

EXCESS GIBBS ENERGIES FOR THE BENZENE + *n*-HEXADECANE SYSTEM AT 298.15 AND 323.15 K

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(Received 20 January 1982)

ABSTRACT

The vapor pressure of the system benzene + *n*-hexadecane is measured by means of a static apparatus. Excess Gibbs energies are calculated using a modified Barker's method, and fitted to an equation proposed by Marsh. The regression analysis is based on the principle of maximum likelihood. The selection of the best set of estimates of the parameters is also discussed. The results obtained in this work are compared with those reported by other authors for the same system. Due to the lack of heat capacity data for this system, an approximation to calculate temperature dependence is studied.

INTRODUCTION

Benzene + *n*-alkane binary systems have often been studied and several of their thermodynamical properties (H^E , V^E , G^E) have been measured. However, it is still difficult to find a complete set of accurate data at the same temperature. This paper reports vapor pressure measurements and excess Gibbs energy calculations for the benzene + *n*-hexadecane system at two temperatures for which very few vapor pressure data exist although they have been chosen for other thermodynamical determinations.

EXPERIMENTAL

Vapor pressure experiments were carried out using an apparatus similar to that described by McGlashan and Williamson [1]. Descriptions of the experimental technique, and the outgassing method used for pure substances have been reported previously [2].

Benzene used in this work was the same as that used in ref. 2. The *n*-hexadecane used was Fluka (Puriss type) and was distilled at low pressure and stored over sodium wire. Estimated purity by gas chromatography is better than 99.5%. The density and refractive index of *n*-hexadecane at 25

TABLE I
Experimental and calculated variables for the benzene + *n*-hexadecane system

X_1	$10^5 \Delta X$	P (kPa)	ΔP (Pa)	G^E (J mole ⁻¹)	ΔG^E (J mole ⁻¹)	a_1	a_2	TS^E (J mole ⁻¹)
298.15 K								
0.0000	0	<0.001	1	0	0			
0.1796	-3	2.361	9	11	2	0.1883	0.8162	562
0.3278	2	4.464	-6	37	4	0.3532	0.6628	921
0.3468	-2	4.720	8	41	4	0.3745	0.6433	959
0.4228	7	5.833	-26	52	5	0.4594	0.5663	1092
0.4543	-3	6.238	10	68	5	0.4943	0.5348	1126
0.5076	10	7.025	-37	82	5	0.5424	0.4826	1183
0.5562	-10	7.605	37	94	5	0.6040	0.4359	1218
0.6142	2	8.411	-9	108	6	0.6637	0.3817	1235
0.6331	-10	8.601	40	112	6	0.6826	0.3643	1232
0.6881	2	9.329	-11	121	6	0.7357	0.3148	1212
0.6970	-3	9.411	-12	122	6	0.7440	0.3069	1205
0.7569	9	10.155	-33	127	5	0.799%	0.2546	1129

0.7823	1	10.369	-7	127	5	0.8200	0.2326	1079
0.8050	-4	10.612	19	125	5	0.8389	0.2129	1025
1.0000	0	12.695	0	0	0			
323.15 K								
0.0000	0	<0.001	1	0	0			
0.1746	-1	6.173	12	-12	1	0.1818	0.8218	485
0.3212	0	11.730	4	-5	3	0.3283	0.6698	814
0.3419	2	12.560	-20	-3	3	0.3505	0.6484	857
0.4179	2	15.517	-26	6	3	0.4324	0.5703	1008
0.4483	-2	16.633	25	11	3	0.4651	0.5394	1063
0.5035	2	18.833	-20	20	3	0.5243	0.4838	1144
0.5523	-4	20.625	36	29	3	0.5762	0.4354	1191
0.6109	2	22.941	-25	40	3	0.6374	0.3783	1220
0.6289	-2	23.549	26	44	3	0.6560	0.3610	1221
0.6856	2	25.699	-25	54	2	0.7132	0.3074	1206
0.6939	-1	25.943	19	55	2	0.7215	0.2997	1200
0.7555	2	28.175	-25	64	2	0.7811	0.2430	1137
0.7811	2	29.054	-27	66	2	0.8051	0.2198	1097
0.8036	-3	29.728	31	67	2	0.8258	0.1995	1049
1.0000	0	36.162	0	0	0			

and 30°C, respectively, were measured. The values obtained, 0.77010 and 1.43031, compare favorably with the accepted literature values, 0.77001 [3] and 1.43036 [4], respectively.

