Refractive Indices and Densities of the System Acetone + Benzene + Cyclohexane at 298.15 K. Changes of Refractivity and of Volume on Mixing

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Refractive index and density for (acetone + benzene + cyclohexane) at 298.15 K are reported. Changes of refractivity and of volume on mixing over the composition range were derived. Relations for predicting these changes were established and analyzed.

Introduction

Accurate data on physical properties for liquid mixtures, including refractive index and density, are important from the theoretical and practical points of view. Traditionally, the refractive index of a solution can be predicted on the basis of various mixing rules presented in the literature. For binary systems, Heller (*1*) examined the most important mixing rules. If significant changes of refractivity and volume during mixing are present, as a result of physical and/or chemical interactions, some mixing rules will not be suitable for predictive calculations (*1–4*). To predict these changes in two- and three-component systems, Aminabhavi and Munk (*5*) developed a unified phenomenological approach for treating the change in any extensive thermodynamic property during mixing, which is based on the Flory–Huggins theory.

In a recent paper (*4*) the authors presented refractive index and density for acetone + benzene, benzene + cyclohexane, and acetone + cyclohexane at 298.15 K, over the entire composition range. In the present study, refractive index and density for the corresponding ternary system, acetone + benzene + cyclohexane at the same temperature, are measured.

Constituents of this three-component binary system belong to different chemical classes; hence, the presence of various binary and ternary interactions between the components is possible. Since the approach of Aminabhavi and Munk (*5*) seems to be promising for treating the investigated system, an attempt is made to examine its ability (a) to correlate satisfactorily the experimental data and (b) to help in better understanding of the interactions between the molecules from the points of view of the Flory–Huggins theory.

Experimental Section

Chemicals. Analytical grade acetone (Merck, molar mass M_A = 58.08 g mol^{-1}) was dried over anhydrous calcium chloride (Merck) and fractionated before use. Analar benzene (BHD, molar mass M_B = 78.11 g mol^{-1}) was shaken with concentrated sulfuric acid until the yellow color in the acid layer disappeared, washed with water, and dried with sodium. Finally, it was distilled twice. Only the middle cuts were used for experimental work. RP cyclohexane from Carlo Erba (molar mass M_C = 84.16 g mol^{-1}) was stirred with a mixture of HNO_3 and H_2SO_4 to remove benzene, washed with NaOH solution and water, dried with sodium, and fractionated.

Table 1. Comparison of Refractive Indices n_D and Densities ϱ of Pure Compounds with Selected Literature Data at 298.15 K

	n_D[a]		ϱ/(g cm^{-3})	
compd	exptl	lit.	exptl	lit.
acetone	1.3557	1.35599 (*7*) 1.35609	0.78508	0.78501 (*7*) 0.78507 0.78508
benzene	1.4978	1.49792 (*8*)	0.87360	0.8736 (*8a*)
cyclohexane	1.4231	1.42354 (*8*)	0.77386	0.77389 (*8b*)

[a] Data apply to the sodium D line.

The quality of the purified chemicals was checked by determining their refractive indices and densities at 298.15 K. These are in good agreement with selected literature values, as given in Table 1.

Measurements. To prepare systematically and accurately three-component mixtures of the constituents having different volatilities, the mixing cell and experimental procedure described by Radojković et al. (*6*) were used. All weighings of the individual components and of their mixtures were performed using a Mettler H20 balance with an accuracy of 0.1 mg. Typical masses of the liquid weighed were approximately 4.5 g.

Temperature was measured with an accuracy of ±0.01 K. Refractive indices were measured at the sodium D line with a Carl Zeiss Abbe refractometer at 298.15 ± 0.01 K. The precision of the instrument was ±0.0001 refractive index unit. It is believed that the overall uncertainty in refractive index measurements of the pure liquids and of their mixtures was about ±0.0003 refractive index unit.

Densities of the pure components and of the ternary mixtures were measured at 298.15 ± 0.01 K with an oscillatory-type densimeter (*9*), Model DMA 02C, developed by Anton Paar K.G., Austria. The accuracy of the density measurements was estimated to be within ±0.00001 g cm^{-3}.

The volume fraction error of the mixtures studied was estimated to be within ±0.0001, depending on composition.

