Vapor-Liquid Equilibrium Measurements on Benzene + n-Decane Systems at 298.15 and 323.15 K

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Vapor-pressures for benzene + n-decane mixtures have been measured using a static technique. Values for the excess Gibbs energy have been calculated using a modified Barker's method and fitted to a Padé approximant equation. The selection of the most adequate approximant is discussed. Results are compared with those corresponding to other benzene + alkane systems. The value for the activity coefficient of benzene at infinite dilution calculated from these data agrees very well with the values obtained by gas-liquid chromatography.

1. INTRODUCTION

Although it is possible to find excess enthalpy (H^E) and excess volume (V^E) data for the system benzene + n-decane in the literature [1, 2], vapor-pressure data have not been available to date [3]. Total vapor-pressure measurements and excess Gibbs energy (G^E) calculations for this system at 298.15 and 323.15 K are reported in this paper. Values of G^E are compared with those obtained for other benzene + alkane systems.

2. EXPERIMENTAL PROCEDURE AND MATERIALS

Vapor-pressure measurements were performed using a static method similar to the one described by McGlashan and Williamson [4]. Details of

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the experimental technique and the degassing method used for pure substances have been reported elsewhere [5]. The accuracy of the experimental measurements of pressure, temperature, and mole fraction where 8 Pa, 0.01 K, and 10^{-4}, respectively. Temperature is expressed on the IPTS-68 scale.

The benzene used in this work was Carlo Erba (RS chromat) and was distilled over sodium wire. A purity of 99.9% was determined by gas chromatography. Values of 0.87370 g · cm^{-3} and 1.49481 were obtained for the density at 298.15 and the refractive index (n_D) at 303.15 K, respectively. These values are in agreement with those reported in the literature (0.87370 g · cm^{-3} at 298.15 K [6] and 1.49468 at 303.15 K [7]). The n-decane used was from Phillips Petroleum (research grade). A purity of 99.7% was determined by gas chromatography. The density at 298.15 K (0.74525 g · cm^{-3}) and the refractive index ($n_D = 1.41757$) agree well with their respective values from the literature: 0.74516 g · cm^{-3} [6] and 1.41755 [7]. The n-dodecane was stored over sodium wire after distillation at reduced pressure.

The vapor pressures of the pure components were found to be 12.695 and 36.162 kPa for benzene at 298.15 and 323.15 K, respectively, and 0.173 and 0.867 kPa for n-decane at the same temperatures. These values are in good agreement with those obtained from the equation proposed by Ambrose [8] for benzene (12.690 and 36.168 kPa, respectively), and from the Antoine equation using coefficients given by Dreisbach [7] for n-decane (0.173 kPa and 0.859 kPa, respectively). Deviations between both sets of values are smaller than those reported by Messow et al. [9], for n-decane at 313.15 K.

3. RESULTS AND DISCUSSION

The vapor pressures of the system benzene + n-decane were measured at 298.15 and 323.15 K. The molar volumes of pure components were taken from the API Tables [6]. The excess volume data, which are necessary in order to estimate the volume of the vapor phase in the measurements cell were taken from Díaz Peña and Nuñez Delgado [2]. Values for the second virial coefficient of n-decane were estimated using the McGlashan and Potter equation [10]. Although a difference of 1000 cm^3 · mol^{-1} is found with respect to the values provided by the method of Pitzer and Curl [11] at 298.15, the G^E values are not affected because of the low volatility of n-decane. The second virial coefficient of the mixture was estimated using the Lorentz–Berthelot combination rule.

