Densities and Excess Volumes of Benzene + Hexane between 298.15 and 473.15 K

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This paper reports the results of measurements of the densities for benzene + hexane using a high-pressure stainless steel pycnometer system at various temperatures between 298.15 and 473.15 K. The results were compared with those predicted by the Hankinson–Brobst–Thomson correlation (HBT) and the Spencer and Danner modified Rackett equation (SDR). The HBT equation showed an average deviation of about 0.74% from the experimental results while the SDR equation showed a 0.20% average absolute deviation. The excess molar volumes, V^E, calculated from the density values have been found to be positive for all the concentrations and temperatures considered.

Introduction

The densities and/or the excess molar volumes for benzene + hexane have been previously investigated by some researchers, which include among others Diaz Pena and Nunez Delgado (*1*), Letcher (*2*), Nigam et al. (*3*), Schmidt et al. (*4*), Heric and Brewer (*5*), Ridgway and Butler (*6*), Battino (*7*), and Jain et al. (*8*). The limitation in the studies of these investigations was the small temperature range considered, which was mostly between 298.15 and 323.15 K. This paper reports the densities and excess molar volumes of the binary mixtures of benzene with hexane in the temperature range of 298.15–473.15 K. The wide range of temperature considered in the present study may provide more insight into the effect of temperature on the densities and excess volumes of the binary mixtures of benzene + hexane. The experimental results can then be compared with the data reported in the literature. Comparison between the experimentally obtained densities and those predicted by the available correlations can also be made.

Experimental Section

Materials. Analytical grade benzene and hexane were obtained from BDH Limited, Poole, England, with a purity of 99.7 mol % each. An attempt was made to further purify each of the two samples by means of a simple distillation technique, with the first and last 20% of the distillate being discarded. Precision refractometry indicated that the purity of each product was not significantly enhanced.

Sample Preparation. The binary mixtures were prepared just before their use by mass using a Mettler balance PC-2000 (precision of 10^{-2} g) and air-tight stoppered bottles. It was ensured that the components were adequately mixed before being transferred into the density cell. The mixing was done at temperatures below ambient to minimize evaporation losses. The cumulative error in the mole fractions is estimated to be less than 7×10^{-4}.

Apparatus and Procedure. Density measurements were carried out using a 40 cm^3 double-ended 316 stinless steel cylinder with 35-mm female threads on both ends. The volume of the cylinder (i.e., the pycnometer) was calibrated as a function of temperature using mercury as the density standard. The density of mercury was taken from the *Smithsonian Physical Tables* (*9*). The principle of the density measurement involves measurement of the mass of the test sample contained in a pycnometer of known volume at any desired temperature. The experimental system was designed to operate in a temperature range from ambient to 500 K and at pressures up to 125 bar.

For the measurement of the density of the test sample, the pycnometer was first evacuated by connecting it to a vacuum line, after which it was weighed carefully on a Mettler balance PC-2000. The pycnometer was subsequently reconnected to the system. The test sample, already prepared and stored in a sample reservoir, was then forced into the pycnometer under pressure from a nitrogen gas stored in a standard nitrogen cylinder. The test sample in the pycnometer was kept in the liquid state through the application of a pressure of approximately 15 kPa above the estimated saturation pressure of the sample at the operating temperature. The saturation pressures of the samples were estimated from the generalized Riedel correlation (*10*). The mixture pseudocritical temperature and pressure, T_{cm} and P_{cm}, and the mixture acentric factor, ω_m, needed to obtain an estimate of the saturation pressures were calculated using the mixing rules proposed by Hankinson and Thomson (*11*). A digital pressure gauge with an accuracy of 1% of full scale (11 MPa) monitored the pressure in the high-pressure line. The schematic diagram of the experimental setup has been given elsewhere (*12*).

The pycnometer now containing the sample was then immersed in a constant-temperature bath which had already attained a steady-state predetermined operating temperature. After thermal equilibrium had been achieved, the density cell was disconnected from the system, properly cleaned, dried, and weighed. The density was then determined from the weight of the sample and the volume of the density cell.

