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Excess Volume and Excess Polarizability during Mixing of Binary Solvents

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Refractive-index and density data are presented for 10 binary solvent mixtures comprising benzene, chlorobenzene, bromobenzene, toluene, acetophenone, dimethyl sulfoxide, carbon tetrachloride, and water. All of these data were collected at 20 °C over the entire composition ranges of the mixtures. Previously developed relations for the excess volume and excess polarizability of mixing were employed to analyze the binary data.

Introduction

In an earlier study (*1–3*), we measured the hydrodynamic properties of binary solvent mixtures. In this study, as part of a general program to pursue our investigation of the properties of binary mixtures, we have undertaken an extensive investigation of the measurement of refractive index at three different wavelengths (589, 546, and 436 nm) and density at 20 °C as a function of composition of the mixtures. The 10 binary mixtures studied were benzene (1)–acetophenone (2), bromobenzene (1)–acetophenone (2), acetophenone (1)–chlorobenzene (2), acetophenone (1)–toluene (2), dimethyl sulfoxide (1)–bromobenzene (2), water (1)–dimethyl sulfoxide (2), benzene (1)–chlorobenzene (2), carbon tetrachloride (1)–chlorobenzene (2), bromobenzene (1)–benzene (2), and bromobenzene (1)–chlorobenzene (2). These binary data were further analyzed by using the relations developed earlier (*1*, *4*, *5*).

Experimental Part

The solvents used in this study were of reagent grade. All of the solvents were purified by fractionating through a 6-ft column. Further purity of these solvents was tested by using gas chromatography. The various physicochemical properties of the solvents used together with mol % impurity are presented in Table I. Double-distilled water was used throughout the entire work. Particular care was taken in handling hygroscopic liquids as the slightest traces of water were found to affect the data of pure solvents quite markedly.

The solvent mixtures were prepared by weighing appropriate volumes of pure solvents; the volume fractions were calculated from the weights and from densities of pure components. Refractive indexes of pure solvents and solvent mixtures were measured with a Bausch and Lomb precision refractometer equipped with mercury and sodium light sources. The precision of the instrument as quoted by the manufacturer is ±0.000 03 unit. The initial calibration of the instrument was made at 20 °C by using the standard glass test piece provided by the manufacturer. Calibration checks were made routinely with distilled water, and occasional rechecks were made with the glass test piece. Samples were applied to the prism of the refractometer as quickly as possible to minimize possible evaporation and changes in composition. all measurements were made at 20 °C by using the sodium (589 nm) line and the mercury green (546 nm) and blue (436 nm) lines. All densities were measured with a precision density meter, Model DMA 02C, manufactured by Anton Paar K.G., Austria, by a procedure described earlier (*6*). The data for density and refractive index for pure solvents agreed very well (Table I) with the literature values (*11*).

Results and Discussion

The experimental data for both density and refractive index are presented in Tables II–XI. In the calculation of the excess properties from these data, we have used the following relations for the changes in volume and refractivity during mixing (*1*, *4*, *5*):

$$\Delta V_{mix} = (\sum_{i=1}^{2} N_i V_i) A_{12} \phi_1 \phi_2 \quad (1)$$

$$\Delta R_{mix} = (\sum_{i=1}^{2} N_i V_i) B_{12} \phi_1 \phi_2 \quad (2)$$

Here, N_i, V_i, and ϕ_i represent the number of moles, the molar volume, and the volume fraction ($\phi_i \equiv N_i V_i / \sum_j N_j V_j$) of the ith

