Thermochimica Acta, 65 (1983) 69–79
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EXCESS MAGNITUDES FOR THE BENZENE + *n*-DODECANE SYSTEM AT 298.15 AND 323.15 K

R.G. RUBIO, J.A.R. RENUNCIO * and M. DIAZ PEÑA

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, Madrid-3 (Spain)

(Received 1 December 1982)

ABSTRACT

The vapor pressures for benzene + *n*-dodecane mixtures have been measured using a static apparatus. Values for the excess Gibbs energy have been calculated using a modified form of Barker's method and fitted to a Padé approximant equation. Selection of the most adequate approximant is made according to objective criteria. The results are compared with those corresponding to other benzene + *n*-alkane systems. The values for the activity coefficient of benzene at infinite dilution calculated from these data agrees very well with the values obtained by gas–liquid chromatography.

INTRODUCTION

Over the years, the benzene + alkane systems have been studied in our laboratories. Excess volumes [1], excess enthalpies [2], and compressibilities [3] have been reported for benzene + *n*-alkane systems where the *n*-alkane varies from *n*-pentane to *n*-hexadecane and the temperature may be 298.15 or 323.15 K or both. Vapor pressure measurements and the calculated excess Gibbs energies have also been reported for the benzene + *n*-decane [4], benzene + *n*-pentadecane [5], benzene + *n*-hexadecane [6], and benzene + *n*-tetradecane [7] systems at the same two temperatures. In this paper total vapor pressure measurements of the benzene + *n*-dodecane system at 298.15 and 323.15 K are reported. The excess Gibbs energies are calculated and compared with those obtained for other benzene + *n*-alkane systems.

EXPERIMENTAL

Vapor pressure experiments were carried out using an apparatus similar to the one described by McGlashan and Williamson [8]. Details of the experi-

---

* Present address: Facultad de Química, Universidad de Oviedo, Oviedo, Spain.

mental technique and the degassing method used for the pure substances have been reported elsewhere [5]. The benzene used in this work was the same as that previously described [6]. The n-dodecane was obtained from Phillips Petroleum (Research grade) which was stored over sodium wire. The estimated purity by gas chromatography is better than 99.8%. The density at 298.15 K (0.74525 g cm^{-3}) and the refractive index ($n_D^{30} = 1.41757$) agree well with the respective values from the literature (0.74516 g cm^{-3} and 1.41755, respectively) [9].

The vapor pressures of both pure components were determined and found to be in good agreement with the literature values. The values obtained for benzene were: 12.696 and 36.162 kPa at 298.15 and 323.15 K, respectively, while the literature reports values of 12.690 and 36.168 kPa, respectively [10].

The values obtained for n-dodecane were 0.021 and 0.087 kPa at the same two temperatures. These values are in good agreement with the values calculated using the Antoine equation and the coefficients reported by Dreisbach [9].

The accuracy of the experimental measurements of pressure, temperature and mole fraction were, 8 Pa, 0.01 K and 10^{-4}, respectively.

RESULTS AND DISCUSSION

The vapor pressures of the system benzene(1) + n-dodecane(2) were measured at 298.15 and 323.15 K. The molar volumes of pure components were taken from the A.P.I. tables [11]. The excess volume data which are necessary in order to estimate the volume of the vapor phase in the measurement cell, were taken from Díaz Peña and Nuñez Delgado [1]. Second virial coefficient data are also required to assume a non-ideal behavior in the vapor phase. Values for the second virial coefficient of benzene were taken from Dïaz Peña et al. [12]. Values for the second virial coefficient of n-dodecane were estimated using the McGlashan and Potter equation [13]. Although these values differ from those provided by the method of Pitzer and Curl [14], the G^E values are not affected by these discrepancies because of the low volatility [15]. The second virial coefficient of the mixture, B_{12}, was estimated using the Lorentz–Berthelot combination rule.

