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Light Scattering in Binary Liquid Mixtures. I. Isotropic Scattering

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The isotropic light scattering in liquid mixtures of small nonelectrolyte molecules was studied from both the theoretical and the experimental point of view. The necessity of the cross-term in the isotropic Rayleigh ratio resulting from the correlation of fluctuations in density and concentration is discussed. A new expression for this term is derived and compared with the previously derived expression. Isotropic scattering of various pure liquids and liquid mixtures is determined at the wavelengths 546 and 436 nm and the reliability of experimental data is discussed in great detail. Mixtures of cyclohexane, *n*-heptane and carbon tetrachloride (component 1) with benzene and carbon disulfide (component 2) were examined. The possibility of the determination of molecular weights from light scattering experiments on such systems is discussed. The reliability of the excess free energy of mixing data obtained by light scattering is carefully considered. It is concluded that light scattering phenomena can be explained by thermodynamics, but the light scattering method is generally inferior to vapour pressure methods both in sensitivity and accuracy, and because of the complexity of the evaluation of data.

INTRODUCTION

In the last decade several papers have appeared dealing with the problems of light scattering in liquid mixtures of small nonelectrolyte molecules. Some of them are theoretical discussions on the various parts of the Rayleigh scattering arising from fluctuations in density, orientation, concentration *etc.*¹⁻³ Others report on the application of the light scattering method in the determination of activity coefficients and the excess free energy of mixing. Most of the results have been obtained with binary mixtures of nonelectrolytes⁴⁻⁸, but the method has been applied also to electrolyte solutions⁹. In general, good agreement has been obtained in comparing experimental data based on the so-called »high« values of the Rayleigh ratios with theoretical results and data obtained with experimental techniques¹⁰. One of the points which have not as yet been elucidated is the necessity to take into account the cross-term in the Rayleigh ratio resulting from the correlation of fluctuations in density and concentration. Bullough¹¹ was the first to call attention to this term, but whereas Sicotte³ advocates the necessity of this term, Pethica and Smart⁹ consider its use incorrect. Coumou and Mackor² are inclined to think that this term has a negligible influence on the other parts of the Rayleigh ratio.

The aim of this paper is to discuss the necessity of the cross-term based on thermodynamic consideration and on comparison with the experimental con-

centration Rayleigh ratio. On the basis of the experimental data collected with several binary liquid mixtures, the applicability of the light scattering method for the determination of thermodynamic excess function of mixing is reviewed. Since the determination of these quantities depends on the reliability and accuracy of the absolute values of the Rayleigh ratios, the methods for the determination of the Rayleigh ratios are compared and discussed.

THEORETICAL PART

In liquids consisting of small molecules light scattering phenomena can be treated as a consequence of the random thermal motion of molecules which causes fluctuation in the dielectric constant. The Smoluchowski-Einsten theory^{12,13} gives the expression:

$$R_u = (\pi^2/2 \lambda_0^4) v \langle (\Delta \epsilon)^2 \rangle, \quad (1)$$

where v is a volume element, small in comparison to the wavelength but large enough to obey the laws of statistical thermodynamics. Here $\langle (\Delta \epsilon)^2 \rangle$ is the mean-square fluctuation of the dielectric constant ϵ (measured at optical frequencies) around its mean value, and R_u is the so-called total Rayleigh ratio¹⁰ determined at the scattering angle 90° with the light of the wavelength in vacuo λ_0 .

The quantity R_u can be separated into two parts: the isotropic Rayleigh ratio R_{is} and the anisotropic Rayleigh ratio R_{anis} , and it holds:

$$R_u = R_{is} + R_{anis} \quad (2)$$

with R_{is} and R_{anis} defined as

$$R_{is} = (\pi^2/2 \lambda_0^4) \cdot F_{is} \quad (3)$$

and

$$R_{anis} = (13 \pi^2/10 \lambda_0^4) \cdot F_{anis}, \quad (4)$$

where F_{is} and F_{anis} are the isotropic and anisotropic molecular scattering factors respectively¹⁰.

R_{anis} can be determined directly by measuring the partial Rayleigh ratios V_h or H_v . From the expression

$$V_h = H_v = (\pi^2/5 \lambda_0^4) \cdot 3 F_{anis} \quad (5)$$

it follows that

$$R_{anis} = (13/6) V_h. \quad (6)$$

On the other hand, R_{is} is not directly experimentally accessible, and has to be determined as the difference

$$R_{is} = R_u - R_{anis}. \quad (7)$$

A method to eliminate F_{anis} which is more often used consists in measuring at 90° the polarization ratio $D_u = H_u/V_u$ and dividing R_u by C , the well known Cabannes factor:

$$R_{is} = R_u/C \quad (8)$$

with

$$C = (6 + 6 D_u) / (6 - 7 D_u). \quad (9)$$

Consequently, the mean-square fluctuation $\langle (\Delta \varepsilon)^2 \rangle$ can also be separated into the isotropic and the anisotropic part.

$$\langle (\Delta \varepsilon)^2 \rangle = \langle (\Delta \varepsilon^{is})^2 \rangle + \langle (\Delta \varepsilon^{anis})^2 \rangle, \quad (10)$$

where both fluctuations are supposed to be statistically independent.

In the following we shall concentrate on the isotropic fluctuations only. As shown elsewhere¹⁰

$$F_{is} = v \langle (\Delta \varepsilon^{is})^2 \rangle. \quad (11)$$

If a liquid contains only one component, only density fluctuations are of importance¹⁴, and R_{is} can be determined from physical constants only:

$$R_{is} = (\pi^2/2 \lambda_0^4) kT \kappa_T (N \partial \varepsilon / \partial N)^2 \quad (12)$$

Here k is the Boltzmann constant, T the absolute temperature, κ_T the isothermal compressibility, and $\varepsilon = n^2$, n being the refractive index of the dense medium.

If a liquid is a binary mixture of molecules exhibiting different polarizabilities, additional fluctuations in ε have to be taken into account.

By following the treatment of Einstein¹³ and of Kirkwood and Goldberg¹⁵ the isotropic mean-square fluctuations can be expressed as a sum of the terms containing both the fluctuations in density and the fluctuations in concentration. Since the variables density and concentration are statistically correlated, one has

$$\langle (\Delta \varepsilon^{is})^2 \rangle = \langle (\Delta \varepsilon^d)^2 \rangle + \langle (\Delta \varepsilon^c)^2 \rangle + 2 \langle (\Delta \varepsilon^d) (\Delta \varepsilon^c) \rangle, \quad (13)$$

where indices d and c stand for density and concentration, respectively. Expressing $\langle (\Delta \varepsilon^{is})^2 \rangle$ in terms of number density N and of the mole fraction of one of the components x_2 ($= 1 - x_1$) one obtains

$$\begin{aligned} \langle (\Delta \varepsilon^{is})^2 \rangle = & (\partial \varepsilon / \partial N)^2 \langle (\Delta N)^2 \rangle + (\partial \varepsilon / \partial x_2)^2 \langle (\Delta x_2)^2 \rangle + \\ & + 2 (\partial \varepsilon / \partial N) (\partial \varepsilon / \partial x_2) \langle (\Delta N \cdot \Delta x_2) \rangle. \end{aligned} \quad (14)$$

Written in the form of the Rayleigh ratios

$$R_{is} = R_d + R_c + R\#, \quad (15)$$

with

$$R_d = (\pi^2/2 \lambda_0^4) v (\partial \varepsilon / \partial N)^2 \langle (\Delta N)^2 \rangle. \quad (16)$$

$$R_c = (\pi^2/2 \lambda_0^4) v (\partial \varepsilon / \partial x_2)^2 \langle (\Delta x_2)^2 \rangle, \quad (17)$$

$$R\# = (\pi^2/\lambda_0^4) v (\partial \varepsilon / \partial N) (\partial \varepsilon / \partial x_2) \langle (\Delta N \cdot \Delta x_2) \rangle \quad (18)$$

