Ultrasound Absorption in Mixtures of Phenol with Carbontetrachloride and Cyclohexane

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(Z. Naturforsch. **31 a**, 1671 – 1673 [1976]; received August 16, 1976)

Ultrasound absorption has been measured in binary mixtures of phenol with carbontetrachloride and cyclohexane covering the complete concentration range at 20, 30, 40, and 50 °C. Absorption maxima in dilute phenolic solutions are interpreted as arising from cyclic association of phenol to trimers or tetramers.

I. Introduction

Ultrasound absorption measurements were done [1] in solutions of phenol in carbontetrachloride and cyclohexane, and peculiar absorption maxima at low phenol mole fraction were noted. In connection with other measurements [2], it was thought of the possibility of ascribing these absorption maxima to trimeric or tetrameric cyclic associates [3], and the measurements were extended over the complete concentration range.

II. Experimental

Measurements were made by means of a two crystal pulse technique [4], comparing the attenuation caused by the liquid with that of a reference pulse of same length and frequency in a calibrated attenuator. X-cut quartz crystals with eigenfrequencies of about 5 MHz were excited in their odd harmonics up to 57 MHz. Temperature error may be ± 0.05 K, mole fraction error ± 0.0002. The absorption α/f^2 (α being the linear amplitude absorption coefficient, f the frequency) varied with frequency between $3-5\%$ in case of strong absorption, and $5-10\%$ in case of weak absorption. This variation was nonsystematic and considered to be within the limits of experimental error; values for different frequencies were averaged; most of the cyclohexane mixtures were measured only at 26 and 36 MHz.

Carbontetrachloride and phenol were purified and stored as described elsewhere [2]. Cyclohexane (p. A., Merck) was used without additional purification. Refractive index of carbontetrachloride was $n_D^{20} = 1.46019$. Melting points of phenol and cyclohexane were 40.89 °C and 6.36 °C, resp.

III. Results and Discussion

Table 1 and Fig. 1 show the results for phenol + carbontetrachloride, and Table 2 and Fig. 2 for phenol + cyclohexane. In the figures, the measured

Table 1. $(\alpha/f^2)/10^{-17}\,\mathrm{cm^{-1}\,s^2}$ for x_{Ph} phenol + $(1-x_{\mathrm{Ph}})$ carbon tetrachloride.

T/°C x_{Ph}	19.6	29.7	39.4	50.2
0.0	548	568	579	—
0.0199	612	582	542	—
0.0476	564	526	514	500
0.0736	499	470	460	—
0.2021	312	295	286	280
0.4664	196	175	161	150
0.6598	—	140	125	115
1.0	—	—	89 [a]	78

[a] at 42.1 °C.

Table 2. $(\alpha/f^2)/10^{-17}\,\mathrm{cm^{-1}\,s^2}$ for x_{Ph} phenol + $(1-x_{\mathrm{Ph}})$ cyclohexane.

T/°C x_{Ph}	20.0	30.0	39.5	49.3
0.0	192	201	210	230
0.0306	266	256	244	240
0.0719	226	223	220	220
0.1457	—	186	188	191
0.2578	—	163	161	163
0.2992	—	159	154	152
0.4556	—	142	137	133
0.5666	—	—	121	112
0.6409	—	—	121	115
0.6564	—	—	111	105
0.7325	—	—	103	96
0.8100	—	—	98	86

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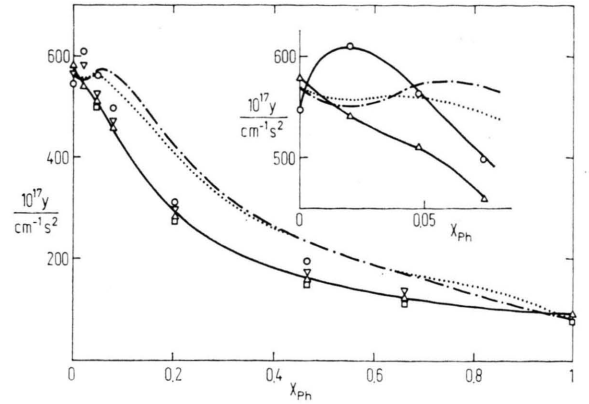

Fig. 1. $y = \alpha/f^2$ for the mixture $x_{Ph}\ C_6H_5OH + (1 - x_{Ph})\ CCl_4$. Experimental points are at 20° (○), 30° (▽), 39.5° (△), and 49.3 °C (□). Model calculations correspond roughly to 50 °C and are made for trimerisation (dotted curve) and tetramerisation (dash-dotted curve). Small phenol concentrations are shown on enlarged scale in the insert.

