x_2 mole fraction of the second component, i.e., solvent
y mole fraction of the acid in vapor phase

Registry No. $(CH_3)_2CHCOOH$, 79-31-2; $(CH_3)_3CCOOH$, 75-98-9; c-C_6H_{12}, 110-82-7; n-C_7H_{16}, 142-82-5.

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Predicting Refractive Index and Density Increments of Binary Solvent Mixtures

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Refractive indices and densities of six binary liquid mixtures measured at 20 °C for three wavelengths (589, 546, and 436 nm) have been used to predict their increments. Dependence of refractive index and density increments has been discussed as a function of composition of the mixture.

For a satisfactory thermodynamic treatment of polymers in mixed solvents it seemed important to have accurate values of refractive index and density increments (*1-3*). While these increments can be measured experimentally for polymer solutions, no accurate procedure exists to measure them in neat solvent mixtures. In this study, an attempt is made to present equations which could be successfully used to predict both refractive index and density increments of solvent mixtures by using refractive index and density data on pure solvents and their mixtures. Accordingly, refractive indices and densities have been measured for six binary mixtures comprising benzene, cyclohexane, ethyl acetate, and carbon tetrachloride at 20 °C over the entire range of composition for each mixture. The data are used to predict refractive index and density increments of solvent mixtures; a dependence of these quantities on mixture composition is also discussed.

Theory

To incorporate the changes of volume and refractivity, we use the following relations (*2*, *4*)

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

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

where A_{12} and B_{12} are the empirical parameters which depend on composition of the mixture; ϕ_i is the volume fraction of the ith component in a mixture.

Lorentz-Lorenz relation leads to the definition of molar refractivity, R_i, of pure substance i as (*5*)

$$R_i = [(n_i^2 - 1)/(n_i^2 + 2)](M_i/\rho_i) \quad (3)$$

where n_i, M_i, and ρ_i represent the refractive index, molecular weight, and density of the ith component in the mixture. However, the refractivity, R, of a mixture is defined as the product of polarizability P and volume V of the system (*6*). Thus

$$R \equiv PV \quad (4)$$

so that

$$P \equiv (n^2 - 1)/(n^2 + 2) \quad (5)$$

where n is the refractive index of the mixture. For binary mixtures the following relations are feasible

$$\rho = (\phi_1\rho_1 + \phi_2\rho_2)/(1 + A_{12}\phi_1\phi_2) \quad (6)$$

$$P = (\phi_1 P_1 + \phi_2 P_2 + B_{12}\phi_1\phi_2)/(1 + A_{12}\phi_1\phi_2) \quad (7)$$

where P_1, P_2 are the polarizability of component 1 and 2 of the mixture; ρ_1, ρ_2 and ϕ_1, ϕ_2 represent their respective densities and volume fractions. Routine calculations from eq 6 and 7 lead to the desired quantities

$$(d\rho/d\phi_1) = \frac{(\rho_1 - \rho_2) + \rho D}{(1 + A_{12}\phi_1\phi_2)} \quad (8)$$

$$(dn/d\phi_1) = \left[(n^2 + 2)\left\{ \left[(P_1 - P_2) + B_{12}(\phi_2 - \phi_1) + \frac{dB_{12}}{d\phi_1}(\phi_1\phi_2) \right] - PD \right\} \right] \Big/ [6n(1 + A_{12}\phi_1\phi_2)] \quad (9)$$

where

$$D = \left[A_{12}(\phi_2 - \phi_1) + \frac{dA_{12}}{d\phi_1}(\phi_1\phi_2) \right]$$

Experimentally calculated values of A_{12} and B_{12} (using eq 6 and 7) may be fitted to the following quadratic equations in order to evaluate the coefficients a_0, a_1, a_2, and b_0, b_1, and b_2.

$$A_{12} = a_0 + a_1(\phi_2 - \phi_1) + a_2(\phi_2 - \phi_1)^2 \quad (10)$$

$$B_{12} = b_0 + b_1(\phi_2 - \phi_1) + b_2(\phi_2 - \phi_1)^2 \quad (11)$$

Equations 10 and 11 are used to compute the derivatives $(dA_{12}/d\phi_1)$ and $(dB_{12}/d\phi_1)$ whose values are then inserted into eq 8 and 9 along with others to predict the incremental values

