

THERMODYNAMICS OF LIQUID MIXTURES STUDIED BY LIGHT SCATTERING

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(Received 14 September 1990)

ABSTRACT

The light scattering method for measuring interactions in binary mixtures has been applied to three groups of mixtures of carbonyl compounds with aromatic hydrocarbons; namely, alkyl acetate–benzene mixtures, alkyl acetate–toluene mixtures, and butanone–aromatic hydrocarbon mixtures. The interaction coefficients are rather small and, within each group, they exhibit well defined trends. This behavior is explained as a result of a specific interaction between an electron accepting aromatic ring and an electron donating carbonyl.

INTRODUCTION

In our previous papers [1,2], we reported that by improving the precision for gathering the Rayleigh scattering data and by incorporating the concept of excess isothermal compressibility of liquid mixtures, the light scattering technique can be successfully used for the characterization of thermodynamic interactions in binary mixtures in an effective and simple way. We also discussed the dependence of attainable accuracy of interaction parameters on various factors. The key elements are the difference between the refractive indices of the two components and the experimental accuracy in determination of isotropic Rayleigh ratio and of isothermal compressibility.

Thermodynamic interaction data for liquid mixtures are usually obtained from measurements of vapor–liquid equilibria. As a consequence, the majority of such data refer to the vicinity of the boiling temperatures of the liquids involved. The interaction data at ambient temperatures are relatively rare. In ongoing research, we are trying to remedy this situation by studying families of binary mixtures using the light scattering technique at 20°C. In this paper, we present the results of our studies of mixtures of aromatic hydrocarbons with alkyl acetates and with butanone.

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THEORY

Light scattering of a liquid is usually measured using unpolarized light and is expressed in terms of the Rayleigh ratio. The total scattering Rayleigh ratio, R_t , consists of two parts, isotropic scattering R_{is} and anisotropic scattering R_{an} ; R_{is} can be further divided into the density scattering R_d and the compositional scattering R_c :

$$R_t = R_{is} + R_{an} = R_d + R_c + R_{an} \quad (1)$$

R_t and R_{an} are obtained experimentally by measuring the intensity and the depolarization of the scattered light. R_d is calculated as

$$R_d = \left(\pi^2 kT / 2\lambda_0^4 \right) \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T^2 \beta \quad (2)$$

where β , ϵ and ρ are the isothermal compressibility, dielectric constant and density of the liquid, respectively; λ_0 is the wavelength of the light in vacuo; k and T have their usual meanings. The value of $(\rho \partial \epsilon / \partial \rho)$ is calculated using Eykman's relation [1,3].

The isothermal compressibility β of mixtures is usually quite close to the volume fraction weighted average of the compressibilities of its components β_i ; the deviation from the average is conveniently expressed by the composition-dependent excess compressibility β^E that must be determined from an independent experiment. The appropriate relation reads

$$\beta = \beta_1 \phi_1 + \beta_2 \phi_2 + \beta^E \phi_1 \phi_2 \quad (3)$$

where ϕ_i is the volume fraction of the i th component.

The compositional scattering R_c is related to the chemical potential of the components of the liquid μ_i as

$$R_c = \left(\frac{2\pi^2 kT}{\lambda_0^4} \right) V x_1 \bar{n}^2 \left[\frac{(d\bar{n}/dx_2)^2}{(\partial \mu_2 / \partial x_2)_{P,T}} \right] \quad (4)$$

where x_i is the mole fraction of the i th component, V is the molar volume of the mixture, and \bar{n} is its refractive index.

Similarly to our previous paper [2], we are describing the thermodynamic behavior of the mixture by means of interaction functions $g^{(x)}$ and $F^{(x)}$ defined as

$$\Delta G_{\text{mix}} \equiv RT \left[n_1 \ln x_1 + n_2 \ln x_2 + (n_1 + n_2) x_1 x_2 g^{(x)} \right] \quad (5)$$

$$F^{(x)} \equiv g^{(x)} + (x_2 - x_1) \frac{dg^{(x)}}{dx_2} - \frac{x_1 x_2}{2} \left(\frac{d^2 g^{(x)}}{dx_2^2} \right) \quad (6)$$

There, ΔG_{mix} is the change of Gibbs energy upon mixing, R is the gas constant, and n_i is the number of moles of the i th component. Using

standard thermodynamic manipulations, eqn. (4) is combined with eqns. (5) and (6) yielding

$$F^{(x)} = (1/2) \left[1/x_1 + 1/x_2 - (2\pi^2/N_A\lambda_0^4) \bar{n}^2 (d\bar{n}/dx_2)^2 V/R_c \right] \quad (7)$$

where N_A is the Avogadro number.

Once the function $F^{(x)}$ has been measured for the whole range of compositions of the mixture, $g^{(x)}$ is obtained by integration.

