

Excess Volume of Mixing for Binary Mixtures of Pyridine, Acrylonitrile, Anisole & Acetylacetone with Carbon Tetrachloride

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Excess volumes of mixing of binary mixtures of pyridine, acrylonitrile, anisole, and acetylacetone in carbon tetrachloride determined dilatometrically are reported over the complete mole fraction range and at 303.15 K. The results are discussed in terms of the specific interaction between the components.

CARBON tetrachloride is known to show specific interaction of the charge transfer type with electron donors. In continuation of our work^{1a,b,c,d} on the excess thermodynamic properties of mixtures containing carbon tetrachloride as one of the components, we report here the excess volumes for mixtures of four *n*-donor, namely pyridine, acrylonitrile, anisole, and acetylacetone in carbon tetrachloride over the complete range of mole fractions and at 303.15 K.

Materials and Methods

All the chemicals were stored over pre-dried molecular sieves (4 Å). The methods of purification of carbon tetrachloride (BDH, AR) and cyclohexane (Pfizer-Duchem; LR) are described elsewhere^{1a}. Benzene (BDH, AR) was distilled twice over sodium using a 1 m column; the middle fraction of the second distillate being used. Pyridine (Pfizer-Duchem; AR) of minimum 99.5% GLC assay was used as such. Acrylonitrile and acetylacetone (BDH LR), and anisole (Bush Company Limited) were dried over fused calcium chloride and then fractionally distilled (acetylacetone and anisole under reduced pressure). The densities of pure components at 303.15 K are given in Table 1 along with the corresponding literature values. Mercury was purified according to literature method³.

The U-shaped dilatometer used to measure the volume change on mixing was of the Keyes and Hildebrand² type. The pear-shaped bulbs were replaced by the two cylindrical bulbs of different capacities and, also in contrast, the precision-bore capillary at the top of each bulb was parallel to latter's vertical axis. Each of the eight dilatometers, bulb-capacities ranging from 1 cm³ to 8 cm³, used to measure the excess volume over the complete mole fraction range utilized 2 cm³ of pure degassed mercury to isolate the two components in the bulbs. The components, degassed to less than 13 Pa by six freeze-thaw cycles, were introduced into the bulbs with the help of long hypodermic needle; amount of each component being determined by weighing the dilatometer. The procedure for the measurements was essentially the same as described by earlier workers² except that the mixing was accomplished outside the water thermostat and the liquid menisci in the capillaries were read relative to the fiducial marks on the capillaries by a 1 m OSAW cathetometer (least count ± 0.01 mm).

The capillaries were calibrated by weighing measured length of mercury thread in each capillary and then by calculating its volume. Appropriate corrections were made for the hemispherical menisci on each end of the thread. The ratio of volume

TABLE 1 — DENSITIES OF PURE COMPONENTS AT 303.15 K

Component	$\rho/g\text{ cm}^{-3}$	Component	$\rho/g\text{ cm}^{-3}$
Carbon tetrachloride	1.5747 (1.57458) ⁵	Acrylonitrile	0.7951 (0.7948) ^(a)
Cyclohexane	0.7692 (0.76914)	Anisole	0.9845 (0.98462)
Benzene	0.8683 (0.8684)	Acetylacetone	0.96945 (0.96942) ^(b)
Pyridine	0.9734 (0.97319)	—	—

Values in the parentheses are the literature values (ref. 4).

(a) Determined by extrapolation of values at 293.15 and 298.15 K.

(b) at 298.15 K (ref. 6).

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to the corrected length of the thread was used as the calibration factor of the capillary. Only those capillaries were used for which the calibration factor varied within 0.1% over the entire capillary length of 15 cm. The internal radii of these capillaries were ~ 0.7 mm.