Table I gives the experimental values of the total vapor pressure (p), and the mole fraction of benzene (x) obtained for the system studied here. The excess Gibbs energies were calculated using a modified Barker's

Table I. Experimental and Calculated Quantities, and their Deviations from the "True" Values for Benzene + *n*-Decane

x	$10^5\Delta x$	p (kPa)	Δp (Pa)	G^E (J·mol^{-1})	ΔG^E (J·mol^{-1})	γ_1	γ_2	TS^E (J·mol^{-1})
				$(T = 298.15$ K$)$				
0.		0.173						
0.1073	− 4	0.173	12	98.8	0.7	1.4196	1.0026	161
0.1453	− 4	2.700	12	131	1	1.3980	1.0048	237
0.9161	7	3.553	− 19	171	1	1.3702	1.0090	337
0.2463	2	4.318	− 5	207	1	1.3439	1.0149	428
0.3000	− 8	5.089	26	243	2	1.3169	1.0023	511
0.3443	3	5.763	− 8	269	2	1.2954	1.0304	568
0.3763	− 0	6.198	6	287	2	1.2803	1.0372	602
0.4050	8	6.626	− 27	301	2	1.2670	1.0442	630
0.4438	− 5	7.098	17	318	2	1.2493	1.0551	670
0.4749	7	7.542	− 21	331	2	1.2353	1.0652	678
0.4989	− 4	7.810	15	339	2	1.2246	1.0741	690
0.5340	6	8.285	− 23	349	2	1.2090	1.0889	703
0.5487	− 8	8.413	26	353	2	1.2025	1.0958	707
0.5869	0	8.898	− 6	360	2	1.1856	1.1164	711
0.6303	− 1	9.267	6	364	2	1.1708	1.1380	708
0.6373	− 2	9.458	5	365	2	1.1632	1.1509	704
0.7019	3	10.160	− 12	360	2	1.1339	1.2121	671
0.7283	− 1	10.408	3	355	1	1.2116	1.2458	647
0.7461	1	10.586	− 2	349	1	1.1131	1.2725	628
1.0		12.690						
				$(T = 323.15$ K$)$				
0.		0.867						
0.1042	4	5.537	− 4	74.0	0.3	1.2782	1.0022	207
0.1413	− 16	7.095	17	97.4	0.4	1.2611	1.0041	277
0.1920	8	9.218	− 9	127.0	0.5	1.2391	1.0076	368
0.2412	−2	11.182	2	152.99	0.6	1.2190	1.0122	449
0.2957	11	13.322	− 13	178.4	0.7	1.1980	1.0187	532
0.3394	14	14.984	− 17	196.3	0.7	1.1822	1.0250	590
0.3718	− 14	16.153	17	208.0	0.7	1.1710	1.0304	628
0.3999	− 13	17.185	16	217.0	0.8	1.1616	1.0356	658
0.4395	− 14	18.613	17	228.4	0.8	1.1489	1.0439	695
0.4706	10	19.749	− 12	235.7	0.8	1.1393	1.0513	717
0.4956	10	20.626	− 13	240.7	0.8	1.1318	1.0578	733
0.5304	7	21.828	− 10	246.1	0.8	1.1216	0.0679	749
0.5469	5	22.345	− 7	248.0	0.8	1.173	1.0727	754
0.5836	− 11	23.610	15	251.0	0.8	1.1066	1.0861	760
0.6179	5	24.777	− 7	251.8	0.7	1.0973	1.1001	757
0.6346	0	25.318	0	251.4	0.7	1.0928	1.1076	753
0.6999	−9	27.412	13	245.0	0.7	1.0756	1.1437	716
0.7267	−4	28.260	6	239.8	0.7	1.0686	1.1625	691
0.7448	8	28.840	− 12	235.3	0.6	1.0638	1.770	670
1.0		36.168						

method, fitting G^E values to the equation

$$G^E/\{RTx(1 - x)\} = \sum_{i=0}^{n} A_i(2x - 1)^i \Big/ \left\{1 + \sum_{j=1}^{m} B_j(2x - 1)^j\right\} \quad (1)$$

which was first proposed by Marsh [12]. Equation (1) is a Padé approximant of degree (n/m), where A_i and B_j are adjustable coefficients, and RT is the thermal energy. A regression method based on the maximum likelihood principle as developed by Anderson et al. [13] was used to determine the values of coefficients A_i and B_j. This method provides not only the values of coefficients, A_i and B_j, but also the so-called "true" values of the variables (x, p, T), which are the smoothed values of experimental data within the method's uncertainty interval. The deviations between experimental and "true" values (residuals) of the variables (Δx and Δp) are given in Table I. The temperature residuals are not reported because they are negligible.