Tables 1 and 2 give the experimental values of the total vapor pressure, p, and the mole fraction of benzene, x, at 298.15 and 323.15 K, respectively. The excess Gibbs energies were calculated using a modified form of Barker's method [6]. The resulting values for G^E were fitted to the equation

$$\frac{G^E}{RTx(1-x)} = \frac{\sum_{i=0}^{i=n} A_i(2x-1)^i}{1 + \sum_{j=1}^{j=m} B_j(2x-1)^j} \qquad (1)$$

TABLE 1

Experimental and calculated variables for the benzene + *n*-dodecane system at 298.15 K

x_1	$\Delta x \times 10^5$	p (kPa)	Δp (Pa)	G^E (J mole^{-1})	ΔG^E (J mole^{-1})	γ_1	γ_2	TS^E (J mole^{-1})
0.0000	0	0.021	0	0	0	1.3455	1.0000	0
0.1887	9	3.100	−26	127	2	1.2856	1.0049	402
0.1943	−5	3.142	16	131	2	1.2839	1.0052	411
0.2570	−1	4.113	2	167	2	1.2651	1.0095	519
0.3220	3	5.088	−10	202	2	1.2459	1.0159	620
0.3321	−1	5.220	4	207	2	1.2430	1.0170	635
0.4387	−9	6.697	31	254	3	1.2117	1.0335	771
0.4831	3	7.341	−10	271	3	1.1985	1.0433	811
0.5135	2	7.742	−8	288	3	1.1893	1.0519	826
0.5571	3	8.309	−12	293	3	1.1757	1.0653	853
0.5862	−8	8.630	31	299	3	1.1664	1.0767	860
0.6433	9	9.387	−33	308	2	1.1474	1.1054	851
0.7189	0	10.208	−2	308	2	1.1199	1.1648	793
0.7734	−4	10.746	20	297	2	1.0980	1.2353	713
0.8091	1	11.112	−6	284	2	1.0824	1.3045	641
1.0000	0	12.690	0	0	0	1.0000	4.2362	0

TABLE 2

Experimental and calculated variables for the benzene + n-dodecane system at 323.15 K

x	$\Delta x \times 10^5$	p (kPa)	Δp (Pa)	G^E (J mole^{-1})	ΔG^E (J mole^{-1})	γ_1	γ_2	TS^E (J mole^{-1})
0.0000	0	0.087	0	0	0	1.1293	1.0000	0
0.1798	7	7.362	−7	57.1	0.7	1.1299	0.9992	419
0.1895	8	7.756	−9	60.3	0.9	1.1301	0.9991	439
0.2449	−23	9.941	25	79	1	1.1302	0.9991	625
0.3104	7	12.608	−8	100	1	1.1282	0.9998	658
0.3261	−17	13.196	19	105	1	1.1274	1.0001	682
0.3975	12	16.053	−14	127	1	1.1218	1.0030	777
0.4282	7	17.236	−9	136	1	1.1186	1.0051	810
0.4779	−13	19.102	14	150	1	1.1121	1.0099	853
0.5042	7	20.118	−7	157	1	1.1081	1.0134	870
0.5820	−12	22.919	16	173	1	1.0941	1.0291	898
0.6358	20	24.843	−26	180	1	1.0825	1.0464	893
0.7138	−9	27.364	12	181	1	1.0633	1.0863	848
0.7697	6	29.127	−9	174.1	0.9	1.0484	1.1319	779
0.8067	10	30.244	−17	164.3	0.8	1.0382	1.1739	714
0.8251	−15	30.740	22	157.7	0.7	1.0331	1.1995	675
1.0000	0	36.162	0	0	0	1.0000	1.7929	0

which was first proposed by Marsh [16]. 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 enunciated by Anderson et al. [17] was used to determine the values of coefficients A_i and B_j. This method provides not only the values of the coefficients, but also the so-called "true" values of the variables (x, p, T). The deviations between experimental and true values (residuals) of the variables (Δx and Δp) are given in Tables 1 and 2. The temperature residuals are not reported because they are negligible ($< 10^{-3}$ K).

Several approximants may be found which are able to represent the calculated values of the excess Gibbs energy. The criteria used to select the most adequate of those approximants have been reported previously [6]. The approximant (1/1) is the most adequate for the data at 298.15 K while the approximant (0/2) is most adequate at 323.15 K.