A Tamson TCV-70 constant-temperature bath supplied by Neslab was used for operating temperatures from ambient to 500 K. The bath was provided with an 800-W control heater and a 1750-W booster heater, for quick heating. The temperature in the bath could be maintained within of ±0.02 K. A Neslab DR-2 digital readout compact thermometer that could monitor temperature in the range from 200 to 500 K was used for measuring the operating bath temperatures. A Fluka Model 2180A RTD digital

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Table 1. Densities of Benzene and Hexane at Temperature T

benzene			hexane		
	ϱ/(g·cm^{-3})			ϱ/(g·cm^{-3})	
T/K	present work	lit.	T/K	present work	lit.
298.15	0.8737	0.8736^a 0.87368^b 0.8737^c	298.15	0.6548	0.65479^b 0.6548^d
303.15	0.8683	0.86829^a 0.8683^c	303.15	0.6503^c	0.6503^c
313.15	0.8581	0.8575^c	313.15	0.6409	0.6410^d

[a] Reference 16. [b] Reference 17. [c] Reference 4. [d] Reference 18.

thermometer which had a temperature range from 100 to 500 K and a resolution of ±0.01 K was also used as a double check on the bath temperature measurement.

Results and Discussion

Density. In order to test the accuracy of the experimental system, the density of doubled distilled water was measured from 313.15 to 373.15 K and each observation was repeated. The results were compared with some earlier density of pure water measurements reported in the literature. Kell (*13*) has summarized both recent measurements and older ones to give a precise representation of the volume of water at 1 atm. For convenience, only two such measurements (*14*, *15*) were chosen for comparison with our results. Each of the two reported literature values was found to differ from our experimental measurement by an average absolute deviation of about 0.06%, which does establish the reliability of the system in terms of both its accuracy and its reproducibility. The accuracy in the measurement of the density of the individual components (benzene and hexane) and their mixtures was estimated to be within ±0.07% over the whole range of temperature, taking into account the uncertainties in the measurements of mass, volume, and temperature and the effect of pressure.

Some experimentally determined densities of the pure components used in this work are listed in Table 1 with literature values. The experimental values of the present study compare favorably with these reported literature values. The experimental densities of the pure components and seven of their binary mixtures at 11 temperatures in the $198.15 \leq T/\mathrm{K} \leq 473.15$ range are listed in Table 2.

Experimental density measurements of the binary mixtures of benzene + hexane have been made by such authors as Schmidt et al. (*4*), Heric and Brewer (*5*), Ridgway and Butler (*6*), Mathison and Thynne (*7*), and Jain et al. (*8*) among others in the temperature range of 298.15–323.15 K. Their measurements were carried out at compositions different from those selected for the present studies, making a one to one comparison between our results and their experimental measurements impossible. Nevertheless, it has been possible to compare these literature values with predictions made by an empirical correlation derived from our experimental results.

The saturated molar volumes of the benzene + hexane mixtures calculated from the experimental density data were correlated as a function of composition at temperature T using an equation of the form

$$V = a + bx + cx^2 + dx^3 \tag{1}$$

Values of the coefficients a, b, c, and d along with the percentage absolute deviation (AAD, %) from the experimental data are given in Table 3.

Figure 1 shows curves of deviations from eq 1 for the saturated molar volumes reported by Schmidt et al. (*4*), Heric and Brewer (*5*), and Ridgway and Butler (*6*). It is evident from Figure 1 that our results compare favorably with those of other researchers due to the relatively small deviations obtained.

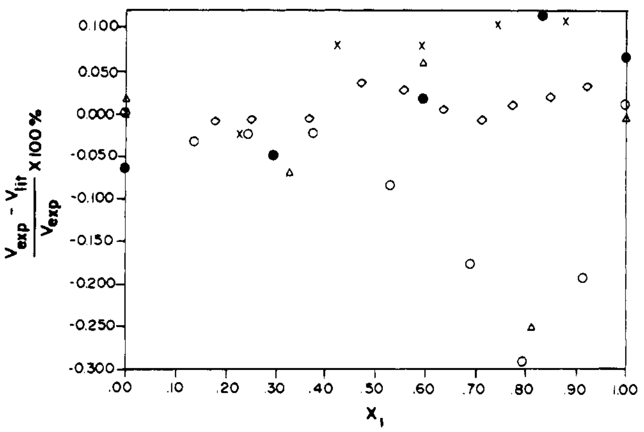

Figure 1. Deviations of experimental molar volumes for the benzene + hexane system from the values given by eq 1: (×) Schmidt et al. (*4*), 298.15 K; (◇) Heric and Brewer (*5*), 298.15 K; (○) Ridgway and Butler (*6*), 298.15 K; (△) Schmidt et al. (*4*), 303.15 K; (●) Schmidt et al. (*4*), 313.15 K.