Several approximants may be found representing the calculated values of the excess Gibbs energy. In order to select objectively the most appropriate approximant, the following criteria have been established [14]:

1. Each set of residuals ($\Delta x, \Delta p$) must present a random distribution around zero.
2. The eigenvalues of the variance-covariance matrix of the parameters, Σ, must be positive or null.
3. The approximant should have a minimal number of parameters, with a statistical significance as high as possible.
4. Uncertainties in G^E, calculated from Σ, must be minimal.
5. Satisfactory agreement must exist between calculated and reported values of other thermodynamic parameters.

The variance-covariance matrix, Σ, enables one to calculate the error of the parameters. The regression method also provides the correlation matrix of the parameters, C, which gives information about the degree of correlation between the parameters. We have found that the approximant (1/1) is the best possible for this system at 298.15 K and 323.15 K.

Table II gives the values of the parameters and their uncertainties, as well as the terms of the Σ and C matrices. The variances of experimental variables are $\sigma(x) = 4 \times 10^{-5}$, $\sigma(p) = 15$ Pa at 298.15 K, $\sigma(x) = 4 \times 10^{-5}$, and $\sigma(p) = 11$ Pa at 323.15 K. Since these values are within the experimental accuracies of the variables, the scattering of experimental points is almost negligible. It may be observed in Table II that the term (2/3) of the correlation matrix is close to unity. This means that the parameters A_i and P_i are correlated in the fit. In principle [15], it is possible to substitute these

Table II. Values for Parameters and Related Quantities for the Best Fit to Eq. (1)

$$T = 298.15 \text{ K}$$

Parameters	Variances
$A_0 = 0.5481 \pm 0.0028$	$\sigma(p) = 15$ (in Pa)
$A_1 = -0.1279 \pm 0.0129$	$\sigma(x) = 4 \times 10^{-5}$
$B_1 = -0.7089 \pm 0.0155$	

Matrices

$$\Sigma = 10^{-4} \begin{pmatrix} 0.0786 & -0.2313 & -0.1895 \\ & 1.6723 & 1.9187 \\ & & 2.4022 \end{pmatrix}$$

$$C = \begin{pmatrix} 1.0 & -0.6328 & -0.4361 \\ & 1.0 & 0.9573 \\ & & 1.0 \end{pmatrix}$$

$$T = 323.15 \text{ K}$$

Parameters	Variances
$A_0 = 0.3599 \pm 0.0010$	$\sigma(p) = 11$ (in Pa)
$A_1 = -0.1407 \pm 0.0053$	$\sigma(x) = 9 \times 10^{-5}$
$B_1 = -0.7537 \pm 0.0103$	

Matrices

$$\Sigma = 10^{-4} \begin{pmatrix} 0.0104 & -0.0327 & -0.0435 \\ & 0.2852 & 0.5317 \\ & & 1.0596 \end{pmatrix}$$

$$C = \begin{pmatrix} 1.0 & -0.6001 & -0.4139 \\ & 1.0 & 0.9671 \\ & & 1.0 \end{pmatrix}$$

two parameters by a linear combination of their values, thus transforming the (1/1) approximant into a (1/0) approximant. Nevertheless, the variances $\sigma(x)$ and $\sigma(p)$, obtained for the resulting (1/0) approximant, are larger than those corresponding to the (1/1) approximant. This behavior has not been found for other systems. Usually, when the number of parameters is reduced by changing from a (m/n) to a $(m - 1/n)$ or $(m/n - 1)$ approximant, the values of the variances or their random distributions are not affected. The change from a (1/1) to a (1/0) approximant here discussed presents the unusual situation of the disappearance of the polynomial denominator in Eq. (1). For the (1/0) approximant, Eq. (1) is a parabolic equation, which one may have difficulties conforming to the recalculated values of $G^E / RTx(1 - x)$.

