

## The Volumetric Behavior of Nitrobenzene in Electron Donating Solvents

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The excess volumes of 18 binary solutions containing nitrobenzene as a weak electron acceptor and various mono- and polysubstituted aromatic donors were evaluated at 25 °C. The partial molal volume of nitrobenzene in these solvents was also evaluated. There is no quantitative correlation between the volumetric behavior of the solutions and the electron donor acceptor abilities of the solution constituents. The results, however, clearly prove that isomers of higher cohesive energy affect the volumetric behavior of solutions less than their lower cohesive energy counterparts. An attempt is made to interpret this observation in terms of the steric effect and the cohesive energy of donors.

It is well known that solutions with strong specific interactions, such as  $\text{H}_2\text{O} + \text{HCl}$ ,  $\text{H}_2\text{O} + \text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O} + \text{HNO}_3$ , acetone + chloroform, methylacetate + chloroform, water + hydrazine and many others frequently exhibit negative deviations from ideal behavior ( $G^E < 0$ ,  $\gamma_1 < 1$ ).<sup>2)</sup> There are systems for which the reasons for negative deviations from ideal behavior are not as obvious as in the above mentioned solutions. The 2,3-dimethyl-2-butene + carbon tetrachloride solution is a good example of this kind of a system.<sup>3)</sup> By comparing the negative  $G^E$  values of this system with the positive  $G^E$  values of the very similar 2,3-dimethyl-2-butene + tetrachloroethylene system one must conclude that the diametrically different thermodynamic behavior of the two solutions is due to charge transfer interactions in the  $\text{C}_2(\text{CH}_3)_4 + \text{CCl}_4$  system. The chlorines in the  $\text{CCl}_4$  molecule have the ability to withdraw  $\pi$ -electrons from the electron rich double bond of the donor molecule  $[(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2]$ ; this charge transfer interaction may eventually lead to complex formation between the donor and acceptor molecules. The chlorines in the  $\text{C}_2\text{Cl}_4$  molecule do not possess such ability. These chlorines saturate themselves with electrons by withdrawing them from the double bond of the  $\text{C}_2\text{Cl}_4$  molecule itself. Consequently, the  $\text{C}_2\text{Cl}_4$  molecule cannot act as an electron acceptor and is unable to participate in complex formation. The partially double bond character of the C—Cl bond in the  $\text{C}_2\text{Cl}_4$  molecule (the C—Cl bond is shorter than in the  $\text{CCl}_4$  molecule) gives strong support for such interpretation.

Electron charge transfer interactions account for the thermodynamic behavior in far more numerous systems than suspected in the past. Deviations of solutions from ideal behavior is frequently due to charge transfer interactions between the solution constituents. Complex formation in binary mixtures of carbon tetrachloride with aromatic donor molecules has been extensively studied and is well established.<sup>3–10)</sup> The great majority of these systems exhibit positive  $G^E$  values in spite of the charge transfer interaction in the solution. This seems to be contradictory and can be explained by the following reasoning. When only charge transfer interactions exist in a solution, or when these interactions control the behavior of a solution, then  $G^E$  is expected to be negative. The discrepancy arises from the practical impossibility of separating the specific and nonspecific interactions in solutions from each other. There is no rigorous method, theoretical

or experimental, which can quantitatively distinguish the contributions to thermodynamic behavior of liquid solutions due to specific and nonspecific interactions. Data appearing recently in the literature<sup>11–13)</sup> indicate that simultaneous thermodynamic and structural investigations might yield some qualitative insight into this extremely important problem.

This work is concerned with the excess volumes and partial molal volumes of nitrobenzene (electron acceptor) in 18 electron donating solvents.

