0.001° C. Temperatures were measured on the International Scale with a calibrated copper-constantan thermocouple and a Pye-type precision vernier potentiometer. The densities were measured in a calibrated pycnometer of the type previously used by Mathot and Desmyter (*11*) and were reproducible to ± 0.0001 gram per ml. The viscosities reported here are accurate to within 0.5%. This margin has been estimated as the maximum limit from the corresponding possible uncertainties in the control of temperature and in the measurements on the times of flow, the compositions, and densities of mixtures. Auxiliary experiments dealing with a large number of observations on the viscosity at equimolar composition showed that the deviations of the individual observations, $(\Delta\eta/\eta) \times 100$, from the mean value η where much less than the 0.05% estimated limit. The results obtained are shown in Tables II and III.

RESULTS AND DISCUSSION

In columns 2 and 4 of Tables II and III are recorded the experimentally observed values of the molar volumes, V, and viscosities, η, against the mole fraction, χ, of one component shown in the corresponding row of column 1.

In column 5 are recorded the corresponding values of the viscosities of the mixtures calculated by using the relation (*8*)

$$\ln \eta_s V_s = \chi \ln \eta_1 V_1 + (1 - \chi) \ln \eta_2 V_2 + \chi(1 - \chi)\omega_{\text{visc}}/RT \quad (1)$$

where the symbols s, 1, and 2 stand for mixture and pure components 1 and 2, respectively; and ω_{visc} is the interaction energy for the activation of flow; R, the gas constant and T, the absolute temperature. A self-consistent value of ω_{visc} for each mixture was calculated by using Relation 1 from the observed values of η_s for an equimolar mixture. The corresponding values of ω_{visc} for each mixture are recorded at the head of Tables II and III.

The composition variations of the viscosities were then calculated by using the above values of ω_{visc} and Relation 1. These values are recorded in column 5 of Tables II and III. Column 3 shows the viscosities of the corresponding ideal mixtures as calculated from Relation 1 with ω_{visc} = zero.

A comparison of the corresponding viscosities for both the mixtures in columns 3 and 4 of Tables II and III shows the large deviations of these mixtures from ideality.

Columns 4 and 5 show that agreement between the experimentally observed values of viscosities and those calculated from Relation 1 for both the mixtures over the entire range of composition is well within the experimental error.

ACKNOWLEDGMENT

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Refractive Indices of Binary Hydrocarbon Mixtures

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Refractive indices, n_D, were determined for five binary hydrocarbon mixtures and correlated by means of a two-constant equation. When volume farctions were used instead of mole fractions, n_D values for four benzene–aliphatic hydrocarbon mixtures could be correlated by a one-constant equation.

IN THE STUDY of thermodynamic properties of mixtures, refractive indices were measured at 25° C. for five binary hydrocarbon mixtures: benzene-*n*-hexane, benzene-*n*-heptane, benzene-*n*-octane, benzene-*n*-decane, and benzene-cyclohexane. Measurements were made using a precision refractometer, and refractive indices were readily determined to 0.00001. The accuracy of reading is, however, of the order of 0.00003. A precision temperature controller was used to maintain the temperature at 25 ± 0.02° C. Spectro grade benzene and cyclohexane, (Matheson, Coleman, and Bell Co.), and research grade *n*-hexane and *n*-heptane, and pure grade *n*-octane and *n*-decane, (Phillips Petroleum Co.), were dried with silica gel and then used without further purifications. Experimental refractive index values of these pure compounds are compared with the literature values in Table I. Refractive indices of the five binary mixtures are listed in Table II. The uncertainty in making up mixtures, in terms of the liquid mole fraction, is estimated to be less than ± 0.0004.

The following equation has been used sucessfully in the literature for correlating thermodynamic properties of binary mixtures.

$$G = x_1G_1 + x_2G_2 + \frac{x_1x_2}{A + B(x_1 - x_2) + \cdots} \quad (1)$$

Table I. Refractive Index of Pure Compounds at 25° C.

Compound	Experimental	Literature (*1*)
Benzene	1.49787	1.49790
n-Hexane	1.37230	1.37226
n-Heptane	1.38525	1.38517
n-Octane	1.39532	1.39505
n-Decane	1.40975	1.40967
Cyclohexane	1.42333	1.42354

Table III. Summary of Differences between the Experimental and Calculated n_D Values

	Maximum Deviation		Average Absolute Deviation	
System	Eq. 2	Eq. 3	Eq. 2	Eq. 3
Benzene–*n*-hexane	0.00008	0.00008	0.00003	0.00003
Benzene–*n*-heptane	0.00005	0.00005	0.00001	0.00001
Benzene–*n*-octane	0.00004	0.00005	0.00002	0.00002
Benzene–*n*-decane	0.00005	0.00006	0.00002	0.00003
Benzene-cyclohexane	0.00008	...	0.00003	...

Table II. Experimental Data at 25° C.

