Excess Volumes of Mixing

Benzene-Cyclohexane and Benzene-Diphenylmethane Systems

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The excess volume of mixing of the binary system benzene-cyclohexane has been measured as a function of composition at 25° and 40° C. using a direct, dilatometric technique. The results are compared with previous determinations, and the comparison confirms the superiority of the direct method of measurement over the more usual indirect technique of calculating volume changes from density measurements. The excess volume of mixing of the system benzene-diphenylmethane has been measured at 30° and 50° C.

THE thermodynamic properties of the binary system benzene-diphenylmethane have been studied intensively during the past few years (*3, 5, 6, 9, 10*), and the results have been used to test various statistical theories of monomer-dimer mixtures. The excess volume of mixing of this system has been measured by Duff and Everett (*3*) and, more recently, by Kortüm and Schreiber (*9*). The former authors quote a value for the equimolar mixture at 30° C. of –0.61 cc. mole^{-1} and this is in very poor agreement with Kortüm and Schreiber's figure of –0.12 cc. mole^{-1} at 35° C. Both groups derived the excess volume of mixing from experimental measurements of the densities of mixtures of known composition. Derivations using this technique are notoriously unreliable, and the present results on this system were obtained using a direct, dilatometric method.

To test the absolute accuracy and precision of the dilatometric technique the excess volume of mixing of the binary system benzene-cyclohexane was measured at 25° and 40° C.

EXPERIMENTAL

The dilatometers used have been described previously (*4*). Veridia capillary tubing of 0.3-mm. internal bore was used to measure the volume changes, and the individual bore diameters were calibrated in the usual way by weighing a mercury thread of known length.

The materials used, benzene, cyclohexane, and diphenylmethane, were purified as described previously (*10*), and all contained less than 0.1 mole % impurity. The measured physical properties are given in Table I.

RESULTS

Benzene-Cyclohexane. Eleven successful measurements were made on this system at 40° C. and six at 25° C. The results are tabulated in Table II and are well represented by Equations 1 and 2, where V^E is the excess volume in cubic centimeters per mole and x_1 and x_2 are the mole fractions of benzene and cyclohexane, respectively.

$$\text{At } 25^\circ\text{ C., } V^E = x_1x_2[2.5564 - 0.0577\,(x_1 - x_2) + 0.0267\,(x_1 - x_2)^2] \quad (1)$$

$$\text{At } 40^\circ\text{ C., } V^E = x_1x_2[2.4878 - 0.0241\,(x_1 - x_2) + 0.3459\,(x_1 - x_2)^2] \quad (2)$$

Table I. Physical Properties of Pure Components

Substance	Freezing Point, ° C.	Density, d_4^{25}
Benzene	5.530	0.87366
Cyclohexane	6.551	0.77384
Diphenylmethane	25.06	0.9998 (Supercooled)

Table II. Excess Volumes of Mixing

	x_1	V^E, Cc. Moles^{-1}	Δ	
BENZENE-CYCLOHEXANE				
$t = 25°$ C.	0.2324	0.4632	0.0003	
	0.3749	0.6023	–0.0006	
	0.5015	0.6394	0.0003	$\sigma = 0.0005$
	0.5046	0.6389	0.0000	
	0.6496	0.5786	0.0001	
	0.7957	0.4114	–0.0001	
$t = 40°$ C.	0.1496	0.3416	0.0013	
	0.2385	0.4688	–0.0025	
	0.2394	0.4773	0.0049	
	0.3137	0.5441	–0.0038	
	0.4441	0.6107	–0.0052	
	0.4975	0.6235	0.0015	$\sigma = 0.0039$
	0.5071	0.6257	0.0040	
	0.5897	0.6065	0.0029	
	0.6949	0.5334	–0.0032	
	0.7991	0.4194	0.0025	
	0.8260	0.3742	–0.0022	
BENZENE-DIPHENYLMETHANE				
$t = 30°$ C.	0.1966	–0.1102	0.0043	
	0.2164	–0.1246	0.0006	
	0.2394	–0.1351	–0.0005	
	0.3076	–0.1649	–0.0016	
	0.4011	–0.1950	–0.0004	$\sigma = 0.0054$
	0.5022	–0.2235	–0.0045	
	0.5184	–0.2227	–0.0012	
	0.5988	–0.2283	–0.0007	
	0.7233	–0.2000	0.0114	
	0.8890	–0.1262	–0.0048	
	0.8933	–0.1230	–0.0053	
$t = 50°$ C.	0.2871	–0.2042	0.0020	
	0.3558	–0.2423	0.0011	
	0.4444	–0.2882	–0.0084	$\sigma = 0.0067$
	0.5096	–0.2941	0.0024	
	0.6029	–0.2962	0.0063	
	0.7188	–0.2784	–0.0034	

In Table II, Δ is the difference between experimental V^E and the value calculated from the above equations, and

σ is the over-all standard deviation and is a measure of the experimental precision.

