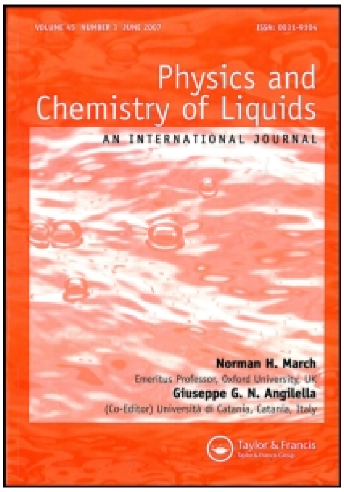

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THE INVESTIGATION OF BENZENE INFLUENCE ON CONFORMATIONAL EQUILIBRIUM IN A SOLVENT USING THE SPECTRAL SHIFT METHOD

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A consequence of an improved model of dissolution process passing through the cavity creation stage is discussed. The improvement consists in accounting for the scales of initial density fluctuations (appropriate vacancies) necessary for creation of the cavities. The radii (R^{v}_{1u}) of the cavities in solvents with flexible molecules containing benzene as a solute, evaluated from solvent-induced spectral shifts, and radii of the vacancies, calculated from volume balance involving the R^{v}_{1u}'s, have been used for determining the changes in conformational equilibrium in the solvents caused by the solute. In free energy balance calculations performed with this aim, the free energy of a cavity is estimated according to Sinanoglu, when the cavity size is equal to or exceeds the size of the room occupied by a solvent molecule, but in the submolecular region it is expressed in terms of the probability of accidental collision of little cavity defects. The reasonable values obtained confirm the picture of dissolution deduced from spectroscopy data.

KEY WORDS: Spectral shift, cavity in a solvent, density fluctuations, conformational equilibrium.

INTRODUCTION

According to modern views as to the nature of dissolution of a substance with not too small molecules in liquids, one of the stages in a dissolution process is the creation of a cavity in a solvent with subsequent accommodation of the solute molecule[1,2]. In the paper[3], it was shown that the effective radii, R^{v}_{1u}, of cavities occupied by benzene molecules are different in various solvents. Also, in[3] it was shown, that in order to perform a dissolution process, it is necessary to have fluctuations of solvent density (appropriate vacancies of R_{bv} radius), the required scales of which depend on the solution components. This important specification in the dissolution picture needs to be examined as to its consistency with other solution properties. In[3] the case of benzene dissolved in water was qualitatively considered in detail. The initial point for consideration was the R^{v}_{1u} value calculated from the shift of the $S_1^* \leftarrow S_0$ benzene *UV*-absorption spectrum, $\Delta\nu^{(10)}$, relative to its position for the gas. In the present paper, starting from similar shifts, we shall discuss to what extent the treatment of the free energy balance during the transfer of a benzene molecule from the liquid phase into non-aqueous solvents, the molecules of which may be subjected to the conformational transition, is self-consistent.

SPECTRAL SHIFTS

The relationship between the $\Delta\nu^{(10)}$ and R_{1u}^{v} values is established as follows[3,4]. First, the role of the vibronic coupling inside benzene molecules is taken into account, i.e., the connection between $\Delta\nu^{(10)}$ and that shift $\Delta\nu$ (of any nature) which would be in the absence of vibronic coupling is determined. Then the shift nature is made concrete, and it is shown (see[3] and Refs cited therein), that for solutions of benzene in widely used liquids, including polar ones, the $\Delta\nu$ value is substantially affected only by dispersion interaction forces and practically not affected by electrostatic fields, because the static field originating from a neighbour solvent particle (dipolar molecule and at least some of univalent ions), acting on a solute benzene molecule, is canceled by the fields borne by other particles. In the quasi-spherical approximation applied to a continuum solvent model, the $\Delta\nu$ value is equal to

$$\Delta\nu = C' \frac{(R_{1u}^{v})^3}{r^3(2R_{1u}^{v} - r)^3} \cdot \frac{n^2 - 1}{n^2 + 2}; \tag{1}$$