System Benzene (1)–*n*-Hexane (2)		System Benzene (1)–*n*-Octane (2)		System Benzene (1)–Cyclohexane (2)		System Benzene (1)–*n*-Decane (2)		System Benzene (1)–*n*-Heptane (2)	
x_1	n_D	x_1	n_D	x_1	n_D	x_1	n_D	x_1	n_D
0.0245	1.37423	0.2094	1.39676	0.0150	1.42405	0.0384	1.41105	0.0366	1.38750
0.0663	1.37765	0.0531	1.39796	0.0352	1.42503	0.0648	1.41196	0.0632	1.38918
0.1616	1.38581	0.1031	1.40053	0.0479	1.42564	0.1698	1.41591	0.0925	1.39109
0.1943	1.38878	0.1175	1.40132	0.0667	1.42659	0.2426	1.41910	0.1193	1.39288
0.3386	1.40272	0.1296	1.40200	0.0967	1.42814	0.2527	1.41956	0.1920	1.39799
0.4894	1.41935	0.2087	1.40662	0.0974	1.42820	0.3683	1.42545	0.3452	1.41014
0.6482	1.43954	0.3450	1.41565	0.1433	1.43061	0.4232	1.42873	0.4932	1.42400
0.7926	1.46090	0.4990	1.42808	0.1580	1.43144	0.5000	1.43376	0.6420	1.44061
0.9500	1.48821	0.5770	1.43552	0.2098	1.43433	0.6059	1.44198	0.7994	1.46214
$A' = -21.27$		0.6405	1.44223	0.2884	1.43899	0.6461	1.44562	0.9501	1.48789
$B' = 7.922$		0.8004	1.46257	0.3505	1.44287	0.6995	1.45098	$A' = -19.16$	
$A'' = -0.01037$		0.9468	1.48711	0.4295	1.44822	0.8305	1.46703	$B' = 8.714$	
		$A' = 18.28$		0.5586	1.45763	0.9484	1.48684	$A'' = -0.01329$	
		$B' = 9.349$		0.5970	1.46059	$A' = -17.94$			
		$A'' = -0.01479$		0.6081	1.46141	$B' = 10.96$			
				0.7483	1.47328	$A'' = -0.01669$			
				0.7553	1.47388				
				0.8749	1.48504				
				0.9474	1.49233				
				0.9500	1.49258				
				$A' = -37.20$					
				$B' = 6.800$					

where G, G_1, and G_2 are the properties of the mixture and pure components 1 and 2, respectively, x_1 and x_2 are the mole fractions of the components, and A and B are constants. Redlich and Kister (*3*) used Equation 1 with two terms in the denominator for obtaining critical pressure of binary mixtures and evaluated the constants A and B from the limiting slopes of the critical pressure-composition curve. Mrazek and Van Ness (*2*) used Equation 1 empirically for representing excess enthalpy of mixing data for alcohol-aromatic binary systems.

In this investigation, Equation 1 with two constants was rearranged to give

$$\frac{x_1 x_2}{n_D - x_1 n_{D1} - x_2 n_{D2}} = A' + B' x_1 \qquad (2)$$

in which n_D, n_{D1}, and n_{D2} refer to the refractive indices of the mixture and pure components 1 and 2, respectively. Values of the constants A' and B' were determined by the least-squares method using a digital computer and are listed in Table II. In the evaluation, equal weight was given to all n_D values obtained between $x_1 = 0.1$ and $x_1 = 0.9$ and only these values were employed. The good representation of the data by means of Equation 2 is illustrated in Figure 1 for the system benzene–*n*-octane.

An attempt was made to employ the volume fraction, ϕ, instead of the mole fraction, x, in Equation 2. For the four benzene-aliphatic hydrocarbon systems, but not for the system benzene-cyclohexane, the following one-constant equation could also be used for representing the data

$$n_D - \phi_1 n_{D1} - \phi_2 n_{D2} = A'' \phi_1 \phi_2 \qquad (3)$$

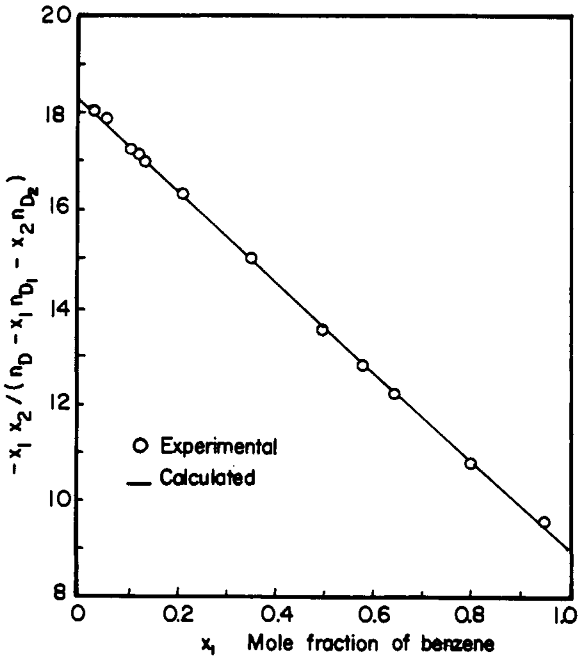

Figure 1. Representation of experimental n_D values for the system benzene–*n*-octane at 25° C. by means of Equation 2