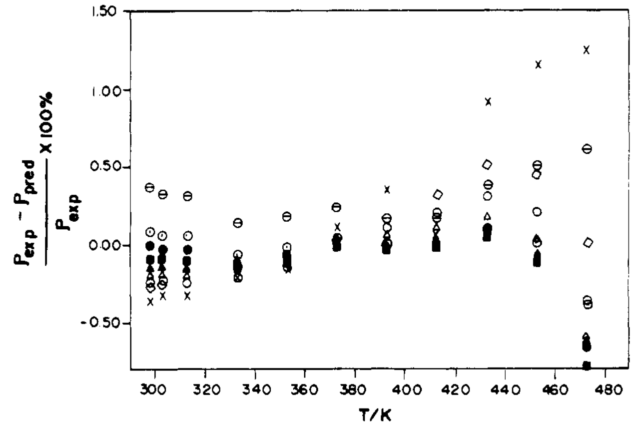

Figure 2. Deviations of experimental densities for the benzene + hexane system from predictions by the SDR equation at the following mole fractions of benzene: (×) 0.0, (tso) 0.2162, (○) 0.3210, (△) 0.4238, (▲) 0.5245, (■) 0.6233, (●) 0.7202, (⊙) 0.8153, (⊖) 1.00.

The proposed correlation (eq 1) has been found to fit the experimental data of Schmidt et al. (*4*), Heric and Brewer (*5*), and Ridgway and Butler (*6*) at 298.15 K with an overall average absolute deviation of 0.049%. Schmidt et al.'s (*4*) data at 303.15 and 313.15 K were predicted with average absolute deviations of 0.066% and 0.052%, respectively.

The density results of the benzene + hexane mixtures were also predicted as a function of temperature by the Hankinson–Brobst–Thomson (HBT) method (*11*) and the Spencer and Danner modified Rackett equation (SDR) (*19*). The Z_{RA} values and the pure component critical property data required to estimate the liquid densities as shown in Table 4 were obtained from Reid et al. (*20*). The HBT correlation showed an average absolute deviation of 0.74% for all the mixtures considered while the SDR equation predicted the experimental density data of the mixtures with an average absolute deviation of 0.20%. Figures 2 and 3 show deviation plots of the predicted densities from the corresponding experimental values. The two correlations predicted higher densities for the benzene + hexane mixtures. This indicates that there exists a scope for improvement of both the HBT and SDR correlations to

Table 2. Experimental Densities for Benzene (1) + Hexane (2) at Temperature *T*

	ϱ/(g·cm^{-3})								
T/K	$x_1 = 1.000$	$x_1 = 0.8153$	$x_1 = 0.7202$	$x_1 = 0.6233$	$x_1 = 0.5245$	$x_1 = 0.4238$	$x_1 = 0.3210$	$x_1 = 0.2162$	$x_1 = 0.000$
298.15	0.8737	0.8168	0.7915	0.7679	0.7459	0.7253	0.7061	0.6880	0.6548
303.15	0.8683	0.8117	0.7865	0.7631	0.7412	0.7207	0.7015	0.6835	0.6504
313.15	0.8581	0.8017	0.7766	0.7532	0.7314	0.7109	0.6918	0.6739	0.6409
333.15	0.8358	0.7803	0.7556	0.7326	0.7112	0.6910	0.6722	0.6545	0.6221
353.15	0.8146	0.7594	0.7348	0.7119	0.6906	0.6706	0.6519	0.6344	0.6023
373.15	0.7926	0.7376	0.7131	0.6904	0.6692	0.6494	0.6308	0.6134	0.5816
393.15	0.7685	0.7139	0.6896	0.6671	0.6461	0.6266	0.6082	0.5910	0.5596
413.15	0.7437	0.6891	0.6648	0.6423	0.6214	0.6019	0.5837	0.5666	0.5355
433.15	0.7188	0.6632	0.6386	0.6158	0.5947	0.5751	0.5568	0.5399	0.5087
453.15	0.6912	0.6337	0.6085	0.5853	0.5639	0.5440	0.5255	0.5083	0.4773
473.15	0.6607	0.5993	0.5727	0.5485	0.5262	0.5058	0.4869	0.4694	0.4381