The vapor pressures of both pure components were determined and found to agree well with literature values. The vapor pressures of benzene at 25 and 50°C were found to be 12.695 and 36.162 kPa, respectively, while literature values [5] at those temperatures are 12.690 and 36.168 kPa. The vapor pressures of hexadecane at 25 and 50°C were lower than 0.001 kPa; these results are in agreement with the values calculated by Dreisbach [4] using Antoine's equation.

RESULTS

The vapor pressures of the system benzene + *n*-hexadecane at 298.15 and 323.15 K were measured. The molar volumes of pure components required for phase equilibria calculations were taken from the A.P.I. tables [3]. The second virial coefficient of benzene was taken from Diaz-Peña et al. [6]. The second virial coefficient of *n*-hexadecane was estimated using the method of McGlashan and Potter [7]. Although there are large discrepancies between the estimations provided by the methods of McGlashan and Pitzer [7], the differences in the calculated excess Gibbs energies are negligible due to the low volatility of *n*-hexadecane. This has already been pointed out by Ott et al. [8] for similar systems. The second virial coefficient of the mixture, B_{12} , was calculated by means of the Lorentz–Berthelot's combination rule.

The excess volumes of the mixture, which are also necessary for estimating the volume of the vapor phase, were taken from Diaz-Peña and Nuñez-De-lgado [9]. The excess Gibbs energy was calculated and fitted to the equation

$$\frac{G^E}{RT X_1 X_2} = \frac{\sum_{i=0}^n A_i (X_1 - X_2)^i}{1 + \sum_{j=1}^m B_j (X_1 - X_2)^j} \quad (1)$$

Equation (1) is a Padé approximant [10] of grade (n/m). The principle of maximum likelihood as described by Anderson et al. [11] was used in the regression method.

Table 1 gives the molar fraction of benzene in the liquid phase X_1 , and the experimental values for the vapor pressure of the mixture, P . As has been already pointed out [2,11], the regression method used in this paper provides values of the parameters A_i and B_j , and the so-called true values of the variables (X , P , T) which are the smoothed values of experimental data within their uncertainty intervals and are determined according to the principle of maximum likelihood. The deviations between experimental and

true values (ΔX , ΔP) are given in Table 1. Deviations for temperature were not taking into account because they are negligible.

It is also possible to obtain the variance-covariance matrix, Σ , and the correlation matrix, C , of the parameters. Matrix Σ enables the calculation of the error in the estimated parameters and matrix C informs about the degree of correlation between each two parameters. The error of any thermodynamical magnitude which can be expressed in terms of the parameters A_i and B_j of eqn. (1), may also be estimated from Σ .

The best set of parameters is chosen among all the different sets obtained by varying the n and m indices according to the following criteria:

(a) deviation from all variables (ΔX , ΔP , ΔT) must follow a random distribution around zero [12] and the mean deviations must be of the same order as deviations estimated from experimental uncertainties [11,13];

(b) the eigenvalue of matrix Σ must be null or positive [14];

TABLE 2

Values for the parameters and related magnitudes for the best fit to eqn. (1)

298.15 K

Parameters

$$A_0 = 0.1261 \pm 0.0085$$

$$A_1 = 0.1442 \pm 0.0196$$

$$B_1 = -0.5407 \pm 0.0435$$

Matrices

$$\Sigma = 10^{-4} \begin{pmatrix} 0.7603 & -1.3960 & -1.9250 \\ & 3.6050 & 6.5040 \\ & & 14.9610 \end{pmatrix}$$

$$C = \begin{pmatrix} 1.0000 & -0.8434 & -0.5706 \\ & 1.0000 & 0.8857 \\ & & 1.0000 \end{pmatrix}$$