In order to obtain all three mean-square fluctuation terms, the minimum energy change in mixing two components should be calculated. According to the laws of statistical mechanics¹⁶, the minimal work E_{\min} arising from fluctuations in the free energy F of the mixture is given as

$$\begin{aligned} E_{\min} = & \frac{1}{2} \{ (\partial^2 F / \partial N^2) (\Delta N)^2 + (\partial^2 F / \partial x_2^2) (\Delta x_2)^2 + \\ & + 2 (\partial^2 F / \partial N \partial x_2) (\Delta N \cdot \Delta x_2) \}. \end{aligned} \quad (19)$$

Both the squares of fluctuations $(\Delta N)^2$ and $(\Delta x_2)^2$ and the correlated fluctuation $(\Delta N \Delta x_2)$ have a Gaussian distribution¹⁶ with a distribution function W proportional to

$$W \sim e^{-(\beta/2) (\Delta X)^2} \quad (20)$$

with $(\Delta X)^2$ standing for $(\Delta N)^2$, $(\Delta x_2)^2$ or $(\Delta N \Delta x_2)$. Here

$$\beta = (\partial^2 F / \partial X^2) / kT = 1 / \langle (\Delta X)^2 \rangle \quad (21)$$

By calculating partial derivatives in (21), all three mean-square fluctuation terms in (14) are obtained (see Appendix):

$$\langle (\Delta N)^2 \rangle = kT \kappa_T N^2 / v \quad (22)$$

$$\langle (\Delta x_2)^2 \rangle = kT x_1 V / (\partial \mu_2 / \partial x_2) v \quad (23)$$

$$\langle (\Delta N \Delta x_2) \rangle = kT \kappa_T N x_1 x_2 / 2 v \quad (24)$$

Here indices 1 and 2 denote component 1 and component 2, respectively. The symbol μ_2 is the chemical potential of component 2 in the mixtures.

By inserting (22), (23) and (24) into (16), (17) and (18), respectively, the density, concentration, and cross-term Rayleigh ratios are obtained:

$$R_d = (\pi^2 / 2 \lambda_0^4) kT \kappa_T (N \partial \varepsilon / \partial N)^2 \quad (25)$$

$$R_c = (\pi^2 / 2 \lambda_0^4) kT V x_1 (\partial \varepsilon / \partial x_2)^2 / \partial \mu_2 / \partial x_2 \quad (26)$$

$$R\# = (\pi^2 / 2 \lambda_0^4) kT \kappa_T x_1 x_2 (N \partial \varepsilon / \partial N) (\partial \varepsilon / \partial x_2) \quad (27)$$

Here $V = N_A / N$ is the molar volume of the mixture, and N_A is the Avogadro number. The density ratio R_d appears to be identical to R_{is} for the pure liquid (12). The concentration ratio R_c can be used for the determination of the excess free energy of mixing². For an ideal mixture $\partial \mu_2 / \partial x_2 = RT / x_2$, thus

$$R_{c, id} = (\pi^2 / \lambda_0^4 N_A) V x_1 x_2 (\partial \varepsilon / \partial x_2) \quad (28)$$

By comparing $R_{c, id}$ calculated from physical constants with R_c obtained from

$$R_c = R_{is} - R_d - R\#, \quad (29)$$

where R_{is} is determined experimentally and R_d and $R\#$ are calculated from (25) and (27), the sign of the excess free energy of mixing as well as the values of the activity coefficients and of the excess free energy can be obtained.

EXPERIMENTAL

Light scattering measurements were carried out by using a Brice-Phoenix Model 2000-DMS Light Scattering Photometer, manufactured by Phoenix Precision Instrument Co., Philadelphia, Pa., U.S.A. The measuring instrument was the Skalengalvanometer manufactured by Zeiss, Jena, Germany. Instead of the original AH-3 high pressure mercury lamp a Philips SP 500 W water-cooled super-pressure mercury lamp was used. This lamp was installed in vertical position. Measurements were made at room temperature (23–26 °C) except for the system cyclohexane-benzene where the temperature was regulated to (20.0 ± 0.5) °C *via* a thermostated jacket. The incident light wavelengths were 546 and 436 nm. The Rayleigh ratios were determined, unless otherwise noted, by applying the Brice formula¹⁷. In order to check the results obtained by Brice's formula, data on pure carbon disulfide were determined by using the standard scatterer method¹⁰. Since the original lamp was replaced by the Philips SP 500 W lamp, it was found necessary to redetermine the constants TD in Brice's formula. In experiments with pure liquids this was done by using benzene as the standard substance. The mean values of three determinations of galvanometer readings as well as the R_u values $16.1 \times 10^{-6} \text{ cm}^{-1}$ and $46.5 \times 10^{-6} \text{ cm}^{-1}$ for wavelengths 546 and 436 nm, respectively, were used¹⁸. In experiments with binary liquid mixtures

it was found necessary to adjust the TD constants separately for benzene and separately for carbon disulfide systems. This was done for each system by using the above R_u values for benzene, and $85 \times 10^{-6} \text{ cm}^{-1}$ and $270 \times 10^{-6} \text{ cm}^{-1}$ for wavelengths 546 and 436 nm, respectively, for carbon disulfide¹⁸. All measurements were made in square cells $30 \times 30 \text{ mm}$ (Phoenix Catalog No. T-101) with the outer back surface painted black.

All liquids were reagent grade chemicals. Except for carbon tetrachloride and carbon disulfide, all liquids were distilled several times over sodium and collected in dust-free bottles for the preparation of mixtures, or collected directly into the cell when pure liquids were measured. Carbon disulfide was shaken for some time with mercury and mercurous chloride. After shaking with distilled water the material was dried and distilled several times over the drying agent. The distilled liquid was kept in dark. Phosphorus pentoxide was used as the drying agent. Carbon tetrachloride was distilled several times over phosphorus pentoxide. The mixtures were prepared by weighing.

The densities of all liquids and liquid mixtures were determined by pycnometers having the shape of a volumetric flask (about 25 cm^3 in volume) with a capillary neck¹⁹. The pycnometers were calibrated with pure benzene.

The refractive indices n were determined by an Abbe type refractometer permitting precision of $\pm (1-2) \times 10^{-4}$ in n to be achieved. A high-pressure mercury lamp was used as the light source, and the refractometer was calibrated with pure cyclohexane, carbon tetrachloride, benzene, and carbon disulfide. Reported n values²⁰ for different wavelengths were plotted as a function of $(1/\lambda_0^2)$ in order to determine values at the wavelengths 546 and 436 nm. The readings on the refractometer scale were plotted versus standard values, and least-square equations of the first order for 546 nm and of the second order for 436 nm were used to determine experimental n values.

The values of excess molar free energies of mixing are expressed in cal/mol. Here 1 cal is the thermochemical unit and equals to 4.184 J.