Table 3. Coefficients *a*, *b*, *c*, and *d* of Eq 1 for Benzene (1) + Hexane (2) at Temperature *T*

T/K	a	b	c	d	AAD/%
298.15	131.608	−40.840	−0.9504	−0.4062	0.0028
303.15	132.500	−41.266	−0.8229	−0.4480	0.0027
313.15	134.462	−42.151	−0.9228	−0.3569	0.0040
333.15	138.529	−43.855	−0.8717	−0.3412	0.0035
353.15	143.081	−45.945	−1.0289	−0.2147	0.0022
373.15	148.176	−48.508	−0.8541	−0.2590	0.0028
393.15	154.001	−54.364	−0.6555	−0.3365	0.0026
413.15	160.930	−54.903	−0.8605	−0.1324	0.0019
433.15	169.397	−59.817	−0.7870	−0.1240	0.0084
453.15	180.558	−66.665	−0.9772	0.0984	0.0039
473.15	196.710	−77.699	−0.8918	0.1101	0.0030

Table 4. Z_{RA} Values and Other Pure Component Critical Property Data

	benzene	hexane		benzene	hexane
T_c/K	562.2	507.5	Z_{RA}	0.2698	0.2635
P_c/bar	48.9	30.1	V^*(cm^3·mol^{-1})	256.4	368.2
V_c/(cm^3·mol^{-1})	259.0	370.0	ω_{SRK}	0.2137	0.3007
Z_c	0.271	0.264	molec wt	78.114	86.178
ω	0.212	0.299			

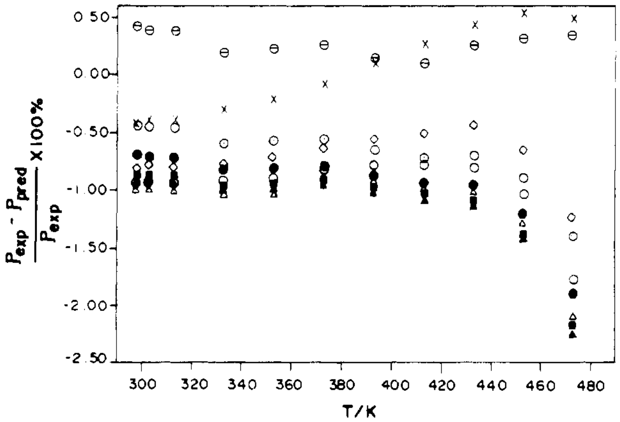

Figure 3. Deviations of experimental densities for the benzene + hexane system from predictions by the HBT correlation at the following mole fractions of benzene: (×) 0.0, (◇) 0.2162, (○) 0.3210, (△) 0.4238, (▲) 0.5245, (■) 0.6233, (●) 0.7202, (⊙) 0.8153, (⊖) 1.00.

more accurately predict the density−temperature behavior of mixtures.

In order to make sure that the test samples did not decompose or were not contaminated during studies at higher temperatures, measurements of the density at ambient temperature were made for all such samples that had been previously exposed to high temperatures. The results obtained were compared with density measurement of a fresh sample. From the results obtained, no evidence of decomposition or contamination of the specimens was found (*12*).

The modified Tait equation included in the HBT (i.e., the COSTALD) correlation (*21*) for predicting the effect of pressure on a liquid was utilized to ascertain the effect of the excess pressure (15 kPa approximately) applied in determining the density of the samples. The effect on the saturated liquid densities was found to be negligible to within a maximum of 0.013% for all the mixtures.

Excess Volumes. The experimental densities ϱ at each temperature were converted into excess molar volumes V^E using the following equation:

$$V^E = (x_1M_1 + x_2M_2)/\varrho - [(x_1M_1/\varrho_1) + (x_2M_2/\varrho_2)] \quad (2)$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 the molar masses of the solvents, and ϱ_1 and ϱ_2 the densities of the pure components. The V^E values are accurate to within ±0.01 cm^3/mol.