323.15 K

Parameters

$$A_0 = 0.0292 \pm 0.0042$$

$$A_1 = 0.1141 \pm 0.0090$$

$$B_1 = -0.6226 \pm 0.0344$$

Matrices

$$\Sigma = 10^{-4} \begin{pmatrix} 0.1795 & -0.3375 & -0.9490 \\ & 0.8123 & 2.7809 \\ & & 11.8020 \end{pmatrix}$$

$$C = \begin{pmatrix} 1.0000 & -0.8839 & -0.6520 \\ & 1.0000 & 0.8982 \\ & & 1.0000 \end{pmatrix}$$

(c) a minimal number of parameters with the highest statistical meaning and independence is desirable;

(d) minimal uncertainties in the excess Gibbs energy and activities of each component are preferred;

(e) best agreement between calculated values and literature data for other thermodynamical magnitudes, i.e. activity coefficient at infinite dilution.

Table 1 gives the values of calculated excess Gibbs energies, G^E , and its error, ΔG^E , as well as the activities and entropies calculated using the heat-of-mixing data reported by Diaz-Peña and Menduina [15] for this system at the same temperatures.

The Padé approximant used for data at both temperatures has been the (1/1). It has only three parameters which are given in Table 2. Estimated errors of the parameters, standard deviations of the variables, and the matrices Σ and C are also reported in Table 2. The estimated uncertainties of experimental variables X , P , and T are: $\sigma(P) = 20$ Pa, $\sigma(X) = 10^{-4}$ and $\sigma(T) = 0.01^\circ\text{C}$, respectively.

TABLE 3

Parameters and related magnitudes obtained using a Padé (3/0) and its comparison with similar results for a Padé (1/1)

$$A_0 = 0.0141 \pm 0.0074$$

$$A_1 = 0.1432 \pm 0.0078$$

$$A_2 = 0.0693 \pm 0.0115$$

$$A_3 = 0.1007 \pm 0.0147$$

$$\sigma(X) = 2 \times 10^{-4}$$

$$\sigma(P) = 24 \text{ Pa}$$

$$\sigma(T) < 0.001^\circ\text{C}$$

$$\Sigma = 10^{-4} \begin{pmatrix} 0.5554 & -0.5194 & 0.7035 & -0.7058 \\ & 0.6101 & -0.7107 & 0.5089 \\ & & 1.3182 & -1.3240 \\ & & & 2.1701 \end{pmatrix}$$

X_1	G^E (J mole ⁻¹)	
	(3/0)	(1/1)
0.1	-26 ± 3	-10 ± 1
0.2	-29 ± 5	-12 ± 2
0.3	-22 ± 5	-7 ± 2
0.4	-8 ± 5	4 ± 3
0.5	9 ± 5	20 ± 3
0.6	30 ± 4	38 ± 3
0.7	50 ± 4	56 ± 2
0.8	63 ± 2	67 ± 2
0.9	54 ± 1	58 ± 1

Selection of the best set of parameters for data at 323.15 K illustrates the decisive importance of meeting all the criteria mentioned above. The approximant (3/0) leads to the results shown in Table 3. Selection criteria (a) and (b) are not relevant in this case. It has been shown that the relation [11,13]

$$t_i = \frac{\sigma(\theta_i)}{\theta_i} \quad (2)$$

where θ_i is a parameter of eqn. (1) and $\sigma(\theta_i)$ is its estimated error, has a Student's t distribution. All the parameters of Padé (1/1) and (3/0) are statistically acceptable according to this criterion, but maximum uncertainty in the parameters shows that parameters of Padé (1/1) are more significant than those of Padé (3/0) (14% and 51%, respectively). The uncertainties in G^E are higher, some of them larger than experimental error ($X_1 \leq 0.4$). The hyperellipsoid representing the region in which the parameter values can be expected to lie at a 99% confidence level is greater in Padé (3/0) than in Padé (1/1). This is in agreement with G^E errors given in Table 3. Similar results can be found using the approximants (1/3), (2/1), (3/1), and (4/0); all lead to large discrepancies in calculated G^E values. The results given in Tables 1 and 2 for both temperatures are thermodynamically consistent according to Van Ness criteria [12], and the vapor pressures of pure components are in excellent agreement with vapor pressure data at intermediate compositions.

