Densities and Molar Volumes of Binary Solutions of Nitrobenzene in Electron Donating Solvents

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Densities and molar volumes of solutions of nitrobenzene in 18 weak electron donating solvents were measured as functions of concentration at 25.00°C. The data were fitted by a least-squares method to a polynomial of the form $y = \sum_{i=0}^{i} a_i x^i$. No obvious relationship is observed between the electron donating ability of the solvents and densities of the solutions.

Electron charge transfer interactions between molecules in solution account for the excess thermodynamic properties in far more numerous systems than suspected in the past (*1, 2, 4, 5*). Nitrobenzene is a weak electron acceptor—a Lewis acid—therefore, it is expected that in a solution with an electron donating solvent—a Lewis base—it will form weak charge transfer complexes, and these will have some effect on the density measurement. The densities and molar volumes of the 18 systems, in combination with other available information, will be used later to discuss the possibility of establishing a correlation between the electron donor–acceptor abilities of the solution constituents and the thermodynamic excess properties of the solutions.

Experimental

All the materials used in this investigation were Fisher analytical grade or spectrograde chemicals. The majority of them were further purified by redistilling with an efficient column using a high reflux ratio. The fractions having physical properties reproducing literature values (*7*) were collected. No trace impurities were detected by gas chromatographic analysis. The difference between the boiling points and condensation temperatures of the individual samples, measured at atmospheric pressure with a Beckmann thermometer in a modified Świętostawski differential ebulliometer (*3*), was less than 3×10^{-3}°C. Nitrobenzene was the most difficult to purify. Its hygroscopic nature and sensitivity to light and atmospheric oxygen made it necessary to redistill (under a reduced nitrogen atmosphere) the sample prior to each measurement.

Density measurements were made with 25-cm^3 single-stem closed pycnometers, calibrated with distilled and degassed water. The inner diameters of the stems were less than $1 \times 10^{-3}M$. Assuming that this varies very little throughout the length of the stem, one can estimate that an error of $\pm 1 \times 10^{-4}M$ in reading the level of the liquid in the stem will cause an error in the volume of about $\pm 7 \times 10^{-5}$ cm^3. Since the volume of the pycnometer is roughly 25 cm^3, this contributes very little to the error in the density measurement. The pycnometers were filled with hypodermic syringes and were placed in a constant temperature bath at 25.00° ± 0.01°C for about 30 min. The bath temperature was monitored with a Beckman thermometer standardized against a calibrated Leeds and Northrup platinum resistance thermometer in a Mueller bridge (G2) circuit. Due to the small vapor space of the pycnometers, the error in the densities caused by evaporation of the solution is calculated to be negligibly small. Buoyancy corrections were considered during all measurements. We estimate the total error in the density measurement is about $\pm 4 \times 10^{-5}$ g/cm^3.

Results

The density vs. mole fraction data for the 18 systems are summarized in Table I. Each density value is the average of at least four measurements not differing by more than $\pm 4 \times 10^{-5}$ g/cm^3. The data were fitted by a least-squares method to a polynomial of the form:

$$d = \sum_{i=0}^{i} a_i x^i \qquad (1)$$

where d is the density, and x is the corresponding mole fraction of the solvent. The number of constants necessary to obtain the best fit was chosen so that the deviation of the experimental densities from the calculated values was within the limits of experimental error ($\pm 4 \times 10^{-5}$ g/cm^3). The standard deviations for the systems listed in Table I vary from 2×10^{-5} to 4×10^{-5} g/cm^3. The constants of the polynomial are given in Table II.

The slight differences in density of the pure nitrobenzene shown for the systems in Tables I and II are explained by the fact that for each system a freshly distilled sample of nitrobenzene was used. It was very difficult to obtain samples of the same purity. The average value 1.19843 ± 0.00003 g/cm^3 is very close to the literature value (*7*).

From the measured densities, we have calculated the molar volumes V_m, according to

$$V_m = \frac{x_1 M_1 + x_2 M_2}{d} \qquad (2)$$

where M_1 and M_2 are the molecular weights of the components. These were again fitted by a least-squares method to a polynomial of the form:

$$V_m = \sum_{i=0}^{i} b_i x^i \qquad (3)$$

The constants of this polynomial are also reported in Table II.

The data do not indicate any obvious relationship between the densities or the molar volumes of the solutions and the electron donor–acceptor abilities of the solution constituents.

