydrous magnesium sulphate and then fractionally distilled [26]. The middle fraction of distilled *n*-butyl acetate was then dried over type 0.3 nm molecular sieves (Merck) in an amber coloured bottle for several days before use. Benzene, toluene, and xylenes (Merck) were shaken repeatedly with 15% (v/v) concentrated sulphuric acid in a separating funnel in order to eliminate thiophene from them until the acid layer was colourless [27]. After each shaking that lasted a few minutes, the mixtures were allowed to settle and the acid was drawn off. The remaining acid was neutralized by sodium bicarbonate solution and the substance of interest was subsequently washed with distilled water and dried over fused calcium chloride for 24 h. It was then fractionally distilled and the middle fraction of the distillate was stored over sodium wire in an amber coloured bottle. The purities of the purified samples were checked by measuring their densities, refractive indices, and vapour pressures at 308.15 K. The densities were measured with a precision of  $\pm 0.05 \text{ kg m}^{-3}$  by a specially designed densimeter, consisting of a bulb of approximate volume  $3.5 \times 10^{-5} \text{ m}^3$  attached to a calibrated capillary through a B-10 standard joint in the manner described by Weissenberger [28]. Air buoyancy correction was also applied to achieve a greater accuracy. Refractive indices were measured with a thermostatically controlled Abbe refractometer (OSAW, India) using sodium D-line with an accuracy of  $\pm 1 \times 10^{-4}$ . The total vapour pressures of the pure components and their various binary mixtures were measured as a function of liquid phase mole fraction of butyl acetate ( $x_A$ ) at 298.15 K by the static method [29] in the manner described by Nigam and Mahl [30]. The height of the mercury column in the manometer was read with a cathetometer (OSAW, India) with a resolution of  $\pm 1 \times 10^{-5} \text{ m}$ . The uncertainties in the vapour pressure measurements due to the manometer were  $\pm 2.66 \text{ Pa}$ . Condensation effect on mercury was avoided by vacuum suction of condensed vapours from

Table 1. Densities ( $\rho$ ), refractive indices ( $n_D$ ) and vapor pressures ( $p$ ) of the pure components at 298.15 K.

Substance	$\rho/(\text{kg m}^{-3})$		$n_D$		$p/(\text{kPa})$	
	This work	Literature	This work	Literature	This work	Literature
Butyl acetate	876.38	876.36 <sup>a</sup>	1.3928	1.3931 <sup>b</sup>	1.665	1.664 <sup>a</sup>
Benzene	873.56	873.60 <sup>a</sup>	1.4977	1.4979 <sup>c</sup>	12.702	12.7 <sup>a</sup>
Toluene	862.24	862.19 <sup>a</sup>	1.3858	1.3859 <sup>c</sup>	3.802	3.8036 <sup>a</sup>
<i>o</i> -Xylene	875.97	875.94 <sup>a</sup>	1.5031	1.50295 <sup>a</sup>	0.880	0.88 <sup>a</sup>
<i>m</i> -Xylene	860.05	860.09 <sup>a</sup>	1.4947	1.4946 <sup>a</sup>	1.098	1.1 <sup>a</sup>
<i>p</i> -Xylene	856.63	856.61 <sup>a</sup>	1.4931	1.4933 <sup>c</sup>	1.201	1.2 <sup>a</sup>

<sup>a</sup>Ref. [26]. <sup>b</sup>Ref. [31]. <sup>c</sup>Ref. [32].

manometer after each measurement and also mercury was changed after every four or five readings. Our experimental values for the density, refractive index, and vapour pressure of the pure compounds compared well with the literature values as shown in table 1. The composition of the liquid phase was determined by measuring the refractive index using an Abbe refractometer in the manner described by Strubl *et al.* [33]. The uncertainties in the liquid phase composition were about 0.01 mol per cent.

### 3. Results and discussion

The measured vapour pressure ( $p$ ) for the present *n*-butyl acetate ( $A$ ) + benzene, or toluene, or *o*-, or *m*-, or *p*-xylene ( $B$ ) systems at 298.15 K over the entire composition range are reported in table 2 and shown graphically in figure 1. The values of excess molar Gibbs free energies of mixing  $G^E$  as a function of composition are calculated by fitting VLE data using Barker's method [25] of minimizing the residual pressure ( $\delta p$ ) to Redlich–Kister equation (1) and are reported in table 2 along with activity coefficients and  $\delta p$  and are shown in figure 2.

