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THE INFLUENCE ON THE IDEAL SOLUTION LAWS OF THE DISTRIBUTION OF POLARITY WITHIN THE MOLECULE

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It has long been known that differences in the degree of polarity between two molecular species tend to produce, in their solutions, deviations from the ideal solution laws.[1] Recent progress in clarifying our ideas concerning polarity, which we owe principally to Debye,[2] has made it possible to measure the electric moments of molecules and to determine how they are influenced by the nature and arrangement of their parts, and it is now possible to test an opinion expressed earlier by the senior author[3] that to understand the effect of polarity on the solution laws it is often necessary to take account of the polarity of the parts of a molecule, and not simply the polarity of the molecule as a whole.

There are only a few systems for which all the necessary data are at hand, and the best for our purpose appear to be the solutions of benzene with nitrobenzene, with the three dinitrobenzenes and with 1-3-5-trinitrobenzene. According to Williams[4] the electric moment of benzene is very small, $< 0.1 \times 10^{-18}$ e.s.u., that of nitrobenzene is 3.90×10^{-18}, for the ortho-, meta- and para-dinitrobenzenes the moments are 6.05×10^{-18}, 3.81×10^{-18} and 0.32×10^{-18}, respectively; for trinitrobenzene the moment is 1.08×10^{-18}. Solutions of nitrobenzene and benzene show deviations from Raoult's law (*vide infra*) in harmony with the difference between their electric moments; if, then, deviations from Raoult's law depend upon the electric moments of the molecule as a whole, we would expect very little deviation for solutions of benzene with para-dinitrobenzene, more for benzene with meta-dinitrobenzene, and most with benzene and ortho-dinitrobenzene. If, on the other hand, the forces between two molecules are determined chiefly by the polarity of the parts which are nearest

to each other, there should be much less difference in the behavior of the three dinitrobenzenes toward benzene.

We have measurements of solubility for the system benzene-nitrobenzene by Dahms,[5] for benzene with the three dinitrobenzenes by Kremann.[6] Since these substances have different melting points and heats of fusion we cannot directly compare their solubility curves, but we can make a comparison sufficiently accurate for our purpose by means of the equation used by the senior author[7] to define a "regular" solution,

$$\bar{F}_2 - \bar{F}_2^i = b N_1^2 \qquad (1)$$

where $\bar{F}_2$ is the partial molal free energy of component X_2 in the regular solution, $\bar{F}_2^i$, its partial molal free energy in an ideal solution, b, a constant which expresses the deviation from Raoult's law and N_1 the mole fraction of the other component, X_1. For regular solutions Eq. (1) is considered to be independent of the temperature; for the solutions here under consideration this may not to be strictly true, but it may, nevertheless, be regarded as sufficiently approximate to serve for the rather rough comparison we wish to make, and the data themselves indicate that this is the case. The free energy of transfer of a mole of X_2 from the ideal to the actual solution is given by

$$\bar{F}_2 - \bar{F}_2^i = RT \, ln(N_2^i/N_2); \qquad (2)$$

the ideal solubility, N_2^i, is calculated from the heat of fusion, ΔH_f, and the absolute melting point, T_m, by the familiar equation:

$$\log N_2^i = \frac{-\Delta H_f}{2.3R}\left(\frac{1}{T} - \frac{1}{T_m}\right). \qquad (3)$$

Values for the heats of fusion and melting points of the several nitrobenzenes were taken from Andrews, Lynn and Johnston.[8] It is hardly necessary to tabulate the figures used and the results of the calculations, since the conclusion is sufficiently well indicated in figure 1 where $\bar{F}_2 - \bar{F}_2^i$ is plotted against N_1^2. The number and positions of the nitro-groups have been indicated in a manner that is self-explanatory.

It will be seen that a single straight line serves for all three dinitrobenzenes, which shows not only that their behavior is satisfactorily expressed by Eq. (1) but that *there is no significant difference between their behaviors toward benzene in spite of the great differences in their electric moments.*

The point for nitrobenzene represents the eutectic point and is doubtless sufficient to give the slope with satisfactory accuracy even though higher values of N_1 are thereby excluded. It is a very striking fact that the slope

of this line is approximately half the slope of the line for the dinitrobenzenes. It will be remembered that this slope represents b in Eq. (1) and expresses the deviation of the solution from the ideal. We may say, accordingly, that the substitution of the nitro-group in the benzene ring causes a deviation from Raoult's law expressed by $b = 320$ cals., while the substitution of two nitro-groups gives rise to nearly twice this deviation, making $b = 580$ cals. One must not, of course, attach too great significance to the apparent simplicity of this relationship unless it is later confirmed for other systems. It is to be hoped that data will be obtained with this end in view.