Alternatively, ΔG_{mix} may be expressed by means of volume fractions ϕ_i as

$$\Delta G_{\text{mix}} \equiv RT \left[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 g^{(\phi,1)} \right] \quad (8)$$

$$F^{(\phi,1)} \equiv g^{(\phi,1)} + (\phi_2 - \phi_1) \frac{dg^{(\phi,1)}}{d\phi_2} - \frac{\phi_1 \phi_2}{2} \left(\frac{d^2 g^{(\phi,1)}}{d\phi_2^2} \right) \quad (9)$$

Unlike eqn. (5), eqn. (8) is not symmetrical with respect to both components. Thus, the introduction of the second identifying superscript is necessary. The function $F^{(\phi,1)}$ is calculated from R_c according to the relation

$$F^{(\phi,1)} = (V_1/2) \left[1/\phi_1 V_1 + 1/\phi_2 V_2 - (2\pi^2/N_A\lambda_0^4) \bar{n}^2 (d\bar{n}/d\phi_2)^2 / R_c \right] \quad (10)$$

For many purposes it is convenient to use still another interaction parameter, B_{12} , defined as

$$\Delta G_{\text{mix}}/V \equiv RT \left[(\phi_1/V_1) \ln \phi_1 + (\phi_2/V_2) \ln \phi_2 \right] + B_{12} \phi_1 \phi_2 \quad (11)$$

It is related to the above defined parameter $g^{(\phi,1)}$ as

$$B_{12} = RTg^{(\phi,1)}/V_1 \quad (12)$$

EXPERIMENTAL

The techniques and equipment used for measuring various experimental data are essentially the same as those given in the previous papers [1,2]. The materials utilized in the present study were ACS certified, having a nominal purity of more than 99%. They were further purified using a 30 cm fractionation column. The mixtures were prepared by direct weighing using a Mettler analytical balance. The refractive indices of the pure liquids and mixtures were obtained at the wavelength of 546 nm using a Bausch and Lomb precision refractometer. Densities were determined with an Anton Paar–Mettler oscillatory densitometer. For light scattering measurement all samples were passed through a 0.45 μm Teflon filter to ensure that they were dust free.

The isothermal compressibilities of pure components were obtained from their isotropic Rayleigh ratio R_{is} (which for pure substances is equal to R_{d}) according to eqn. (2). The excess compressibilities were measured for alkyl acetate–benzene and alkyl acetate–toluene systems. They were obtained

from experimental measurements of compressibility of both pure components (these values agreed reasonably with the values obtained from light scattering) and of a mixture with $\phi_1 = 0.5$. The measurements were made using a piezometer constructed in our own laboratory. While the quality of the results was not completely satisfactory, the estimated error in values of the total compressibility never exceeded 1%.

All measurements were performed at 20 °C.

RESULTS AND DISCUSSION

The present study is devoted to mixtures of aromatic hydrocarbons with compounds containing carbonyl. The data comprise three groups of mixtures: alkyl acetates–benzene, alkyl acetates–toluene, and butanone–aromatic hydrocarbons. The acetates include methyl acetate, ethyl acetate, propyl acetate, and butyl acetate. The aromatics were benzene, toluene, ethylbenzene, and *p*-xylene. The refractive indices \tilde{n} and densities ρ are listed in Table 1. It can be seen that the difference in refractive indices of any measured pair of substances is larger than 0.10. In our previous paper [2] it has been pointed out that the calculated thermodynamic interaction parameters become acceptably accurate for such mixtures.

For the analysis of the light scattering data, refractive indices and excess isothermal compressibilities of the mixtures need to be known as functions of the composition of the mixtures. The dependence of the refractive index on the composition is described as

$$\tilde{n} = \sum_{j=0}^m B_j \phi_2^j \quad (13)$$

The relevant coefficients B_j are collected in Table 2. (B_0 , which is not tabulated, is the refractive index of the component listed first in the table.)

TABLE 1

Refractive indices and densities of pure components at 20 °C

Liquid	\tilde{n} ($\lambda_0 = 546 \text{ nm}$)	ρ (g cm^{-3})
Methyl acetate (MA)	1.3628	0.9320
Ethyl acetate (EA)	1.3738	0.9007
Propyl acetate (PA)	1.3858	0.8880
n-Butyl acetate (BA)	1.3957	0.8820
Butanone (BU)	1.3805	0.8054
Benzene (BE)	1.5052	0.8792
Toluene (TO)	1.5009	0.8669
Ethyl benzene (EB)	1.4990	0.8670
<i>p</i> -Xylene (PX)	1.4993	0.8660

TABLE 2

Coefficients of eqn. (13) for refractive indices, and excess compressibilities for binary mixtures

