CALCULATION OF THE HEATS OF SOLUTIONS OF ALKYLBENZENES IN A NONPOLAR STATIONARY PHASE

S. I. Mel'nikova and A. N. Korol'

Teoreticheskaya i Eksperimental'nyaya Khimiya, Vol. 6, No. 1, pp. 72–78, 1970

UDC 543.544

The heats of solution of 32 alkylbenzenes in nonpolar stationary phases (pentadecane, squalane, and Apiezon L) have been determined by gas-liquid chromatography. It is shown that the heats of solution of these substances may be calculated a priori as the sum of three quantities: a) the calculated dispersion force taking into account intramolecular screening; b) the energy of vacancy formation; and c) the interaction of the solvent molecules and the methyl groups of the solute. The presence of a double bond in the alkyl substituent increases the heat of solution of an alkylbenzene in the nonpolar stationary phase.

In spite of the large number of studies which have been made of the gas chromatographic separation of aromatic hydrocarbons [1–6], the relationship between the heats of solution and the structure of these molecules has not been studied. When Desty and Swanton [1] determined the heats of solution in nonpolar solvents of alkylbenzenes having up to 8 carbon atoms they did not attempt to relate these values with the structure of the solutes; in general, the heats of solution of heavier alkylbenzenes have not been determined. Furthermore, the experimental determination and subsequent calculation of the heats of solution of alkylbenzenes in nonpolar stationary phases is of fundamental importance for the solubility theory of aromatic compounds. The present paper deals with the calculation of the heats of solution of alkylbenzenes in nonpolar solvents, using micro characteristics of the molecules of the substances separated.

The molar heats of solution were calculated from the temperature dependence of the retention volumes by the equations presented in [1–3]; the retention volumes were determined on a Khrom-1 chromatograph, using a flame-ionization detector. Khromosorb G with a grain size of 120–140 mesh, was used as the solid support, the stationary phase being applied from a volatile solvent in the ratio of 0.25 g to 10 ml of support. The experiments were conducted with a column 80 cm long over the temperature range 60–120°C. The error in determining the retention volumes was 0.5–0.8%, for the heats of solution, 0.05 kcal; and the standard was benzene. Pentadecane, squalane, and Apiezon L were used as the nonpolar stationary phases; the 32 hydrocarbons listed in Table 2 were the substances separated.

The heats of solution in the nonpolar stationary phase are determined principally by the dispersion interaction, which can be found from the simplified London equation [7–9]:

\[ D \sim \frac{\alpha_1 \alpha_2}{r^6} \]

where \( D \) is the dispersion interaction index, \( \alpha_1 \) and \( \alpha_2 \) are the ionization potentials of the solute and solvent, and \( r \) is the distance between the particles.

When calculating the interaction of a group of atoms with a solvent, attention should be paid to the intramolecular screening of these groups by groups of atoms chemically combined and arranged in series. The degree of intramolecular screening of each group of atoms present in the alkylbenzenes studied was calculated on the basis of stereochemical spatial models. An example of such a calculation is given for the ethane molecule (Fig. 1).

If we assume for our calculations that the methyl group is a sphere of radius 2 Å and the surface area 50.28 Å², and that the distance between the methyl groups is the length of the ordinary C–C bond, 1.54 Å. Each sphere cuts off from the adjoining one the spherical segments ABD and AB'D whose surface area is deprived of the possibility of interacting effectively with the surrounding solvent medium and is equal to 15.46 Å². To calculate the degree of screening of a segment its surface is divided into a random number of spherical zones and one spherical segment. For each part the average radius \( R_1, \ldots, R_n \) is calculated from trigonometrical relationships. The coefficient for the effective interaction of the parts of the segment is calculated from the equation

\[ 62 \]
The surface of the sphere of the methyl group which interacts effectively with the surrounding medium is calculated as:

$$S_{\text{eff}}^{\text{ABD}} = \sum_{i}^{n} S_{i}^{\text{ABD}}.$$  

Hence the surface of the spherical segment ABD which is inaccessible for interaction is

$$S_{\text{ABD}}^{\text{eff}} = S_{\text{ABD}} - S_{\text{ABD}}^{\text{eff}}.$$  

In this case this quantity represents 23% of the total surface area of the sphere of methyl group and represents the degree of screening of the methyl group in the ethane molecule. The coefficients $K_{i}^{\text{eff}}$ for the screening of all the remaining atomic groups were calculated in the same way (Table 1).

**Aromatic Hydrocarbons with Saturated Alkyl Radicals**

A typically nonpolar stationary phase in an n-paraffin whose relative polarity index is equal to zero [10]. The heat of solution of benzene in an n-paraffin is equal to the sum of the dispersion interaction and the energy expended in the formation of a vacancy in the solvent for the distribution of those solute molecules. The divergence between the calculated and experimental data in this system is attributed to the interaction of the benzene ring with the medium, which was not taken into account. The presence of a linear alkyl radical in aromatic hydrocarbon does not alter the work of formation of a vacancy, because an additional transverse displacement of the chain molecules of the stationary phase does not arise. This is confirmed by the values of $\Delta$ being equal for benzene, ethylbenzene propylbenzene, n-butylbenzene, and n-decane. Then the quantity $D$ for each alkylbenzene is multiplied by $i$; the calculated heats of solution obtained are shown in Table 2.

![Fig. 1. For calculating the screening of methyl groups in the ethane molecule.](image)