$$G^E/RT = x_A x_B \sum_{j=0}^m A_j (x_A - x_B)^j \quad (1)$$

The activity coefficients  $\gamma_A$  and  $\gamma_B$  are obtained by differentiation of above equation

$$\ln \gamma_A = x_B^2 \left[ A_0 + \sum_{j=1}^m \{ A_j (x_B - x_A)^j - 2j A_j x_A (x_B - x_A)^{j-1} \} \right] \quad (2)$$

$$\ln \gamma_B = x_A^2 \left[ A_0 + \sum_{j=1}^m \{ A_j (x_B - x_A)^j - 2j A_j x_B (x_B - x_A)^{j-1} \} \right] \quad (3)$$

where subscript A and B stand for butyl acetate and second component, respectively. The calculated vapour pressure is then given by:

$$P_{\text{calcd}} = x_A \gamma_A P_A^* R_A + x_B \gamma_B P_B^* R_B \quad (4)$$

Table 2. Measured vapour pressure ( $p$ ), activity coefficients ( $\gamma_A$  and  $\gamma_B$ ), residual vapour pressure ( $\delta_p = p_{\text{calcd}} - p_{\text{expd}}$ ), where  $p_{\text{calcd}}$  is obtained from Barker's method, and molar Gibbs energies of mixing ( $G^E$ ) as a function of mole fraction  $x_A$  at 298.15 K for butyl acetate ( $A$ ) + an aromatic hydrocarbon ( $B$ ).

$x_A$	$p$ (kPa)	$\gamma_A$	$\gamma_B$	$\delta p$ (kPa)	$G^E$ /(J mol $^{-1}$ )
<b>Butyl Acetate (<math>A</math>) + Benzene (<math>B</math>)</b>					
0.1501	11.61	1.6276	1.0408	0.0880	250
0.2599	10.71	1.4465	1.0935	-0.0333	323
0.3798	9.60	1.2958	1.1446	-0.0733	346
0.5203	8.12	1.168	1.1853	-0.0213	335
0.6202	7.03	1.1023	1.2144	0.0667	314
0.6797	6.35	1.0715	1.2424	0.0947	295
0.7398	5.33	1.0466	1.288	-0.0973	270
0.8602	4.18	1.0133	1.4844	0.0387	189
0.9099	3.47	1.0055	1.6407	0.0107	137
0.9694	2.40	1.0006	1.9334	-0.0227	54
<b>Butyl Acetate (<math>A</math>) + Toluene (<math>B</math>)</b>					
0.0899	3.45	0.6484	0.9895	-0.0683	-120
0.1501	3.40	0.7208	0.9755	0.0617	-174
0.2798	2.96	0.8203	0.9431	-0.0191	-242
0.3897	2.73	0.859	0.9219	0.0140	-270
0.4703	2.53	0.8756	0.9096	-0.0139	-281
0.5905	2.30	0.8951	0.8857	-0.0048	-285
0.6899	2.11	0.9187	0.8448	0.0057	-275
0.7896	1.93	0.9496	0.7671	0.0068	-239
0.8902	1.79	0.9817	0.6412	-0.0071	-162
0.9201	1.76	0.9895	0.5944	-0.0105	-127
<b>Butyl Acetate (<math>A</math>) + <i>o</i>-Xylene (<math>B</math>)</b>					
0.0702	0.89	0.7331	0.9982	0.0007	-88
0.1401	0.92	0.7668	0.9929	-0.0020	-147
0.2498	1.00	0.8172	0.9778	0.0035	-199
0.3599	1.08	0.8634	0.9545	-0.0028	-220
0.4503	1.16	0.8971	0.9299	-0.0036	-224
0.5197	1.22	0.9206	0.9075	0.0004	-222
0.5905	1.29	0.9415	0.8825	0.0028	-217
0.7498	1.44	0.9778	0.8171	0.0036	-185
0.8295	1.53	0.9896	0.7809	0.0008	-152
0.9101	1.62	0.9971	0.7428	0.0099	-97
<b>Butyl Acetate (<math>A</math>) + <i>m</i>-Xylene (<math>B</math>)</b>					
0.0702	1.07	0.6678	0.9938	-0.0036	-85
0.1601	1.10	0.7797	0.9745	0.0044	-152
0.2598	1.15	0.8696	0.9496	0.0013	-191
0.3703	1.21	0.9095	0.9269	-0.0027	-206
0.4598	1.27	0.9382	0.9138	-0.0084	-206
0.5397	1.33	0.9378	0.9045	0.0005	-200
0.6102	1.39	0.9452	0.8949	0.0051	-193
0.7101	1.47	0.9582	0.8709	0.0067	-174
0.8198	1.56	0.9771	0.8156	0.0031	-138
0.8999	1.63	0.991	0.7463	-0.0211	-93
<b>Butyl Acetate (<math>A</math>) + <i>p</i>-Xylene (<math>B</math>)</b>					
0.0799	1.17	0.6574	0.9928	-0.0083	-91
0.1801	1.19	0.7635	0.9715	0.0021	-167
0.2898	1.23	0.8403	0.9439	0.0053	-215
0.3704	1.26	0.8753	0.9253	0.0003	-236
0.4497	1.29	0.8989	0.9085	-0.0036	-247
0.5495	1.39	0.9202	0.8875	-0.0101	-250
0.5902	1.35	0.9278	0.8777	0.0032	-248
0.7108	1.48	0.9516	0.8367	0.0121	-226
0.8497	1.57	0.9815	0.7467	-0.0087	-160
0.9099	1.65	0.9923	0.6886	-0.0015	-110