System	B_1	B_2	B_3	$\beta^E \times 10^{10}$ ($\text{m}^2 \text{N}^{-1}$)	$\Delta\beta/\beta_{\text{id}}$
MA-BE	0.13185	0.00841	0.00199	0.00	0.00
EA-BE	0.12473	0.00464	0.00202	0.84	0.02
PA-BE	0.11354	0.00366	0.00225	0.00	0.00
BA-BE	0.10373	0.00246	0.00324	0.69	0.02
MA-TO	0.13083	0.00699	0.00	0.53	0.01
EA-TO	0.12406	0.00303	0.00	-0.71	-0.02
PA-TO	0.11283	0.00172	0.00	0.59	0.02
BA-TO	0.10250	0.00252	0.00	0.44	0.01
BU-BE	0.12256	0.00195	0.00		
BU-TO	0.12205	-0.00166	0.00		
BU-EB	0.11954	-0.00083	0.00		
BU-PX	0.11960	-0.00170	0.00		

The values of the excess compressibility coefficient β^E measured at $\phi_2 = 0.5$ are listed in the same table together with the ratio $\Delta\beta/\beta_{\text{id}}$ where β_{id} is the volume-fraction based average of the compressibility of the components of the mixture; $\Delta\beta \equiv \beta^E \phi_1 \phi_2$ is the change in compressibility that is due to the measured excess compressibility. The value of the ratio is listed for $\phi_2 = 0.5$; presumably, it has the highest value at this composition. It is apparent that for all mixtures measured the value of the ratio has about the same magnitude as the acceptable experimental error in the measurement of compressibility (see ref. 2). Thus, for the present study, the introduction of the excess compressibility has only marginal importance and possible errors in our measurement of β^E (and its neglect for butanone-aromatic hydrocarbon mixtures) do not lead to serious deterioration of our interaction data.

The total, isotropic, and compositional Rayleigh ratios for all measured mixtures are listed in Table 3 for alkyl acetate-benzene systems, in Table 4 for alkyl acetate-toluene systems, and in Table 5 for butanone-aromatic hydrocarbon mixtures. It should be noted that a given binary system including both pure components was always measured in one light scattering session and that the values measured for pure components on that particular day were used in the calculations. That explains the slight variations of the values presented in our tables for pure components. The dependence of the compositional scattering ratio R_c on the volume fraction of benzene for the alkyl acetate-benzene mixtures is plotted in Fig. 1.

Figures 2 and 3 illustrate the compositional dependence of $F^{(\phi,1)}$ and $g^{(\phi,1)}$ functions for systems of methyl acetate-benzene and ethyl acetate-benzene, respectively. The error was evaluated according to the assumption that

TABLE 3

Rayleigh ratios and their components for alkyl acetate-benzene mixtures at 20 °C

System	$\phi_2 \times 10^2$	Rayleigh ratio $\times 10^4 \text{ (m}^{-1}\text{)}$			System	$\phi_2 \times 10^2$	Rayleigh ratio $\times 10^4 \text{ (m}^{-1}\text{)}$		
		R_t	R_{is}	R_c			R_t	R_{is}	R_c
MA-BE	0.0	4.44	2.47	0.00	EA-BE	0.0	4.80	2.89	0.00
	8.3	6.28	3.47	0.83		11.7	7.17	4.19	1.03
	19.7	8.57	4.74	1.84		19.7	8.79	5.01	1.66
	30.1	10.68	5.96	2.80		30.1	10.71	5.95	2.35
	39.9	12.40	6.77	3.37		39.8	12.32	6.63	2.79
	50.0	13.93	7.23	3.56		49.8	13.76	7.11	3.03
	60.0	15.08	7.67	3.71		60.1	15.08	7.48	3.13
	69.1	15.88	7.62	3.38		70.3	15.99	7.45	2.84
	80.1	16.58	7.13	2.52		79.8	16.58	7.13	2.27
	91.0	16.83	6.30	1.31		89.5	16.87	6.48	1.38
	100.0	16.70	5.32	0.00		100.0	16.70	5.36	0.00
PA-BE	0.0	4.75	2.92	0.00	BA-BE	0.0	4.73	2.89	0.00
	10.0	6.86	3.89	0.77		9.3	6.57	3.72	0.64
	19.4	8.49	4.73	1.41		29.6	10.10	5.17	1.64
	29.9	10.29	5.46	1.93		39.4	11.65	5.69	1.92
	39.5	11.85	6.08	2.32		49.7	13.13	6.19	2.17
	49.9	13.29	6.65	2.65		60.7	14.43	6.51	2.22
	61.2	14.71	6.82	2.54		69.7	15.42	6.65	2.12
	69.3	15.49	6.90	2.41		80.3	16.21	6.54	1.73
	79.6	16.27	6.84	2.07		100.0	16.70	5.35	0.00
	100.0	16.70	5.38	0.00					