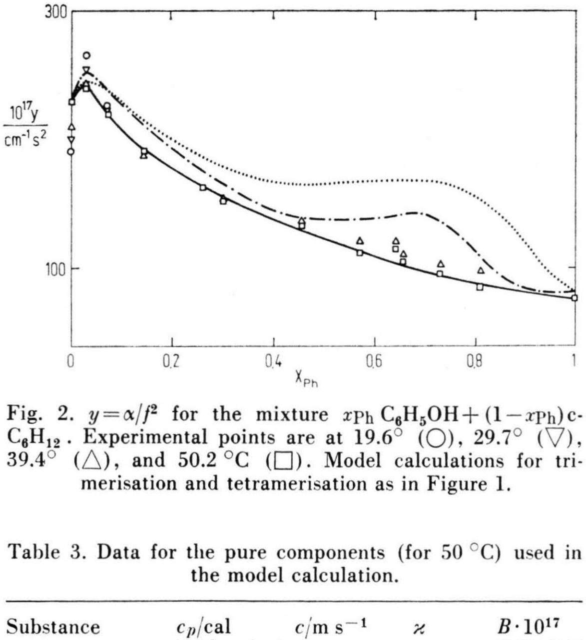

Fig. 2. $y = \alpha/f^2$ for the mixture $x_{Ph}\ C_6H_5OH + (1 - x_{Ph})$ c-C_6H_{12}. Experimental points are at 19.6° (○), 29.7° (▽), 39.4° (△), and 50.2 °C (□). Model calculations for trimerisation and tetramerisation as in Figure 1.

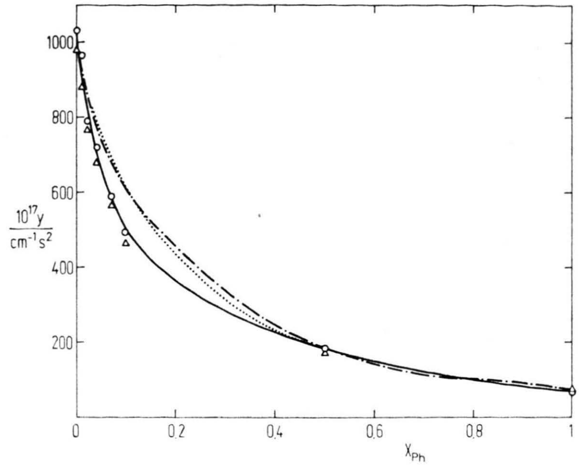

Fig. 3. $y = \alpha/f^2$ for the mixture $x_{Ph}\ C_6H_5OH + (1 - x_{Ph})\ C_6H_6$ according to Reference [5]. Experimental points are shown for 40° (△) and 50 °C (○). Model calculations for trimerisation and tetramerisation as in Figure 1.

Table 3. Data for the pure components (for 50 °C) used in the model calculation.

Substance	c_p/cal K^{-1} mol^{-1}	c/m s^{-1}	$\varkappa$	$B \cdot 10^{17}$ / cm^{-1} s^2
phenol [8, 12]	49.9	1423	1.205 [13]	55
carbon tetrachloride [6, 11]	31.5	844	1.444 [13]	570
cyclohexane [10]	39.2	1133.5	1.384	230
benzene [9]	32.8	1183.5	1.429	1000

curves are compared with a model calculation. The same comparison is done in Fig. 3 for phenol + benzene on the basis of measurements reported in [5].