There are data obtained by Desvergnes[9] for the solubility in benzene of symmetrical trinitrobenzene. Unfortunately, we have no figure for its heat of fusion, but since its solubilities[10] in ortho-dinitrobenzene, in
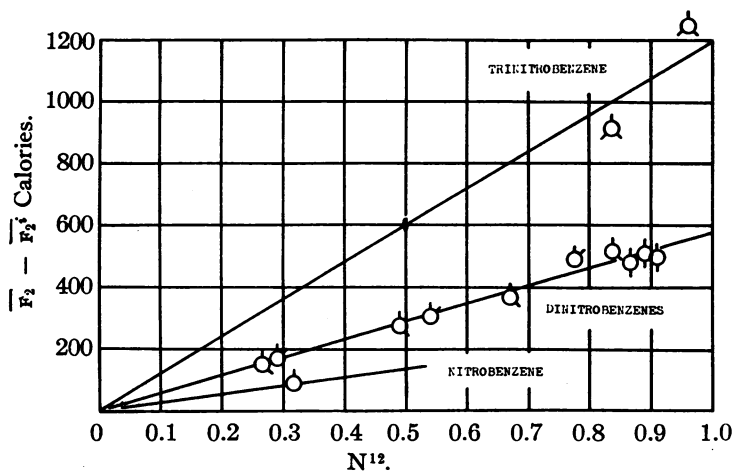

FIGURE 1

Deviations from Raoult's Law shown by solutions of benzene with
various nitrobenzenes.

meta-dinitrobenzene and in 2-4-6-dinitrotoluene are all practically identical they may safely be assumed to be approximately ideal. Fixing the ideal solubility in this way the solubilities in benzene show a departure from Raoult's law, indicated in figure 1, which is approximately twice that for the dinitrobenzenes, corresponding to $b = 1200$ cals. as compared with 580 cals. for the dinitrobenzenes and 320 cals. for nitrobenzene. The addition of the third nitro-group in the symmetrical arrangement apparently leaves so small a non-polar portion exposed that the unlikeness to benzene is more than proportionately increased, although the electric moment of the molecule is thereby much reduced.

We may mention, further, that the three dinitrobenzenes, in spite of the differences in their electric moments, show mutual solubilities agreeing closely with Raoult's law.

The combined weight of this evidence indicates that *it is the number and polarity of the substituent groups rather than the electric moment of the whole molecule which determines deviations from Raoult's law.*

We must not overlook, however, the fact that when the field of a polar bond is sufficiently buried within the molecule its influence upon solubility tends to disappear. Thus, in spite of the polarity of the bond between the carbon atom and the nitro-group, as shown in nitrobenzene and nitromethane, we might expect tetranitromethane to behave in its solutions as a substance of low polarity. Again, stannic chloride is non-polar but stannic fluoride, apparently on account of the smaller halogen atoms, is so polar as to form a high-melting solid.

[1] Cf. Rothmund, *Z. physik. Chem.*, **26,** 433 (1898).
[2] Cf. Debye, *Polar Molecules,* Chem. Catalog. Co., **1929.**
[3] Hildebrand, *Solubility,* Chem. Catalog. Co., **1924,** Chap. 8.
[4] Williams and Schwingel, *J. Am. Chem. Soc.,* **50,** 362 (1928).
[5] Dahms, *Ann. d. Physik. u. Chemie,* **54,** 486 (1895).
[6] Kremann, *Sitz. Akad. Wiss. Wien,* **117,** IIb, 569 (1908).
[7] Hildebrand, *Proc. Nat. Acad. Sci.,* **13,** 267 (1927); *J. Am. Chem. Soc.,* **51,** 66 (1929).
[8] Andrews, Lynn and Johnston, *J. Am. Chem. Soc.,* **48,** 1274 (1926).
[9] Desvergnes, *Mon. Sci.,* **15,** 149 (1925).
[10] Cf. *Tables ann. int. des const. et donnés numeriques,* **5,** 136 (1922).

PENTAVALENT NITROGEN IN ORGANIC COMPOUNDS*

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In connection with some work that we are doing on the constitution of the proteins, it became essential to know in what cases nitrogen in organic compounds will or will not add on hydrogen chloride gas stoichiometrically at room temperature and atmospheric pressure to give what is ordinarily called pentavalent nitrogen.

The following generalizations seem to cover most cases:

I. The tendency for a nitrogenous compound to react stoichiometrically with hydrogen chloride is increased when hydrogen is replaced by an alkyl group and decreased when hydrogen is replaced by a phenyl group. .

II. Introduction of so-called negative radicals such as O, Cl, Br, NO_2, etc., decreases the tendency of the nitrogenous compounds to react stoichiometrically with hydrogen chloride. These radicals have most effect when attached directly to the nitrogen.