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ON THE DETERMINATION OF THERMODYNAMIC FUNCTIONS OF THE INTERACTION OF A SUBSTANCE WITH POLAR SOLVENTS BY THE METHOD OF GAS-LIQUID CHROMATOGRAPHY

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Data on the distribution of a substance between phases can, as is known, be used to study the thermodynamics of interaction with the components of the phases, for example ([1]).

In some cases it is especially convenient and simple to study the distribution of a substance between gas and liquid phases, since the thermodynamic distribution constant of a substance between two phases K and the value of the standard change in free energy ($\Delta\Phi = -RT\ln K$) for infinitely dilute solutions are readily calculated from the distribution coefficients H, determined directly by methods of gas-liquid chromatography ([2]),

$$K = \frac{a'_A}{a''_A} = \frac{C'_A/N'}{PC''_A/N''} = \frac{C'_A}{C''_A}\frac{1}{N'RT} = \frac{H}{N'RT} = \frac{1}{P^0_A\gamma^\infty}, \qquad (1)$$

where a'_A, a''_A and C'_A, C''_A are the activities and concentrations of the distributed substance A in the liquid and gas phases, respectively; N' and N'' are the total numbers of moles per unit volume of the liquid and gas phases; P is the total pressure; P^0_A is the vapor pressure of pure substance A at temperature T; γ^∞ is the activity coefficient of substance A in an infinitely dilute solution of it in the liquid phase, and

$$H = C'_A/C''_A = N'RT/P^0_A\gamma^\infty \qquad (2)$$

([2]). (In deriving (1), ideality of the gas phase is assumed.)
From (1) we obtain

$$\Delta\Phi_A = RT\ln P^0_A\gamma^\infty *. \qquad (3)$$

Since, under the conditions of gas-liquid chromatography, the concentrations of substance A in the gas and liquid phases are very small, then, neglecting the interaction of the molecules of A with one another, the quantity $\Delta\Phi_A$ can be represented as the sum of only two terms

$$\Delta\Phi_A = {}^1/_2\Delta\Phi_{BB} + \Delta\Phi_{AB}, \tag{4}$$

where $\Delta\Phi_{BB}$ is the change in free energy characterizing the process of "separating" the molecules of substance B used as the liquid phase, and $\Delta\Phi_{AB}$ is the change in free energy in the process of interaction of the molecules of substance A with the molecules of the liquid phase B. The value of $\Delta\Phi_{BB}$ is especially large for polar compounds, which, in particular, is manifested in a noticeable association of their molecules.

* In papers ([3,4]) a not quite exact expression is used for $\Delta\Phi_A$: $\Delta\Phi_A = -RT\ln H$, resulting from identifying the thermodynamic distribution constant K with the distribution coefficient H. As is evident from (1), K is proportional to $H/N'-$ the volume of the given substance retained by one mole of stationary liquid.

However, in sufficiently dilute solutions of substance B in an inert solvent, the interaction of molecules of B with one another may be neglected and, consequently, $\Delta\Phi_{AB}$ can be calculated by extrapolating to a mole fraction of substance B equal to 1 the dependence of $\Delta\Phi_A$ on the concentration of B in the liquid phase (which represents dilute solutions of B in a suitable inert solvent).

Let us represent the quantity H, directly determined from chromatographic data, as a function of the mole fraction x of substance B in the liquid phase in the form of a series and, for the region of small values of x, restrict ourselves to the term containing x to the first power:

$$H = H_0\left(1 + \frac{1}{H_0}\frac{dH}{dx}\,x\right), \tag{5}$$

where dH/dx is the value of the derivative at $x = 0$; H_0 is the distribution coefficient of substance A when an inert solvent is used as the liquid phase.

Similarly, the total number N' of moles in 1 cm^3 of the liquid phase in the region of small values of x can be represented as a linear function

$$N' = N_0(1 + ax), \tag{6}$$

where N_0 is the number of moles in 1 cm^3 of the inert solvent.

Hence, from (1), at small values of x we obtain

$$\Delta\Phi_A = \Delta\Phi_0 - RT\left(\frac{1}{H_0}\frac{dH}{dx} - a\right)x, \tag{7}$$

where $\Delta\Phi_0 = -RT\ln(H_0/RTN_0)$. From (3) and (7) we have

$$\ln\gamma^\infty = \ln\gamma_0^\infty - \left(\frac{1}{H_0}\frac{dH}{dx} - a\right)x, \tag{8}$$

where γ_0^∞ is the activity coefficient of substance A in the inert solvent.