in which $\phi_1 = V_1/(V_1 + V_2)$ and $\phi_2 = V_2/(V_1 + V_2)$, and V_1 and V_2 are the volumes of the pure components. The A'' values were calculated using the n_D values obtained near the $x_1 = 0.5$ region, and are also listed in Table II. They may be represented linearly as a function of the number of C atoms of the aliphatic hydrocarbons. The differences between the experimental and calculated n_D values, using either Equation 2 or Equation 3 are summarized in Table III. The average difference is of the same order of accuracy as the refractometer's readings.

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Interfacial Tensions in Two-Liquid-Phase Ternary Systems

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Interfacial tensions over the concentration range corresponding to two liquid phases have been measured in the following ternary systems: 1,1,2-trichloroethane–water–acetone (25.0° C.), 1,1,2-trichloroethane–water–methyl ethyl ketone (25.0° C.), benzene–water–acetone (30.0° C.), benzene–water–methanol (25.0° C), carbon tetrachloride–water–*n*-propanol (20.0° C), perfluoro-*n*-hexane–benzene–*n*-hexane (30.0° C.), and perfluoro-*n*-hexane–carbon disulfide–*n*-hexane (25.0° C.). In the case of the latter two, the ternary phase diagrams were also determined. Mutual solubilities and interfacial tensions were also measured in the binary systems, perfluoro-*n*-hexane–tetradecane (25.0° C.) and tetradecane–methanol (25.0° C.).

INFORMATION about the interfacial tension of two-liquid-phase ternary systems, as it varies with concentration within the systems, is relatively rare. Perhaps the most extensive study of great importance in liquid-liquid extraction, is that of Murphy, Lastovica, and Fallis (*9*), who confined themselves to aqueous systems. In the present study, which also includes aqueous systems, two nonaqueous systems which are regular in the Hildebrand sense (*8*) are included.

EXPERIMENTAL METHODS

Most of the measurements were made with a Cenco-DuNouy ring tensiometer having a platinum-iridium ring 5.999 cm. in circumference. Samples were kept in a constant-temperature bath until just before measurement. During measurement, the temperature was maintained by placing the sample dishes in a larger container and allowing water, pumped from the bath, to circulate around them. Corrections involving the densities of the two liquids, and the diameters of ring and wire (*15*) were then applied.

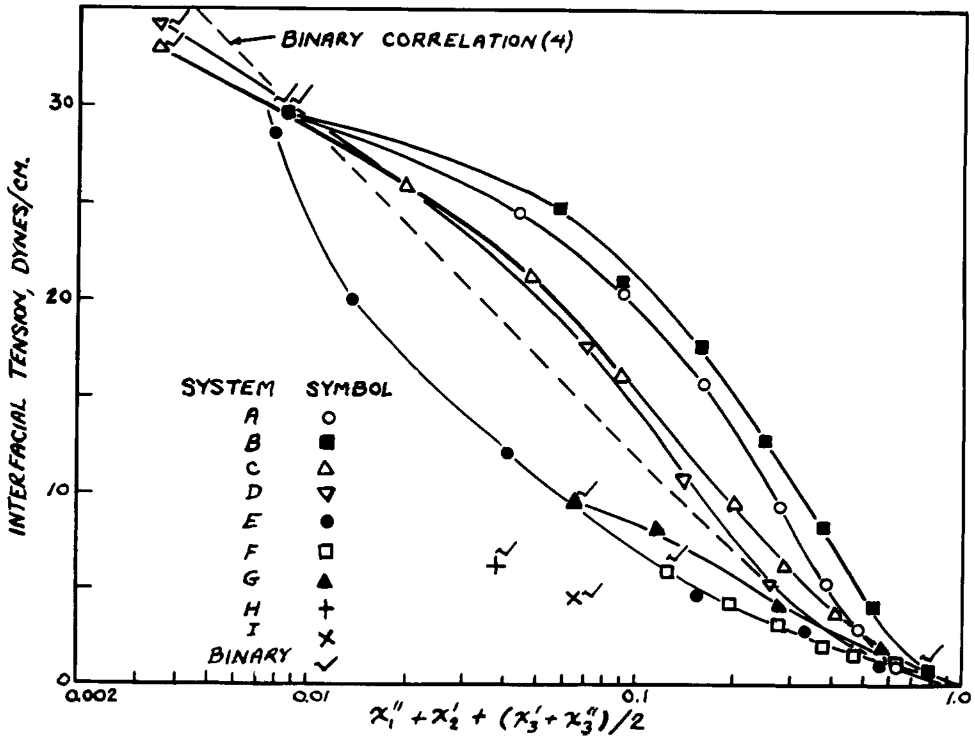

Figure 1. Correlation of interfacial tensions and phase compositions. Binary correlation of Donahue and Bartell (*4*)

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