On the other hand, the random distribution of residuals, Δx and Δp, is also altered when we change from a (1/1) approximant to a (1/0) approximant. The random distribution is checked by the Abbe's test as

described by Linnik [16], which is equivalent to the Van Ness' consistency criterion [17]. Table I also gives the calculated values of G^E and its uncertainties, ΔG^E, as well as the values of the activities of benzene, a_1, and n-decane, a_2, and the excess entropy, S^E. Values of TS^E have been calculated using the H^E data reported for this system at 298.15 K and 323.15 K [1].

Figures 1 and 2 show the values of G^E for the benzene + n-decane system at 298.15 K and 323.15 K together with values for this magnitude previously reported for the benzene + n-hexadecane [14] and benzene + n-pentadecane [15] systems at the same temperatures. The shape and maxima of these G^E curves show a dependence on the chain length similar to that observed for other excess properties of these mixtures.

Excess Gibbs energy data are very often interpolated and even extrapolated using the Gibbs–Helmholtz equation, which may be written as

$$G^E(T_1)/T_1 = G^E(T_0)/T_0 - \int_{T_0}^{T_1} \frac{H^E}{T^2} \, dT \qquad (2)$$

Application of Eq. (2) requires a set of data $G^E(T_0)$ and H^E data covering the temperature range (T_0, T_1) for each mixture composition of interest. These data are not available for a majority of systems, and Eq. (2) is often used assuming that the excess enthalpy does not change with temperature in the $T_0 - T_1$ interval. Very recently, Münsch [18] has described a method for the calculation of the enthalpy of mixing from isothermal vapor-liquid equilibria. This method has been applied successfully to the benzene + n-heptane system. The excess enthalpy may be obtained as

$$H^E = -\overline{H}_1^v \left\{ x(\partial \ln P_1/P_{10}/\partial \ln P_{10})_x + (1 - x)(\partial \ln P_2/P_{20}/\partial \ln P_{20})_x \right\} \quad (3)$$

$\overline{H}_1^v$ being the enthalpy of vaporization of component 1, p_i the partial vapor pressure of component i, and p_{i0} its saturation vapor pressure.

We have applied Eq. (3) to the benzene + n-decane system, using $\overline{H}_i^v = 33.816$ J $\cdot$ mol^{-1} given by Cox and Pilcher [19], and P_i values calculated from Eq. (1). We have assumed a linear variation of $\ln P_i/p_{i0}$ versus $\ln p_{i0}$ as suggested by Münsch [18] for benzene + n-heptane. Results from Eq. (3) reproduce the shape of the H^E versus x curve and the location of the maximum $(x\sim0.63)$, but H^E values are 35% higher than experimental ones.