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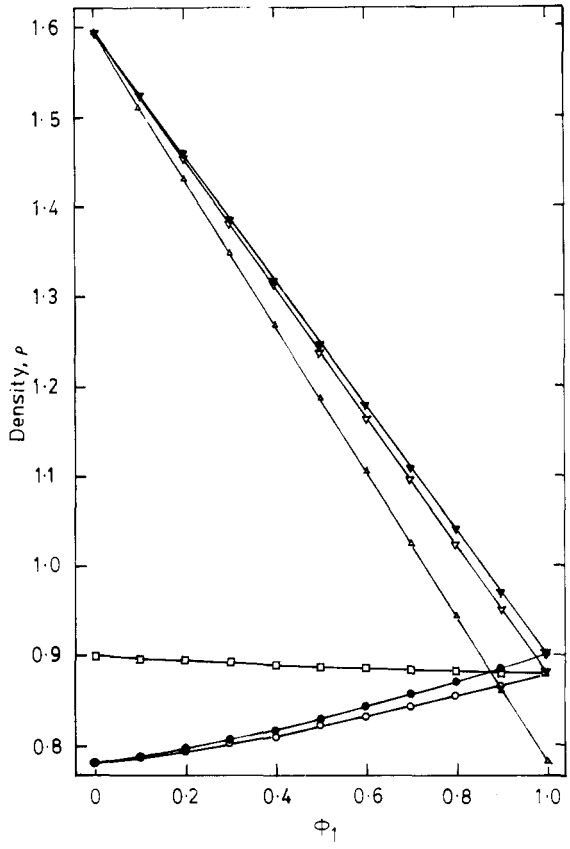

Figure 1. Dependence of density on volume fraction of the first-named component in the mixture at 20 °C: (△) cyclohexane (1)–carbon tetrachloride (2); (▽) benzene (1)–carbon tetrachloride (2); (▼) ethyl acetate (1)–carbon tetrachloride (2); (□) benzene (1)–ethyl acetate (2); (○) benzene (1)–cyclohexane (2); (●) ethyl acetate (1)–cyclohexane (2).

of density and refractive index.

Experimental Section

Solvents used in this work were of reagent grade and were used without further purification. Gas chromatography did not show any impurity except for cyclohexane. Different batches of cyclohexane contained about 0.2–1% impurity and their physical properties varied accordingly. However, each series of experiments was performed with a single batch of cyclohexane and the values of density and refractive index applicable to each batch were used for its evaluation. Solvent mixtures were prepared by weighing appropriate volumes of pure solvents. The volume fractions were calculated from the weights and densities of pure components (*1*).

Densities were measured at 20 ± 0.01 °C with a precision density meter, Model DMA 02C, manufactured by Anton Paar K.G., Austria. A Bausch and Lomb precision refractometer was used to measure the refractive index. The instrument was equipped with mercury and sodium light sources. The precision of the instrument is ±0.000 03 units. Samples were applied to the prism of the refractometer as quickly as possible to minimize evaporation and accompanying changes in composition of the mixture. Measurements were done at 20 ± 0.01 °C by using sodium (589 nm) line, mercury green (546 nm), and blue (436 nm) lines. The experimental data reported here were collected at the university of Texas, Austin, TX (courtesy of Professor Petr Munk).

Results and Discussion

Densities, refractive indices, and their increments as calculated from eq 8 and 9, respectively, are compiled in Table I.