Results and Discussion

Refractive indices n_{123} were measured for 57 ternary composition points. Except for the densities taken from

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Table 2. System Acetone (1) + Benzene (2) + Cyclohexane (3) at 298.15 K: Experimental Refractive Indices n_{123}, Densities ϱ_{123}, and Changes of Specific Refractivity ΔR_{mix} and Specific Volume ΔV_{mix} for Volume Fractions ϕ

ϕ_1	ϕ_2	n_{123}[a]	ϱ_{123}[a]/(g cm^{-3})	$10^3\Delta R_{mix}$[b]/(cm^3 g^{-1})	$10^3\Delta V_{mix}$[c]/(cm^3 g^{-1})
0.0069	0.0129	1.4229	0.77438	0.01	1.16
0.0072	0.1099	1.4287	0.78196	0.01	4.24
0.0066	0.2158	1.4356	0.79106	−0.01	6.40
0.0081	0.4523	1.4524	0.81352	−0.02	8.11
0.0078	0.7141	1.4728	0.84097	0.12	5.90
0.0083	0.8853	1.4871	0.86044	0.10	2.59
0.0089	0.9455	1.4924	0.86761	0.01	1.12
0.0091	0.9800	1.4954	0.87180	−0.08	0.23
0.0348	0.0422	1.4220	0.77559	0.03	4.47
0.0364	0.0847	1.4248	0.77905	0.03	5.72
0.0355	0.1749	1.4305	0.78698	0.02	7.45
0.0372	0.3649	1.4438	0.80469	−0.01	9.02
0.0379	0.4593	1.4504	0.81410	0.01	8.84
0.0386	0.6139	1.4628	0.83046	0.09	7.37
0.0398	0.7289	1.4720	0.84312	0.17	5.44
0.0417	0.8411	1.4814	0.85619	0.12	2.91
0.0409	0.8987	1.4865	0.86296	−0.03	1.44
0.0422	0.9474	1.4906	0.86889	−0.27	0.05
0.0710	0.0429	1.4189	0.77457	0.06	6.95
0.0714	0.0869	1.4215	0.77833	0.04	7.92
0.0755	0.3668	1.4410	0.80496	0.03	10.02
0.0774	0.4673	1.4486	0.81542	0.03	9.36
0.0801	0.6252	1.4610	0.83247	0.14	7.08
0.0818	0.7974	1.4752	0.85235	0.19	3.08
0.0830	0.8560	1.4803	0.85932	0.03	1.39
0.1846	0.0093	1.4072	0.76966	0.22	11.64
0.1872	0.0451	1.4092	0.77289	0.13	12.13
0.1883	0.0914	1.4126	0.77749	0.09	12.50
0.1934	0.2350	1.4227	0.79184	0.13	12.45
0.2042	0.4951	1.4422	0.82026	0.09	8.40
0.2128	0.6615	1.4560	0.84010	0.24	3.52
0.2143	0.7230	1.4613	0.84767	0.27	1.39
0.3159	0.0473	1.4000	0.77321	0.11	14.69
0.3176	0.0968	1.4037	0.77833	0.06	14.42
0.3287	0.2486	1.4141	0.79495	0.17	12.29
0.3364	0.3547	1.4221	0.80705	0.13	9.73
0.3486	0.5243	1.4358	0.82764	0.03	4.02
0.3506	0.5841	1.4409	0.83511	0.06	1.67
0.4090	0.0496	1.3935	0.77407	0.02	15.22
0.4130	0.0992	1.3970	0.77954	−0.04	14.48
0.4420	0.4281	1.4219	0.81891	−0.02	4.54
0.4470	0.4866	1.4268	0.82625	−0.09	1.97
0.5098	0.0508	1.3870	0.77563	−0.16	14.77
0.5156	0.1040	1.3908	0.78174	−0.20	13.42
0.5221	0.1579	1.3949	0.78833	−0.11	11.79
0.5340	0.2696	1.4031	0.80226	0.04	7.68
0.5397	0.3273	1.4076	0.80963	0.01	5.19
0.5472	0.3858	1.4125	0.81733	−0.08	2.36
0.6787	0.0557	1.3770	0.78015	−0.54	11.41
0.6876	0.1113	1.3812	0.78732	−0.51	8.96
0.6974	0.1654	1.3853	0.79451	−0.33	6.26
0.7029	0.2272	1.3901	0.80277	−0.13	3.12
0.7104	0.2748	1.3942	0.80927	−0.07	0.36
0.8642	0.0228	1.3640	0.78232	−0.58	5.64
0.8704	0.0587	1.3668	0.78731	−0.71	3.59
0.8797	0.1065	1.3702	0.79437	−0.57	0.66
0.9368	0.0475	1.3622	0.78852	−0.58	0.80

[a] Experimental measurements. [b] Values obtained from eq 2. [c] Values obtained from eq 1.

our previous work, Radojković et al. (*6*), the new density data for 19 additional compositions close to the binary borders of the triangular composition field were measured. These data along with compositions for each point are shown in the first four columns of Table 2.