DISCUSSION

Figure 1 shows the experimental vapor pressure at 298.15 K. Our results are plotted together with those obtained by Jain and Lark [16] at the same temperature. The agreement between both data sets is excellent except in the benzene rich region. This may be due to the poor agreement between Jain's values for the vapor pressure of pure benzene and the values obtained in the literature. At low temperatures (298.15 K) Jain's values are lower than the literature values, while at higher temperatures (328.15 K) Jain reported a vapor pressure which is 300 Pa higher than the literature value. The presence of impurities in this component could be a possible explanation. On the other hand, Harris and Dunlop [17] found similar discrepancies when they compared their results for the system benzene + *n*-heptane with those obtained by Jain et al. [18].

The activity coefficient of benzene at infinite dilution was also calculated at 298.15 K. We found a value of 0.9924, to be compared with the values 0.9934 obtained by gas-liquid chromatography [19], and 1.975 calculated from Jain and Lark [16] data at the same temperature.

Messow et al. [20] have measured the vapor pressure for this system at

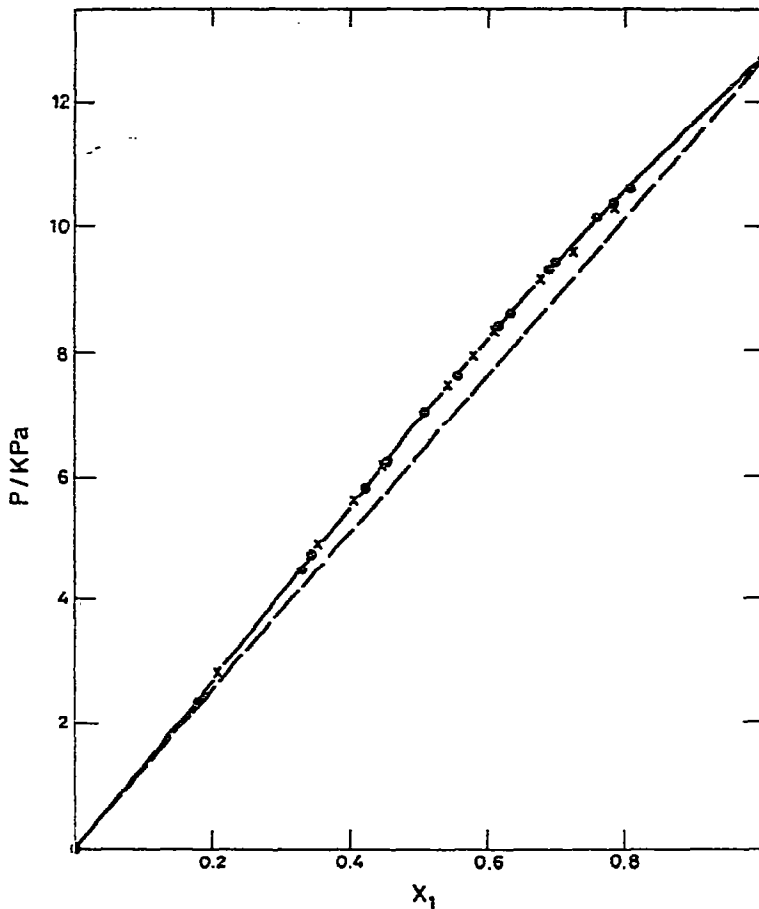


Fig. 1. Vapor pressure for the system benzene(1)+ *n*-hexadecane(2) at 298.15 K. ●, This work; ×, Jain and Lark [16].

313.15 K using ebullometry. Their results are not compatible with the values obtained by us and with those of Jain and Lark [16]. There are also large discrepancies between their results for the vapor pressure of benzene and the literature values.