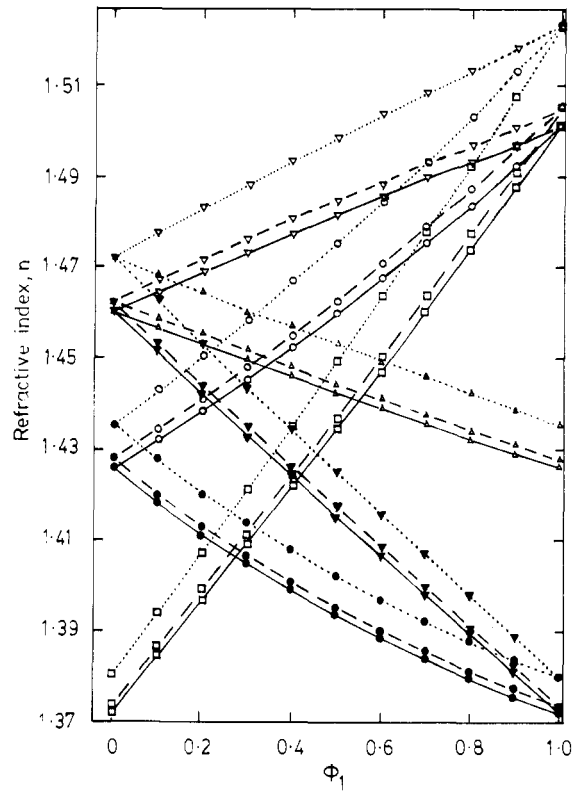

Figure 2. Dependence of refractive index on volume fraction of the first-named component in the mixture at 20 °C (symbols have the same meaning as in Figure 1): dotted line (436 nm); dashed line (546 nm); full line (589 nm).

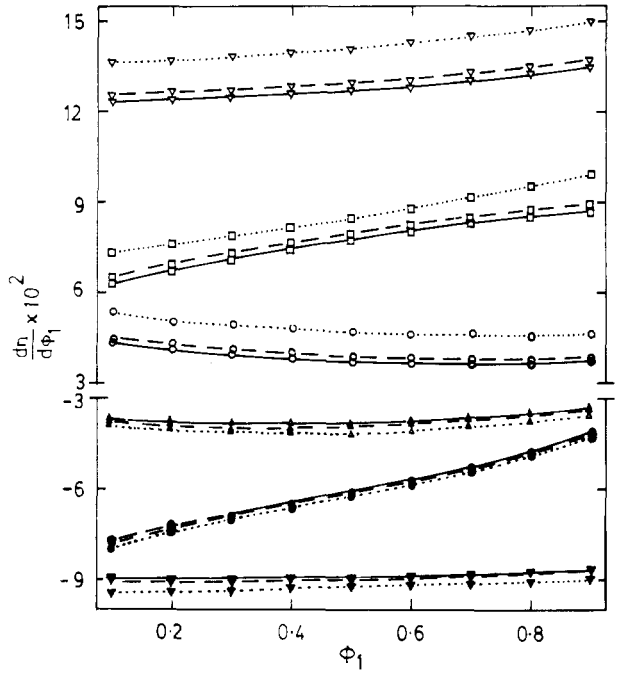

Figure 3. Dependence of refractive index increment on volume fraction of the first-named component in the mixture at 20 °C: (▽) benzene (1)–ethyl acetate (2); (□) benzene (1)–cyclohexane (2); (○) benzene (1)–carbon tetrachloride (2); (▲) cyclohexane (1)–carbon tetrachloride (2); (●) ethyl acetate (1)–cyclohexane (2); (▼) ethyl acetate (1)–carbon tetrachloride (2) (lines have the same meaning as in Figure 2).

Dependence of density on volume fraction (ϕ_1) of the mixture is shown in Figure 1. Mixtures of carbon tetrachloride with benzene, cyclohexane, or ethyl acetate and also benzene (1)–ethyl acetate (2) exhibit linear dependence. However, a slight deviation from straight-line behavior is shown by mixtures

Table I. Densities, Refractive Indices, and Density and Refractive Index Increments for Binary Mixtures at 20 °C