Excess volumes were calculated using Eq. (1)

$$V^E = C(\Delta h_1 + \Delta h_2)/(n_1 + n_2) \quad \dots(1)$$

where C is the calibration factor of capillaries (capillaries of same C were used in one dilatometer), Δh_1 and Δh_2 are the changes in heights of the menisci upon mixing, and n_1 and n_2 are the moles of the two components. The composition dependence of V^E was correlated by Eq. (2)

$$V^E/\text{cm}^3\text{mol}^{-1} = x(1-x)\{v_0 + v_1(2x-1) + v_2(2x-1)^2\} \quad \dots(2)$$

with the coefficients v_0 , v_1 and v_2 determined by least squares fit. Standard deviation $\sigma(V^E)$ were calculated from Eq. (3),

$$\sigma(V^E) = \left\{ \sum (\delta V^E)^2 / (N-3) \right\}^{1/2} \quad \dots(3)$$

where $\delta V^E = V^E$ (Eq. 2) - V^E_{expt} and N is the number of experimental points.

Results and Discussion

Cyclohexane + Benzene — This system has been suggested⁷ as a standard for dilatometry. Our results at 298.15 and 303.15 K are given in Table 2. These were correlated by Eq. (2) with the constants given in Table 3; the standard deviation of the fit being ± 0.003 cm³ mol⁻¹ at both the temperatures. Various reported values⁸ of V^E ($x = 0.5$) at 298.15 K fall in the range 0.639-0.653 cm³ mol⁻¹ and so

does our value 0.643 ± 0.003 cm³ mol⁻¹. The deviations of our results (Eq. 2) from the two best sets^{8,9} are plotted in Fig. 1. In view of relatively large uncertainty in temperature ± 0.01 K as compared to theirs ± 0.001 K, the deviations are not significant. The significantly large deviations of our results at 303.15 K from the densimetric V^E of Satchard *et al.*¹⁰ and Wood and Austin¹¹ are well within the generally accepted limit⁸ of $\pm 10\%$. We are unaware of any dilatometric V data of cyclohexane + benzene at 303.15 K.

Other mixtures — Results for four other mixtures are given in Table 4. No literature data, dilatometric or densimetric, are available for any of these mixtures for comparison. The correlation coeffi-

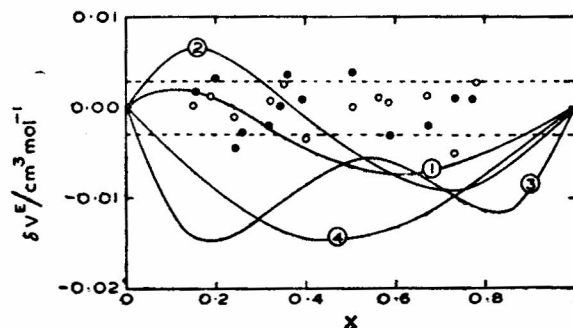


Fig. 1 — Comparison of our V^E results of x cyclohexane + $(1-x)$ benzene with values reported in literature; (O) and (●) this work at 298.15 K and 303.15 K respectively, (---) standard deviation of fit, (1) Stokes *et al.*⁹ at 298.15 K; (2) Stookey, *et al.*⁸ at 298.15 K; (3), Satchard *et al.*¹⁰ at 303.15 K; and (4) Wood and Austin¹¹ at 303.15 K. δV^E is the deviation of Eq. (2) from various results]

TABLE 2 — EXCESS VOLUME FOR $(1-x)$ BENZENE + x -CYCLOHEXANE

[V^E values in cm ³ mol ⁻¹]							
x	V^E	x	V^E	x	V^E	x	V^E
298.15 K							
0.1537	0.333	0.3245	0.560	0.5044	0.643	0.6733	0.571
0.1888	0.391	0.3507	0.580	0.5660	0.633	0.7338	0.516
0.2452	0.474	0.4010	0.619	0.5876	0.626	0.7803	0.448
303.15 K							
0.1562	0.326	0.3213	0.557	0.3958	0.613	0.6738	0.581
0.1967	0.392	0.3451	0.577	0.5034	0.645	0.7335	0.516
0.2462	0.472	0.3585	0.584	0.5885	0.637	0.7760	0.460
0.2596	0.488	—	—	—	—	—	—