the precision of the light scattering measurement $\Delta R_{is}/R_{is}$ and the precision of the compressibility coefficient measurement $\Delta\beta/\beta$ were both equal to 0.01. The F values become less precise near both ends of the composition range where R_c is getting smaller. In the middle portion of the range, the typical error is around ± 0.07 . As a general rule, the g function is much flatter than the F function: consequently, its error is about the same (as the error of the F function) in the middle of the range, but is smaller near the ends of the concentration scale. It is seen from Figs. 2 and 3 that the compositional dependence of $g^{(\phi,1)}$, if present, is masked by experimental errors. This is also true for all other systems studied. We will therefore report the values of $g^{(\phi,1)}$ that correspond to the middle of the concentration range. While eqn. (8), the Flory-Huggins relation, which is based on volume fractions, is routinely used in polymer studies, eqn. (5), which is based on molar fractions is routinely used in thermodynamic studies of mixtures of small molecules. We have therefore evaluated both $g^{(\phi,1)}$ and $g^{(x)}$. It should be obvious that, for mixtures of components with different molar volumes, the fact that $g^{(\phi,1)}$ is composition independent implies that $g^{(x)}$ is composition dependent and vice versa. However, during the evaluation procedure

TABLE 4

Rayleigh ratios and their components for alkyl acetate-toluene mixtures at 20°C

System	$\phi_2 \times 10^2$	Rayleigh ratio $\times 10^4 \text{ (m}^{-1}\text{)}$			System	$\phi_2 \times 10^2$	Rayleigh ratio $\times 10^4 \text{ (m}^{-1}\text{)}$		
		R_t	R_{is}	R_c			R_t	R_{is}	R_c
MA-TO	0.0	4.46	2.52	0.00	EA-TO	0.0	4.81	2.90	0.00
	9.7	6.87	3.84	1.12		20.6	9.55	5.35	2.10
	19.9	9.32	5.18	2.24		30.7	11.73	6.24	2.78
	29.7	11.63	6.36	3.21		40.0	13.46	6.91	3.30
	39.6	13.67	7.26	3.88		50.1	15.18	7.31	3.50
	49.6	15.42	7.78	4.17		60.6	16.65	7.46	3.44
	59.5	16.74	7.89	4.04		70.3	17.79	7.26	3.03
	70.1	17.87	7.51	3.40		80.2	18.73	6.75	2.30
	79.2	18.56	6.87	2.54		90.1	19.40	5.92	1.25
	89.9	19.25	5.91	1.31		100.0	19.95	4.91	0.00
	100.0	19.71	4.85	0.00					
PA-TO	0.0	4.81	2.97	0.00	BA-TO	0.0	4.82	3.01	0.00
	9.7	7.02	3.98	0.84		10.7	7.18	4.01	0.80
	20.3	9.47	4.97	1.63		20.0	8.86	4.64	1.25
	29.9	11.10	5.57	2.03		29.4	10.82	5.27	1.69
	40.1	13.06	6.14	2.41		39.3	12.70	5.86	2.08
	50.6	14.92	6.61	2.69		49.8	14.23	6.15	2.16
	59.9	16.44	6.71	2.62		59.9	16.32	6.62	2.41
	70.4	17.75	6.44	2.16		69.7	16.99	6.40	2.00
	79.7	18.81	6.15	1.69		80.3	18.35	6.25	1.62
	100.0	20.40	4.80	0.00		100.0	20.39	5.05	0.00

the experimental errors masked the dependence of $g^{(x)}$ on composition as well. Consequently, we are reporting both values $g^{(\phi,1)}$ and $g^{(x)}$ as a single value corresponding to the middle of the composition range.

The experimentally found values of $g^{(\phi,1)}$ and $g^{(x)}$ are presented in Table 6. These values are very consistent among themselves: in both the alkyl acetate-benzene group and the alkyl acetate-toluene group the $g^{(\phi,1)}$ values regularly decrease with increasing size of the alkyl group; in the butanone-aromatic hydrocarbon group the values increase with increasing substitution of the benzene ring.

Direct comparison of our results with literature values of $g^{(\phi,1)}$ was not possible; none of these values exists in the literature. We have therefore utilized four different approaches for estimating the $g^{(\phi,1)}$ values from various types of data in the literature. In the first approach we utilized the vapor-liquid equilibrium data of Kraus and Linek [4], Linek et al. [5] and Nagata et al. [6], which were available for six of our twelve binary systems. For every case, the equilibria were measured at a number of compositions and at three temperatures (in 10°C intervals somewhere in the 30–75°C region). Using routine thermodynamic calculations we have evaluated $g^{(\phi,1)}$

TABLE 5

Rayleigh ratios and their components for butanone–aromatic hydrocarbon mixtures at 20 °C