A consideration of Equations 1 and 2 shows that V^E for this system is only slightly dependent on temperature. If, at constant composition, V^E is assumed to be a linear function of temperature, dV^E/dT is represented by Equation 3.

$$dV^E/dT = x_1x_2[-0.0045 + 0.00224\,(x_1 - x_2) + 0.0213\,(x_1 - x_2)^2] \quad (3)$$

The relatively large value of the coefficient of $(x_1 - x_2)^2$ in Equation 3 causes dV^E/dT to be positive for solutions dilute with respect to either component and negative for solutions in the middle of the concentration range.

The excess volume of mixing of benzene-cyclohexane mixtures has been studied by many groups of experimentalists (*1, 2, 8, 11, 13-15*). All the available data are presented in Figure 1, where ΔV^E, the difference between each experimental point and the value of V^E given by Equation 1 is plotted as a function of composition. To enable a consistent comparison to be made, where the original results were obtained at a temperature other than 25° C., the values have been corrected to this temperature using Equation 3. Only the results of Klapproth (*8*) have been excluded from Figure 1, as there is a considerable discrepancy between the tabulated densities and the derived values of V^E given in this publication. The remaining seven sets of data can be divided into two groups. Wood and Austin (*15*), Danusso (*1*), Reddy, Subrahmanyam, and Bhimasenachar (*13*), and Mathieson and Thynne (*11*) derived excess volumes of mixing from density measurements, while the measurements of Diaz-Pena and Cavero (*2*), Watson *et al.* (*14*), and the present results were obtained using direct, dilatometric techniques.

Figure I shows the remarkable precision of the results of Wood and Austin, although their values are systematically higher than the bulk of the more recent measurements. The other sets of measurements in this first group are either of low precision or of low absolute accuracy. Figure I also shows the second group of measurements, the present results and the equation of Watson *et al.* (*14*) are in excellent agreement, the agreement being exact for the equimolar mixture. This is especially satisfactory because the two sets of measurements were obtained using two entirely different types of dilatometer. The actual experimental points of Watson and associates are not available, but a standard deviation of $\sigma = 0.007$ cc. mole^{-1} is quoted. The agreement of the equation of Watson *et al.* with the present results is well within this limit. The dilatometric results of Diaz-Pena and Cavero (*2*) are in contrast, of rather lower precision.

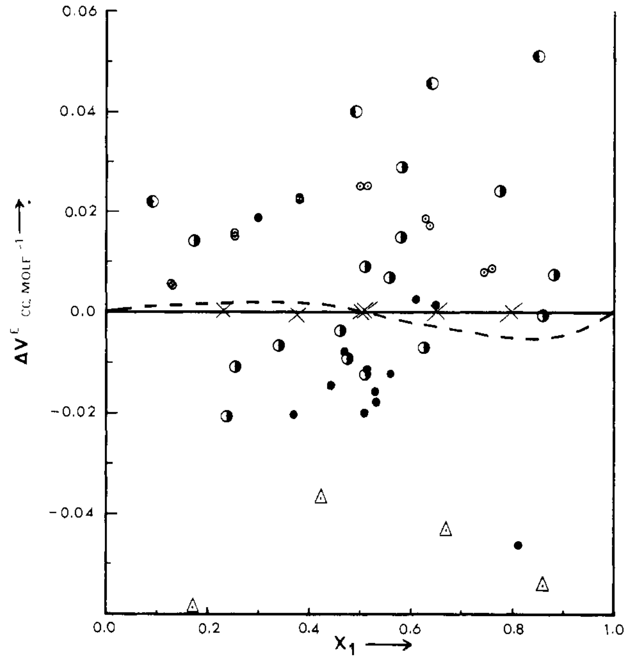

Figure 1. Deviations of experimental excess volumes of mixing of the system benzene-cyclohexane from the values given by Equation 1

⊙ Wood and Austin (*15*)
◐ Danusso (*1*)
△ Reddy, Subrahmanyam, and Bhimasenachar (*13*)
◑ Mathieson and Thynne (*11*)
• Diaz-Pena and Cavero (*2*)
X Present results
---- Equation of Watson *et al.* (*14*)

Figure I emphasizes how difficult it is to measure excess volumes of mixing to better than ±2% and indicates that dilatometric results are almost always preferable to excess volumes derived from density measurements. In the present case, for equimolar solutions, an error of as little as $\pm 3 \times 10^{-6}$ in density measurements would give rise to an uncertainty of ±2% in V^E. The dilatometric technique is easier and quicker than pycnometry and also requires smaller amounts of material. The authors suggest that benzene-cyclohexane be used in the future as a test system for excess volume measurements.