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Table I. Some Physicochemical Properties of Pure Solvents at 20 °C

solvent	impurity, mol %	mol wt	bp, °C	density, g/mL this work	density, g/mL lit.[a]	n_D this work	n_D lit.[a]
benzene	<0.002	78.12	80.0	0.878 66	0.878 65	1.501 11	1.501 10
chlorobenzene	0.01	112.56	132.2	1.105 86	1.105 84	1.524 12	1.524 10
bromobenzene	0.015	157.02	156.1	1.495 04	1.495 04	1.559 71	1.559 70
acetophenone	0.025	120.16	202.2	1.028 16	1.028 14	1.537 19	1.537 18
carbon tetrachloride	0.02	153.82	76.54	1.594 03	1.594 04	1.460 11	1.460 10
dimethyl sulfoxide	<0.03	78.13	190.0	1.101 45	1.101 44	1.477 04	1.477 00
toluene	0.01	92.15	110.9	0.866 95	0.866 94	1.496 12	1.496 10

[a] Reference *11*.

Table II. Density and Refractive-Index Data for Acetophenone (1)-Benzene (2) Mixture at 20 °C

ϕ_2	density, g/mL	refractive index 589 nm	546 nm	436 nm
0.0	1.028 16	1.537 19	1.536 62	1.558 16
0.1004	1.013 28	1.529 78	1.534 58	1.555 75
0.1962	0.999 49	1.526 85	1.531 55	1.552 34
0.2948	0.985 15	1.523 92	1.528 55	1.549 06
0.3975	0.970 06	1.520 75	1.525 32	1.545 44
0.4948	0.955 44	1.517 65	1.522 18	1.541 83
0.5991	0.939 97	1.514 33	1.518 78	1.538 17
0.6947	0.925 70	1.511 27	1.515 63	1.534 66
0.7977	0.910 14	1.507 73	1.512 06	1.530 73
0.8991	0.894 75	1.504 22	1.508 55	1.526 68
1.0	0.878 66	1.501 11	1.504 85	1.522 58

Table III. Density and Refractive-Index Data for Acetophenone (1)-Bromobenzene (2) Mixture at 20 °C

ϕ_2	density, g/mL	refractive index 589 nm	546 nm	436 nm
0.0	1.028 16	1.537 19	1.536 62	1.558 16
0.1019	1.074 69	1.535 59	1.540 43	1.561 97
0.2009	1.120 40	1.538 08	1.542 88	1.564 26
0.2991	1.165 81	1.540 58	1.545 39	1.566 73
0.4005	1.212 70	1.542 93	1.547 76	1.568 95
0.4993	1.258 50	1.545 71	1.550 48	1.571 53
0.5996	1.304 81	1.548 33	1.553 13	1.574 08
0.6961	1.349 51	1.550 89	1.555 63	1.576 49
0.7974	1.396 62	1.553 58	1.558 35	1.579 09
0.8968	1.443 08	1.556 19	1.561 00	1.581 63
1.0	1.495 04	1.559 71	1.563 64	1.584 20

Table IV. Density and Refractive-Index Data for Chlorobenzene (1)-Acetophenone (2) Mixture at 20 °C

ϕ_2	density, g/mL	refractive index 589 nm	546 nm	436 nm
0.0	1.105 86	1.524 12	1.528 40	1.546 66
0.1048	1.098 51	1.525 12	1.529 45	1.548 08
0.1988	1.091 18	1.526 09	1.530 44	1.549 36
0.2963	1.083 36	1.526 97	1.531 40	1.550 67
0.3957	1.075 43	1.527 89	1.532 37	1.551 99
0.4941	1.067 86	1.528 69	1.533 25	1.553 21
0.5950	1.059 76	1.529 61	1.534 21	1.554 48
0.6970	1.051 90	1.530 47	1.535 12	1.555 75
0.7969	1.043 93	1.531 34	1.536 07	1.557 01
1.0	1.028 16	1.537 19	1.536 62	1.558 18

component. The phenomenological parameters A_{12} and B_{12} represent the contact terms between two solvents, and both are functions of composition of the mixture. They can be easily calculated by using the following relations:

$$A_{12} = (\phi_1\rho_1 + \phi_2\rho_2 - \rho)/(\phi_1\phi_2\rho) \quad (3)$$

$$B_{12} = [p(\phi_1\rho_1 + \phi_2\rho_2)/\rho - p_1\phi_1 - p_2\phi_2]/(\phi_1\phi_2) \quad (4)$$