Figure 2 shows a plot of the excess Gibbs energy versus composition at several temperatures. The two isotherms reported in this paper are in agreement with Jain and Lark's isotherms [16] but not with those of Messow et al. [20]. Plots of G^E/T vs. $1/T$ at constant composition show fairly linear behavior for $0.5 \leq X_1 \leq 0.7$ molar fractions, which correspond to the highest values of heat-of-mixing and excess Gibbs energy data. Nevertheless, values of H^E calculated from least squares fittings of these data disagree with the experimental values given by Diaz-Peña and Menduiña [15] up to 300 J mole^{-1} in the vicinity of the maximum of the curve. Marsh et al. [21] assumed a linear variation of H^E with temperature

$$H^E = a + bT \quad (3)$$

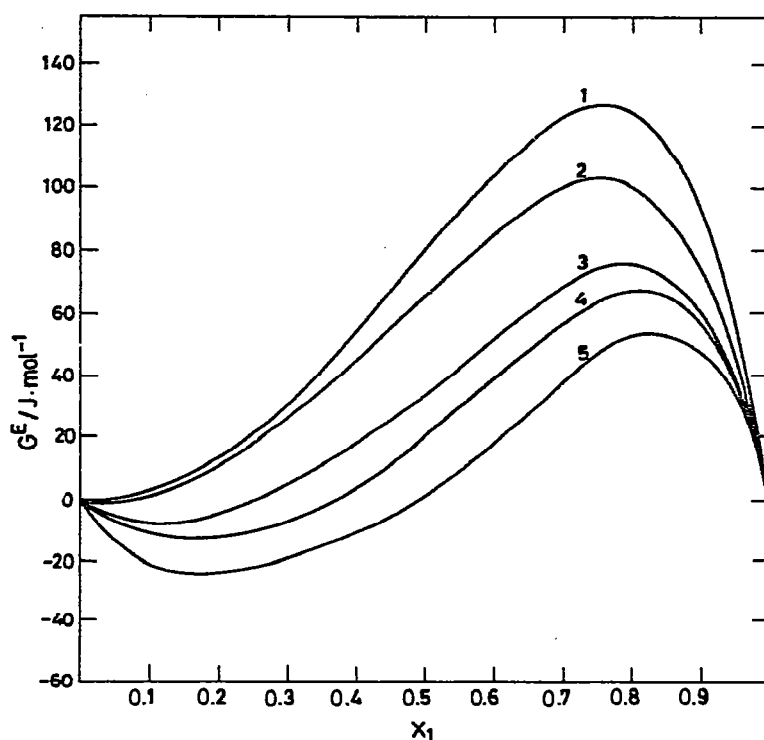


Fig. 2. Excess Gibbs energy for the system benzene + *n*-hexadecane at several temperatures. Curves 1 (25°C) and 4 (50°C), this work; curves 2 (35°C), 3 (45°C) and 5 (55°C) from Jain and Lark [16].

for systems formed by *n*-hexane plus an *n*-alkane. With this assumption it is possible to express G^E at temperature T_2 in terms of its value at another temperature T_1 and values of coefficients a and b in eqn. (3).

$$G_2^E/T_2 = G_1^E/T_1 + a(T_2^{-1} - T_1^{-1}) - b \ln(T_2/T_1) \quad (4)$$

Using the data of Diaz-Peña and Menduïña [15] to calculate a and b ($a = 2901.29$ K; $b = -5.52$), and values of G^E at 298.15 K, we can estimate values of G^E at 323.15 K at each composition. We obtained a value of -13 J mole $^{-1}$ for the equimolar mixture at 323.15 K. This value must be compared with the experimental value given in Table 1 (20 J mole $^{-1}$).

We may conclude that the approximation of constant heat capacity introduced by eqn. (3) is not adequate for the system and temperature range studied in this paper. On the other hand, it should be noticed that Bhattacharyya and Patterson [22] have reported values of excess heat capacities for cyclohexane + *n*-alkane which vary up to 20% within our temperature range; Diaz-Peña and Renuncio [23] have also found variations of heat capacities up to 25% for the *n*-hexane + *n*-hexadecane system.

Finally, the benzene + *n*-hexadecane system presents positive values of G^E at 298.15 K (see Table 1) while at 323.15 K the G^E plot is S-shaped, with a

minimum occurring in the *n*-hexadecane rich region and a maximum at the opposite side of the concentration range. This system contrasts with mixtures of this alkane with other substances (cyclohexane [24], *n*-hexane [1], 2,2-dimethylbutane [25]) which present negative values of G^E even at 298.15 K.

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