System	$\phi_2 \times 10^2$	Rayleigh ratio $\times 10^{-4} (\text{m}^{-1})$			System	$\phi_2 \times 10^2$	Rayleigh ratio $\times 10^4 (\text{m}^{-1})$		
		R_t	R_{is}	R_c			R_t	R_{is}	R_c
BU–BE	0.0	4.48	3.05	0.00	BU–TO	0.0	4.59	3.13	0.00
	10.5	6.68	4.09	0.83		20.5	9.09	5.21	1.70
	20.6	8.64	4.94	1.47		29.9	11.05	6.03	2.34
	30.6	10.35	5.77	2.07		39.7	12.85	6.50	2.63
	40.6	12.00	6.41	2.50		49.8	14.29	6.88	2.82
	50.1	13.24	6.78	2.64		60.3	15.86	6.99	2.75
	60.4	14.47	7.02	2.65		70.1	17.22	6.91	2.49
	69.8	15.33	6.97	2.38		80.0	17.97	6.32	1.73
	80.2	16.11	6.66	1.82		90.0	18.85	5.73	0.97
	90.8	16.47	6.10	1.00		100.0	19.72	4.92	0.00
	100.0	16.70	5.33	0.00					
BU–EB	0.0	4.51	3.05	0.00	BU–PX	0.0	4.53	3.09	0.00
	11.1	7.20	4.44	1.21		10.4	7.36	4.35	1.09
	19.7	8.93	5.34	1.96		19.5	10.40	5.40	1.99
	30.1	10.91	6.26	2.72		30.3	12.25	6.30	2.73
	40.4	12.65	6.89	3.18		40.2	14.46	6.93	3.21
	49.8	13.98	7.27	3.41		49.9	16.62	7.26	3.40
	60.3	14.97	7.18	3.15		59.8	18.12	7.20	3.21
	69.8	15.76	6.96	2.80		69.7	20.20	6.98	2.86
	78.8	16.21	6.31	2.02		80.0	21.95	6.31	2.07
	89.3	16.60	5.47	1.04		88.2	23.10	5.52	1.19
	100.0	16.85	4.56	0.00		100.0	25.65	4.47	0.00

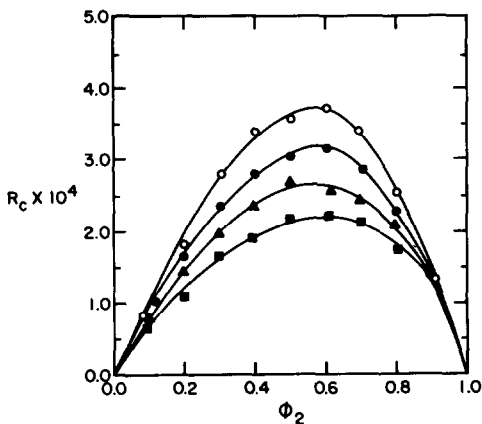


Fig. 1. Dependence of the compositional Rayleigh ratio R_c for the alkyl acetate–benzene mixtures, on benzene volume fraction ϕ_2 : \circ , MA–BE; \bullet , EA–BE; \blacktriangle , PA–BE; \blacksquare , BA–BE.

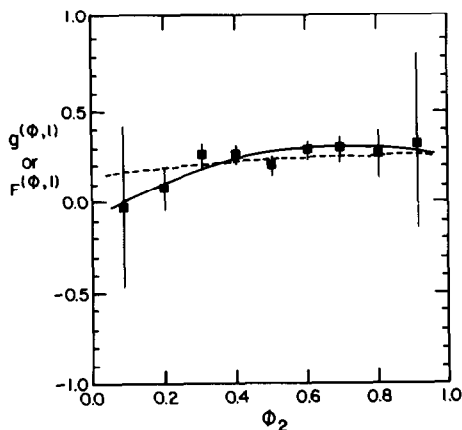


Fig. 2. Dependence of the interaction functions $F^{(\phi,1)}$ (full line) and $g^{(\phi,1)}$ (broken line) for the methyl acetate–benzene mixtures on benzene volume fraction ϕ_2 .

for all experimental points. While the values for compositions close to both ends of the concentration scale were slightly erratic (the apparent slope and curvature of the dependence on the composition changing erratically from temperature to temperature), the values in the middle of the scale seemed to be quite dependable. The temperature dependence of the values at $\phi_2 = 0.5$ was small, scattered, and clearly within the experimental error. We have chosen the following method of evaluation: the composition dependences were approximated by a polynomial of second order; the values interpolated for $\phi_2 = 0.5$ were then averaged for the three temperatures. The results are reported in the fourth column of Table 6; we estimate that they are accurate within ± 0.02 .

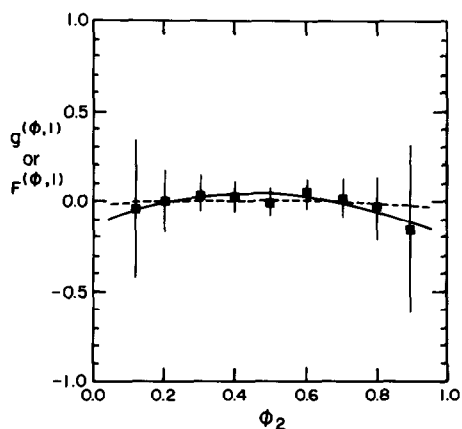


Fig. 3. Dependence of the interaction functions $F^{(\phi,1)}$ (full line) and $g^{(\phi,1)}$ (broken line) for the ethyl acetate–benzene mixtures on benzene volume fraction ϕ_2 .