The system exhibits positive deviations from ideality at all the temperatures considered (Table 5). The positive deviations are probably ascribable to the inefficient packing in the mixtures of these components as a result of their incompatible structures: benzene, rigid with flat structure; hexane, flexible chain structure. But as the molecular motion in the mixtures increases with increasing temperature, the spaces between the molecules become occupied by the flexible hexane chain structure, causing packing to be more efficient. This may explain why the excess molar volume becomes less positive with increasing temperature.

The V^E data were correlated as a function of composition using a three-constant Redlich−Kister expansion:

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1(1 - x_1)[A + B(1 - 2x_1) + C(1 - 2x_1)^2] \quad (3)$$

Values of the coefficients A, B, and C along with the percentage absolute deviation (AAD, %) determined by a linear regression using statistical analysis with all points weighted equally are given in Table 6. Further attempt was made to express the excess volume of the mixture as a function of both composition and temperature by correlating the coefficients of the Redlich−Kister expansion (eq 3) as a function of temperature:

$$A = A_0 + A_1T + A_2T^2 \quad (4)$$

$$B = B_0 + B_1T + B_2T^2 \quad (5)$$

$$C = C_0 + C_1T + C_2T^2 \quad (6)$$

Values of the coefficients A_i, B_i, and C_i are listed in Table 7. These coefficients reproduce the V^E data with an overall percentage absolute deviation of 2.14%. The values of the excess molar volume have been presented graphically in Figure 4 together with the trend of eq 3.

One to one comparison of our excess molar volume results with those obtained by previous researchers is not

Table 5. Excess Molar Volumes V^E of Benzene (1) with Hexane (2) at Temperature T

	$V^E/(cm^3 \cdot mol^{-1})$						
T/K	$x_1 = 0.8153$	$x_1 = 0.7202$	$x_1 = 0.6233$	$x_1 = 0.5245$	$x_1 = 0.4238$	$x_1 = 0.3210$	$x_1 = 0.2162$
298.15	0.26	0.33	0.38	0.39	0.38	0.32	0.24
303.15	0.25	0.32	0.36	0.37	0.36	0.31	0.23
313.15	0.24	0.31	0.35	0.36	0.36	0.31	0.22
333.15	0.23	0.30	0.34	0.34	0.34	0.29	0.22
353.15	0.22	0.28	0.32	0.33	0.33	0.29	0.21
373.15	0.20	0.27	0.30	0.31	0.30	0.27	0.20
393.15	0.19	0.25	0.28	0.30	0.27	0.24	0.19
413.15	0.16	0.22	0.26	0.26	0.26	0.22	0.17
433.15	0.14	0.19	0.23	0.25	0.24	0.21	0.15
453.15	0.13	0.17	0.19	0.20	0.20	0.19	0.16
473.15	0.10	0.15	0.16	0.19	0.17	0.16	0.14

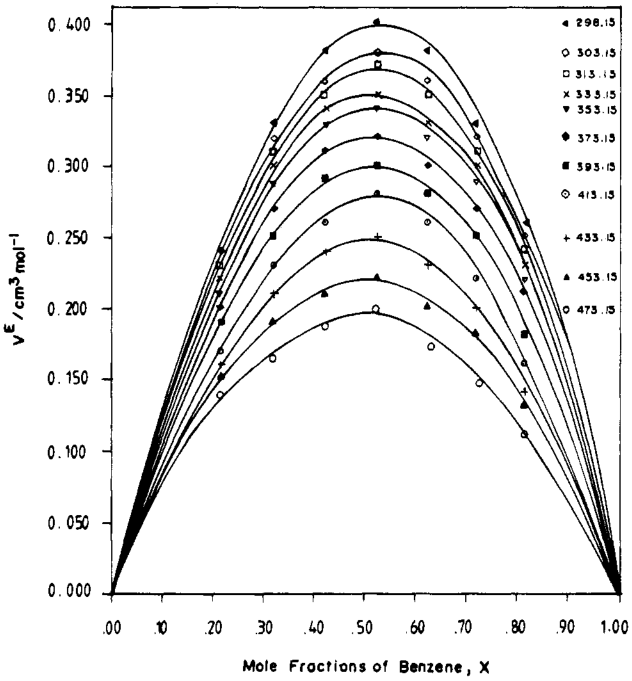

Figure 4. Excess molar volumes, V^E, for benzene (1) + hexane (2) from 298.15 to 473.15 K.