Here, $\rho_i \equiv 1/V_i$ is the density of pure component i, and p is the Lorentz–Lorenz polarizability $p \equiv (n^2 - 1)/(n^2 + 2)$, with n as refractive index. In the analysis of the data, the experimentally

Table V. Density and Refractive-Index Data for Toluene (1)-Acetophenone (2) Mixture at 20 °C

ϕ_2	density, g/mL	refractive index 589 nm	546 nm	436 nm
0.0	0.866 95	1.496 12	1.500 12	1.517 20
0.1008	0.883 70	1.500 20	1.504 29	1.521 83
0.2025	0.900 37	1.504 27	1.508 40	1.526 40
0.3028	0.916 14	1.507 41	1.511 65	1.529 97
0.4051	0.932 68	1.511 86	1.516 18	1.535 07
0.5039	0.948 97	1.515 65	1.520 04	1.539 42
0.6036	0.964 63	1.519 20	1.523 69	1.543 47
0.7002	0.981 07	1.522 84	1.527 38	1.547 67
0.8004	0.996 74	1.526 27	1.530 99	1.551 68
0.9011	1.012 43	1.529 69	1.534 77	1.555 58
1.00	1.028 16	1.537 19	1.536 63	1.558 20

Table VI. Density and Refractive-Index Data for Bromobenzene (1)-Dimethyl Sulfoxide (2) Mixture at 20 °C

ϕ_2	density, g/mL	refractive index 589 nm	546 nm	436 nm
0.0	1.495 04	1.559 71	1.563 68	1.584 20
0.1010	1.451 81	1.551 40	1.555 91	1.575 62
0.2019	1.412 46	1.543 64	1.548 09	1.566 95
0.3031	1.373 36	1.535 49	1.539 71	1.557 61
0.4054	1.333 91	1.527 63	1.531 76	1.548 74
0.5047	1.295 20	1.519 93	1.523 82	1.539 83
0.6029	1.257 28	1.511 99	1.515 41	1.530 21
0.7039	1.217 48	1.503 32	1.506 71	1.520 96
0.8034	1.179 81	1.495 14	1.498 15	1.511 50
0.8984	1.143 20	1.487 66	1.490 35	1.502 82
1.0	1.101 45	1.477 04	1.481 66	1.493 19

Table VII. Density and Refractive-Index Data for Dimethyl Sulfoxide (1)-Water (2) Mixture at 20 °C

ϕ_2	density, g/mL	refractive index 589 nm	546 nm
0.0	1.101 45	1.477 04	1.481 67
0.1022	1.103 64	1.467 70	1.470 16
0.1973	1.103 20	1.455 95	1.458 35
0.2951	1.098 47	1.442 37	1.444 57
0.3955	1.088 65	1.427 69	1.429 88
0.4976	1.075 67	1.412 19	1.414 17
0.5968	1.059 97	1.395 64	1.397 27
0.6951	1.043 62	1.378 91	1.380 58
0.7976	1.027 85	1.363 64	1.364 61
0.8974	1.012 88	1.349 42	1.350 28
1.0	0.998 23	1.334 98	1.335 43

obtained values of A_{12} and B_{12} were fitted to the following quadratic equations to evaluate the coefficients from a nonlinear least-squares method using an IBM 4341 computer:

$$A_{12} = a_1 + a_2(\phi_2 - \phi_1) + a_3(\phi_2 - \phi_1)^2 \quad (5)$$

$$B_{12} = b_1 + b_2(\phi_2 - \phi_1) + b_3(\phi_2 - \phi_1)^2 \quad (6)$$

The coefficients for A_{12} and B_{12} are tabulated in Tables XII and XIII, respectively. The back calculation of density and

Table VIII. Density and Refractive-Index Data for Chlorobenzene (1)-Benzene (2) Mixture at 20 °C