(a more exact solution is expressed in terms of spherical functions[4]). In Eq. (1) C' is the positive proportionality coefficient, r is the radius of collision for benzene molecules being in the liquid phase[5], and n is the refractive index of the solvent. The dependence of $\Delta\nu^{(10)}$ on $\Delta\nu$ is approximated by the parabola

$$\Delta\nu^{(10)} = -C|\Delta\nu|^{1.926}, \tag{2}$$

where the index of a power on the right side is evaluated from spectral shifts of the solutions of benzene in liquified noble gases reported by Zelikina and Meister[6]; for such solutions R_{1u}^{v} takes its minimum constant value[7]. Detailed analysis of the $\Delta\nu^{(10)}$ function on $\Delta\nu$ is presented in Ref. 4. Combining Eqs (1) and (2) we can find R_{1u}^{v} from the ratio of $\Delta\nu^{(10)}$ for the solution under consideration to that for the benzene solution CCl_4 equal to $-440\,\text{cm}^{-1}$, taking into account that the magnitude of R_{1u}^{v} for the latter solution is $3.279 \cdot 10^{-10}\,\text{m}$.[3]

BALANCES OF VOLUMES AND FREE ENERGIES

The values of $\Delta\nu^{(10)}$ and R_{1u}^{v} thus determined for the solutions of benzene in cyclohexane, 1,4-dioxane, *n*-pentane, *n*-hexane, and for comparison in chloroform are given in Table 1. The R_{bv} values also shown in this Table are calculated from the volume balance[3]

$$V_{1u}^{v} = V_{av} = V_{1u} + V_{bv} + V^E, \tag{3}$$

where V^E is macroscopic excess volume of mixing, and indices on other terms (here and below, while describing free energies) mean the following. The first subscript indicates the quantity of molecules of species denoted by the second subscript located in the cavity of volume V, with v and u denoting a sol$\underline{v}$ent and sol$\underline{u}$te, respectively. The superscript shows a medium in which the molecules described by the second subscript

Table 1 Spectral shifts and local geometric characteristics of benzene solutions[a].

Solvent	$-\Delta\nu^{(10)}$, cm^{-1}	R^{v}_{1u}, 10^{-10} m	V^E, $cm^3\ mol^{-1}$	R_{bv}, 10^{-10} m	R_{1v}, 10^{-10} m
$CHCl_3$	386	3.318	0.52(12)	1.029	2.675
c-C_6H_{12}	268	3.603	2.774(13)	2.186	3.499
1,4-$C_4H_8O_2$	276	3.468	−0.101(12)	1.867	2.730
n-C_5H_{12}	218	3.510	0.3862(14)	1.984	3.584
n-C_6H_{14}	231	3.535	1.3056(15)	2.076	3.737

[a] The shift values are taken from (16), the R_{1v} values are calculated from the data given in (17, 18).

are immersed, but when the superscript coincides with the second subscript, it is omitted. The a and b numbers are equal to V_{av}/V_{1v} and V_{bv}/V_{1v}, respectively[3].

The excess chemical potential, μ^E, of the benzene molecule transfer into infinitely diluted solution is described by the expression

$$\mu^E = \mathring{\mu}^E + \Delta G. \tag{4}$$

Here the contributions of pure non-perturbed components are collected in $\mathring{\mu}^E$, and ΔG is the contribution of the solute-solvent interface. According to[3],

$$\mathring{\mu}^E = G^i_{av} + G^c_{av} - G^i_{bv} - G^c_{bv} - G^i_{1u} - G^c_{1u}, \tag{5}$$

where the i superscript shows that we are concerned with the free energy of the interaction of former content in cavity described by the subscript with the rest of liquid, and the c superscript indicates the free energy of the surface of the respective cavity. Taking into account, that[8,9]

$$G^i = -2G^c, \tag{6}$$

it is convenient to rewrite Eq. (5) as follows:

$$\mathring{\mu}^E = G^i_{av} + G^c_{av} + G^c_{bv} + G^c_{1u}. \tag{7}$$

In turn,

$$\Delta G = \Delta G^i + \Delta G^c, \tag{8}$$

where ΔG^i is the difference in the free energy of the interaction between the given and former cavity contents and the solvent after the substitution a solute molecule for a drop consisting of $(a - b)$ solvent molecules, and ΔG^c is the analogous difference for the cavity surface energy[3].