Some brief remarks about accuracy and reliability of the work should be given. Since, by our knowledge, refractive index and density data for the ternary system under study were not reported by other authors, the worth of the present data could not be evaluated by comparison. But, taking into consideration the quality of the results for pure substances (Table 1) and for the corresponding binary systems (our previous papers, refs 4, 6, and 10), a similar quality of the measurements for the ternary mixtures (Table 2) could be supposed to exist. As in most other instances, the inaccuracy of the present ternary data is expected to increase toward regions of higher dilution, i.e. for nearly binary mixtures.

The change in specific volume on mixing ΔV_{mix} and change in specific refractivity ΔR_{mix} were calculated

$$\Delta V_{mix}/(\text{cm}^3\ \text{g}^{-1}) = [V_{123} - \sum_{i=1}^{3}(\omega_i V_i)] \quad (1)$$

$$\Delta R_{mix}/(\text{cm}^3\ \text{g}^{-1}) = [R_{123} - \sum_{i=1}^{3}(\omega_i R_i)] \quad (2)$$

where ω_i denotes mass fraction of component i; V_i and V_{123} (both in cm^3 g^{-1}) stand for the specific volume of component i and of the ternary mixture, respectively. The ΔV_{mix} and ΔR_{mix} values are shown in the last two columns of Table 2.

The specific refractivity R_{123} is defined as

$$R_{123}/(\text{cm}^3\ \text{g}^{-1}) = P_{123}V_{123} \quad (3)$$

where the polarizability P_{123} is related to the refractive index n_{123} by the Lorentz–Lorenz relation (*5*)

$$P_{123} = \frac{n_{123}^2 - 1}{n_{123}^2 + 2} \quad (4)$$

Correlation of the ΔV_{mix} and ΔR_{mix} values from Table 2 was based on the relationships proposed by Aminabhavi and Munk (*5*):

$$\Delta V_{mix} = (\sum_{i=1}^{3}\omega_i V_i)[A_{12}\phi_1\phi_2 + A_{23}\phi_2\phi_3 + A_{31}\phi_3\phi_1 + A_{123}\phi_1\phi_2\phi_3] \quad (5)$$

$$\Delta R_{mix} = (\sum_{i=1}^{3}\omega_i V_i)[B_{12}\phi_1\phi_2 + B_{23}\phi_2\phi_3 + B_{31}\phi_3\phi_1 + B_{123}\phi_1\phi_2\phi_3] \quad (6)$$

ϕ_i (i = 1, 2, 3) denotes the volume fraction of component i; A_{ij} and B_{ij} are binary, whereas A_{123} and B_{123} represent ternary interaction parameters.

According to this approach, the parameters A_{ij} and B_{ij} were evaluated from the corresponding experimental data reported in Table 2 of ref 4 by employing the relations

$$A_{ij} = (\phi_i\varrho_i + \phi_j\varrho_j - \varrho_{ij})/(\phi_i\phi_j\varrho_{ij}) \quad (7)$$

$$B_{ij} = \{[P_{ij}(\phi_i\varrho_i + \phi_j\varrho_j)/\varrho_{ij}] - P_i\phi_i - P_j\phi_j\}/(\phi_i\phi_j) \quad (8)$$

In eqs 7 and 8, ϱ and P denote density and polarizability of the corresponding component (i or j), respectively, whereas ϱ_{ij} represents density of the mixture; P_{ij} stands for the Lorentz–Lorenz polarizability $P_{ij} = (n_{ij}^2 - 1)/(n_{ij}^2 + 2)$. The obtained values for A_{ij} and B_{ij} were fitted to the equations

$$A_{ij} = \sum_{l=0}^{k} a_l(2\phi_j - 1)^l \quad (9)$$

Table 3. Coefficients of Equations 9 (a_l) and 10 (b_l), Their Standard Deviations, and Standard Deviations of the Fits for the Binary Systems at 298.15 K