Table 3 gives the values of the parameters and their uncertainties, as well as the terms of the variance–covariance, Σ of the parameters and their correlation matrices, C. The variances of experimental variables are also reported. Since these values are within the experimental accuracies of the variables, the scattering of experimental points is almost negligible. The same conclusion may be derived from the values of the weighted root mean square deviation, WRMSD, reported in Table 3 [18].

It may be observed in Table 3 that the term (2,3) of the correlation matrix is close to unity. This means that the parameters A_1 and B_1 are correlated in this fit. In principle, it is possible [19] to substitute these two parameters by a linear combination of its values, thus transforming the (1/1) approximant into a (1/0) approximant. Nevertheless, the variances, $\sigma(x)$ and $\sigma(p)$,

TABLE 3

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

298.15 K		*333.15 K*	
Parameters	*Variances*	*Parameters*	*Variances*
$A_0 = 0.4466 \pm 0.0038$	$\sigma(P)/\text{Pa} = 17$	$A_0 = 0.2341 \pm 0.0014$	$\sigma(P)/\text{Pa} = 15$
$A_1 = -0.0695 \pm 0.0129$	$10^5 \sigma(x) = 5$	$B_1 = -0.7624 \pm 0.0118$	$10^4 \sigma(x) = 1$
$B_1 = -0.7389 \pm 0.0150$		$B_2 = 0.1633 \pm 0.0140$	
Matrices		*Matrices*	
$\Sigma = 10^{-4} \begin{pmatrix} 0.1454 & -0.3181 & -0.2130 \\ & 1.6628 & 1.7850 \\ & & 2.2550 \end{pmatrix}$		$\Sigma = 10^{-4} \begin{pmatrix} 0.0219 & 0.1426 & -0.1371 \\ & 1.6329 & -0.8312 \\ & & 2.3059 \end{pmatrix}$	
$C = \begin{pmatrix} 1.0000 & -0.6467 & -0.3718 \\ & 1.0000 & 0.9218 \\ & & 1.0000 \end{pmatrix}$		$C = \begin{pmatrix} 1.0000 & 0.7545 & -0.6104 \\ & 1.0000 & -0.9437 \\ & & 1.0000 \end{pmatrix}$	
WRMSD = 0.9628		WRMSD = 0.8471	

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 an (m/n) to an $(m-1/n)$ or $(m/n-1)$ approximant, the values of the variances or the random distributions are not affected. The change from a (1/1) to a (1/0) approximant discussed here presents the unusual situation of the disappearance of the polynomial denominator in eqn. (1). For the (1/0) approximant, eqn. (1) is a parabolic equation which may have difficulties in accommodating the calculated values of $G^{\mathrm{E}}/RTx(1-x)$.

On the other hand, the random distribution of residuals, Δx and Δp, is also disturbed when we change from a (1/1) to a (1/0) approximant. The random distribution is checked by the Abbe test [20]. This is equivalent to the Van Ness consistency criterion [21].

Tables 1 and 2 also give the calculated values of G^{E} and its uncertainties, ΔG^{E}, as well as values of the activity coefficients, γ_1 and γ_2, and the excess entropy, S^{E}. Values of TS^{E} have been calculated using the H^{E} data reported by Díaz Peña and Menduiña [2] for this system at 298.15 and 323.15 K.

Figures 1 and 2 show the values of G^{E} as a function of composition for the benzene + n-alkane systems reported at 298.15 and 323.15 K, respectively. The shape and maxima of these curves show a dependence on the chain length similar to that observed for other excess properties of these mixtures [1–3]. Table 4 gives the smoothed values of various excess properties for rounded mole fractions.