ϕ_1	density, g/cm³	refract. index 589 nm	refract. index 546 nm	refract. index 436 nm	density increment	refract. index increment 589 nm	refract. index increment 546 nm	refract. index increment 436 nm
			I. Benzene (1)–Ethyl Acetate (2)					
1.0	0.879 16	1.501 11	1.505 21	1.523 03				
0.9	0.880 73	1.487 56	1.491 34	1.507 92	−0.0162	0.1349	0.1375	0.1497
0.8	0.882 09	1.473 93	1.477 40	1.492 78	−0.0183	0.1327	0.1352	0.1471
0.7	0.884 41	1.460 84	1.464 13	1.478 35	−0.0200	0.1307	0.1331	0.1448
0.6	0.886 38	1.447 80	1.450 73	1.463 79	−0.0213	0.1288	0.1313	0.1427
0.5	0.888 59	1.434 85	1.437 70	1.449 61	−0.0223	0.1272	0.1297	0.1409
0.4	0.890 85	1.422 06	1.424 57	1.435 38	−0.0232	0.1258	0.1282	0.1393
0.3	0.893 11	1.409 55	1.411 80	1.421 53	−0.0239	0.1246	0.1270	0.1379
0.2	0.895 59	1.396 96	1.399 02	1.407 59	−0.0246	0.1236	0.1261	0.1368
0.1	0.898 08	1.384 65	1.386 38	1.393 95	−0.0255	0.1228	0.1253	0.1359
0.0	0.900 68	1.372 26	1.373 82	1.380 27				
			II. Benzene (1)–Carbon Tetrachloride (2)					
1.0	0.879 16	1.501 11	1.505 21	1.523 03				
0.9	0.951 14	1.497 19	1.501 10	1.518 17	−0.7186	0.0371	0.0387	0.0462
0.8	1.022 31	1.493 40	1.497 19	1.513 50	−0.7166	0.0366	0.0382	0.0458
0.7	1.094 26	1.489 46	1.493 10	1.508 60	−0.7152	0.0364	0.0380	0.0466
0.6	1.165 44	1.485 57	1.488 97	1.503 74	−0.7144	0.0365	0.0382	0.0461
0.5	1.236 99	1.481 53	1.484 72	1.498 71	−0.7143	0.0371	0.0388	0.0469
0.4	1.308 30	1.477 42	1.480 45	1.493 63	−0.7146	0.0380	0.0398	0.0480
0.3	1.379 33	1.473 20	1.476 05	1.488 39	−0.7151	0.0393	0.0411	0.0494
0.2	1.451 10	1.468 91	1.471 63	1.483 08	−0.7156	0.0410	0.0428	0.0513
0.1	1.522 68	1.464 56	1.467 03	1.477 63	−0.7155	0.0430	0.0449	0.0535
0.0	1.594 27	1.460 03	1.462 39	1.472 14				
			III. Benzene (1)–Cyclohexane (2)					
1.0	0.879 16	1.501 11	1.505 21	1.523 03				
0.9	0.867 35	1.492 41	1.496 34	1.513 02	0.1173	0.0871	0.0895	0.0993
0.8	0.855 80	1.483 82	1.487 52	1.503 12	0.1144	0.0853	0.0876	0.0955
0.7	0.844 59	1.475 61	1.479 01	1.493 57	0.1108	0.0831	0.0853	0.0918
0.6	0.833 81	1.467 67	1.470 82	1.484 33	0.1067	0.0805	0.0828	0.0884
0.5	0.823 44	1.459 93	1.462 87	1.475 36	0.1023	0.0776	0.0799	0.0851
0.4	0.813 52	1.452 52	1.455 22	1.466 71	0.0975	0.0745	0.0767	0.0820
0.3	0.804 15	1.445 54	1.448 02	1.458 47	0.0925	0.0710	0.0732	0.0790
0.2	0.795 26	1.438 80	1.441 14	1.450 64	0.0874	0.0672	0.0694	0.0763
0.1	0.786 70	1.432 30	1.434 46	1.443 06	0.0823	0.0632	0.0654	0.0737