TABLE 6

Interaction coefficients of twelve binary mixtures at $\phi_1 = 0.5$ ^a

System	$g^{(x)}$	$g^{(\phi,1)}$					B_{12} (J cm ⁻³)
	(LS)	LS	V-L	PFP	IGC	UNIFAC	
MA-BE	0.24	0.23	0.37	0.42	0.25	0.28	7.1
EA-BE	0.00	0.00	0.10	0.11	0.11	0.14	0.1
PA-BE	-0.15	-0.14			0.01	0.05	-3.0
BA-BE	-0.27	-0.27			-0.03	0.00	-5.0
MA-TO	0.36	0.35			0.37	0.24	10.7
EA-TO	0.23	0.22	0.26		0.22	0.08	5.5
PA-TO	-0.20	-0.21			0.10	-0.02	-4.5
BA-TO	-0.29	-0.31			0.04	-0.09	-5.7
BU-BE	-0.04	-0.04	0.18	-0.05	0.23	0.28	-1.1
BU-TO	0.06	0.06	0.27	0.13	0.35	0.27	1.6
BU-EB	0.27	0.27	0.37	0.13	0.43	0.38	7.4
BU-PX	0.35	0.33				0.23	9.0

^a LS, light scattering; V-L, vapor-liquid; PFP, Prigogine-Flory-Patterson; IGC, inverse gas chromatography.

In our second approach we have employed the Prigogine-Flory-Patterson (PFP) theory [11] of liquid mixtures and the published data of enthalpies of mixing. These data were available for five of our binary systems [7-10]. According to the PFP theory, the interaction parameter χ^* (which is identical to function $g^{(\phi,1)*}$, which in turn is an equivalent of function $g^{(\phi,1)}$ expressed in core volumes) may be expressed as a sum of an enthalpic parameter χ_H^* and an entropic parameter χ_S^* . These parameters can be calculated as [11]

$$\chi_H^* = \frac{V_1^*}{RT} \left[\frac{\theta_2}{\phi_2^*} X_{12} \bar{v}^{-1} - \frac{P_1^*}{\phi_2^*} (\bar{v}^{-1} - \bar{v}_1^{-1}) - \frac{P_2^*}{\phi_1^*} (\bar{v}^{-1} - \bar{v}_2^{-1}) \right] \quad (14)$$

$$\chi_S^* = -\frac{3V_1^*}{R} \left[\frac{P_1^*}{T_1^* \phi_2^*} \ln \left(\frac{\bar{v}^{1/3} - 1}{\bar{v}_1^{1/3} - 1} \right) + \frac{P_2^*}{T_2^* \phi_1^*} \ln \left(\frac{\bar{v}^{1/3} - 1}{\bar{v}_2^{1/3} - 1} \right) \right] \quad (15)$$

Here V_i^* , P_i^* , and T_i^* are, respectively, the core volume, characteristic pressure, and characteristic temperature of the i th component, ϕ_i^* is the core volume fraction, \bar{v}_i , and \bar{v} are the reduced volumes of component i and of the mixture, respectively. X_{12} is the contact interaction parameter of the mixture, θ_i is the surface fraction of i th component. Further relevant relations of the PFP theory define the reduced quantities \bar{v} , \bar{P} , and \bar{T} as

$$\bar{v} = v/v^* \quad \bar{P} = P/P^* \quad \bar{T} = T/T^* \quad (16)$$

$$\bar{T} = (\bar{v}^{1/3} - 1)/\bar{v}^{4/3} \quad (17)$$

These relations are applied to both components as well as to the mixture. For pure components, the quantities \bar{v}_i , and P_i^* are calculated from

TABLE 7

Parameters used in the Prigogine–Flory–Patterson (PFP) approach for calculating interaction parameters at 25°C

Liquid	$\alpha_i \times 10^3$ (K ⁻¹) ^a	$\beta_i \times 10^3$ (cm ³ J ⁻¹) ^a	S_i	V_i (cm ³ mol ⁻¹)	V_i^* (cm ³ mol ⁻¹)	P_i^* (J cm ⁻³)	T_i^* (K)	\tilde{v}_i
MA	1.41 [13]	1.14 [13]	1.274	79.90	60.25	649.5	4403	1.326
EA	1.37 [13]	1.17 [13]	1.183	98.51	74.69	607.3	4461	1.320
BU	1.31 [14]	1.16 [15]	1.151	90.17	68.94	576.0	4555	1.308
BE	1.22 [16]	0.97 [16]	1.261	89.40	69.24	625.1	4715	1.291
TO	1.09 [16]	0.92 [16]	1.200	106.87	84.42	569.1	4994	1.266
EB	1.02 [17]	0.87 [17]	1.173	123.08	98.16	554.9	5147	1.254