RESULTS

Rayleigh Ratios of Pure Components

Two methods have mostly been used for the determination of the Rayleigh ratios: (a) the Brice working standard method and (b) the standard scatterer method. It has been pointed out¹⁰ that although it is frequently recognized that Brice's method leads to reliable absolute intensities, some care has to be taken to avoid systematic errors if the geometry of the apparatus has been changed. Schmidt⁴ has recently reported on Rayleigh ratios determined by a modified standard scatterer method. Table I summarizes data obtained with carbon disulfide for the wavelengths 546 and 436 nm by using the expressions written here for the case when $\vartheta = 90^\circ$:

standard scatterer method (columns 2 and 3):

$$R_i = (n/n_s)^2 [R_{i,s}/F_s G_{i,s}(90)] FG_i(90) \quad (30)$$

Schmidt's method⁴ (columns 4 and 5):

$$R_i = \frac{n^2 a (R_w/R_c) (r/r') R_{i,s}}{n_s^2 a_s (R_w/R_c)_s (r/r')_s F \{G(90)/G(0)\}_{i,s}} \times F \{G(90)/G(0)\}_i \quad (31)$$

Brice's method¹⁷ (column 6):

$$R_i = \frac{TD a n^2 (R_w/R_c) (r/r')}{1.049 h \pi} F \{G(90)/G(0)\}_i \quad (32)$$

Here subscript i stands for a particular Rayleigh ratio (thus R_i replaces R_u , V_u ,

TABLE I

Rayleigh Ratios* and Polarization Ratios of Carbon Disulfide at $\vartheta = 90^\circ$ and Room Temperature Determined by Different Methods

	$\lambda_0 = 546 \text{ nm}$					
	(1)	(2)	(3)	(4)	(5)	(6)
$R_u \times 10^6$	86	86	86	84	83	89
$V_u \times 10^6$	105	101	102	101	100	106
$H_u \times 10^6$	67	66	66	65	66	72
$V_v \times 10^6$	71	69	68	70	69	72
$V_h \times 10^6$	34	33	34	33	34	35
$H_v \times 10^6$	34	33	33	33	33	37
$H_h \times 10^6$	34	33	34	34	34	35
D_u	0.64	0.65	0.65	0.64	0.66	0.68
D_v	0.48	0.48	0.50	0.47	0.49	0.49
D_h	1.00	1.00	7.03	1.03	1.03	1.06
$\sqrt{\langle d^2 \rangle}$	—	2.7	2.3	2.6	2.8	4.9

	$\lambda_0 = 436 \text{ nm}$					
	(1)	(2)	(3)	(4)	(5)	(6)
$R_u \times 10^6$	265	285	274	287	269	290
$V_u \times 10^6$	320	324	322	324	350	332
$H_u \times 10^6$	211	218	220	221	239	227
$V_v \times 10^6$	214	215	212	225	229	216
$V_h \times 10^6$	105	106	108	106	106	110
$H_v \times 10^6$	105	108	108	113	118	112
$H_h \times 10^6$	105	107	109	106	107	111
D_u	0.66	0.67	0.68	0.68	0.68	0.68
D_v	0.49	0.49	0.51	0.47	0.46	0.51
D_h	1.00	1.01	0.99	1.07	1.10	1.01
$\sqrt{\langle d^2 \rangle}$	—	3.4	3.0	5.0	8.2	6.1

* All Rayleigh ratios in cm^{-1}

- (1) — Deželić and Vavra, Ref. 18, Table III, column (3);
 - (2) — Standard scatterer method, standard Brice-Phoenix photometer stops;
 - (3) — Standard scatterer method, circular stops 4 mm in diameter;
 - (4) — Schmidt's method, Eq. (31), standard stops;
 - (5) — Schmidt's method, Eq. (31), circular 4 mm stops;
 - (6) — Brice's method, Eq. (32).
- $\langle d^2 \rangle$ — mean-square percent deviation from data in column (1)

H_u , V_v , etc.), and subscript s stands for the standard (in the particular case it was benzene). Quantities $G(90)$ and $G(0)$ denote galvanometer deflections at scattering angles 90° and 0° , respectively, and F is the attenuation factor of the combination of neutral filters. The quantities a , (R_v/R_c) , (r/r') , TD and h are as defined in the Brice-Phoenix Photometer manual²¹. The quantity $\langle d^2 \rangle$ is the mean square percentage deviation from the values in column (1).

In Table II data on several pure liquids measured at 546 and 436 nm are collected. The Rayleigh ratios in this Table were determined by the Brice equation.

TABLE II

Rayleigh Ratios* and Polarization Ratios of Several Pure Liquids at $\theta = 90^\circ$ and Room Temperature Determined by Brice's Equation (32)

	$\lambda_0 = 546 \text{ nm}$				
	Benzene	Cyclohexane	n-Hep-tane	Carbon tetra-chloride	Carbon di-sulfide
$R_u \times 10^6$	17.0	4.9	4.8	5.8	89
$V_u \times 10^6$	23.6	9.6	9.2	11.3	106
$H_u \times 10^6$	10.3	0.54	0.89	0.55	72
$V_v \times 10^6$	18.3	9.2	8.5	10.9	72
$V_h \times 10^6$	5.0	0.31	0.47	0.31	35
$H_v \times 10^6$	5.3	0.27	0.44	0.29	37
$H_h \times 10^6$	5.0	0.32	0.46	0.29	35
D_u	0.44	0.056	0.096	0.049	0.68
D_v	0.27	0.029	0.052	0.026	0.49
D_h	1.06	1.12	1.02	1.05	1.06

$\lambda_0 = 436 \text{ nm}$					
$R_u \times 10^6$	47.0	12.9	13.0	14.9	290
$V_u \times 10^6$	65.5	24.6	24.4	28.0	332
$H_u \times 10^6$	29.2	1.85	2.60	1.43	227
$V_v \times 10^6$	48.2	23.6	22.0	26.6	216
$V_h \times 10^6$	14.7	0.94	1.29	0.72	110
$H_v \times 10^6$	14.0	0.90	1.28	0.70	112
$H_h \times 10^6$	14.8	1.00	1.27	0.72	111
D_u	0.45	0.074	0.107	0.051	0.68
D_v	0.30	0.038	0.058	0.027	0.51
D_h	0.95	0.90	1.01	0.97	1.01

* All Rayleigh ratios in cm^{-1}

Table III gives isotropic ratios R_{is} calculated from Eqs. (7) and (8) as well as the relative errors (coefficients of variation) s_r . The error of R_{is} , $s_r(R_{is})$, was estimated by

$$s_r(R_{is}) = \sqrt{s_r^2(R_u) + \{13 s_r(V_h)/6\}^2} \quad (33)$$

whereas that determined by Eq. (8) follows from

$$s_r(R_{is}) = \sqrt{s_r^2(R_u) + s_r^2(C)}. \quad (34)$$

Here C' is the reciprocal of the Cabannes factor, $C' = (6 - 7D_u)/(6 + 6D_u)$, and

$$s_r(C') = \{13 D_u / [(1 + D_u)(6 - 7 D_u)]\} s_r(D_u). \quad (35)$$

The error $s_r(D_u)$ was taken in all cases to be equal to 2%, *i. e.* as the average error of four galvanometer readings needed for the Brice equation (32).