Extrapolating (7) to the region of pure substance B, i.e., to $x = 1$, we obtain the value of the quantity $\Delta\Phi_A = \Delta\Phi_{AB}$, corresponding to the distribution of substance A between the gas phase and substance B in a hypothetical state in which there is no interaction of the molecules of B with one another; accordingly, from (8) we have

$$\ln[\gamma^\infty] = \ln\gamma_0^\infty - \left(\frac{1}{H_0}\frac{dH}{dx} - a\right), \tag{9}$$

where $[\gamma^\infty]$ is the activity coefficient of substance A at infinite dilution in substance B, which is in the above-mentioned state.

From the temperature dependence of $[\gamma^\infty]$, using the known expression (5), one can calculate the excess molar heat ΔH_{AB} of dissolution of substance A in "nonassociated" substance B.

In the present work, expression (9) was used to calculate thermodynamic functions for the system saturated hydrocarbons C_4 and C_5—benzonitrile.

In connection with the fact that the literature contains data on considerable association of molecules of nitrile compounds ([6,7]), it was of interest to determine $\Delta\Phi_{BB}$—the change in free energy upon dissociation of associated benzonitrile molecules

$$\Delta\Phi_{BB} = 2(\Delta\Phi_A - \Delta\Phi_{AB}) = RT\ln\{(\gamma^\infty)^2/[\gamma^\infty]^2\}, \tag{10}$$

where γ^∞ is the activity coefficient of substance A at infinite dilution in substance B.

From (10) it follows that

$$K_{\text{diss}} = [\gamma^\infty]^2/(\gamma^\infty)^2, \tag{11}$$

where K_{diss} is the dissociation constant of complexes formed by benzonitrile molecules.

To calculate the thermodynamic functions of interaction of unsaturated hydrocarbons with benzonitrile it was necessary, as is clear from (9), to determine the dependence of the distribution coefficient H on the mole fraction of benzonitrile in an inert solvent. In this connection, *n*-dodecane was chosen as the

Fig. 1. Dependence of the distribution coefficients H for unsaturated hydrocarbons on the mole fraction of benzonitrile x in the liquid phase. 1—pentene-1; 2—2-methylbutene-1; 3—2-methylbutene-2; 4—2-methylbutadiene-1,3; 5—trans-pentadiene-1,3; 6—cis-pentadiene-1,3. a—$T = 20^\circ$, b—$T = 30^\circ$.

Figure 1: Fig. 1. Dependence of the distribution coefficients H for unsaturated hydrocarbons on the mole fraction of benzonitrile x in the liquid phase. 1—pentene-1; 2—2-methylbutene-1; 3—2-methylbutene-2; 4—2-methylbutadiene-1,3; 5—trans-pentadiene-1,3; 6—cis-pentadiene-1,3. a—$T = 20^\circ$, b—$T = 30^\circ$.

solvent for benzonitrile, since it excludes the possibility of donor–acceptor and dipole–dipole interaction with benzonitrile, has a comparatively high boiling point (216°), and dissolves benzonitrile sufficiently well (30.4 wt.% at +20°).

In the work, an ordinary chromatographic setup was used, similar to that described previously ([8]). The application of the liquid phase onto the solid support (INZ-600) was carried out in a hermetically closed vessel according to a known procedure ([9,10]).

The distribution coefficient H was calculated from the chromatographic data by the usual method ([5]). The error in determining the absolute values of H was 1-2%.

The data presented in Fig. 1 confirmed the applicability of equation (5), the linear character of the curves being retained over a fairly wide concentration range, up to $x = 0.20$-0.25.

Fig. 1. Dependence of the distribution coefficients H for unsaturated hydrocarbons on the mole fraction of benzonitrile x in the liquid phase. 1—pentene-1; 2—2-methylbutene-1; 3—2-methylbutene-2; 4—2-methylbutadiene-1,3; 5—trans-pentadiene-1,3; 6—cis-pentadiene-1,3. a—$T = 20^\circ$, b—$T = 30^\circ$.