It is possible to calculate the excess Gibbs energy at any temperature from the value at a given temperature making use of the Gibbs–Helmholtz equation

$$\frac{G^{\mathrm{E}}(T_1)}{T_1}=\frac{G^{\mathrm{E}}(T_0)}{T_0}-\int_{T_0}^{T_1}\frac{H^{\mathrm{E}}}{T^2}\mathrm{d}T \tag{2}$$

In fact, this equation requires knowledge of H^{E} as a function of temperature. We have assumed that the excess enthalpy varies linearly with temperature as given by

$$H^{\mathrm{E}}(T)=H^{\mathrm{E}}(T_0)+C_p^{\mathrm{E}}(T-T_0) \tag{3}$$

which is equivalent to the assumption that C_p^{E} is constant with temperature. The experimental value of C_p^{E} at 310.65 K given by Trejo and Patterson [22] has been taken in eqn. (3). Table 4 also gives the deviations, δ, between the experimental and calculated values of G^{E} making use of eqns. (2) and (3). Values of δ indicate that the assumption given by eqn. (3) is not adequate for this system. This is in accordance with the results obtained for the benzene + n-hexadecane system, but contrast with those for the benzene + n-tetradecane system [7]. Although excess heat capacity data are not available at other temperatures, it may be expected that C_p^{E} varies significantly in this

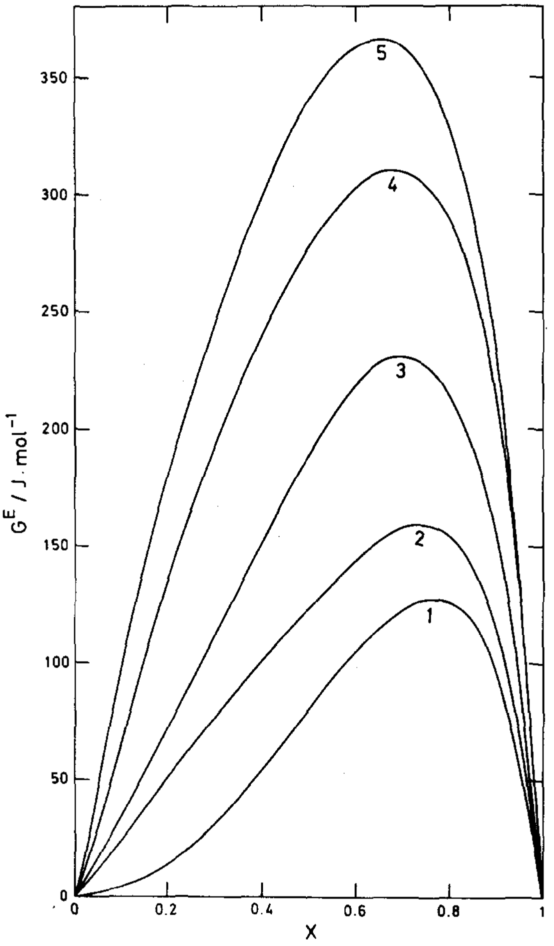

Fig. 1. Excess Gibbs energy for benzene (1) + *n*-alkane (2) systems at 298.15 K. 1, *n*-Hexadecane; 2, *n*-pentadecane; 3, *n*-tetradecane; 4, *n*-dodecane; 5, *n*-decane.

system. Bhattacharyya and Patterson [23] have reported changes in C_p^E as high as 22% within a temperature interval of 25 K for the cyclohexane + *n*-dodecane system.

The activity coefficient of benzene at infinite dilution, γ_1^∞, has also been calculated from eqn. (1). It may be expressed by

$$\gamma_1^\infty = \exp\left(\frac{A_0 - A_1}{1 - B_1}\right) \tag{4}$$

for the (1/1) approximant. The calculated value for benzene at 298.15 K is 1.3455 which is in good agreement with the value of 1.33 obtained by gas–liquid chromatography as reported by Letcher and Jerman [24]. It is important to take into account that the activity coefficients obtained by

TABLE 4

Excess magnitudes at rounded mole fractions for benzene + n-dodecane

x_1	$H^{E\,a}$ (J mole^{-1})	$V^{E\,b}$ (cm^3 mole^{-1})	$G^{E\,c}$ (J mole^{-1})	$\kappa^{E\,d}$ (T Pa^{-1})	$TS^{E\,c}$ (J mole^{-1})	$-C_p^{E\,e}$ (J mole^{-1} K^{-1})	δ^{f} (J mole^{-1})
298.15 K							
0	0	0	0	987.6	0	0	
0.1	303.3	0.2572	70.3	997.3	233.0	1.491	
0.2	555.8	0.4793	134	1002.3	422	2.624	
0.3	777.9	0.6804	190	1005.2	588	3.512	
0.4	965.2	0.8275	238	1007.9	727	4.209	
0.5	1100.9	0.9404	276	1010.9	825	4.710	
0.6	1162.0	0.9923	302	1013.5	860	4.951	
0.7	1122.2	0.9588	309	1013.9	813	4.811	
0.8	942.2	0.8089	288	1009.0	661	4.108	
0.9	589.1	0.5044	213	994.8	385	2.604	
1.0	0	0	0	965.9	0	0	