TABLE III

Isotropic Rayleigh Ratios, R_{is} , and Percentage Errors, $s_r(R_{is})$ for Several Pure Liquids Determined from Experimental Data (TABLE II) by Eqs. (7) and (8), and from Physical Constants by Eq. (12)

Liquid	$\lambda_0 = 546 \text{ nm}$						$\lambda_0 = 436 \text{ nm}$					
	Eq. (8)		Eq. (7)		Eq. (12)		Eq. (8)		Eq. (7)		Eq. (12)	
	$R_{is} \times 10^6$ (cm^{-1})	$s_r(R_{is})$ (%)	$R_{is} \times 10^6$ (cm^{-1})	$s_r(R_{is})$ (%)	$R_{is} \times 10^6$ (cm^{-1})	$s_r(R_{is})$ (%)	$R_{is} \times 10^6$ (cm^{-1})	$s_r(R_{is})$ (%)	$R_{is} \times 10^6$ (cm^{-1})	$s_r(R_{is})$ (%)	$R_{is} \times 10^6$ (cm^{-1})	$s_r(R_{is})$ (%)
Benzene	5.7	3.6	6.2	3.0	5.9	3.4	15.4	3.4	15.2	3.1	16.1	3.1
Cyclohexane	4.3	2.0	4.2	7.8	4.2	2.0	11.0	2.0	10.9	5.4	10.9	5.4
<i>n</i> -Heptane	3.9	2.1	3.8	4.6	4.1	2.1	10.3	2.1	10.2	3.7	10.6	3.7
Carbon Tetrachloride	5.2	2.2	5.1	9.9	5.0	2.1	13.3	2.1	13.3	7.8	13.0	7.8
Carbon disulfide	10.9	8.5	13.0	3.0	12.2	8.5	35.7	8.5	52.0	3.5	36.3	3.5

each having an error of 1%. The error of V_h was greater since the values of one of the four galvanometer readings, $G(90)$, for liquids having low optical anisotropy, were low and allowed errors exceeding 1% (from 2 to 4%).

Binary Liquid Mixtures

Physical constants. — Experimental data on the density ρ and refractive index were fitted to the second order least-square equations by computer processing. The data are collected in Tables IV and V.

TABLE IV

Coefficients for the Second-order Equations Correlating the Density of Mixtures, ρ with the Mole Fraction of the Second Component x_2 ; $\rho = a_0 + a_1x_2 + a_2x_2^2$, ρ_1 and ρ_2 . Densities of Pure Components 1 and 2, Respectively. All Densities and Coefficients in g/cm^3

Component (1)	t ($^{\circ}C$)	a_0	a_1	a_2	ρ_1	
					exptl.	literature*
Component (2): Benzene**						
Cyclohexane	20	0.7788	0.0585	0.0412	0.7786	0.7783—0.7785
<i>n</i> -Heptane	25	0.6810	0.0794	0.0398	0.6796	0.6794—0.6796
Carbon Tetrachloride	25	1.5867	—0.6514	—0.0609	1.5853	1.5843—1.5846
Component (2): Carbon Disulfide, $\rho_2 = 1.2564$ (lit.* 1.2559)						
Cyclohexane	25	0.7779	0.1689	0.3043	0.7738	0.7738—0.7739
<i>n</i> -Heptane	25	0.6904	0.0643	0.4874	same as above	
Carbon Tetrachloride	25	1.5815	—0.1873	—0.1364	same as above	

* Ref. (20); ** densities of benzene taken as standard values in pycnometer calibration.

The molar volume of mixture V was determined from

$$V = M/\rho \quad (36)$$

with $M = M_1 + (M_2 - M_1)x_2$ being the average molecular weight of the mixture.

The isothermal compressibilities, κ_T , were determined from the values for the pure components, $\kappa_{T,1}$ and $\kappa_{T,2}$, by including the volume change upon mixing⁴ from the expression

$$\kappa_T = \rho (x_1\kappa_{T,1}/\rho_1 + x_2\kappa_{T,2}/\rho_2). \quad (37)$$

The dielectric constant increment ($N\partial\epsilon/\partial N$) was determined from the equation

$$(N\partial\epsilon/\partial N) = f(n^2 - 1)(n^2 + 2)/3, \quad (38)$$

where f is the factor arising from the density dependence of polarizability^{4,22}. An empirical value $f = 0.912$, corresponding to the corrections for benzene and carbon disulfide²², was used.

TABLE V

Coefficients of the Second Order Equations Correlating the Refractive Index of Mixtures, n , with the mole Fraction of the Second Component x_2 :

$$n = a_0 + a_1x_2 + a_2x_2^2$$

Component (1)	t (°C)	λ_0 (nm)	a_0	a_1	a_2
Component (2): Benzene					
Cyclohexane	20	546	1.4300	0.0314	0.0391
		436	1.4385	0.0363	0.0427
<i>n</i> -Heptane	25	546	1.3917	0.0323	0.0789
		436	1.3988	0.0367	0.0849
Carbon Tetrachloride	25	546	1.4596	0.0421	0.0002
		436	1.4693	0.0502	-0.0001
Component (2): Carbon Disulfide					
Cyclohexane	25	546	1.4276	0.0597	0.1419
		436	1.4354	0.0693	0.1597
<i>n</i> -Heptane	25	546	1.3919	-0.0085	0.2298
		436	1.4014	-0.0002	0.2639
Carbon Tetrachloride	25	546	1.4610	0.0675	0.1023
		436	1.4711	0.0774	0.1180

TABLE VI

Coefficients of the Fourth Order Equations Correlating the Refractive Index Increment of Mixtures, $\partial n/\partial x_2$, with the Mole Fraction of the Second Component, x_2 :

$$\frac{\partial n}{\partial x_2} = \sum_{j=0}^4 b_j x_2^j$$

Component (1)	t (°C)	λ_0 (nm)	b_0	b_1	b_2	b_3	b_4
Component (2): Benzene							
Cyclohexane	20	546	0.06399	-0.17066	0.69930	-1.03188	0.60200
		436	0.08337	-0.30224	1.09920	-1.50752	0.80880
<i>n</i> -Heptane	25	546	0.04825	0.15290	-0.31344	0.55200	0.21990
		436	0.06362	0.05838	-0.03774	0.29676	-0.14730
Carbon Tetrachloride	25	546	0.03832	0.05266	-0.16809	0.17920	-0.05525
		436	0.05040	-0.01080	0.08640	-0.19444	0.12540
Component (2) Carbon Disulfide							
Cyclohexane	25	546	0.10188	-0.01288	0.80253	-1.27960	0.82300
		436	0.11912	-0.07346	1.21200	-1.97748	1.21975
<i>n</i> -Heptane	25	546	0.09574	-0.01432	0.93600	-1.79240	1.47315
		436	0.06061	0.39046	-0.14916	-0.53472	1.00250
Carbon Tetrachloride	25	546	0.09999	0.00754	0.30306	-0.22568	0.12530
		436	0.11161	0.00772	0.48270	-0.58504	0.34610

Instead of the dielectric constant increment ($\partial\epsilon/\partial x_2$), the refractive index increment ($\partial n/\partial x_2$) was determined from the measured n vs. x_2 values. The p -th order least-squares polynomials

$$n = \sum_{i=0}^p a_i x_2^i$$

were computed, and the increments

$$(\partial n/\partial x_2) = \sum_{i=1}^p i a_i x_2^{i-1} = \sum_{j=0}^q b_j x_2^j$$

(with $q = p - 1$) were derived from the polynomials showing the best fit to experimental values. Polynomials up to $p = 7$ were computed and by determining the mean-square deviations of the experimental values from the fitted ones. The polynomials with the minimum deviation were taken for determining $\partial n/\partial x_2$. In all systems the fifth order polynomials (fourth order for the refractive index increment) were found to give the best fit to experimental data. Table VI gives a summary of the 4-th order coefficients used for the determination of $(\partial n/\partial x_2)$.

Concentration Rayleigh ratios. — The summary of experimental data on the total Rayleigh ratios R_u and polarization ratios D_u for the six binary mixtures is given in Tables VII (mixtures with benzene) and VIII (mixtures with carbon disulfide).