The G^c at $R \geq R_1$ may be estimated according to Sinanoglu[8,9]:

$$G^c \approx \gamma\sigma[1 - (\sigma_1/\sigma)(1 - \kappa_1)], \tag{9}$$

where γ is the macroscopic surface tension coefficient, σ is the surface area and κ_1 is determined by the expression

$$\kappa_1 = (\sigma_1\gamma)^{-1}[\Delta G^0 + kT\ \ln(kT/p_0 V_1)], \tag{10}$$

where ΔG^0 is the free energy of transfer of a molecule from the pure liquid into vacuum and p_0 is the pressure in the standard state[9]. Since

$$\Delta G^0 = kT \ln K, \tag{11}$$

where K is the liquid–vapour equilibrium constant, then in quasi-spherical approximation we have

$$\kappa_1 \approx (4\pi R_1^2)^{-1} kT \ln(kT/p_s V_1), \tag{12}$$

where p_s is the pressure of saturated vapour.

At $V \leq V_1$ both Eq. (9) and a quasi-spherical approximation for the G^c evaluation cease to be valid, and the accuracy of Eq. (6) must be retained in the next step. Unlike[3,8,9] we shall consider a liquid to be continuous, if all its molecules occupy equal volumes, V_1, in the liquid (the comparison may be performed, for example, having constructed the Voronoi polyhedron for every molecule). Otherwise the local increases of density (the overlaps of the Voronoi polyhedrons constructed for the continuous liquid) and the cavities (free from polyhedrons space parts), associated with the deviation of intermolecular distances from the average ones, take place. In this model the quasi-spherical approximation for the G^c evaluation is retained when $V \geq V_1$. We shall suppose that, at $V \leq V_1$, the free energy of the fluctuation cavity creation has pure entropy origin, for example, as elasticity of rubbers on elongation[10]. Then while considering a cavity of a great diameter as a result of an accidental collision between particles of gas of little cavity defects, we find that the probability, w, to detect the cavity of $V = \lambda V_1$, where $0 < \lambda < 1$, in the given space point is equal to

$$w = w_0^{B\lambda}, \tag{13}$$

where w_0 and B are the constants. Then the cavity formation free energy is described by

$$G^i(\lambda) + G^c(\lambda) = -\bar{C}kT\lambda = \bar{\bar{C}}\lambda. \tag{14}$$

On the basis of such considerations, the total free energy of the interaction of the former total contents in all the cavities, the volume sum of which is V_{1v}, with the environment, is equal to the free energy for the interaction of the environment with the former content of a cavity having the volume of V_{1v}, i.e., it is G^i_{1v}, or

$$G^i_v = \lambda G^i_{1v}. \tag{15a}$$

Substituting this expression in (14), we have

$$G^c_v = \lambda G^c_{1v}, \tag{15b}$$

i.e., within the submolecular region the free energy on the cavity surface is proportional to the increase in the distance between molecules, which resulted in the creation of this cavity. In principle, Sinanoglu's approach to the evaluation of cavity free energy for cavities of molecular size[8,9] may be extended to the submolecular region. Then, in particular, in the quasi-ellipsoidal approximation the surface tension coefficient within a submolecular region is described by the expression

$$\gamma_\lambda = 2\gamma\kappa_1\lambda/[1 + A(\lambda)], \tag{16}$$

with

$$A(\lambda) = \lambda/(1 - \lambda^2)^{1/2} \ln[1 + (1 - \lambda^2)^{1/2}/\lambda].$$