It may be of some interest to notice the relatively small values of a_1 and b_1 for the systems containing solvents of very small electron donating ability (bromobenzene, benzonitrile, chlorobenzene, and aniline). Also for these systems, except chlorobenzene, only three constants are required for the polynomial. The small value of a_1 for the 1,2,3,4-tetramethylbenzene system, when compared with the values of a_1 for the *n*-butylbenzene and isobutylbenzene systems, may also be of some significance. More discussion of these systems will be given in a second paper.

[1] This paper is dedicated to the memory of H. N. Wachter, a graduate student, who passed away recently.
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Table I. Densities of Binary Solutions of Nitrobenzene in Electron Donating Solvents at 25.00 ± 0.01°C

Benzene(1)–nitrobenzene(2)		Toluene(1)–nitrobenzene(2)		*o*-Xylene(1)–nitrobenzene(2)		*p*-Xylene(1)–nitrobenzene(2)	
x_1	d, g/cm³	x_1	d, g/cm³	x_1	d, g/cm³	x_1	d, g/cm³
0.0000	1.19847	0.0000	1.19849	0.0000	1.19845	0.0000	1.19845
0.0693	1.17896	0.0222	1.19806	0.0184	1.19154	0.0735	1.16948
0.1778	1.14770	0.0596	1.17829	0.0331	1.18612	0.1417	1.14314
0.3076	1.10906	0.1154	1.15947	0.0871	1.16643	0.2837	1.09050
0.4499	1.06498	0.2971	1.09832	0.1220	1.15389	0.3969	1.05022
0.5490	1.03308	0.3926	1.06630	0.2478	1.10980	0.5486	0.99849
0.6908	0.98562	0.4903	1.03351	0.3615	1.07137	0.7016	0.94857
0.8214	0.93992	0.5922	0.99930	0.4580	1.03971	0.8750	0.89445
0.9357	0.89813	0.6916	0.96595	0.4931	1.02847	0.9434	0.87370
1.0000	0.87384	0.7924	0.93213	0.5621	1.00651	1.0000	0.85686
		0.8770	0.90370	0.6654	0.97445		
		0.9161	0.89057	0.7718	0.94237		
		0.9588	0.87621	0.9542	0.88911		
		0.9801	0.86906	0.9750	0.88316		
		1.0000	0.86231	1.0000	0.87601		

m-Xylene(1)–nitrobenzene(2)		Ethylbenzene(1)–nitrobenzene(2)		Styrene(1)–nitrobenzene(2)		*n*-Propylbenzene(1)–nitrobenzene(2)	
0.0000	1.19846	0.0000	1.19842	0.0000	1.19847	0.0000	1.19842
0.1374	1.14567	0.0675	1.17230	0.0768	1.17338	0.0638	1.17007
0.2779	1.09410	0.1411	1.14457	0.1207	1.15929	0.1310	1.14149
0.4419	1.03669	0.2807	1.09374	0.2481	1.11912	0.2663	1.08744
0.5551	0.99868	0.3908	1.05520	0.4298	1.06381	0.3723	1.04819
0.6739	0.96008	0.5536	1.00052	0.6035	1.01285	0.5267	0.99529
0.8758	0.89719	0.6929	0.95574	0.6652	0.99513	0.7020	0.94058
1.0000	0.86001	0.8735	0.90020	0.8674	0.93833	0.8651	0.89397
		0.9386	0.88080	0.9283	0.92154	0.9377	0.87434
		1.0000	0.86276	1.0000	0.90192	1.0000	0.85796

Isopropylbenzene(1)–nitrobenzene(2)		1,2,4-Trimethylbenzene(1)–nitrobenzene(2)		1,3,5-Trimethylbenzene(1)–nitrobenzene(2)		*n*-Butylbenzene(1)–nitrobenzene(2)	
0.0000	1.19844	0.0000	1.19846	0.0000	1.19844	0.0000	1.19842
0.1263	1.14390	0.0652	1.17122	0.0597	1.17243	0.1923	1.10855
0.2353	1.10020	0.1264	1.14656	0.1275	1.14400	0.3847	1.03289
0.4263	1.03025	0.2132	1.11309	0.2596	1.09177	0.6252	0.95420
0.6043	0.97166	0.3770	1.05438	0.3682	1.05179	0.7817	0.91040
0.8136	0.90942	0.5253	1.00569	0.5224	0.99905	0.9258	0.87392
0.9218	0.87948	0.6967	0.95400	0.6917	0.94603	1.0000	0.85627
1.0000	0.85862	0.8642	0.90733	0.8702	0.89476		
		0.9372	0.88805	0.9366	0.87671		
		1.0000	0.87187	1.0000	0.85995		