TABLE VII

Total Rayleigh Ratios R_u and Polarization Ratios D_u for Binary Liquid Mixtures of Benzene with Cyclohexane, *n*-Heptane, and Carbon Tetrachloride

x_2	$\lambda_0 = 546 \text{ nm}$		$\lambda_0 = 436 \text{ nm}$	
	$R_u \times 10^6$ (cm^{-1})	D_u	$R_u \times 10^6$ (cm^{-1})	D_u
Cyclohexane (1) — Benzene (2)				
0.000	4.67	0.054	12.7	0.070
0.083	6.02	0.113	16.0	0.133
0.230	8.10	0.199	21.3	0.232
0.368	9.32	0.228	25.8	0.206
0.521	11.1	0.258	32.3	0.265
0.650	12.5	0.306	35.9	0.292
0.777	13.5	0.327	39.7	0.334
0.912	15.4	0.372	44.7	0.373
1.000	16.1	0.418	46.5	0.425
<i>n</i> -Heptane (1) — Benzene (2)				
0.000	4.91	0.094	13.0	0.103
0.137	7.03	0.154	18.7	0.159
0.295	9.36	0.192	26.0	0.200
0.388	11.0	0.206	31.4	0.209
0.518	13.1	0.222	37.6	0.222
0.637	15.4	0.237	46.0	0.237
0.751	17.2	0.260	51.0	0.256
0.869	17.6	0.310	52.1	0.310
1.000	16.1	0.422	46.5	0.428

TABLE VII (Continued)

Carbon Tetrachloride (1) — Benzene (2)				
0.000	5.67	0.047	14.8	0.050
0.177	8.31	0.155	22.9	0.164
0.307	9.78	0.216	27.3	0.225
0.437	11.5	0.248	32.2	0.274
0.556	12.5	0.308	35.4	0.315
0.719	14.4	0.352	41.8	0.358
0.865	15.7	0.391	45.6	0.404
1.000	16.1	0.423	46.5	0.428

TABLE VIII

Total Rayleigh Ratios R_u and Polarization Ratios D_u for Binary Liquid Mixtures of Carbon Disulfide with Cyclohexane, *n*-Heptane, and Carbon Tetrachloride

x_2	$\lambda_0 = 546 \text{ nm}$		$\lambda_0 = 436 \text{ nm}$	
	$R_u \times 10^6$ (cm^{-1})	D_u	$R_u \times 10^6$ (cm^{-1})	D_u
Cyclohexane (1) — Carbon Disulfide (2)				
0.000	4.84	0.056	11.9	0.074
0.157	11.6	0.277	33.1	0.294
0.272	17.8	0.342	51.5	0.354
0.394	25.8	0.389	76.4	0.392
0.530	38.0	0.410	116.9	0.416
0.769	60.0	0.480	189.0	0.480
0.889	72.9	0.548	231.0	0.548
1.000	85.0	0.657	270.0	0.669
<i>n</i> -Heptane (1) — Carbon Disulfide (2)				
0.000	4.97	0.097	12.2	0.105
0.139	9.81	0.235	25.7	0.243
0.259	14.6	0.294	39.7	0.300
0.371	21.1	0.313	57.9	0.330
0.482	28.4	0.333	79.3	0.340
0.600	38.6	0.348	113.0	0.334
0.753	60.0	0.352	181.2	0.360
0.834	67.2	0.390	208.6	0.375
0.938	82.6	0.500	252.4	0.505
1.000	85.0	0.646	270.0	0.661
Carbon Tetrachloride (1) — Carbon Disulfide (2)				
0.000	5.64	0.048	13.9	0.050
0.196	14.5	0.304	41.0	0.324
0.312	20.9	0.372	60.2	0.381
0.433	28.8	0.422	83.5	0.429
0.583	40.3	0.464	122.0	0.465
0.757	56.8	0.518	172.9	0.519
0.888	69.9	0.585	217.5	0.589
1.000	85.0	0.660	270.0	0.660

Isotropic Rayleigh ratios R_{is} derived from data in Tables VII and VIII by using Eq. (8) and Rayleigh ratios R_d and $R^\#$ derived from physical constants and Eqs. (25) and (27), were used for the evaluation of the concentration Rayleigh ratios R_c .

These data, together with the concentration ratios valid for ideal mixtures, $R_{c, id}$, derived from Eq. (28), are given in Tables IX and X.

TABLE IX

Concentration Rayleigh Ratios R_c and $R_{c, id}$ for Binary Liquid Mixtures of Benzene with Cyclohexane, *n*-Heptane and Carbon Tetrachloride

x_2	$\lambda_0 = 546 \text{ nm}$		$\lambda_0 = 436 \text{ nm}$	
	$R_c \times 10^6$ (cm^{-1})	$R_{c, id} \times 10^6$ (cm^{-1})	$R_c \times 10^6$ (cm^{-1})	$R_{c, id} \times 10^6$ (cm^{-1})
Cyclohexane (1) — Benzene (2)				
0.000	— 0.10	0	— 0.15	0
0.083	0.49	0.18	0.55	0.65
0.230	0.77	0.37	1.52	1.10
0.368	1.03	0.56	2.92	1.66
0.521	1.41	0.77	4.68	2.42
0.650	1.22	0.92	4.77	2.91
0.777	1.15	1.02	4.00	3.22
0.912	0.88	0.94	3.19	2.81
1.00	— 0.05	0	0.41	0
<i>n</i> -Heptane (1) — Benzene (2)				
0.000	— 0.15	0	— 0.39	0
0.137	0.60	0.50	2.06	1.52
0.295	1.46	1.24	4.87	3.34
0.388	2.16	1.69	7.55	4.92
0.518	2.97	2.40	10.1	7.25
0.637	3.68	3.06	13.1	9.35
0.751	3.86	3.44	14.0	10.4
0.869	2.64	2.93	10.1	8.60
1.000	— 0.19	0	0.04	0
Carbon Tetrachloride (1) — Benzene (2)				
0.000	0.17	0	0.35	0
0.177	0.47	0.21	1.66	0.70
0.307	0.31	0.30	1.33	1.04
0.437	0.60	0.33	1.44	1.19
0.556	0.07	0.31	0.76	1.15
0.719	0.19	0.26	1.54	0.90
0.865	0.09	0.17	0.83	0.55
1.000	— 0.12	0	0.29	0

TABLE X

Concentration Rayleigh Ratios R_c and $R_{c,id}$ for Binary Liquid Mixtures of Carbon Disulfide with Cyclohexane, *n*-Heptane and Carbon Tetrachloride

x_2	$\lambda_0 = 546 \text{ nm}$		$\lambda_0 = 436 \text{ nm}$	
	$R_c \times 10^6$ (cm^{-1})	$R_{c,id} \times 10^6$ (cm^{-1})	$R_c \times 10^6$ (cm^{-1})	$R_{c,id} \times 10^6$ (cm^{-1})
Cyclohexane (1) — Carbon Disulfide (2)				
0.000	0.14	0	—0.64	0
0.157	1.50	1.37	4.57	4.38
0.272	2.86	2.79	8.73	9.05
0.394	4.30	4.45	14.0	15.9
0.530	7.34	6.27	23.9	21.4
0.769	8.92	8.45	30.5	27.2
0.889	6.50	7.05	23.8	22.8
1.000	—0.27	0	—0.82	0
<i>n</i> -Heptane (1) — Carbon Disulfide (2)				
0.000	0.04	0	—0.90	0
0.139	1.50	1.35	3.71	3.62
0.259	2.75	3.04	7.60	9.40
0.371	5.10	4.94	13.0	16.0
0.482	7.31	7.00	20.0	22.1
0.600	10.4	9.80	33.8	28.7
0.753	17.9	13.3	54.1	40.3
0.834	17.3	14.8	59.7	47.6
0.938	12.0	11.5	36.9	36.2
1.000	0.54	0	1.00	0
Carbon Tetrachloride (1) — Carbon Disulfide (2)				
0.000	0.14	0	—0.50	0
0.196	1.37	1.42	3.72	4.69
0.312	2.43	2.42	6.84	8.18
0.433	3.18	3.58	9.52	12.2
0.583	4.43	5.03	15.1	16.9
0.757	5.17	5.77	17.2	19.1
0.888	3.05	4.13	10.9	13.8
1.000	—0.47	0	1.10	0