323.15 K						
0	0	0	0	1212	0	0
0.1	275.5	0.2172	33.0	1220	242.55	−16
0.2	524.2	0.4421	66	1229	458.2	−30
0.3	738.0	0.6398	99	1234	639	−42
0.4	907.7	0.7922	130	1243	778	−52
0.5	1023.8	0.8906	157	1252	867	−58
0.6	1074.4	0.9283	177	1262	900	−60
0.7	1041.5	0.8933	183	1273	858	−56
0.8	893.6	0.7612	167.2	1269	726.4	−47
0.9	576.1	0.4874	114.3	1265	461.8	−28
1.0	0	0	0	1186	0	0

---

[a] From ref. 2.

[b] From ref. 1.

[c] This work.

[d] From ref. 3.

[e] From ref. 22 at 310.65 K.

[f] Calculated as described in text.

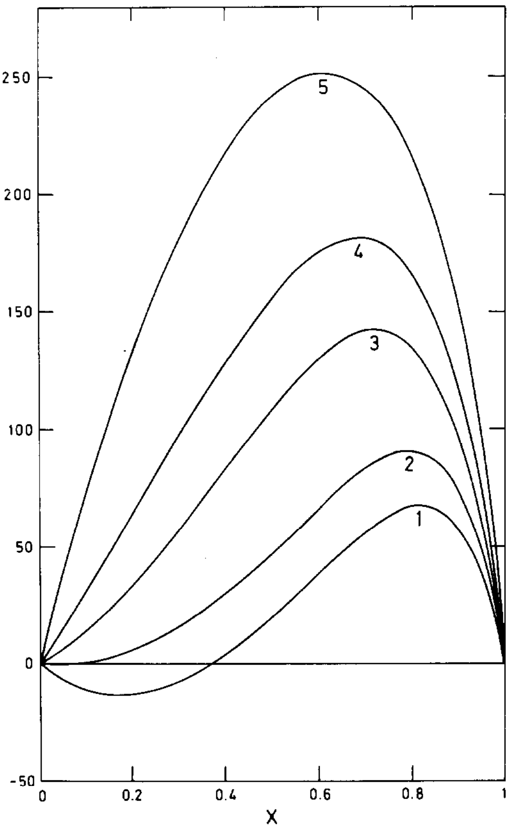

Fig. 2. Excess Gibbs energy for benzene (1)+ *n*-alkane (2) systems at 323.15 K. 1, *n*-Hexadecane; 2, *n*-pentadecane; 3, *n*-tetradecane; 4, *n*-dodecane; 6, *n*-decane.

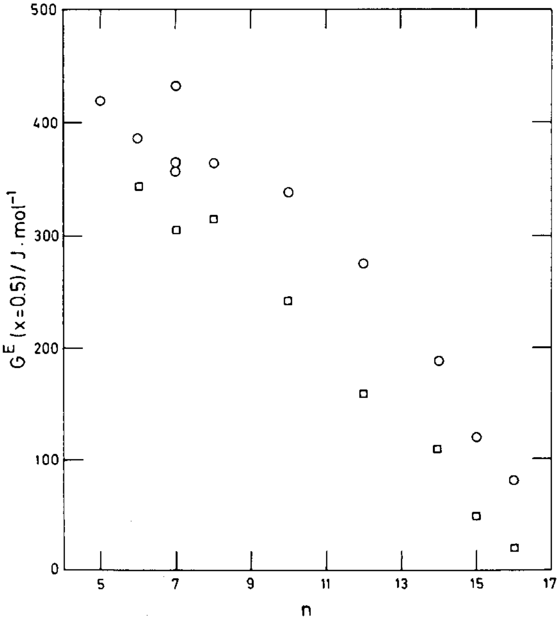

Fig. 3. Equimolecular excess Gibbs energy for benzene (1)+ *n*-alkane systems as a function of the number of carbon atoms, *n*. ○, 298.15 K; □, 323.15 K.

extrapolation of vapor pressure data are always larger than those obtained by gas–liquid chromatography [25].