TABLE 3 — VALUES OF PARAMETERS OF EQ. (2) AND STANDARD DEVIATIONS AT 303.15 K

Mixture	v_0	v_1	v_2	$\sigma(V^E)/\text{cm}^3 \text{mol}^{-1}$
$(1-x) \text{C}_6\text{H}_{12} + x\text{C}_6\text{H}_6$	2.5720 ^(a)	0.0651 ^(a)	0.0660 ^(a)	± 0.003 ^(a)
	2.5951	0.1272	-0.0429	± 0.003
$(1-x) \text{C}_6\text{H}_5\text{N} + x\text{CCl}_4$	-1.9424	0.4066	0.1548	± 0.005
$(1-x) \text{CH}_3\text{CHCN} + x\text{CCl}_4$	-0.4304	0.1576	0.1002	± 0.005
$(1-x) \text{CH}_3\text{OC}_6\text{H}_5 + x\text{CCl}_4$	-0.4447	0.0552	0.0292	± 0.003
$(1-x) \text{CH}_3\text{COCH}_2\text{COCH}_3 + x\text{CCl}_4$	0.2696	0.3599	0.2789	± 0.003

(a) At 298.15 K.

TABLE 4—EXCESS VOLUME AT 303.15 K
 [VE Values in Cm³ mol⁻¹]

x	V^E	x	V^E
$(1-x)C_6H_5N+xCCl_4$		$(1-x)CH_2CHCN+xCCl_4$	
0.1177	-0.231	0.1231	-0.058
0.1688	-0.303	0.1626	-0.068
0.1792	-0.312	0.1656	-0.072
0.1795	-0.311	0.1787	-0.072
0.2778	-0.424	0.2206	-0.079
0.3874	-0.476	0.3076	-0.096
0.4273	-0.484	0.3234	-0.101
0.5270	-0.485	0.3730	-0.108
0.5771	-0.451	0.4717	-0.109
0.6203	-0.439	0.5362	-0.108
0.7132	-0.361	0.5383	-0.110
0.7918	-0.269	0.6338	-0.090
0.8182	-0.242	0.7208	-0.066
0.8832	-0.154	0.7764	-0.046
		0.8926	-0.030
$(1-x)CH_3OC_6H_5+xCCl_4$		$(1-x)CH_3COCH_2COCH_3+xCCl_4$	
0.1790	-0.072	0.1543	0.020
0.2111	-0.076	0.2107	0.024
0.2546	-0.088	0.2387	0.029
0.3098	-0.094	0.3787	0.046
0.4032	-0.110	0.4294	0.056
0.4218	-0.111	0.4747	0.066
0.4235	-0.113	0.5876	0.084
0.4764	-0.114	0.6362	0.090
0.5890	-0.105	0.6839	0.089
0.6395	-0.096	0.7467	0.096
0.6692	-0.091	0.8032	0.093
0.7424	-0.079	0.8364	0.090
0.7995	-0.068	0.8858	0.075
0.8452	-0.050		

coefficients of Eq. (2) for the mixtures are included in Table 3 along with the standard deviations.

The excess volume for pyridine + carbon tetrachloride, acrylonitrile + carbon tetrachloride, and anisole + carbon tetrachloride is negative over the complete mole fraction range and $V^E(x)$ are symmetrical about $x \approx 0.5$. The results are quite interesting for acetylacetone + carbon tetrachloride as V^E values are low and positive ($0.067 \text{ cm}^3 \text{ mol}^{-1}$, $x = 0.5$) and $V^E(x)$ is maximum around $x \approx 0.7$. These are in contrast to acetone + carbon tetrachloride^{12,13} which has negative V^E values of the

order of $0.1 \text{ cm}^3 \text{ mol}^{-1}$ in the range 293.15-318.15 K and $V^E(x)$ is minimum around $x \approx 0.5$. This can be expected from the keto-enol tautomerism¹⁴ in acetylacetone. In the enolic form electron donor capacity of acetylacetone to carbon tetrachloride would be less. The V^E values increase in the sequence pyridine < anisole = acrylonitrile < acetylacetone. The results indicate the presence of strong specific interactions between the components.

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