mixture	l	$10^3 a_l$	$10^3\sigma(a_l)^a$	$10^3 b_l$	$10^3\sigma(b_l)^a$	$10^3\sigma(A_{ij})^b$	$10^3\sigma(B_{ij})^b$
acetone (1) + benzene (2)	0	−2.83	0.27	−0.60	0.58	0.79	0.92
	1	−2.90	0.47	1.44	1.72		
	2			9.32	4.62		
	3			−0.03	3.29		
	4			−22.47	6.46		
benzene (2) + cyclohexane (3)	0	25.66	0.14	−0.02	0.20	0.26	0.37
	1	3.23	0.51	−0.64	0.26		
	2	1.32	0.39	0.97	0.55		
	3	1.08	0.97				
cyclohexane (3) + acetone (1)	0	49.35	0.34	0.52	0.48	0.60	0.86
	1	−5.52	1.16	−2.44	0.63		
	2	8.28	1.01	−1.93	1.34		
	3	−12.74	2.33				

[a] $\sigma_{coeff} = (c_{l,l})^{0.5}\sigma_{fit}$, $l = 0, 1, ..., k$; coeff = a_l for eq 9 or coeff = b_l for eq 10. [b] $\sigma_{fit} = \{\sum_{l=1}^{n} [f(2\phi_j - 1)_{l,exptl} - f(2\phi_j - 1)_{l,calcd}]^2/(n - k - 1)\}^{0.5}$, $j = 1, 2, 3$; $f = A_{12}$ for eq 9 or $f = B_{12}$ for eq 10.

$$B_{ij} = \sum_{l=0}^{k} b_l(2\phi_j - 1)^l \qquad (10)$$

Values of the coefficients a_l and b_l are collected in Table 3.

To establish the expressions for ΔV_{mix} and ΔR_{mix}, values of the parameters A_{123} and B_{123} should be known. For their evaluation, two calculational procedures were performed. At first, the values of A_{123} and B_{123} were chosen to be zero, so that ΔV_{mix} and ΔR_{mix} were expressed only by the binary parameters A_{ij} and B_{ij} (calculated according to eqs 9 and 10, and using the a_l and b_l values from Table 3) as follows:

$$\Delta V_{mix} = (\sum_{i=1}^{3} \omega_i V_i)[A_{12}\phi_1\phi_2 + A_{23}\phi_2\phi_3 + A_{31}\phi_3\phi_1] \qquad (11)$$

$$\Delta R_{mix} = (\sum_{i=1}^{3} \omega_i V_i)[B_{12}\phi_1\phi_2 + B_{23}\phi_2\phi_3 + B_{31}\phi_3\phi_1] \qquad (12)$$

The second calculational procedure tested consisted of employing eqs 5 and 6 in which only parameters A_{123} and B_{123}, respectively, were regarded as unknown quantities; their best values were computed from the corresponding data of Table 2 by the least-squares method as $A_{123} = 3.0 \times 10^{-4}$ and $B_{123} = 3.3 \times 10^{-5}$.

To assess the reliability of the above correlating procedures, standard deviations $\sigma(\Delta V_{mix})$ and $\sigma(\Delta R_{mix})$ have been computed. For each of the procedures mentioned, the same values $\sigma(\Delta V_{mix}) = 0.00038$ g cm^{-3} and $\sigma(\Delta R_{mix}) = 0.00017$ refractive index unit, respectively, were obtained, so that simpler forms of eqs 11 and 12 can be proposed. When densities and refractive indices were recalculated, and compared with the experimental data, the following average absolute deviations $\delta(\pi)$

$$\delta(\pi) = \frac{1}{n}\sum_{l=1}^{n} |\pi_{exptl} - \pi_{calcd}|_l, \ \pi = \varrho_{123} \text{ or } n_{123} \qquad (13)$$

were computed: $\delta(\varrho_{123}) = 0.0002_1$ g cm^{-3} and $\delta(n_{123}) = 0.0002_1$. These results indicate that the refractive indices are reproduced with an inaccuracy close to the experimental error, whereas the corresponding error for density was greater; however, the obtained correlation used for back calculation of density can be regarded as acceptable if the reproduction of the experimental data within two units of the fourth decimal place is sufficient.

As outlined above, both ternary interaction parameters have negligibly small values. Hence, it could be plausibly stated that only binary interactions between the constituents are relevant for adequate interpretation of the changes of refractivity and volume on mixing. However, complete evidence of the behavior of the investigated system is still lacking with which to draw definite conclusions on the structure of this liquid mixture. In that respect, the results of the present work could be regarded as a contribution to a better insight into relevant molecular interactions.

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