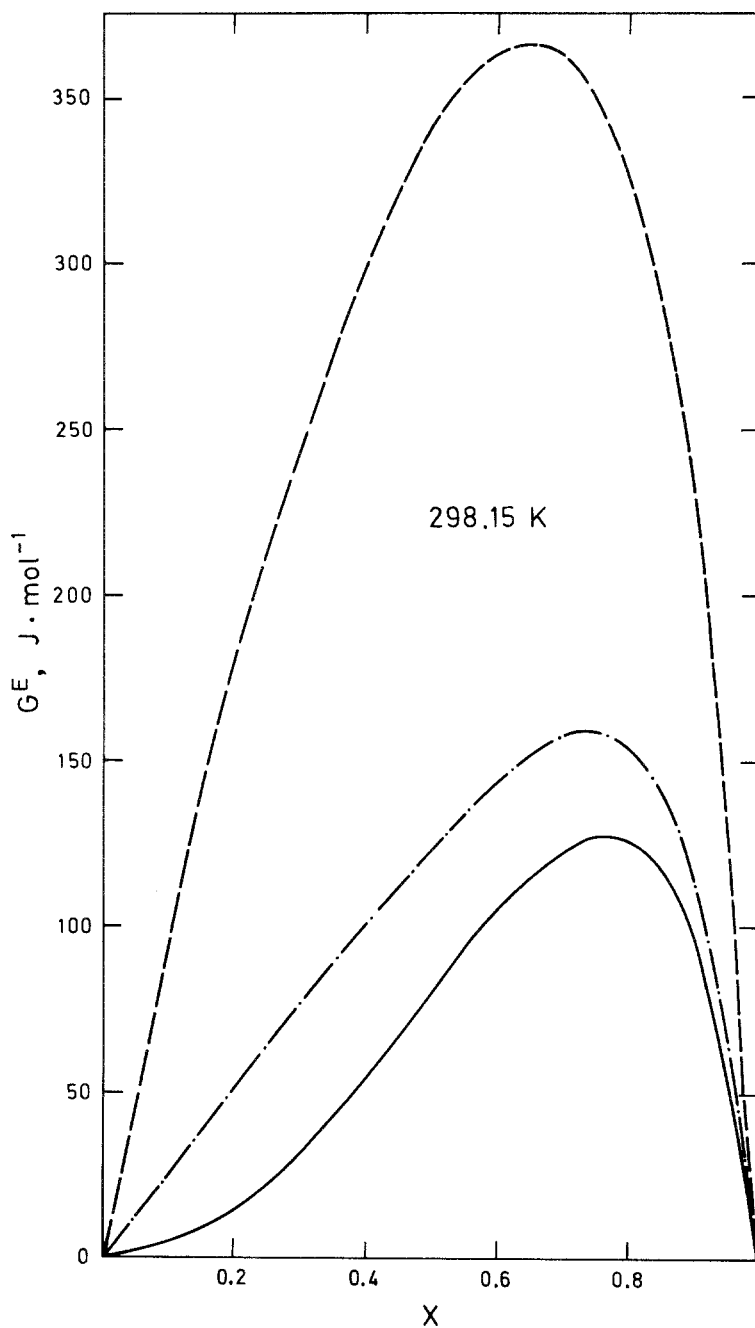The method proposed by Münsch [18] needs $H^E(x)$ curves at different