^a References are given in brackets.

literature values of the thermal expansivity α_i and the isothermal compressibility β_i as

$$\tilde{v}_i^{1/3} = 1 + \alpha_i T / 3(1 + \alpha_i T) \quad (18)$$

$$P_i^* = \alpha_i T \tilde{v}_i^2 / \beta_i \quad (19)$$

The core molar volume V_i^* is calculated from the experimentally accessible molar volume V_i and from \tilde{v}_i ; the core column fractions ϕ_i^* and surface fractions θ_i are calculated as

$$\phi_1^* = 1 - \phi_2^* = x_1 V_1^* / (x_1 V_1^* + x_2 V_2^*) \quad (20)$$

$$\theta_2 = x_2 V_2^* S_2 / (x_1 V_1^* S_1 + x_2 V_2^* S_2) \quad (21)$$

Here S_i is the specific surface per unit core volume of the i th component. The experimental values of α_i , β_i , V_i , and S_i are collected in Table 7 together with the values derived from them: V_i^* , P_i^* , T_i^* and \tilde{v}_i . (T_i^* is calculated from eqns. 16 and 17). The S_i values were adopted from the paper by Munk et al. [12]. The characteristic temperature of the mixture T^* is related to other relevant parameters as

$$T^* = \frac{\phi_1^* P_1^* + \phi_2^* P_2^* - \phi_1^* \theta_2 X_{12}}{\phi_1^* P_1^* / T_1^* + \phi_2^* P_2^* / T_2^*} \quad (22)$$

The starting point for our calculations was the experimental data for molar enthalpy of mixing ΔH_{mix} ; these data were available either in the form of the coefficients of the Redlich–Kister equation [9,10], or as individual points [7,8]. The ΔH_{mix} values are related to χ_H^* as

$$\Delta H_{\text{mix}} = x_1 \phi_2^* \chi_H^* / RT \quad (23)$$

The calculation consists of an evaluation of the remaining variables of the mixture, namely \tilde{v} , X_{12} , and T^* (or \tilde{T}). These variables were obtained by a computer numerical solution of eqns. (14), (17) and (22). Once \tilde{v} is known,

TABLE 8

Reduced volume and interaction parameters of five binary mixtures calculated from PFP theory at $\phi_1 = 0.5$

System	\tilde{v}	X_{12}	χ_H^*	χ_S^*	χ^*
MA-BE	1.313	22.08	0.55	-0.14	0.41
EA-BE	1.305	4.70	0.13	-0.03	0.10
BU-BE	1.299	-2.54	-0.08	0.03	-0.05
BU-TO	1.291	5.16	0.14	-0.01	0.13
BU-EB	1.281	5.07	0.13	0.01	0.14

χ^* is evaluated easily; its transformation into $g^{(\phi,1)}$ (which is based on volume fractions, not core volume fractions) is straightforward. For all our systems, χ^* and $g^{(\phi,1)}$ differ only in the third decimal place. We have evaluated the χ^* values at 25°C for the whole compositional range (using the experimental or Redlich-Kister value of ΔH_{mix} at each point). However, all the values (with a few minor exceptions close to the ends of the compositional range) were within ± 0.03 of the value calculated for $\phi_2 = 0.5$. The χ_H^* , χ_S^* , \tilde{v} and X_{12} values for the five systems are reported in Table 8; the $g^{(\phi,1)}$ value is also included in Table 6.

In our third approach we have utilized the concept of modified solubility parameters we have reported elsewhere [12]. According to this approach, the cohesive energy of a pure substance (subscript 1) ϵ_1 , and the interaction coefficient B_{12} of a mixture can be expressed by means of five parameters per component; namely, reduced molecular surface per unit volume S_i (the same quantity as in eqn. 21); the van der Waals solubility parameter $\delta_{i,w}$; the polar solubility parameter $\delta_{i,p}$; and the electron donor and electron acceptor solubility parameters $\delta_{i,d}$ and $\delta_{i,a}$, respectively. The relevant relations read

$$\epsilon_1 = S_1(\delta_{1,w}^2 + \delta_{1,p}^2 + \delta_{1,a}\delta_{1,d}) \quad (24)$$

$$B_{12} \equiv \frac{RTg^{(\phi,1)}}{V_1} = \frac{S_1S_2}{S_1\phi_1 + S_2\phi_2} \times \left[(\delta_{1,w} - \delta_{2,w})^2 + (\delta_{1,p} - \delta_{2,p})^2 + (\delta_{1,a} - \delta_{2,a})(\delta_{1,d} - \delta_{2,d}) \right] \quad (25)$$

The five parameters were evaluated for a large number of solvents using the technique of inverse gas chromatography at 100°C [12]. The data referring to components of our mixtures are presented in Table 9; the $g^{(\phi,1)}$ values evaluated for our mixtures at $\phi_1 = 0.5$ are included in Table 6.