Benzene-Diphenylmethane. Eleven successful measurements were carried out on this system at 30° C. and six at 50° C. Occasional difficulty was experienced when filling the dilatometers with diphenylmethane owing to the material's solidifying in the hypodermic needle. The results are given in Table II and can be represented by Equations 4, 5, and 6.

$$\text{At } 30^\circ\text{ C., } V^E = -x_1x_2[0.8747 + 0.3387(x_1 - x_2) + 0.1519\,(x_1 - x_2)^2] \quad (4)$$

$$\text{At } 50^\circ\text{ C., } V^E = -x_1x_2[1.1786 + 0.4087\,(x_1 - x_2) + 0.0153\,(x_1 - x_2)^2] \quad (5)$$

$$dV^E/dT = x_1x_2[0.0152 + 0.0035\,(x_1 - x_2) - 0.00683\,(x_1 - x_2)^2] \quad (6)$$

The present results are plotted in Figure 2 with the pycnometric results of Duff and Everett (*3*) and the recent results of Kortüm and Schreiber (*9*), which were also derived from density measurements. The present results lie between the other sets of data, and Figure 2 demonstrates con-

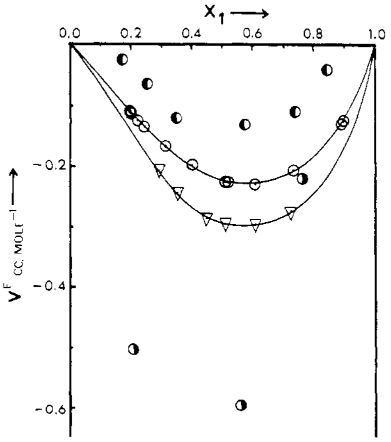

Figure 2. Excess volume of mixing of the system benzene-diphenylmethane

◑ Duff and Everett (*3*) at 30° C.
◐ Kortüm and Schreiber (*9*) at 35° C.
⊙ Present results at 30° C.
▽ Present results at 50° C.

clusively the superiority of the dilatometric technique. The value of dV^E/dT given by Duff and Everett, −0.0060 cc. mole^{-1} degree^{-1} for an equimolar solution, is in quite reasonable agreement with the present value of −0.0038 cc. per mole degree. A previous anomaly has been resolved in that both V^E and dV^E/dT for the system benzene-diphenylmethane have now been shown to be comparable in sign, magnitude, and composition dependence to the experimental values for other binary systems in which the ratio of the molar volumes of the two pure components is approximately two—e.g., benzene-diphenyl (*7*), cyclohexane-dicyclohexyl, cyclohexane-dicylohexylmethane (*12*). The experimental free energy, enthalpy, and volume of mixing for benzene-diphenylmethane will be used to test various statistical theories of monomer-dimer mixtures in a subsequent publication.

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Vapor Pressures of Liquid Oxygen between the Triple Point and Critical Point

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Vapor pressure measurements reported in the literature for liquid oxygen have been subjected to a rigorous analysis to establish the constants of the Frost-Kalfwarf vapor pressure equation. This investigation has considered all pertinent measurements reported since 1884 and includes in excess of 423 values. A screening procedure reduced this number to 259 reliable points which have served to define the constants of this vapor pressure equation as follows:

$$\log P = 13.4275 - \frac{469.150}{T} - 2.7391 \log T + 0.1155 \frac{P}{T^2}$$

where P is millimeters of mercury and T is the temperature in ° K. This relationship covers the range included between the triple point and critical point and has the capability to reproduce the more accurate experimental measurements with an average deviation of 0.43%. The triple point, T_t = 54.363° K., P_t = 1.125 mm. of Hg and the critical point, T_c = 154.33° K., P_c = 49.713 atm. were deduced from the analysis of these data.

VAPOR PRESSURE measurements on oxygen have appeared in the literature since the early studies of Wroblewski (*13*). Since then, additional measurements have appeared until the last studies reported by Hoge (*8*). Virtually no attempts have been made to obtain further vapor pressure measurements since 1950.

Altogether, 12 sources of information were consulted to obtain vapor measurements for liquid oxygen. Of particular interest is the work reported by Kamerlingh Onnes, Dorsman, and Holst (*9*) and that of Hoge (*8*). Both of these studies present vapor pressure measurements in the critical region, which have enabled the independent establishment of the critical constants of oxygen. The critical values, corrected to the National Bureau of Standards 1955 temperature scale of 273.15° K. reported by these two references, are as follows:

Reference	T_c, ° K.	P_c, Atm.	d_c, G./Cc.
(*9*)	154.33	49.713	0.4295
(*8*)	154.77	50.14	0.38

The critical value reported by Hoge was estimated by comparing the isotherms for oxygen in the vicinity of the critical point with those for carbon dioxide reported by Michels, Blaisse, and Michels (*10*). In this investigation, the critical values reported by Kamerlingh Onnes, Dorsman, and Holst (*9*) have been accepted. However, the low pressure measurements of Hoge (*8*) have enabled the establishment of the triple point as T_t = 54.363° K. and P_t = 1.125 mm. of Hg.

TREATMENT OF VAPOR PRESSURE MEASUREMENTS

The Frost-Kalkwarf vapor pressure equation has received considerable attention because of its ability to account for