Fig. 1. Excess Gibbs energy of benzene + *n*-alkane systems at 298.15 K. ———, *n*-hexadecane; -··-, *n*-pentadecane; - - -, *n*-decane.
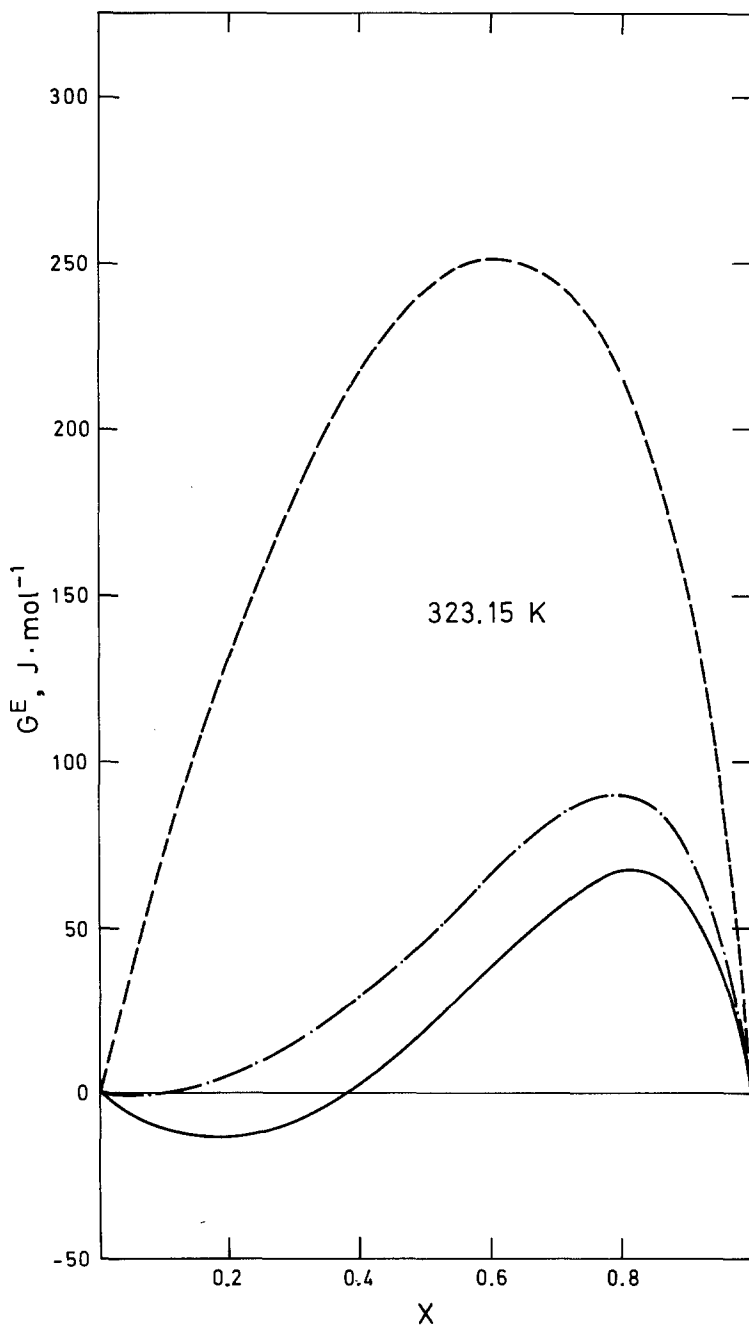
Fig. 2. Excess Gibbs energy of benzene + n-alkane systems at 323.15 K. ————, n-hexadecane; - ·-, n-pentadecane; - - -, n-decane.

temperatures to be similar in shape. It is known that correlations of molecular order (CMO) have important contributions in *n*-alkane systems. Those CMO contributions are higher at low temperature, and have a skewed shape in the composition range. This could explain the different shape in the H^E curves obtained at 298.15 and 323.15 K [1], and that Eq. (3) is not able to reproduce experimental H^E data.

Results of the benzene + *n*-hexadecane system [14] suggest a linear dependency of G^E/T on $1/T$. We have assumed this behavior for benzene + *n*-decane, and we have obtained $H^E(x = 0.5) = 1030$ J · mol^{-1} for 298.15 and 323.15 K. The activity coefficient of benzene at infinite dilution, γ_1^∞, has been also calculated using the values of the coefficients A_i and B_j given in Table II. γ_1^∞ is given, for the Padé (1/1), by

$$\gamma_1^\infty = \exp|(A_0 - A_1)/(1 - B_1)| \tag{4}$$

resulting in values for γ_1^∞ of 1.4852 and 1.3304 at 298.15 and 323.15 K, respectively. We have interpolated γ_1^∞ from reported values for benzene + *n*-alkane systems at 298.15 K [20], obtaining $\gamma_1^\infty = 1.45$. Lichtenthaler et al. [21] have pointed out that γ_1^∞ values obtained by extrapolation of vapor-liquid equilibrium data are always higher than gas-liquid chromatographic results, which is in accordance with the result obtained in this work. The prediction of activity coefficients may be considered as an additional measure of the consistency of the reported data.

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