Viscosities of Binary Mixtures Involving Benzene, Carbon Tetrachloride, and Cyclohexane

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Accurate measurements of viscosities as functions of composition of binary mixtures of benzene + cyclohexane, carbon tetrachloride + cyclohexane, and carbon tetrachloride + benzene which very nearly satisfy the conditions of S-regular solutions are reported. The results, along with the accurate measurements of Grunberg on the same systems, have been interpreted in terms of the relation proposed by Katti and Chaudhri. Throughout the entire concentration range, the agreement between the observed and the calculated values of viscosities is within 0.5%.

PREVIOUS COMMUNICATIONS (*2*, *3*) have discussed the results of the authors' investigations on the viscosities of binary mixtures of benzyl acetate with dioxane, aniline, and *meta*-cresol; and of carbon tetrachloride with methanol and isopropyl alcohol. This article reports results on the viscosities of binary mixtures of benzene + cyclohexane, carbon tetrachloride + cyclohexane, and carbon tetrachloride + benzene at 25° C.

EXPERIMENTAL

Throughout the investigations, best available grades of Merck's carbon tetrachloride and B.D.H. (British Drug House) "analar" benzene and cyclohexane have been used. Pure liquids from freshly opened bottles were subjected to futher purification whenever it was found necessary. The following procedure was adopted for each of the pure liquids:

Benzene was allowed to stand in contact with pure sulphuric acid with frequent shaking for two weeks. The treated benzene was then fractionally distilled and dried over sodium.

Carbon tetrachloride was further purified by repeated fractional distillation and then thoroughly dried.

Cyclohexane was treated with a mixture of concentrated nitric and sulphuric acids to nitrate any benzene that may have been present. After repeated washings with distilled water, with caustic soda pellets, and with anhydrous sodium sulphate, it was fractionally distilled.

The boiling points, densities, and viscosities of the pure liquids used for investigations are shown in Table I along with the corresponding values quoted in the literature. The agreement is satisfactory. The experimental methods for the determination of the densities and viscosities of pure liquids and binary mixtures of various concentrations, temperature measurements on the International Scale, thermostatic control of temperature, and the methods of estimation of the limit of accuracy have been discussed in detail in the previous article (*3*). The viscosities reported here have been estimated to be accurate to within 0.5%.

RESULTS AND DISCUSSION

The authors' results on the three binary systems are recorded in Tables II, III, and IV. Viscosity measurements of Grunberg have been made using a U-tube viscometer which at 20° C. gave for distilled water a time flow of 1805.8 seconds. Also, from the comparison of the data on the pure liquids used by Grunberg (Table I) with those for the liquids used by us, it can be seen that there is a close correspondence between the specimens used and the procedures employed for the measurements of the times of flow in the present investigation and that of Grunberg. Therefore, it seemed worthwhile to include Grunberg's accurate measurements (claimed by Grunberg to be accurate to within ±0.2%) for discussion on the composition variation of the viscosities of these binary mixtures.

In Tables II–IV, the columns 1 show the mole composition, 'x', of one of the pure components; columns 2 show the molar volumes, 'V', and columns 3 show the observed values of viscosities, 'η'$_{\text{obsd}}$. In columns 4 are recorded the corresponding values of viscosities 'η'$_{\text{calcd.}}$ of the mixtures containing a mole fraction, 'x', of one the components calculated by using the relation (*2*)

$$\ln \eta_s V_s = x \ln \eta_1 V_1 + (1 - x) \ln \eta_2 V_2 + x(1 - x) \left[(\omega_{\text{visc.}}) / (RT) \right] \quad (1)$$

where the symbols 's', 1, and 2 stand for mixtures of pure components 1 and 2, respectively, 'R' the gas constant, and 'T' the absolute temperature. The self-consistent value of 'ω'$_{\text{visc.}}$, the interaction energy for the activation of flow,

Table I. Data for the Samples of Benzene, Carbon Tetrachloride, and Cyclohexane Used

	Densities at 25° C., G./Ml.			Boiling Points in ° C. under a Pressure of 760mm. of Mercury			Viscosities at 25° C., in Centipoise		
Component	For specimen used		From literature (*5*)	For specimen used		From literature (*5*)	For specimen used		From literature
Benzene	0.8735	0.8736[a]	0.8736	80.10	80.10[a]	80.10	0.5996	0.5996[a]	0.599(*5*)
Carbon tetrachloride	1.5843	1.5845[a]	1.5843	76.70	76.75[a]	76.7	0.9019	0.9019[a]	0.902(*4*)
Cyclohexane	0.7736	0.7737[a]	0.7738	80.74	80.74[a]	80.75	0.8856	0.8856[a]	0.860(27° C.) 0.930(22° C.) (*5*)

[a] Grunberg's observations (*1*).

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Table II. Viscosities in Centipoise of Benzene (Component 1) and Cyclohexane (Component 2) at 25° C.