0.0	0.778 76	1.426 26	1.428 11	1.435 73				
			IV. Ethyl Acetate (1)–Cyclohexane (2)					
1.0	0.900 68	1.372 26	1.373 82	1.380 27				
0.9	0.885 42	1.375 85	1.377 51	1.384 04	0.1505	−0.0417	−0.0419	−0.0428
0.8	0.870 64	1.379 99	1.381 56	1.388 16	0.1448	−0.0476	−0.0479	−0.0488
0.7	0.856 53	1.384 22	1.385 89	1.392 59	0.1394	−0.0526	−0.0528	−0.0539
0.6	0.843 02	1.388 92	1.390 59	1.397 35	0.1339	−0.0568	−0.0571	−0.0582
0.5	0.830 23	1.393 95	1.395 67	1.402 57	0.1277	−0.0605	−0.0608	−0.0620
0.4	0.818 17	1.399 37	1.401 06	1.408 14	0.1205	−0.0641	−0.0644	−0.0657
0.3	0.806 87	1.405 10	1.406 81	1.413 95	0.1117	−0.0678	−0.0682	−0.0695
0.2	0.796 26	1.411 37	1.413 16	1.420 45	0.1011	−0.0720	−0.0724	−0.0739
0.1	0.786 71	1.418 39	1.420 15	1.427 61	0.0882	−0.0771	−0.0775	−0.0791
0.0	0.778 76[a]	1.426 22[a]	1.428 09[a]	1.435 72[a]				
			V. Ethyl Acetate (1)–Carbon Tetrachloride (2)					
1.0	0.900 68	1.372 26	1.373 82	1.380 27				
0.9	0.969 84	1.380 85	1.382 42	1.389 15	−0.6931	−0.0865	−0.0871	−0.0900
0.8	1.039 47	1.389 54	1.391 20	1.398 24	−0.6930	−0.0873	−0.0878	−0.0908
0.7	1.108 34	1.398 20	1.399 87	1.407 28	−0.6929	−0.0879	−0.0885	−0.0916
0.6	1.177 59	1.406 88	1.408 70	1.416 38	−0.6928	−0.0885	−0.0891	−0.0922
0.5	1.246 88	1.415 66	1.417 58	1.425 65	−0.6930	−0.0890	−0.0896	−0.0928
0.4	1.316 36	1.424 47	1.426 41	1.434 76	−0.6934	−0.0893	−0.0901	−0.0934
0.3	1.384 65	1.433 16	1.435 16	1.443 87	−0.6943	−0.0900	−0.0904	−0.0938
0.2	1.454 87	1.442 04	1.444 18	1.453 21	−0.6958	−0.0897	−0.0906	−0.0941
0.1	1.524 28	1.451 04	1.453 27	1.462 62	−0.6982	−0.0898	−0.0908	−0.0944
0.0	1.594 27	1.460 03	1.462 39	1.472 14				
			VI. Cyclohexane (1)–Carbon Tetrachloride (2)					
1.0	0.778 66[b]	1.426 24[b]	1.428 08[b]	1.435 73				
0.9	0.859 49	1.429 32	1.431 15	1.439 00	−0.8118	−0.0330	−0.0335	−0.0355
0.8	0.941 32	1.432 57	1.434 47	1.442 54	−0.8134	−0.0349	−0.0354	−0.0375
0.7	1.023 62	1.435 93	1.437 87	1.446 14	−0.8144	−0.0365	−0.0370	−0.0390
0.6	1.103 62	1.439 24	1.441 20	1.449 68	−0.8149	−0.0376	−0.0381	−0.0402
0.5	1.184 63	1.442 54	1.444 57	1.453 27	−0.8151	−0.0383	−0.0388	−0.0409
0.4	1.266 07	1.446 02	1.448 08	1.457 01	−0.8155	−0.0389	−0.0397	−0.0412
0.3	1.347 84	1.449 46	1.451 61	1.460 70	−0.8168	−0.0384	−0.0390	−0.0411
0.2	1.429 77	1.452 99	1.455 21	1.464 51	−0.8201	−0.0379	−0.0384	−0.0406
0.1	1.511 18	1.456 52	1.458 76	1.468 29	−0.8263	−0.0369	−0.0375	−0.0397
0.0	1.594 27	1.460 03	1.462 39	1.472 14				