### Results and Discussion

The purity of the chemicals employed in this investigation, the experimental technique used for density measurements, and the density *versus* concentration data were reported elsewhere.<sup>14)</sup>

The molar volumes of the solutions,  $v$ , evaluated from experimental densities,  $d$ , by using the formula

$$v = \frac{x_1 M_1 + x_2 M_2}{d} \quad (1)$$

where  $M_i$  and  $x_i$  are the molecular weight and mole fraction of the two solution constituents, were fitted by a least-squares method to a polynomial of the form:

$$v = \sum_{i=0}^i b_i x_1^i \quad (2)$$

The number of constants necessary to obtain the best fit was chosen so that the deviation of the experimental molar volumes from the correlated volumes was within the limit of experimental error ( $\pm 0.003 \text{ cm}^3 \text{ mol}^{-1}$ ). Most systems required four constants to obtain such accuracy. The constants for the 18 systems are summarized in Table 1. The slight fluctuation in the molar volume of pure nitrobenzene ( $v_2 \equiv b_0$ ) is explained by the fact that for each system a freshly distilled and dried sample was used. It was practically impossible to obtain samples exactly of the same purity. The average value of  $b_0 = 102.723 \text{ cm}^3 \text{ mol}^{-1}$  is, however, very close to the literature value.<sup>15)</sup>

The assumption was made that in dilute donor solutions the specific interactions control the behavior of the solutions. If this assumption was correct then the constant  $b_1 \left( \equiv \frac{v - b_0}{x_1} \right)$  could be considered as a measure of charge transfer interactions, at least in dilute solutions. As the data in Table 1 indicate, the systems with little or no specific interactions at all

TABLE 1. COEFFICIENTS OF EQ. 2 EXPRESSING THE DEPENDENCE OF MOLAR VOLUME OF THE SOLUTION ( $\text{cm}^3 \text{mol}^{-1}$ ) ON THE DONOR MOLE FRACTION AT  $25.00 \pm 0.01^\circ \text{C}$ 

System	$b_0^a$	$b_1$	$b_2$	$b_3$
Benzene + nitrobenzene	102.722	-13.604	-0.3065	0.5798
Toluene + nitrobenzene	102.731	3.1129	0.4169	0.5852
<i>o</i> -Xylene + nitrobenzene	102.736	17.710	0.2216	0.5180
<i>p</i> -Xylene + nitrobenzene	102.725	20.214	-0.0297	1.0025
<i>m</i> -Xylene + nitrobenzene	102.723	19.646	0.3139	0.7646
Ethylbenzene + nitrobenzene	102.729	19.426	0.2608	0.6382
Styrene + nitrobenzene	102.719	12.531	-0.5439	0.7682
<i>n</i> -Propylbenzene + nitrobenzene	102.722	36.645	0.1057	0.6148
Isopropylbenzene + nitrobenzene	102.719	36.361	-0.0904	0.9898
1,2,4-Trimethylbenzene + nitrobenzene	102.717	34.344	0.0712	0.7207
1,3,5-Trimethylbenzene + nitrobenzene	102.720	35.799	0.7479	0.4975
Butylbenzene + nitrobenzene	102.721	53.405	0.1712	0.4436
Isobutylbenzene + nitrobenzene	102.717	54.365	0.420	0.5387
1,2,3,4-Tetramethylbenzene + nitrobenzene	102.719	46.204	-0.0232	0.3286
Bromobenzene + nitrobenzene	102.727	2.9179	-0.1823	—
Benzonitrile + nitrobenzene	102.723	-0.0480	0.3749	—
Chlorobenzene + nitrobenzene	102.719	-0.7958	0.0917	0.1892
Aniline + nitrobenzene	102.723	-10.106	-0.8458	-0.2468

a) Average value  $102.723 \text{ cm}^3 \text{mol}^{-1}$ .

have very small  $b_1$  values (bromobenzene + nitrobenzene, chlorobenzene + nitrobenzene, and benzonitrile + nitrobenzene). The small  $b_1$  values of these systems may, however, also result from the fact that their molar volume ratios  $v_2/v_1$  (see Table 2) are very close to unity. Because of this and also because the other 15 systems do not show any obvious correlations between complex formation and the  $b_1$  values, the assumption made above cannot be recommended