CONFORMATIONAL CHANGES IN SOLVENTS

If we confine ourself to the consideration of the solutions of benzene in liquids, the molecules of which do not differ too much from benzene molecules as regards the size and the pair intermolecular interaction potentials and are not subjected to strong orientation interactions, but may undergo conformational transformations, then in the description of the solvent thermodynamics the shift of conformation equilibrium in a solvent should practically be revealed only in the ΔG^c value, and we may write the approximate equation

$$G^i_{av} + \Delta G^i \approx \xi G^i. \tag{17}$$

Combining Eq. (17) with Eq. (7), we get

$$\mathring{\mu}^W + \Delta G^i \approx -[(2\xi - 1)G^c_{av} - G^c_{bv} - G^c_{1u}], \tag{18}$$

where $\xi = (\delta_u/\delta_v)$ and δ is Hildebrand's solubility parameter. Having subtracted $\mathring{\mu}^E + \Delta G^i$ from the experimental μ^E value, we can determine ΔG^c. The values necessary for evaluation of the terms in the right side of Eq. (18) are given in Table 2, and the $\mathring{\mu}^E + \Delta G^i$ and ΔG^c values are shown in Table 3.

From all solvents of benzene listed in Table 3, only chloroform molecules can not suffer the conformation transformation. Accordingly, only a solution of benzene in chloroform shows a small negative ΔG^c value which is hardly beyond the scope of the usual measurement accuracy of μ^E. The sign possibly indicates the increase of short-range ordering in the weakly polar chloroform molecules arrangement near benzene, but the effect is practically equal to zero. In the remaining cases ΔG^c has a positive sign, that should be considered as evidence that a part of the solvent

Table 2 Energetic characteristics of solvents.

Solvent	γ,[a] mN/m^2	κ_1[b]	δ,[c] $J^{1/2}/cm$	G^{conf}/kT
C_6H_6	28.25	0.831	18.8	
$CHCl_3$	26.58	0.870	19.0	
cyclo-C_6H_{12}	24.34	0.813	16.8	6.8(19)
1,4-$C_4H_8O_2$	35.42	0.768	20.0	3.8(20)
n-C_5H_{12}	15.55	0.941	14.3	1.1(21)
n-C_6H_{14}	17.89	0.895	14.9	0.9(21)

[a] Refs (18, 22).

[b] The κ_1 values are taken from (9) or calculated according to Eq. (10) on the data given in the former column and in (17, 18).

[c] The data are taken from (23, 24), except δ for dioxane, which is calculated according to (23) from the data in (18).

Table 3 Energetic characteristics of solutions of benzene.

Solvent	$(\mathring{\mu}^E + \Delta G^i)/kT$	μ^E/kT	$\Delta G^c/kT$	ΔN^{conf}
$CHCl_3$	−0.002	−0.120(25)	−0.118	
cyclo-C_6H_{12}	−0.383	0.535(26)	0.918	0.1
1,4-$C_4H_8O_2$	−0.037	0.096(27)	0.133	0.03
n-C_5H_{12}	−0.106	0.679(28)	0.785	0.7
n-C_6H_{14}	0.002	0.506(28)	0.504	0.6

molecules take up energetically disadvantageous conformations under the disturbance in symmetry of the force field acting on solvent molecules, caused by the change of one of its neighbours for a benzene molecule. In the last column in Table 3 the evaluations of additional conformational transition quantities induced by a benzene molecule are given. They are equal:

$$\Delta N^{\mathrm{conf}} = \Delta G^c/G^{\mathrm{conf}}, \tag{19}$$

where G^{conf} is the average conformational transition free energy in the solvent. For cyclic molecules (cyclohexane and especially dioxane) the additional transition number is very small, and only for chain pentane and hexane an average quantity of additional trans-gosh transitions is comparable with that of added benzene molecules.

CONCLUSION

The evaluation of ΔN^{conf}, arising under the influence of benzene, perhaps, has proved possible for the first time. The values appear to be quite plausible and suggest that the refinement of the dissolution picture with the cavity creation, consisting in accounting for the role of solvent density fluctuations (vacancies of R_{bv} radius), has no obvious inherent inconsistences. As far as the possibility of using the spectral shift method for evaluating the conformational equilibrium shift in a solvent is concerned, this appears feasible in those not too frequent cases, in which the R_{1u}^{v} value is sensitive to a solvent (for conditions see Refs (7, 11)), as occurs in the case of the benzene solutions examined in this work.

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