The fourth approach employed the concept of group contributions to the interactive behavior of mixtures. We have followed the UNIFAC method as described in ref. 18. This method yields the activity coefficients γ_1 and γ_2 . From these coefficients, $g^{(x)}$ is easily evaluated as

$$g^{(x)}x_1x_2 = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (26)$$

TABLE 9

Surface ratio and components of the solubility parameter of pure components at 100 °C

Liquid	S_i	$\delta_{i,w}$	$\delta_{i,p}$	$\delta_{i,a}$	$\delta_{i,d}$
MA	1.274	6.837	2.846	0.795	1.271
EA	1.183	6.854	2.456	0.531	1.156
PA	1.155	6.950	2.164	0.345	1.067
BA	1.120	7.021	1.966	0.240	0.940
BU	1.151	7.143	3.012	0.302	1.420
BE	1.261	7.157	1.692	0.600	0.273
TO	1.200	7.244	1.482	0.412	0.223
EB	1.173	7.243	1.367	0.298	0.251

$g^{(\phi,1)}$ is then obtained from $g^{(x)}$ in a straightforward way. The values of $g^{(\phi,1)}$ calculated for our mixtures for 20 °C and $\phi_2 = 0.5$ are presented in the seventh column of Table 6.

While the four methods used for the estimates yield $g^{(\phi,1)}$ values that differ both from our light-scattering values and among themselves, the trends in the values within each family of mixtures are the same for the light-scattering data and for all four approaches used. Consequently, we are convinced that these trends are real and that they reflect the nature of the chemical composition of the components involved. It is difficult to establish which data in Table 6 are the best. The vapor-liquid equilibrium data are probably the most dependable. However, they are accessible only at temperatures that are typically 40 °C higher than our experimental temperature of 20 °C. The interaction coefficients are expected to be temperature dependent; hence the differences from light-scattering values are not surprising. These differences are expected to be even larger for the method of modified solubility parameters which utilized data measured at 100 °C. The predictions of the PFP theory depend too heavily on the PFP model; specifically, the calculation of χ_S^* may be based on oversimplified relations. The weakness of the UNIFAC method lies in the fact that the effect of the size of the molecules on the thermodynamic behavior is not accounted for, i.e. the equation-of-state effects are totally neglected. The light-scattering results are measured at the temperature of interest and are based on a firm theoretical foundation. Their uncertainty is related solely to experimental errors in measurement of scattered intensities and compressibilities. They agree with the values from other methods reasonably closely proving that the experimental errors are of the expected order of magnitude. Indeed, the largest deviation of the light-scattering data from the rest is observed for the butanone mixtures, which were evaluated assuming that the excess compressibility is negligible. This assumption may have led to a larger experimental error.

The interaction coefficients in all our mixtures are relatively small, some of them even negative. In other words, their deviation from ideal behavior is

rather small. Such a behavior may seem surprising for mixtures of components differing so much chemically. In our opinion, it is a result of a specific interaction between a carbonyl (which is a much stronger electron donor than it is electron acceptor) and an aromatic ring, (which is more an acceptor than a donor). The negative contribution of this specific interaction to the value of the interaction coefficient is counterbalanced by the positive contribution from the (more generally recognized) van der Waals and polar interactions. The exact contribution of the latter factors depends primarily on the size and/or number of the alkyl groups attached to the components of the mixture. This interpretation is reflected quantitatively by the concept of modified solubility parameters.

CONCLUSIONS

(1) The light scattering method for measurement of interaction coefficients in binary liquid mixtures yields data that are internally consistent within given groups of binary mixtures. The results generally agree with data obtained by other methods. While the precision of the measured values of $g^{(\phi,1)}$ is about ± 0.07 , we estimate that their overall accuracy is about ± 0.15 .

(2) Four alternative methods for obtaining the interaction coefficients were employed. The vapor-liquid equilibrium method requires rather precise data that are rarely available at ambient temperatures. The PFP method relies heavily on model considerations. The solubility parameters method is the easiest to use, but the literature data are at present available only at 100°C ; the inverse gas chromatography technique, on which they are based would have many technical difficulties at ambient temperatures. Finally, the UNIFAC method, while easy to use, is not based on any measurement involving the components of interest; it relies heavily on an assumption that a given chemical group behaves in a certain way irrespective of the structure of the rest of the molecule. In our opinion, the accuracy of all these four methods is comparable to that of the light scattering method.

(3) The interaction coefficients of all mixtures studied are rather small. This is explained as a result of a specific interaction between electron-accepting aromatic structures and electron-donating carbonyls.

ACKNOWLEDGMENT

The authors are grateful to The Robert A. Welch Foundation (grant F-1072) for supporting this work.

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