Isobutylbenzene(1)–nitrobenzene(2)		1,2,3,4-Tetramethylbenzene(1)–nitrobenzene(2)		Bromobenzene(1)–nitrobenzene(2)		Benzonitrile(1)–nitrobenzene(2)	
0.0000	1.19842	0.0000	1.19840	0.0000	1.19846	0.0000	1.19847
0.1584	1.12184	0.0564	1.17488	0.0466	1.21223	0.0606	1.18668
0.3933	1.02633	0.1160	1.15113	0.0980	1.22737	0.1222	1.17469
0.5694	0.96642	0.2525	1.10081	0.2413	1.26948	0.2368	1.15226
0.7993	0.89976	0.3566	1.06595	0.3916	1.31341	0.4328	1.11372
0.9060	0.87219	0.5090	1.01963	0.5732	1.36619	0.5554	1.08948
1.0000	0.84923	0.6725	0.97536	0.7565	1.41910	0.7539	1.05001
		0.8604	0.93002	0.8964	1.45923	0.8763	1.02555
		0.9345	0.91348	0.9463	1.47350	0.9374	1.01331
		1.000	0.89940	1.0000	1.48881	1.0000	1.00071

Chlorobenzene(1)–nitrobenzene(2)		Aniline(1)–nitrobenzene(2)	
0.0000	1.19846	0.0000	1.19843
0.0489	1.19395	0.0440	1.19071
0.1494	1.18455	0.1533	1.17158
0.2948	1.17076	0.3022	1.14520
0.4482	1.15610	0.4016	1.12743
0.5444	1.14670	0.5268	1.10483
0.6952	1.13202	0.6632	1.07998
0.8512	1.11646	0.8693	1.04193
0.9486	1.10660	0.9423	1.02827
1.0000	1.10131	1.0000	1.01749

Table II. Coefficients in Equations 1 and 3 Expressing Dependence of Density (g/cm³) and Molar Volume (cm³) on Mole Fraction at 25.00° ± 0.01°C

System	a_0	a_1	a_2	a_3	b_0	b_1	b_2	b_3
Benzene–nitrobenzene	1.198475	−0.279094	−0.034102	−0.011425	102.722	−13.604	−0.3065	0.5798
Toluene–nitrobenzene	1.198369	−0.337346	0.003104	−0.001764	102.731	3.1129	0.4169	0.5852
o-Xylene–nitrobenzene	1.198335	−0.371161	0.058746	−0.009857	102.736	17.710	0.2216	0.5180
p-Xylene–nitrobenzene	1.198453	−0.399674	0.071263	−0.013204	102.725	20.214	−0.0297	1.0025
m-Xylene–nitrobenzene	1.198456	−0.393063	0.066100	−0.011475	102.723	19.646	0.3139	0.7646
Ethylbenzene–nitrobenzene	1.198347	−0.390075	0.064789	−0.010286	102.729	19.426	0.2608	0.6382
Styrene–nitrobenzene	1.198475	−0.329716	0.041988	−0.008810	102.719	12.531	−0.5439	0.7682
n-Propylbenzene–nitrobenzene	1.198383	−0.452588	0.143877	−0.031732	102.722	36.645	0.1057	0.6148
Isopropylbenzene–nitrobenzene	1.198432	−0.448992	0.141744	−0.032571	102.719	36.361	−0.0904	0.9898
1,2,4-Trimethylbenzene–nitrobenzene	1.198456	−0.426174	0.127350	−0.027769	102.717	34.344	0.0712	0.7207
1,3,5-Trimethylbenzene–nitrobenzene	1.198421	−0.443233	0.132277	−0.027523	102.720	35.799	0.7479	0.4975
n-Butylbenzene–nitrobenzene	1.198403	−0.507609	0.223259	−0.057820	102.721	53.405	0.1712	0.4436
Isobutylbenzene–nitrobenzene	1.198395	−0.517824	0.227544	−0.058941	102.717	54.365	0.420	0.5387
1,2,3,4-Tetramethylbenzene–nitrobenzene	1.198382	−0.426080	0.167951	−0.040901	102.719	46.204	−0.0232	0.3286
Bromobenzene–nitrobenzene	1.198452	0.295674	−0.005318	...	102.727	2.9179	−0.1823	...
Benzonitrile–nitrobenzene	1.198496	−0.194397	−0.003387	...	102.723	−0.0480	0.3749	...
Chlorobenzene–nitrobenzene	1.198519	−0.093384	−0.001963	−0.001852	102.719	−0.7958	0.0917	0.1892
Aniline–nitrobenzene	1.198401	−0.173906	−0.007015	...	102.723	−10.106	−0.8458	−0.2468

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