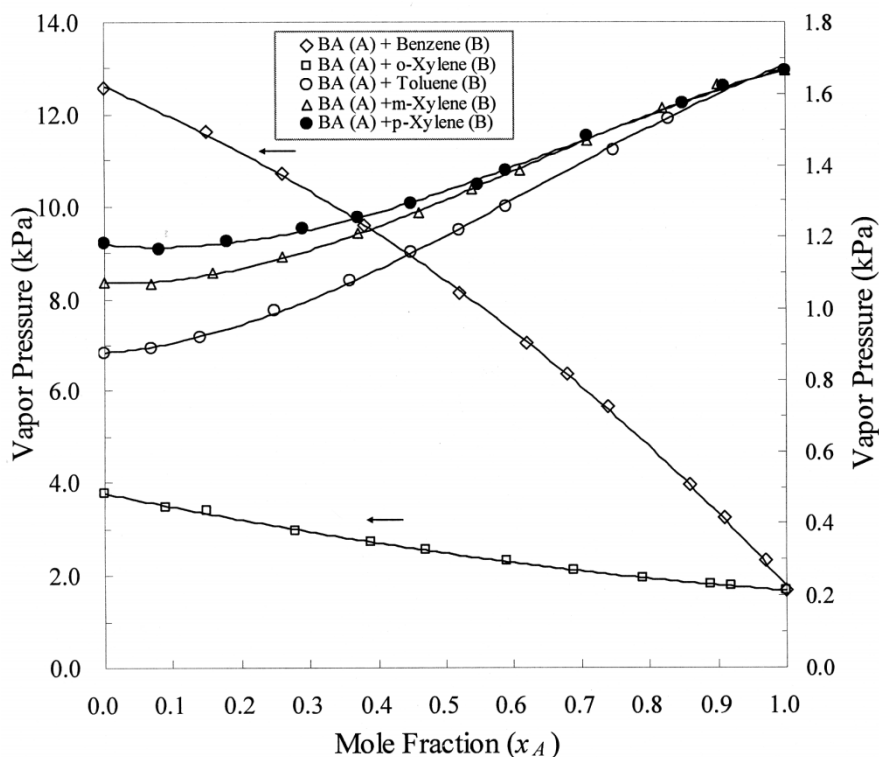


Figure 1. Experimental vapour pressures as a function of mole fraction of butyl acetate ( $x_A$ ) at 298.15 K; the smooth lines represent the calculated vapour pressures for the corresponding systems.

using for non-ideality of the vapour phase the corrections:

$$R_A = \exp\left[\frac{\{(V_A^* - \beta_{AA})(p - p_A^*) - p\delta_{AB}y_B^2\}}{RT}\right] \quad (5)$$

$$R_B = \exp\left[\frac{\{(V_B^* - \beta_{BB})(p - p_B^*) - p\delta_{AB}y_A^2\}}{RT}\right] \quad (6)$$

where  $V_A^*$  and  $V_B^*$  are the molar volumes,  $y_A$  and  $y_B$  are the vapour phase mole fractions of butyl acetate and second component, respectively and  $\delta_{AB}$  is the cross second virial coefficient of the (A + B) binary mixture and defined as:

$$\delta_{AB} = 2\beta_{AB} - \beta_{AA} - \beta_{BB} \quad (7)$$

where  $\beta_{AA}$ ,  $\beta_{BB}$ , and  $\beta_{AB}$  are the second virial coefficients of butyl acetate, second component, and (A + B) mixture, respectively. In this case  $\delta_{AB} = 0$ , as we assume that vapour is an ideal mixture of imperfect gases i.e.