DISCUSSION

In the critical survey by Kratochvil *et al.*²³ various calibration procedures concerning the accuracy of the absolute R_{ii} values were carefully examined. However, the precision of various methods has not been compared either in the work quoted or in other reports. During our present experimental work in which we determined absolute Rayleigh ratios by the Brice method, Eq. (32), systematic errors in some values for several liquids were noted. Especially high deviations were found for carbon disulfide. For this reason a comparison between the methods mentioned in the section Results appeared desirable. In Table I the results obtained with the standard scatterer method, the Schmidt method (a modified standard scatterer method), and the Brice method are compared. As seen from the mean-square percent deviations $\langle d^2 \rangle$ calculated

by taking values in column (1) as standards (these values were determined from R_u and D_u data only), the standard scatterer method with narrower stops (circular 4 mm stops, smaller solid angle) appears to give the best results. The results obtained with the Brice method show a high scatter in absolute values, rendering results in R_u and polarization ratio values unreliable. The precision of the Schmidt method is nearer to that of the Brice method than to that of the standard scatterer method. This is due to the fact that both Brice's and Schmidt's method are based on the determination of at least four galvanometer deflections (the ratios $G(90)/G(0)$, the constants a , and in some cases the r/r' ratios). It can therefore be concluded that in precise measurements the standard scatterer method has the advantage over other methods. In routine work, however, the Brice method demanding no preparation of standard liquid samples can be regarded as satisfactory. The Schmidt method does not offer any particular advantage over the Brice method and is inferior to the standard scatterer method. Data in Table II obtained by Brice's method confirm the above statements. The R_u values, although slightly higher, do not differ significantly from the literature values.

Since there is no method for a direct determination of isotropic scattering and R_{is} has to be determined either *via* the Cabannes factor or *via* the V_h ratio, it was of interest to compare the experimental errors of the values determined by these two methods. The $s_r(R_{is})$ values in Table III show that in the determination of R_{is} for liquids of low optical anisotropy more precise results are obtained with Eq. (8), whereas Eq. (7) is superior in the case of strongly optically anisotropic liquids. Good agreement was achieved with theoretical values determined from physical constants by Eq. (12). The only exception with carbon disulfide at $\lambda_0 = 436$ nm could be ascribed to a value of R_u not followed by a systematic increase in V_h . Here the $s_r(R_{is})$ value is certainly underestimated.

It was stated earlier^{18,22} that the error of both the measured and calculated Rayleigh ratios was of the order of 5 to 10%. The present data confirm this statement. The maximal error of concentration Rayleigh ratios can therefore be estimated at 10 to 20%. These estimations are based on considering both the random and the systematic errors which are always present in absolute light scattering measurements.

The cross-term $R^\#$ derived by Eq. (27) varied from system to system. Expressed relatively to R_c values as $A^\# = 100 R^\#/R_c$ it decreased with increasing concentration of benzene and carbon disulfide, having the smallest values for the system *n*-heptane-carbon disulfide (9 — 4%) and the highest values for the system carbon tetrachloride-carbon disulfide (15 — 11%). A graphical presentation of these data is given in Fig. 1. The results show that in most cases the absolute value of $R^\#$ is comparable with the experimental error of R_c . Thus the cross-term should not be assumed to be a negligible quantity, since its omitting would increase the total error of R_c , doubling it in many cases.

A correct $R^\#$ term must meet two requirements: (1) it should always be smaller than R_c , and (2) it should approach zero as both x_1 and x_2 approach zero. Our $R^\#$ term, Eq. (27), satisfies both requirements. The term suggested by Bullough¹¹ and used by other authors^{3,4},

$$R^\# = (\pi^2/\lambda_0^4) kT\alpha_T (N\partial\epsilon/\partial N) (c_2\partial\epsilon/\partial c_2), \quad (39)$$

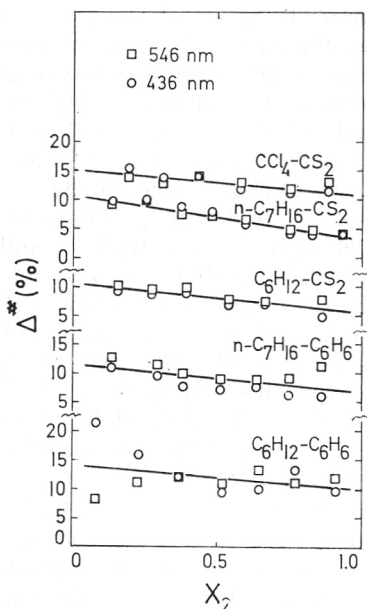


Fig. 1. Percent ratio $\Delta^{\#}$ of the Rayleigh ratios $R^{\#}$ and R_c for various liquid mixtures.

should therefore be regarded as incorrect, since it tends to increase sharply with increasing c_2 , the concentration of the second component. In Fig. 2 both expressions are compared for the system cyclohexane-benzene, but all other systems follow the same pattern.

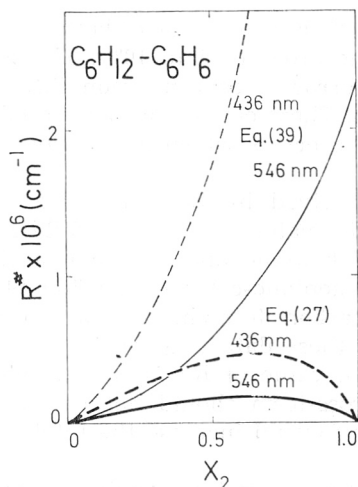


Fig. 2. Cross-term Rayleigh ratio $R^{\#}$ as calculated from Bullough's¹¹ (Eq. 39) and our (Eq. 27) expression.

It is of interest to examine whether our data can be applied to the estimation of thermodynamic quantities, *i. e.* to the determination of the excess free energy of mixing. Extrapolations of the kind applied by Sicotte and

Rinfret¹ (determination of c_2/R_c at $c_2 \rightarrow 0$) did not give satisfactory results and a significant curvature at higher c_2 values was always noted, since for c_2 tending to maximal values (pure component (2)), $R_c \rightarrow 0$, and $c_2/R_c \rightarrow \infty$. It was, therefore, attempted to perform extrapolations with values R_c/Hx_1x_2 , where $H = 2\pi^2n^2 (\partial n/\partial x_2)^2/\lambda_0^4N_{A0}$, vs. x_2 . From Eq. (28) it follows

$$R_{c, id}/Hx_1x_2 = M_1 + (M_2 - M_1)x_2. \quad (40)$$

Consequently, for ideal mixtures the R_c/Hx_1x_2 values should lie on a straight line defined by $M_1 + (M_2 - M_1)x_2$. Any deviation from this line shows the existence of a finite value of the excess free energy of mixing in the real mixture. Figs. 3—7 show experimental results for all the systems measured, with the exception of the system carbon tetrachloride-benzene, whose R_c values are very low and R_c/Hx_1x_2 data are irregularly scattered around the ideal values. The extrapolated R_c/Hx_1x_2 values extrapolated to $x_2 = 0$ should give M_1 , whereas those extrapolated to $x_2 = 1$ render M_2 .