Figure 3 shows the values of G^E for equimolar mixtures at 298.15 K vs. the number of carbon atoms, n. Values for $n = 5$, 6 and 8 are taken from Funk and Prausnitz [25], values for $n = 7$ are taken from refs. 25–27, and values for $n = 10$, 14–16 were obtained in our laboratory [4–7].

REFERENCES

1 M. Díaz Peña and J. Nuñez Delgado, An. Quím., 70 (1974) 678; J. Chem. Thermodyn., 7 (1975) 201.
2 M. Díaz Peña and C. Menduiña, J. Chem. Thermodyn., 6 (1974) 387, 1097.
3 M. Dīaz Peña, G. Tardajos, R.L. Arenosa and C. Menduiña, J. Chem. Thermodyn., 11 (1979) 951.
4 R.G. Rubio, J.A.R. Renuncio and M. Díaz Peña, Int. J. Thermophys., in press.
5 R.G. Rubio, J.A.R. Renuncio and M. Díaz Peña, J. Chem. Thermodyn., 14 (1982) 983.
6 M. Díaz Peña, J.A.R. Renuncio and R.G. Rubio, Thermochim. Acta, 56 (1982) 199.
7 R.G. Rubio, J.A.R. Renuncio and M. Díaz Peña, J. Solution Chem., in press.
8 M.L. McGlashan and A.G. Williamson, Trans. Faraday Soc., 57 (1961) 588.
9 R.R. Dreisbach, Physical Properties of Chemical Compounds, Vol II, American Chemical Society, Washington, 1959.
10 D. Ambrose, Pure Appl. Chem., 49 (1977) 1437.
11 D. Rossini, K.S. Pitzer, R.L. Arnett, R.-M. Braun and G.C. Pimentel, Selected Values of Physical and Thermodynamic Properties of Hydrocarbon and Related Compounds, A.P.I. Research Project 44, 1954.
12 M. Díaz Peña, C.P. Sotomayor and J.A.R. Renuncio, An. Quím., 69 (1973) 273.
13 M.L. McGlashan and D.J.B. Potter, Proc. R. Soc. London, Ser. A, 267 (1962) 478.
14 K.S. Pitzer and R.F. Curl, J. Am. Chem. Soc., 79 (1957) 2369.
15 B.J. Ott, K.N. Marsh and R.H. Stokes, J. Chem. Thermodyn., 13 (1981) 371.
16 K.N. Marsh, J. Chem. Thermodyn., 9 (1977) 719.
17 T.F. Anderson, D.S. Abrams and E.A. Grens, AIChE J., 24 (1978) 20.
18 A. Peneloux, R. Deyrieux and E. Neau, J. Chim. Phys., 72 (1975) 1107.
19 J. Fabries and H. Renon, AIChEJ., 21 (1975) 735.
20 J.W. Linnik, Die Metode der Kleinsten Quadrate in Moderner Darstellung, VEB Deutsche Verlag der Wissenschaften, Berlin, 1961.
21 H.C. Van Ness, S.M. Byer and R.E. Gibbs, AIChEJ., 19 (1973) 238.
22 A.T. Trejo and D. Patterson, J. Chem. Soc. Faraday Trans. 2, 78 (1982) 917.
23 S.N. Bhattacharyya and D. Patterson, J. Phys. Chem., 83 (1979) 2979.
24 T.M. Letcher and P.J. Jerman, J.S. Afr. Chem. Inst., 29 (1976) 55.
25 E.W. Funk and J.M. Prausnitz, Ind. Eng. Chem., 62 (1970) 8.
26 K.R. Harris and P.J. Dunlop, J. Chem. Thermodyn., 2 (1970) 8.
27 V. Rodica and S. Florica, Rev. Roum. Chem., 11 (1966) 175.