(see further discussion). The volume of mixing per mole of solution for the 18 systems was calculated from the formula:

$$v_{\text{mix}} = v^E = v - x_1 v_1 - x_2 v_2 \\ = x_1 x_2 \left[ \left( -b_2 - \frac{3}{2} b_3 \right) - \frac{b_3}{2} (x_1 - x_2) \right] \quad (3)$$

where  $b_2$  and  $b_3$  are the constants listed in Table 1,

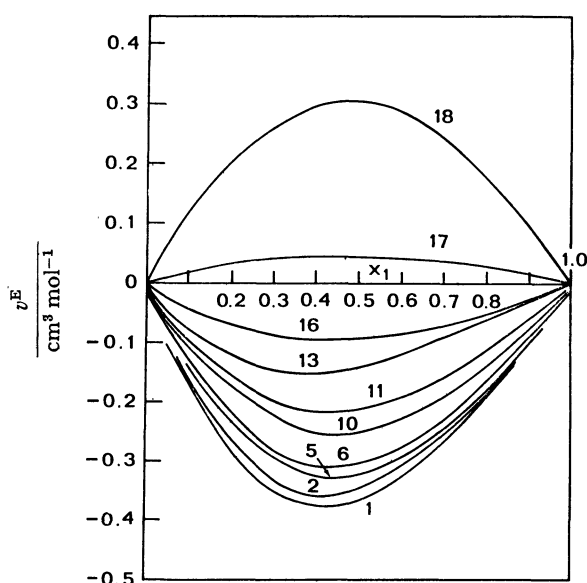


Fig. 1. Excess volume as a function of donor mole fraction at  $25^\circ \text{C}$ . Systems: *p*-xylene(1), 1,3,5-trimethylbenzene(2), toluene(5), isobutylbenzene(6), *o*-xylene(10), *n*-butylbenzene(11), benzene(13), chlorobenzene(16), bromobenzene(17), aniline(18). Nitrobenzene is the acceptor in all the solutions.

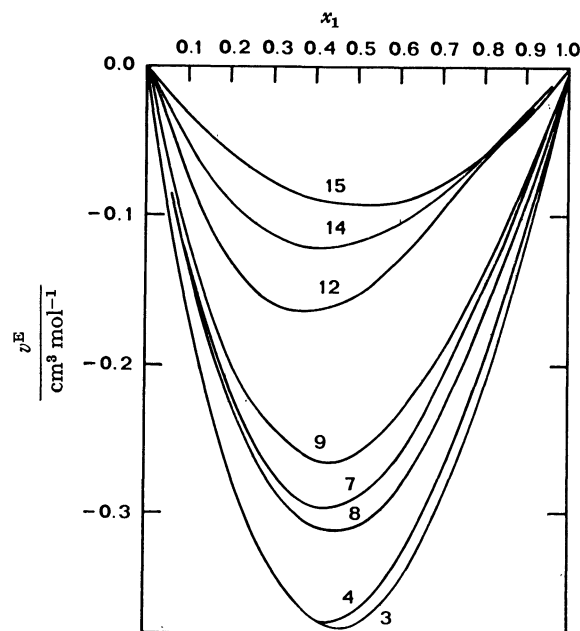


Fig. 2. Excess volume as a function of donor mole fraction at  $25^\circ \text{C}$ . Systems: *m*-xylene(3), isopropylbenzene(4), ethylbenzene(8), 1,2,4-trimethylbenzene(7), *n*-propylbenzene(9), styrene(12), 1,2,3,4-tetramethylbenzene(14), benzonitrile(15). Nitrobenzene is the acceptor in all the solutions.

$v_1$  and  $v_2$  are the molar volumes of the donor and acceptor respectively, and  $x_1$  and  $x_2$  are their respective mole fractions. The  $v^E$  vs.  $x_1$  data for 18 systems are shown in Figs. 1 and 2, respectively. The binary systems containing bromobenzene, chlorobenzene and benzonitrile are again readily distinguishable from all the other solutions. The  $b_3$  values of these systems are very small and consequently their  $v^E$  vs.  $x_1$  curves are symmetrical. The curves representing the other systems, except the one for the aniline system, are more or less skewed, depending on their  $b_3$  values, and have minima between  $x_1=0.4$  and  $x_1=0.5$ . The skewed shape is indicative of specific interactions. The bromobenzene, chlorobenzene and benzonitrile systems seem to be the only solutions within this group with little or no specific interactions at all. The question of how much specific interaction there is in a solution cannot be answered from the shape of the curve alone. Only qualitative observations can be made from these curves and from the data listed in Table 2. Some of them are as follows:

1. The longer the chain of the substituent on the donor the smaller is  $|v^E|$ . In the series of donors, toluene, ethylbenzene, propylbenzene and butylbenzene, the toluene system exhibits the largest and the butylbenzene system the smallest  $|v^E|$ . This is just the opposite of the conclusion for NMR studies that the longer the chain of the substituent on the donor the greater the extent of complexation in the solution.

The difference in  $v^E$  for the toluene and ethylben-

zene systems in  $0.020 \text{ cm}^3 \text{ mol}^{-1}$  at equimolar concentration. For the ethylbenzene and propylbenzene systems the difference amounts to  $0.045 \text{ cm}^3 \text{ mol}^{-1}$  and remains very much the same for the *n*-propylbenzene and butylbenzene systems.

2. The  $v^E$  vs. mole fraction data indicate that the branched donors have a more profound effect on  $|v^E|$  than do the unbranched donors:

$$(v_{\text{isopropyl}}^E - v_{\text{propyl}}^E) = (v_{\text{isobutyl}}^E - v_{\text{butyl}}^E) = 0.095 \text{ cm}^3 \text{ mol}^{-1}$$

3. The monosubstituted ethylbenzene affects  $v^E$  less than its disubstituted isomers, *m*- and *p*-xylenes (for *o*-xylene see below). This is in agreement with NMR measurements, according to which polysubstituted donors are superior to their monosubstituted counterparts in complex formation.

4. Donors having substituents in neighboring (*ortho*) positions have in general a smaller effect on  $v^E$  than similar donors with substituents in non-neighboring positions. The *o*-xylene system when compared with the other two xylene systems illustrates this fact. This is also seen from comparison of the 1,2,4-trimethylbenzene and the 1,3,5-trimethylbenzene systems. The relatively small  $|v^E|$  values of the 1,2,3,4-tetramethylbenzene system very clearly proves the "neighboring substituent effect". The steric effect of the *ortho* substituted donors, as well as their stronger intermolecular forces, indicated by higher enthalpies of vaporization, may be responsible for the diametrically different volumetric behavior of the

TABLE 2. COMPARISON OF SOME CHARACTERISTIC PROPERTIES OF THE DIFFERENT SYSTEMS

Donor <sup>a)</sup>	$v_1$ $\text{cm}^3 \text{ mol}^{-1}$	$l_{\text{vap}}$ $\text{cal g}^{-1}$	$v_1$ $v_2$	$\left(\frac{v^E}{x_1 x_2}\right)_{x_1=0.5}$ $\text{cm}^3 \text{ mol}^{-1}$	$(\bar{v}_2 - v_2)_{x_1 \rightarrow 1}^{\text{b)}}$ $\text{cm}^3 \text{ mol}^{-1}$
<i>iso</i> -Butylbenzene	158.041	—	1.538	-1.23	-1.504
<i>n</i> -Butylbenzene	156.741	—	1.526	-0.84	-1.060
1,2,3,4-Tetramethylbenzene	149.228	80.2	1.452	-0.47	-0.638
1,2,3,5-Tetramethylbenzene	—	78.0 <sup>c)</sup>	—	—	—
<i>iso</i> -Propylbenzene	139.979	77.6	1.362	-1.39	-1.896
<i>n</i> -Propylbenzene	140.088	79.1	1.363	-1.03	-1.337
1,3,5-Trimethylbenzene	139.764	80.6	1.360	-1.49	-1.746
1,2,4-Trimethylbenzene	137.853	81.5	1.342	-1.15	-1.519
1,2,3-Trimethylbenzene	—	83.2 <sup>c)</sup>	—	—	—
<i>p</i> -Xylene	123.911	84.9	1.206	-1.48	-1.974
<i>m</i> -Xylene	123.448	85.3	1.200	-1.46	-1.843
<i>o</i> -Xylene	121.185	86.5	1.178	-1.00	-1.245
Ethylbenzene	123.054	84.3	1.200	-1.22	-1.539
Styrene	115.475	90.0	1.124	-0.61	-0.996
Toluene	106.846	—	1.040	-1.29	-1.578
Benzonitrile	103.050	—	1.003	-0.38	-0.375
Chlorobenzene	102.204	—	0.998	-0.37	-0.474
Bromobenzene	105.463	—	1.026	+0.18	+0.186
Aniline	91.530	—	0.890	+1.22	+1.343
Benzene	89.391	—	0.870	-0.58	-0.854