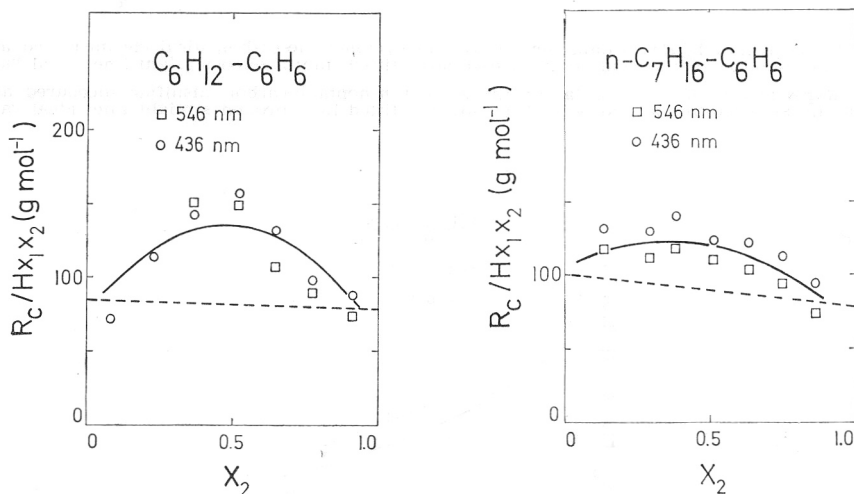


Fig. 3. Experimental R_c/Hx_1x_2 data for the system cyclohexane-benzene measured at 546 and 436 nm. Solid curve: second-order least-squares fitted line; broken straight line: ideal values.
Fig. 4. Experimental R_c/Hx_1x_2 data for the system *n*-heptane-benzene measured at 546 and 436 nm. Solid curve: second-order least squares fitted line; broken straight line: ideal values.

From thermodynamic theory² it follows that mixtures with positive excess free energies of mixing should have $R_c/Hx_1x_2 > R_{c, id}/Hx_1x_2$, whereas the opposite is valid for mixtures with negative energies. For regular mixtures, and all our systems should be regarded as being practically regular, the excess molar free energy of mixing g^E can be determined from the expression

$$g^E = RT/2 (1 - R_{c, id}/R_c). \quad (41)$$

As seen from the results, mixtures with benzene (Figs. 3 and 4) show a positive deviation from the ideal straight line, whereas mixtures with carbon disulfide (Figs. 5 and 6) tend to express a very weak deviation from ideality. The more pronounced negative deviation in the system carbon tetrachloride-

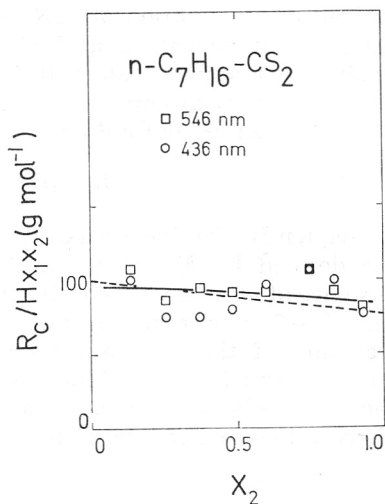
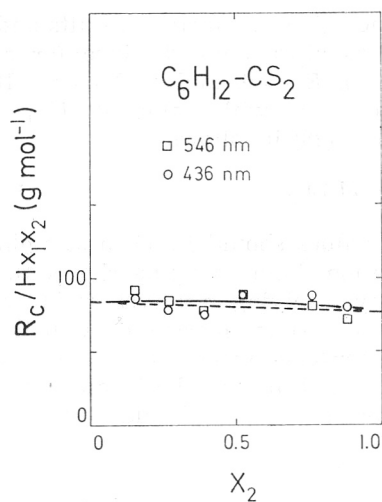


Fig. 5. Experimental R_c/Hx_1x_2 data for the system cyclohexane-carbon disulfide measured at 546 and 436 nm. Solid curve: second-order least-squares fitted line; broken straight line: ideal values.

Fig. 6. Experimental R_c/Hx_1x_2 data for the system *n*-heptane-carbon disulfide measured at 546 and 436 nm. Solid curve: second-order least-squares fitted line; broken straight line: ideal values.

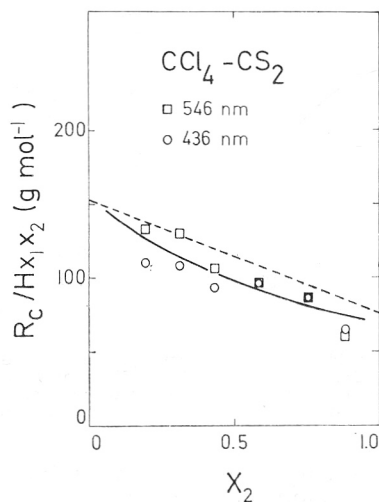


Fig. 7. Experimental R_c/Hx_1x_2 data for the system carbon tetrachloride-carbon disulfide measured at 546 and 436 nm. Solid curve: second-order least-squares fitted line; broken straight line: ideal values.

-carbon disulfide (Fig. 7) does not seem to be significant as noted later in this discussion.

The values of the molecular weights obtained by extrapolation, together with percent deviations from the formula molecular weight Δ are given in Table XI. The scatter of the R_c/Hx_1x_2 values around the fitted curves, expressed as the standard errors of estimate, is appreciable, as seen in Table XI.

TABLE XI

Molecular Weights and Relative Standard Errors of Estimate for Second Order Fitted Curves R_c/Hx_1x_2 vs. x_2 for Various Binary Mixtures (Evaluated Relative to R_c/Hx_1x_2 for $x_1 = x_2 = 0.5$)

System		Extrapolated values				Relative standard error of estimate
Component (1)	Component (2)	M_1 (g mol ⁻¹)	Δ (%)	M_2 (g mol ⁻¹)	Δ (%)	(%)
cyclohexane	benzene	78.3	-7.0	64.4	-17.5	12.7
<i>n</i> -heptane	benzene	106.2	6.0	72.1	-7.7	9.2
cyclohexane	carbon disulfide	83.9	-0.4	76.7	0.8	6.5
<i>n</i> -heptane	carbon disulfide	95.9	-4.3	84.9	11.6	12.5
carbon tetrachloride	carbon disulfide	152.0	-1.2	70.3	-7.6	10.2

Represented as plots $(1 - R_{c, id}/R_c)$ vs. x_2 these data are shown in Fig. 8. Here the curves were calculated from the best fitted values from Figs. 3—7.

The curves for benzene mixtures (Fig. 8a) appear to reproduce the regular behaviour assumed before. However, the absolute g^E values determined by Eq. (41) are higher than those obtained by vapour pressure measurements reported in the literature. For the system cyclohexane-benzene at $x_2 = 0.5$ Scatchard *et al.*²⁴ reported $g^E = 74$ cal/mol as an average between 40° and 70 °C, whereas from Boublik's²⁵ data on activity coefficients at 10 °C one derives $g^E = 88$ cal/mol. From the curve in Fig. 8a one obtains $g^E = 116$ cal/mol at

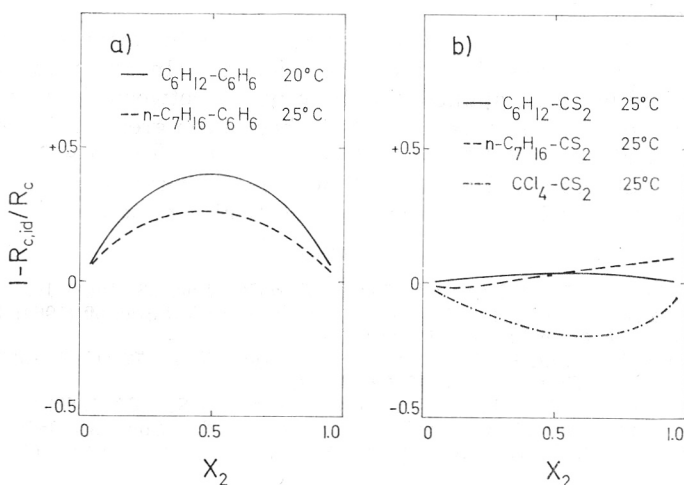


Fig. 8. Second-order least-squares fitted curves of $(1 - R_{c, id}/R_c)$ vs. x_2 data of binary mixtures: a) with benzene; b) with carbon disulfide.