ϕ_2	density, g/mL	refractive index 589 nm	546 nm	436 nm
0.0	1.105 86	1.524 12	1.528 40	1.546 69
0.0990	1.084 10	1.521 64	1.525 89	1.544 10
0.1964	1.061 75	1.519 29	1.523 55	1.541 74
0.2965	1.038 96	1.516 88	1.521 14	1.539 28
0.3977	1.015 97	1.514 47	1.518 69	1.536 74
0.4968	0.993 47	1.512 14	1.516 35	1.534 40
0.5970	0.970 72	1.509 81	1.514 05	1.532 02
0.6953	0.948 36	1.507 56	1.511 72	1.529 68
0.7967	0.925 40	1.505 16	1.509 34	1.527 26
0.8981	0.902 38	1.502 79	1.507 00	1.524 84
1.0	0.878 66	1.501 11	1.504 83	1.522 60

Table IX. Density and Refractive-Index Data for Chlorobenzene (1)-Carbon Tetrachloride (2) Mixture at 20 °C

ϕ_2	density, g/mL	refractive index 589 nm	546 nm	436 nm
0.0	1.105 86	1.524 12	1.528 40	1.546 69
0.1017	1.156 28	1.518 79	1.522 78	1.540 28
0.2033	1.205 62	1.512 74	1.517 04	1.533 86
0.3074	1.254 10	1.506 80	1.510 47	1.526 16
0.4044	1.303 46	1.500 34	1.503 96	1.519 20
0.5028	1.351 30	1.494 10	1.497 46	1.511 85
0.6008	1.399 57	1.487 96	1.490 96	1.504 20
0.7013	1.446 54	1.481 86	1.484 51	1.497 00
0.7971	1.495 02	1.474 49	1.477 40	1.489 00
0.9008	1.545 92	1.467 43	1.469 94	1.480 66
1.00	1.594 03	1.460 11	1.462 57	1.472 30

Table X. Density and Refractive-Index Data for Bromobenzene (1)-Benzene (2) Mixture at 20 °C

ϕ_2	density, g/mL	refractive index 589 nm	546 nm	436 nm
0.0	1.495 04	1.559 71	1.563 65	1.584 20
0.0992	1.432 11	1.553 76	1.558 42	1.578 74
0.1993	1.371 74	1.547 77	1.558 26	1.567 03
0.2995	1.311 83	1.541 87	1.546 34	1.566 14
0.4003	1.249 60	1.535 81	1.540 35	1.559 82
0.4985	1.189 31	1.530 12	1.534 51	1.553 73
0.5994	1.127 68	1.524 10	1.528 53	1.547 45
0.6990	1.065 25	1.518 38	1.522 69	1.541 31
0.7981	1.004 35	1.514 12	1.516 80	1.535 07
0.8993	0.941 76	1.506 56	1.510 70	1.528 78
1.00	0.878 66	1.501 11	1.505 21	1.523 04

Table XI. Density and Refractive-Index Data for Chlorobenzene (1)-Bromobenzene (2) Mixture at 20 °C

ϕ_2	density, g/mL	refractive index 589 nm	546 nm	436 nm
0.00	1.105 86	1.524 12	1.528 41	1.546 67
0.0994	1.144 85	1.527 63	1.531 44	1.550 76
0.2016	1.184 18	1.531 08	1.535 54	1.554 16
0.2989	1.221 52	1.534 47	1.538 82	1.557 80
0.3977	1.259 64	1.537 82	1.542 29	1.561 47
0.4977	1.297 87	1.541 33	1.545 84	1.565 19
0.5987	1.336 91	1.544 86	1.549 41	1.569 07
0.7024	1.376 68	1.548 09	1.552 71	1.572 54
0.8000	1.414 25	1.551 93	1.556 58	1.576 66
0.8995	1.452 55	1.555 46	1.560 20	1.580 52
1.00	1.495 04	1.559 71	1.563 66	1.584 19

refractive index for all mixtures using the evaluated values of the parameters A_{12} and B_{12} reproduced the data within three units in the fourth decimal place. It should be noted that for mixtures such as dimethyl sulfoxide (1)–bromobenzene (2) and carbon tetrachloride (1)–chlorobenzene (2) the term B_{12} is greater as compared to the rest of the mixtures. A dependence of B_{12} on wavelength was also observed in most cases, but