$$\beta_{AB} = (\beta_{AA} + \beta_{BB})/2 \quad (8)$$

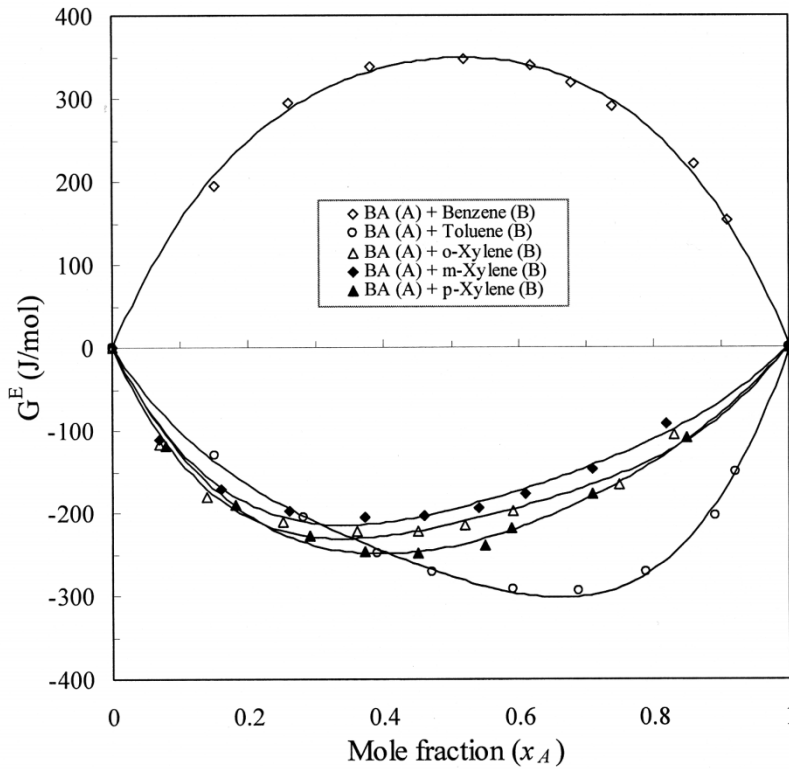


Figure 2. Molar excess Gibbs free energies as a function of mole fraction of butyl acetate ( $x_A$ ) at 298.15 K.

The virial coefficients required for these calculations are calculated from Berthelot's equation [34] and critical constant data used therein are taken from literature [35].

$$\beta = 9RT_C/128P_C - 27RT_C^3/64PT_C^2 \quad (9)$$

The virial coefficients of binary mixtures are taken as the arithmetic mean of second virial coefficients of pure components. The standard deviations are defined by:

$$s(p) = \left[ \sum_{i=1}^N (\delta p)_i^2 / (N - m) \right]^{1/2} \quad (10)$$

where  $\delta p_i$ s are the residual pressures according to Barker's method,  $N$  is the number of experimental points and  $m$  is the number of parameters in the corresponding analytical equation.

The  $s(p)$  along with  $A_j(j=2-4)$  parameters of equation (1) are reported in table 3. The  $G^E$  values are found to be positive for the system containing benzene and negative for other systems over the entire composition range and for an equimolar

Table 3. Adjustable parameters  $A_j(j=0-2)$  of equation (1) and standard deviation  $s(p)$ .

System	$A_0(\text{J mol}^{-1})$	$A_1(\text{J mol}^{-1})$	$A_2(\text{J mol}^{-1})$	$S(p)/(\text{kPa})$
Butyl Acetate (A) + Benzene (B)	0.5459	-0.1161	0.3321	0.068
Butyl Acetate (A) + Toluene (B)	-0.4568	-0.0570	-0.2726	0.034
Butyl Acetate (A) + <i>o</i> -Xylene (B)	-0.3598	0.0296	-0.2145	0.004
Butyl Acetate (A) + <i>m</i> -Xylene (B)	-0.3283	0.0527	-0.2018	0.009
Butyl Acetate (A) + <i>p</i> -Xylene (B)	-0.4027	-0.0264	-0.1715	0.008

composition  $G^E$  values follow the sequence: benzene > *m*-xylene > *o*-xylene > *p*-xylene > toluene (table 3).

### Acknowledgements

Sanjeev Maken thanks the Korean Federation of Science and Technology for the award of a fellowship under Brain Pool and Mr. Dharam Vir (IAS), Principal Secretary, Technical Education, Government of Haryana, for award of study leave from C.R. State College of Engineering, Haryana, India.

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