20 °C. For the system *n*-heptane-benzene the literature vapour pressure values are $g^E = 65$ cal/mol at 80 °C²⁶ and 60 cal/mol at 85 °C²⁷. The curve in Fig. 8a gives 77 cal/mol at 25 °C.

The curves for carbon disulfide mixtures (Fig. 8b) do not suggest the existence of finite g^E values. In this respect the negative deviation of the carbon tetrachloride-carbon disulfide curve appears to be systematically erroneous since vapour pressure measurements give positive g^E values approaching some 40 cal/mol at 25 °C at the most²⁸. The non-availability of vapour pressure data for the two other systems does not permit any conclusions on the reliability of light scattering curves.

Regarding the determination of thermodynamic quantities of binary mixtures by light scattering, one can conclude that light scattering phenomena can be explained by thermodynamics, but the light scattering method is generally inferior to vapour pressure methods both in sensitivity and accuracy, and because of the complexity of data evaluation. For mixtures having g^E smaller than some 50 cal/mol the light scattering measurements of thermodynamic quantities cannot be regarded to be reliable unless the accuracy of all physical constants and Rayleigh ratios needed in Eq. (29) is increased, preferably by an order of magnitude. It is hardly believable that such efforts could pay if considering the simplicity of vapour pressure methods. For systems having higher g^E values, the mixtures with polar molecules such as the benzene-alcohol mixtures serving as an example, the light scattering experiments lead to more satisfactory results, as is reported in the literature^{2,4,8}.

As was expressed earlier², the amount of the difference in refractive indices of the components in the mixture plays an important role in the determination of g^E and of activity coefficients. As seen from the results in this paper, the reliability of such values, if determined by light scattering, depends also on other factors such as the method for the determination of R_{is} (for liquids with low optical anisotropy the evaluation *via* the Cabannes factor is superior to the method with V_h , whereas for highly anisotropic liquids the opposite is true), the calibration of the light scattering photometer, the determination of reliable physical constants, etc.

Finally, the existence of a finite $R^\#$ -term whose importance increases with the decrease of R_c values should not be neglected. In our measurements, if the $R^\#$ -term had not been applied, the discrepancy between the light scattering and the vapour pressure results would have been even greater. For our benzene mixtures the neglecting of $R^\#$ would lead to higher g^E values. In this respect the literature data obtained either without the $R^\#$ -term or with the term in the form proposed by Bullough should be critically reviewed.

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APPENDIX

Calculation of the second order partial derivatives of the free energy F

The calculation of the derivatives $\partial^2 F/\partial N^2$ and $\partial^2 F/\partial x_2$, is already known as these derivatives are included in Eqs. (25) and (26). Since the calculation of $\partial^2 F/\partial N \partial x_2$ is based on the method used in determining $\partial^2 F/\partial N^2$ and $\partial^2 F/\partial x_2^2$, both methods of calculation are reviewed here.

1) *The derivative $\partial^2 F/\partial N^2$*

The number density of the mixture N can be replaced by the volume v :

$$N = N_A n/v$$

where n is the number of moles in the mixtures in the volume v . It follows:

$$\partial N/\partial v = -N/v$$

and

$$\partial^2 F/\partial N^2 = (\partial^2 F/\partial v^2)(\partial v/\partial N)^2.$$

From basic thermodynamics one has

$$\partial^2 F/\partial v^2 = -\partial p/\partial v = 1/\kappa_T v,$$

and consequently

$$\partial^2 F/\partial N^2 = v/N^2 \kappa_T.$$

2) *The derivative $\partial^2 F/\partial x_2^2$*

In calculating the first order derivative $\partial F/\partial x_2$ it is straightforward to substitute x_2 by n_2 , the number of moles of component (2) in the volume v of the mixture.

One obtains:

$$\partial F/\partial x_2 = (\partial F/\partial n_2) (\partial n_2/\partial x_2)$$

From $x_2 = n_2/(n_1 + n_2)$ and $x_1 + x_2 = 1$ one obtains $\partial n_2/\partial x_2 = n_1/x_1^2$. Since $\partial F/\partial n_2 = \mu_2$, where μ_2 is the chemical potential of the component (2), the final result is

$$\partial^2 F/\partial x_2^2 = (n_1/x_1) (\partial \mu_2/\partial x_2),$$

or expressed by the molar volume of the mixture $V = v/(n_1 + n_2) = vx_1/n_1$,

$$\partial^2 F/\partial x_2^2 = v (\partial \mu_2/\partial x_2)/Vx_1.$$

3) The derivative $\partial^2 F/\partial N \partial x_2$

The variables N and x_2 are transformed to v and n_2 :

$$\partial^2 F/\partial N \partial x_2 = (\partial^2 F/\partial v \partial n_2) (\partial v/\partial N) (\partial n_2/\partial x_2).$$

It follows:

$$\partial^2 F/\partial v \partial n_2 = \partial \mu_2/\partial v.$$

With a second transformation

$$\partial \mu_2/\partial v = (\partial \mu_2/\partial p) (\partial p/\partial v),$$

and since from basic thermodynamics¹⁶

$$\partial \mu_2/\partial p = N_A/nx_2,$$

one has

$$\partial^2 F/\partial v \partial n_2 = -N_A/vN\kappa_T x_2.$$

Observing that $N = N_A/V$ the final result is

$$\partial^2 F/\partial N \partial x_2 = v/N\kappa_T x_1 x_2.$$

IZVOD

Rasipanje svjetlosti u binarnim tekućim smjesama. I. Izotropno rasipanje

N. Šegudović i Gj. Deželić

Izotropno rasipanje svjetlosti u tekućim smjesama malih molekula neelektrolita proučavano je s teorijskog i eksperimentalnog stajališta. Razmatrana je potreba uzimanja u obzir korelacijskog člana u izotropnom Rayleighovom omjeru, koji je posljedica korelacije u fluktuaciji u gustoći i koncentraciji. Novi izraz za taj član izveden je i uspoređen s prethodno izvedenim izrazom. Određivano je izotropno rasipanje različitih čistih tekućina i tekućih smjesa kod valnih dužina 546 i 436 nm i detaljno je razmatrana pouzdanost eksperimentalnih podataka. Mjerene su smjese cikloheksana, *n*-heptana i ugljikova tetraklorida (komponenta 1) s benzenom i ugljikovim disulfidom (komponenta 2). Razmatrana je mogućnost određivanja molekularne težine u takvim sistemima pomoću rasipanja svjetlosti. Detaljno je analizirana pouzdanost podataka za dodatnu slobodnu energiju miješanja dobivenih rasipanjem svjetlosti. Zaključeno je da se fenomeni rasipanja svjetlosti mogu objašnjavati termodinamikom, ali je metoda rasipanja svjetlosti općenito neprikladnija od metoda tlaka para kako s obzirom na manju osjetljivost i točnost, tako i na složenost u obradi podataka.

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