[a] For the batch of cyclohexane used for the ethyl acetate (1)–cyclohexane (2) mixture. [b] For the batch of cyclohexane used for the cyclohexane (1)–carbon tetrachloride (2) mixture.

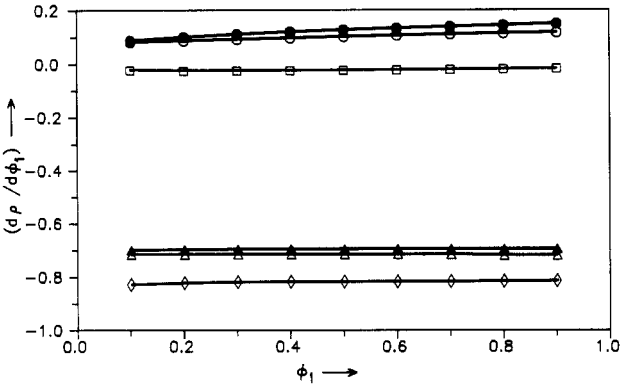

Figure 4. Dependence of density increment on volume fraction of the first-named component in the mixture at 20 °C: (○) benzene (1)–cyclohexane (2); (●) ethyl acetate (1)–cyclohexane (2); (△) benzene (1)–carbon tetrachloride (2); (▲) ethyl acetate (1)–carbon tetrachloride (2); (□) benzene (1)–ethyl acetate (2); (◇) cyclohexane (1)–carbon tetrachloride (2).

of cyclohexane with benzene or ethyl acetate.

Variation of refractive index for all the three wavelengths (589, 546, and 436 nm) as a function of ϕ_1 is shown in Figure 2. As expected, refractive index is higher for the mercury blue line (436 nm) than the mercury green line (546 nm). However, for sodium yellow line (589 nm) lower values of refractive indices than at either 546 or 436 nm are observed. For all the systems, the refractive index versus ϕ_1 curves are slightly deviated from a straight-line behavior.

Dependence of refractive index increment on ϕ_1 is shown in Figure 3. Mixtures of benzene with ethyl acetate, carbon tetrachloride or cyclohexane exhibit positive values for the increment for all the wavelengths. However, mixtures of ethyl acetate with cyclohexane or carbon tetrachloride and cyclohexane (1)–carbon tetrachloride (2) exhibit negative refractive index increments. In all the cases, the refractive index increments have shown increasing tendencies with a decrease in wavelength. The highest (and positive) values of refractive index increments are observed for the benzene (1)–ethyl acetate (2) system and the lowest (and negative) values are observed in the case of cyclohexane (1)–carbon tetrachloride (2) system. No strict linearity is observed for any of the systems as seen in Figure 3.

Dependence of density increment on volume fraction of the first component of the mixture is shown in Figure 4. For the systems benzene (1)–ethyl acetate (2), benzene (1)–carbon tetrachloride (2), ethyl acetate (1)–carbon tetrachloride (2), and cyclohexane (1)–carbon tetrachloride (2), the density increment is negative over the entire range of composition of the mixture. However, for the systems benzene (1)–cyclohexane (2) and ethyl acetate (1)–cyclohexane (2), the density increment is positive; for the latter system it is largest of all. For mixtures exhibiting positive refractive index increments the density increment is negative (see, for instance, mixtures I and II given in Table I). A reverse situation exists in the case of ethyl acetate (1)–cyclohexane (2) wherein the density increment is positive but refractive index increment is negative. On the other hand, for a few mixtures (see, for instance, mixtures V and VI given in Table I) both the increments are negative; in one case (mixture III) both the increments are positive. Thus, there appears to be no strict correlation between either the sign or magnitudes of these increments. From a general observation, it is apparent that if the first component of the mixture possesses higher values of either density or refractive index than the second component, then the increments are found to be positive. If on the other hand, the first component has lower values than the second then negative values of the increments are prevalent.

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Registry No. Benzene, 71-43-2; cyclohexane, 110-82-7; ethyl acetate, 141-78-6; carbon tetrachloride, 56-23-5.

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Densities and Viscosities of Binary Liquid Mixtures at 45 °C

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Densities and viscosities for 14 binary liquid mixtures comprising carbon tetrachloride, cyclohexane, methyl ethyl ketone, benzene, *p*-xylene, bromobenzene, dimethyl sulfoxide, dimethylformamide, nitromethane, ethyl acetate, and methanol at 45 °C over the whole range of mixture compositions are presented.

Introduction

In our earlier studies (*1–3*) densities and viscosities have been measured at 25 and 35 °C for several binary mixtures comprising carbon tetrachloride, cyclohexane, methyl ethyl ketone, dimethyl sulfoxide, dimethylformamide, nitromethane, benzene, bromobenzene, ethyl acetate, *p*-xylene, and methanol. In continuation of this research we now present additional data of densities and viscositites of 14 binary mixtures comprising the same solvents. The properties were studied over the entire range of composition of the mixture.

Experimental Section

All chemicals used were of commercial products of the highest available purity (BDH). These were further purified by

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