Table XII. Computer Evaluation of the Coefficients Needed to Calculate A_{12} from Eq 5

mixture	$10^3 a_1$	$10^4 a_2$	$10^4 a_3$
benzene (1)-acetophenone (2)	−5.83	6.07	0.34
bromobenzene (1)-acetophenone (2)	2.36	9.64	3.78
acetophenone (1)-chlorobenzene (2)	−0.45	−7.39	−19.79
acetophenone (1)-toluene (2)	−4.11	−7.56	−85.43
dimethyl sulfoxide (1)-bromobenzene (2)	2.19	3.03	10.90
water (1)-dimethyl sulfoxide (2)	−89.43	521.74	256.69
benzene (1)-chlorobenzene (2)	0.86	−7.26	−0.77
carbon tetrachloride (1)-chlorobenzene (2)	2.03	16.07	−11.26
bromobenzene (1)-benzene (2)	−11.14	19.62	2.56
bromobenzene (1)-chlorobenzene (2)	0.47	2.11	−0.31

Table XIII. Computer Evaluation of the Coefficients Needed To Calculate B_{12} from Eq 6

mixture	wavelength, nm	$10^4 b_1$	$10^4 b_2$	$10^4 b_3$
benzene (1)-acetophenone (2)	589	4.00	−19.04	9.84
	546	4.70	−17.33	17.09
	436	5.40	−17.16	14.05
bromobenzene (1)-acetophenone (2)	589	12.80	−16.90	33.83
	546	13.60	−16.92	38.64
	436	13.90	−19.00	39.91
acetophenone (1)-chlorobenzene (2)	589	13.40	14.18	5.23
	546	14.80	13.94	8.59
	436	15.60	14.42	8.41
acetophenone (1)-toluene (2)	589	14.80	22.96	7.47
	546	15.20	24.03	12.31
	436	15.00	24.22	10.83
dimethyl sulfoxide (1)-bromobenzene (2)	589	40.10	−3.30	5.44
	546	44.30	−7.17	−5.75
	436	46.30	−10.28	2.31
water (1)-dimethyl sulfoxide (2)	589	−96.00	6.86	28.18
	546	−87.00	11.04	22.98
benzene (1)-chlorobenzene (2)	589	−6.80	−10.96	−20.70
	546	−6.40	−8.55	−10.77
	436	−5.80	−10.45	−17.51
carbon tetrachloride (1)-chlorobenzene (2)	589	60.90	6.22	13.58
	546	62.00	1.42	18.09
	436	55.60	−27.93	−21.33
bromobenzene (1)-benzene (2)	589	−29.10	−8.36	13.90
	546	−29.10	−3.52	−3.50
	436	−29.90	2.04	−14.72
bromobenzene (1)-chlorobenzene (2)	589	−1.20	−0.57	4.16
	546	0.10	0.67	5.66
	436	0.10	0.33	7.84

such a dependence was not significant. Negative values of B_{12} were observed for some systems such as water (1)–dimethyl sulfoxide (2), bromobenzene (1)–benzene (2), and benzene (1)–chlorobenzene (2). For these latter two mixtures, the values of B_{12} were almost equal to zero, indicating thereby that the interactions between components of these mixtures are negligible. Such a behavior was also observed with the binary data of Sumer et al. (7), who studied the mixtures benzene (1)–xylene (2), benzene (1)–toluene (2), and xylene (1)–toluene (2) by using the sodium yellow line at three different temperatures (20, 30, and 40 °C). The dependence of B_{12} on temperature was not noticeable in their data. However, intermediate values were observed for the rest of the systems. Similarly, negative values were observed for the parameter A_{12} in the systems,