a) In all the systems nitrobenzene is the acceptor. b) The average value  $v_2 = 102.723 \text{ cm}^3 \text{ mol}^{-1}$ . c) Given just for comparison. 1,2,3,5-Tetramethylbenzene has lower cohesion energy than 1,2,3,4-tetramethylbenzene. 1,2,4-Trimethylbenzene has lower cohesion energy than 1,2,3-trimethylbenzene. The specific enthalpies of vaporization were evaluated from vapor pressure-temperature data at the respective boiling points of the donors.

*ortho* substituted donor solutions. The heat of vaporization per gram,  $l_{\text{vap}}$ , for some of the donors is listed in Table 2. As these data indicate, donors having substituents in neighboring positions exhibit larger  $l_{\text{vap}}$  values; consequently they must have larger intermolecular forces and exhibit smaller molar volumes.

It may be argued that  $|v^E|$  values will depend on both the electron donor ability of the base and the intermolecular forces in the base.

Addition of acceptor molecules to the pure donor will result in charge transfer interaction and consequently in a lowering of the volume of the solution. Due to these interactions it might be reasonable to expect that the distance between the donor and acceptor molecules will be shorter than between two donor molecules. NMR measurements show that the three xylene isomers have approximately the same donor ability and therefore it is expected that the lowering of the molar volume of the solution caused by charge transfer interactions will be the same regardless of whether or not the donor is *ortho* or non *ortho* substituted.

The *ortho* substituted donors, due to their larger cohesive forces, represent more densely packed solvents (see  $v_1$  in Table 2). For donor and acceptor molecules to interact they must approach each other. Molecules of the solvent must separate from each other in order to make space for the approaching nitrobenzene molecule. Because of the closer packing of molecules in the *ortho* substituted donors, relatively larger separation is required. Thus, the volume increase in these solvents will be larger than in the other donors. The charge transfer interaction effect and the separation effect when combined together will therefore result in smaller  $|v^E|$  values for the *ortho* substituted solvents.

Similar arguments can also be used for the other systems studied and especially for the ethylbenzene and styrene systems. The relatively high cohesion energy in styrene is probably responsible for the unexpectedly smaller  $|v^E|$  value for the styrene-nitrobenzene system.

5. There is no obvious correlation between  $|v^E|$  and  $v_1/v_2$ . For the three isomeric xylenes  $v_1/v_2$  is approximately the same and yet  $|v^E|$  of the *o*-xylene system differs significantly from  $|v^E|$  of the other two xylene systems. The chlorobenzene and toluene systems have very close  $v_1/v_2$  values and yet their  $|v^E|$  differ substantially. Similar conclusions can be made for the  $\text{C}_9\text{H}_{12}$  isomeric solutions and for the  $\text{C}_{10}\text{H}_{14}$  isomeric solutions (see Table 2).

6. There is no obvious correlation between  $|v^E|$  and the polarity of the donor molecules. Systems containing the polar *m*-xylene and the nonpolar *p*-xylene exhibit roughly the same  $|v^E|$  values. Solutions of nonpolar 1,3,5-trinitrobenzene seem to be more nonideal than solutions of polar 1,2,4-trimethylbenzene.