In considering Table 1, where the values of $[\gamma^\infty]$ are given, it should first of all be noted that $[\gamma^\infty]$ is considerably smaller than γ^∞, the activity coefficient of the hydrocarbons in pure benzonitrile; moreover, for dienic hydrocarbons at +20°, $[\gamma^\infty]$ is even less than 1, which corresponds to a negative deviation from Raoult' s law.

Table 1

Comparison of the values of $[\gamma^\infty]$, calculated from equation (9), with γ^∞ in benzonitrile

Hydrocarbon	γ_0^∞ 20°	γ_0^∞ 30°	$\frac{1}{H_0}\frac{dH}{dX}$ 20°	$\frac{1}{H_0}\frac{dH}{dX}$ 30°	$[\gamma^\infty]$ 20°	$[\gamma^\infty]$ 30°	γ^∞ 20°	γ^∞ 30°	$[\gamma^\infty]^2/(\gamma^\infty)^2$ 20°	$[\gamma^\infty]^2/(\gamma^\infty)^2$ 30°
3-Methylbutene-1	0.95	0.94	0.18	—	1.44	—	3.69	3.61	0.15	—
Pentene-1	0.93	0.92	0.24	—	1.32	—	3.42	3.36	0.15	—
2-Methylbutene-1	0.90	0.91	0.23	—	1.29	—	3.14	3.08	0.17	—
2-Methylbutene-2	0.87	0.89	0.31	0.15	1.16	1.35	2.98	2.97	0.15	0.21
Butadiene-1,3	0.91	0.90	0.62	—	0.88	—	1.78	1.74	0.24	—
2-Methylbutadiene-1,3	0.94	0.93	0.54	0.36	0.98	1.16	2.08	2.04	0.22	0.32
trans-Pentadiene-1,3	0.98	0.97	0.67	0.39	0.91	1.17	1.93	1.91	0.22	0.38
cis-Pentadiene-1,3	0.99	0.98	0.68	0.41	0.90	1.15	1.86	1.88	0.23	0.37

These observations could be explained only by the presence in the system under consideration of an intense interaction between the unsaturated hydrocarbons and "unassociated" benzonitrile.

Consequently, the dependences observed in Fig. 1 are explained in the same way as, for example, analogous dependences for unsaturated hydrocarbons when solutions of silver salts ([9]) are used as stationary liquids, i.e., by the formation in the liquid phase of dissociating complexes between benzonitrile and unsaturated hydrocarbons.

From the data in Table 2 it follows that the excess molar heats of solution ΔH_{AB}, calculated from the temperature dependence $[\gamma^\infty]$, for some hydrocarbons (for the remaining hydrocarbons the slope of the H–x curves at +30° was too small for quantitative calculations) are, in order of magnitude (3000–5000 cal/mol), comparable with the energy of a hydrogen bond.

Table 2

Excess heat of solution of unsaturated hydrocarbons in "nonassociated" benzonitrile

Hydrocarbon	ΔH_{AB}, cal/mol
2-Methylbutene-2	−3000
2-Methylbutadiene-1,3	−3400
trans-Pentadiene-1,3	−5000
cis-Pentadiene-1,3	−5000

As noted above, using equations (10) and (11) one can calculate the thermodynamic functions of association of benzonitrile molecules. From (11) it follows that the ratio $[\gamma^{\infty}]^2/(\gamma^{\infty})^2 = K_{\text{diss}}$ must be constant for different hydrocarbons, which, as a first approximation, is confirmed by the data in Table 1. This ratio is especially constant within each class of hydrocarbons. Some difference between the values of K_{diss} for diene hydrocarbons and the corresponding values for olefinic hydrocarbons is possibly associated with the interaction of hydrocarbons with associates of benzonitrile molecules, and, consequently, equation (4) is not entirely accurate.

Estimating approximately the association energy of benzonitrile molecules from the more reliable values of K_{diss}, found experimentally (for +20 and +30°) for diene hydrocarbons, we obtain

$$\varepsilon_{\text{acc}} = RT^2 \frac{\Delta(\ln K_{\text{diss}})}{\Delta T} \simeq 8000 \text{ cal/mol}.$$

This value of the association energy of benzonitrile molecules coincides with the association energy of nitrile compounds reported in work [11].

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Note: Figure translations are in progress. See original paper for figures.