bromobenzene (1)–benzene (2), water (1)–dimethyl sulfoxide (2), acetophenone (1)–toluene (2), acetophenone (1)–chlorobenzene (2), and benzene (1)–acetophenone (2). For the remaining mixtures we obtained positive values for A_{12}. However, for bromobenzene (1)–chlorobenzene (2) mixtures, the excess-volume parameter, A_{12}, was negligibly small. In the data of Sumer et al. (7), the values of A_{12} for toluene (1)–benzene (2) were ~5 times larger than in our systems. Further, they also studied the dependence of A_{12} on temperature, and it was found to be decreasing with increasing temperature for all of their systems. (A study along these lines is in progress for our systems.) The magnitudes of the parameters A_{12} and B_{12} depend strongly on the nature of reacting groups. Similar observations were made by several earlier workers (8–10).

Conclusions

Both refractive indexes and densities were measured for 10 carefully selected binary systems. The properties such as excess volume and excess polarizability of mixing were studied. Obviously, it seems to be quite clear that both of the parameters A_{12} and B_{12} are necessary to get a better insight into the structure of liquid mixtures. Obviously, data on more systems containing different chemical groups are needed to arrive at definite conclusions.

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Vapor–Liquid Equilibria in Binary Systems Containing 1,3-Dioxolane at Isobaric Conditions. 2. Binary Mixtures of 1,3-Dioxolane with Toluene

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Vapor–liquid equilibrium data of binary mixtures of 1,3-dioxolane with toluene were obtained with a Stage–Müller apparatus at pressures of 150, 300, 500, 650, and 740 mmHg. The values of the activity coefficients were correlated by means of the Wilson expression, whose parameters show a marked dependence on the temperature. The values of the activity coefficients lead to the conclusion that the system is nearly ideal in the liquid phase.

In two previous papers (1, 2) we have studied the vapor–liquid equilibria of the following systems: (a) 1,3-dioxolane–water (1); (b) 1,3-dioxolane–*trans*-1,2-dichloroethylene (2); (c) 1,3-dioxolane–trichloroethylene (2); (d) 1,3-dioxolane–tetrachloroethylene (2). The values of the liquid-phase activity coefficients, evaluated from the experimental data, show that system a is strongly nonideal, systems b and c are almost ideal, and system d is appreciably nonideal.

In this paper we extend our study to the system 1,3-dioxolane–toluene. The vapor–liquid experimental data are correlated by means of the Wilson equation.

Experimental Section

1,3-Dioxolane (Fluka product, analytical grade, 99%) was purified following the procedure given in ref 1. The toluene (Carlo Erba RPE product) was used without purification. The vapor–liquid measurements were carried out with a Stage–Müller apparatus, described elsewhere (4), at P = 150, 300, 500, 650, and 740 mmHg.

Table I and Figure 1 collect the experimental t–x_1–y_1 values (where t is the temperature and x_1 and y_1 are the mole fractions of 1,3-dioxolane in the liquid and vapor phases, respectively). The values of x_1 and y_1 were determined with an Abbe refractometer; the refractive index–composition data of the system 1,3-dioxolane–toluene are reported in Table II. The experimental errors for the measured properties P, t, x_1, and y_1 are 2 mmHg, 0.1 °C, 0.2%, and 0.2%, respectively. The literature refractive index of toluene is n^{25}_D = 1.4941 (3); the toluene molar volume is obtained from the density of the pure component at 20 °C (3). The vapor pressures of the pure toluene and 1,3-dioxolane are expressed by the usual relation $\log P^0 = A + B/T$ (P^0 in mmHg) obtained from the vapor–liquid data of this work with a least-squares method. For the component toluene A = 7.711 and B = −1851.1, whereas for

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