7. Of the 18 systems presented here only the two containing bromobenzene and aniline exhibit positive  $v^E$  values. The large positive values of  $v^E$  for the aniline system ( $0.305 \text{ cm}^3 \text{ mol}^{-1}$  at  $x_1=x_2=0.5$ ) is probably due to some structure breaking in the aniline. Aniline is known as a highly associated liquid. The

nitrobenzene molecules break some of the bulky aniline conglomerates into smaller units and separate them from each other. Consequently, there is a volume increase during mixing.

A number of methods have been suggested for the determination of partial molal volumes from density measurements.<sup>16,17</sup> In this investigation we have used a method which establishes an empirical equation to describe the experimental molar volumes of the solution as a function of mole fraction

$$v = b_0 + b_1x_1 + b_2x_1^2 + b_3x_1^3 \quad (2)$$

where  $v_2 \equiv b_0$ . It is then simple to evaluate the derivatives at any point and therefore to determine the partial molal quantity. In this way we obtain for the partial molal volume of the acceptor (nitrobenzene)

$$\bar{v}_2 = v_2 - b_2x_1^2 - 2b_3x_1^3 \quad (4)$$

The constants  $b_2$  and  $b_3$  are those listed in Table 1.

The function  $\bar{v}_2 - v_2$  for the 18 systems is plotted against  $x_1$  in Fig. 3. The limiting values of  $\bar{v}_2 - v_2$  for  $x_1 \rightarrow 1$ , listed in Table 2, are of theoretical significance. Friedman and Sheraga<sup>18</sup> derived a very simple but illustrative theory that evaluates the contribution of nonpolar groups to the partial molal volume in dilute aqueous alcoholic solutions from the limiting values. We were unable to apply this theory to our systems.

The presence of an inflection point on the  $v^E$  vs.  $x_1$

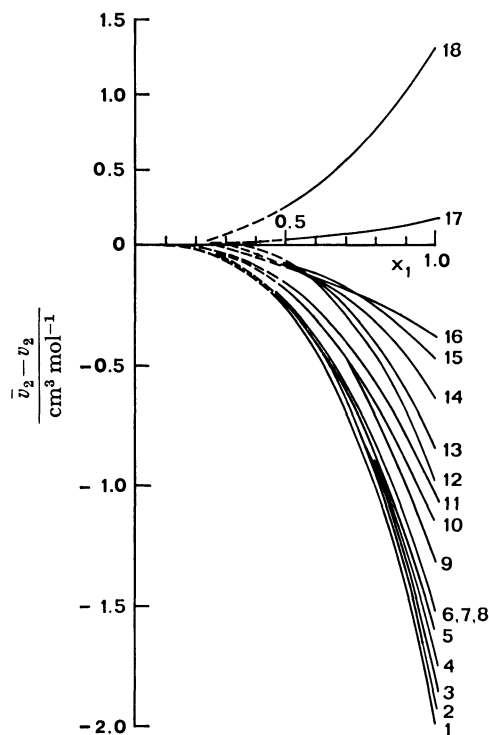


Fig. 3. Partial molal volume of nitrobenzene in electron donating solvents as function of donor mole fraction at 25 °C. Systems: *p*-xylene(1), isopropylbenzene(2), *m*-xylene(3), 1,3,5-trimethylbenzene(4), toluene(5), ethylbenzene(6), 1,2,4-trimethylbenzene(7), isobutylbenzene(8), *n*-propylbenzene(9), *o*-xylene(10), *n*-butylbenzene(11), styrene(12), benzene(13), 1,2,3,4-tertamethylbenzene(14), chlorobenzene(15), benzonitrile(16), bromobenzene(17), aniline(18).

curve indicates the occurrence of extrema on the partial molal volume *vs.*  $x_1$  curves (minimum for one component and maximum for the other component). No such inflection points were observed for our systems. Consequently, no extrema are expected on the  $\bar{v}_2$  *vs.*  $x_1$  curves. Frequently, such extrema occur in the limits of low ( $x_1 \rightarrow 0$ ) and high concentrations ( $x_1 \rightarrow 1$ ). We investigated these regions thoroughly and found no evidence of extrema for these systems.

Since there is direct relationship between  $v^E$  and  $\bar{v}_2$ , all the conclusions drawn from the excess volumes apply equally to the partial molal volumes.

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### References

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