Table 6. Coefficients A, B, and C of Eq 3 for Benzene (1) + Hexane (2) at Temperature T

T/K	A	B	C	ADD/%
298.15	1.56	−0.22	−0.05	1.02
303.15	1.49	−0.24	0.03	1.04
313.15	1.46	−0.21	−0.08	1.97
333.15	1.38	−0.17	0.13	1.16
353.15	1.35	−0.12	−0.01	1.11
373.15	1.24	−0.12	0.12	0.76
393.15	1.15	−0.15	0.08	1.45
413.15	1.06	−0.06	−0.06	1.39
433.15	0.99	−0.03	−0.26	1.44
453.15	0.82	0.08	0.28	1.26
473.15	0.72	0.08	0.06	3.59

Table 7. Coefficients A_i, B_i, and C_i of Eqs 4−6 for the System Benzene + Hexane

A	B	C
$A_0 = 1.5$	$B_0 = 0.35$	$C_0 = 0.58$
$A_1 = 2.9 \times 10^{-3}$	$B_1 = -4.1 \times 10^{-3}$	$C_1 = -3.3 \times 10^{-3}$
$A_2 = -9.5 \times 10^{-6}$	$B_2 = 7.4 \times 10^{-6}$	$C_2 = 4.6 \times 10^{-6}$
	AAD/% = 2.14	

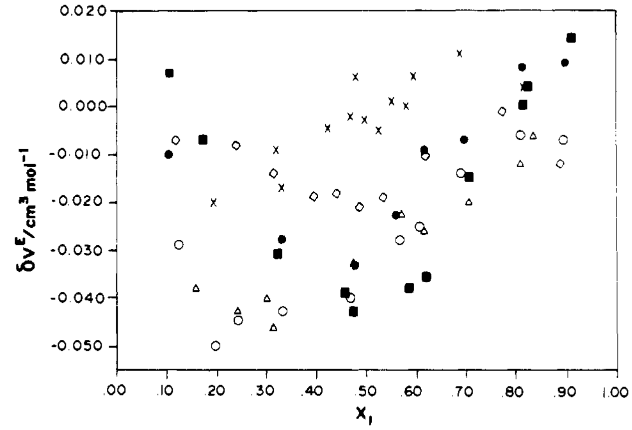

Figure 5. Deviations of experimental excess volumes for the benzene + hexane system from the values given by eq 3: (×) Diaz Pena and Nunez Delgado (*1*), 323.15 K; (◇) Letcher (*2*), 298.15 K; (○) Nigam et al. (*3*), 288.15 K; (△) Nigam et al. (*3*), 298.15 K; (●) Nigam et al. (*3*), 303.15 K; (■) Nigam et al. (*3*), 308.15 K.

possible because the concentrations they considered are different from those selected for the present study. However, it has been possible to compare a representative of these reported literature values with predictions made by the three-constant Redlich−Kister expansion, eqs 3−6.

Figure 5 shows curves of deviations of excess volumes for the predictions made by eq 3 to the experimental results reported by various researchers (*1−3*):

$$\delta V^E = V^E(\text{eq } 3) - V^E(\text{lit.}) \qquad (7)$$

Equation 3 predicted the excess volumes at 323.15 K reported by Diaz Pena and Nunez Delgado (*1*) with an average absolute deviation (AAD) of 2.06%. Letcher's (*2*) excess volume data at 298.15 K were predicted with an average absolute deviation of 4.08%. The values reported by Nigam et al. (*3*) were predicted with relatively higher average absolute deviations of 9.65%, 8.88%, 5.25%, and 6.10% for the data at 288.15, 298.15, 303.15, and 308.15 K, respectively. The correlation does not seem to accurately predict excess volumes at temperatures below ambient as shown by the relatively high AAD of 9.65% for the data at 288.15 K.

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