$'\omega'_{\text{visc.}} = -383.1$ cal./mole

Mole Fraction of Component 1, $'x'$	Molar Volume, $'V'$, Ml. Mole^{-1}	$'\eta'_{\text{obsd.}}$	$'\eta'_{\text{calcd.}}$	$'\eta'_{\text{ideal}}$	$100\left[\frac{'\eta'_{\text{ideal}}}{'\eta'_{\text{obsd.}}} - 1\right]$	$100\left[\frac{'\eta'_{\text{calcd.}}}{'\eta'_{\text{obsd.}}} - 1\right]$
0.0000	108.7900	0.8856	0.8856	0.8856	0.00	0.00
0.1500	105.0107	0.7725	0.7737	0.8401	8.75	0.15
0.2438^a	104.0193	0.7115	0.7126	0.8029	12.85	0.15
0.3500	102.9391	0.6571	0.6581	0.7624	16.02	0.15
0.5000	99.9199	0.6120	0.6120	0.7194	17.55	0.00
0.5490^a	98.7642	0.6011	0.6025	0.7071	17.63	0.23
0.6500	96.8931	0.5853	0.5865	0.6795	16.09	0.20
0.7848^a	94.7975	0.5740	0.5753	0.6417	11.79	0.22
0.9000	93.3195	0.5761	0.5750	0.6092	5.75	−0.19
1.0000	89.4218	0.5996	0.5996	0.5996	0.00	0.00

^{a}Taken from Grunberg (*1*)

Table III. Viscosities in Centipoise of Carbon Tetrachloride (Component 1) and Cyclohexane (Component 2) at 25° C.

$'\omega'_{\text{visc.}} = 98.8$ cal./mole

Mole Fraction of Component 1, $'x'$	Molar Volume, $'V'$, Ml. Mole^{-1}	$'\eta'_{\text{obsd.}}$	$'\eta'_{\text{calcd.}}$	$'\eta'_{\text{ideal}}$	$100\left[\frac{'\eta'_{\text{ideal}}}{'\eta'_{\text{obsd.}}} - 1\right]$	$100\left[\frac{'\eta'_{\text{calcd.}}}{'\eta'_{\text{obsd.}}} - 1\right]$
0.0000	108.7900	0.8856	0.8856	0.8856	0.00	0.00
0.2720^a	105.7460	0.8580	0.8588	0.8877	3.46	0.09
0.5000	103.0303	0.8551	0.8551	0.8915	4.26	0.00
0.5295^a	102.7723	0.8568	0.8551	0.8913	4.03	−0.20
0.6250	101.7609	0.8594	0.8579	0.8919	3.78	−0.18
0.7707^a	99.9220	0.8670	0.8698	0.8959	3.33	0.32
1.0000	97.1028	0.9019	0.9019	0.9019	0.00	0.00

^{a}Taken from Grunberg (*1*).

Table IV. Viscosities in Centipoise of Carbon Tetrachloride (Component 1) and Benzene (Component 2) at 25° C.

$'\omega'_{\text{visc.}} = +16.9$ cal./mole

Mole Fraction of Component 1, $'x'$	Molar Volume, $'V'$, Ml. Mole^{-1}	$'\eta'_{\text{obsd.}}$	$'\eta'_{\text{calcd.}}$	$'\eta'_{\text{ideal}}$	$100\left[\frac{'\eta'_{\text{ideal}}}{'\eta'_{\text{obsd.}}} - 1\right]$	$100\left[\frac{'\eta'_{\text{calcd.}}}{'\eta'_{\text{obsd.}}} - 1\right]$
0.0000	89.4218	0.5996	0.5996	0.5996	0.00	0.00
0.1250	90.2848	0.6346	0.6344	0.6316	−0.48	−0.04
0.2348^a	91.2382	0.6652	0.6628	0.6596	−0.84	−0.36
0.4835^a	93.1213	0.7352	0.7352	0.7300	−0.70	−0.00
0.5000	93.2199	0.7404	0.7404	0.7351	−0.71	−0.00
0.6500	94.3918	0.7872	0.7870	0.7815	−0.72	−0.03
0.7767^a	95.3747	0.8291	0.8272	0.8229	−0.75	−0.23
0.9000	96.3869	0.8691	0.8654	0.8652	−0.45	−0.42
1.0000	97.1028	0.9019	0.9019	0.9019	0.00	0.00

^{a}Taken from Grunberg (*1*).

has been chosen to satisfy relation 1 for the observed values of viscosities at equimolar concentrations ($x = 0.5$). These values are recorded at the head of each of Tables II-IV.

The calculated values of viscosities of the corresponding ideal mixtures, $'\eta'_{\text{ideal}}$, (obtained by putting $'\omega'_{\text{visc.}}$ = zero in relation 1) are recorded in columns 5.

Columns 6 and 7 of Tables II–IV show the % deviations of the ideal and calculated values of viscosities, respectively, from the observed values. Column 6 of each Table shows that the deviations from ideality for the three systems benzene + cyclohexane, carbon tetrachloride + cyclohexane, and carbon tetrachloride + benzene, vary between 5.7 and 17.7%, 3.3 and 4.3%, and −0.45 to −0.84% respectively. The corresponding values in column 7 of Tables II-IV show that over the entire range of concentrations the viscosities of all the three systems are represented by relation 1 to within ±0.5%.

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