The model calculation is a very crude one, considering only the association reaction between phenol monomers and phenol (cyclic) trimers or tetramers as responsible for additional absorption [first term of Eq. (1)], and neglecting the influence of all other reaction steps on ultrasound absorption. Association constants and interaction parameters between all molecular species are the same as used earlier [2] for the approximate description of various other properties of phenolic mixtures. The absorption (low frequency limit) is given by

$$y = \frac{\alpha}{f^2} = \frac{\pi}{c}\,\frac{\varepsilon}{f_r} + B\,, \tag{1}$$

where α is the absorption coefficient, f the frequency (f_r the relaxation frequency), c the ultrasound velocity, ε the relaxation strength, and B the term which summarizes the absorption due to all other influences (classical + high frequency relaxation). Now ε/f_r is given by

$$\frac{\varepsilon}{f_r} = \frac{\varkappa - 1}{c_p}\,\frac{n\,\Phi^2}{n_s\,x_c}\,\frac{2\,\pi\,R\,(\Delta H/R\,T)^2}{\bar{k}\,f_c}\,. \tag{2}$$

In Eq. (2) (the nomenclature is in close analogy to previous papers [6, 3]) $\varkappa$ denotes the ratio of isobaric heat capacity c_p to isochoric heat capacity c_v, n the sum over the mole numbers of all species (monomer, chain polymers, cyclic trimer or tetramer, solvent), n_s the total formal mole number ($n_s = \sum_i i\,n_i + n_B$, where i is the number of monomeric groups in the phenolic species, and B is solvent), Φ is a stoichiometric factor including interaction parameters between different species, x_c is the mole fraction of the cyclic trimer or tetramer, R the gas constant, ΔH the heat of formation of the cyclic associate, $\overline{k}$ its dissociation rate, and f_c its activity coefficient (thought to be identical with that of the activated complex). The second factor in Eq. (2) is given by the model, the third factor should be constant over the whole concentration range. In the first factor, $\varkappa$ and c_p, and similarily the sound velocity c in Eq. (1), are assumed to be additive over the concentration range. Data for the pure components are summarized in Table 3. Finally, assumptions have to be introduced about the concentration dependence of the B-term in Eq. (1), and about the B-term of pure phenol. The concentration dependence of B is assumed to follow a modified Pinkerton formula [7]

$$B = B_{\mathrm{Ph}} (c_s x_s / c_{\mathrm{Ph}} + x_{\mathrm{Ph}}) \cdot \left[x_s \left(\frac{c_{\mathrm{Ph}} B_{\mathrm{Ph}}}{c_s B_s} x_s + x_{\mathrm{Ph}} - A x_s x_{\mathrm{Ph}} \right)^{-1} + x_{\mathrm{Ph}} \right] \tag{3}$$

composed of B-values, sound velocities and mole fractions of phenol and (more absorbing) solvent, and an empirical constant A set equal to $A = 0.6$. The modifying term $A x_s x_{\mathrm{Ph}}$ serves to hinder the B-term to decrease too rapidly for very small phenol concentrations. Here the B-term was estimated in the carbon tetrachloride system [1] and gives practically the whole absorption in the benzene system. The B-term of pure phenol was assumed to be $55 \cdot 10^{-17}\ \mathrm{cm}^{-1}\ \mathrm{s}^2$, which is about twice the classical value ($30 \cdot 10^{-17}\ \mathrm{cm}^{-1}\ \mathrm{s}^2$), and which leaves $29 \cdot 10^{-17}\ \mathrm{cm}^{-1}\ \mathrm{s}^2$ for the first term of Eq. (1) in the case of pure phenol. This serves to determine the constant third factor in Equation (2). Depending on the value of $\Delta H / R T$ (between 10 and 20), this gives for $\overline{k}/\mathrm{s}^{-1}$ a value between $3 \cdot 10^8$ and 10^9, which appears to be reasonable.

The model calculation is only intended to demonstrate that cyclic trimerisation or tetramerisation of phenol can effect a remarkable additional absorption in nonpolar solvents, in spite of rather low absorption of pure phenol itself. This is in contrast to the case of acetic acid, where the sound absorption due to cyclic dimerisation decreases rapidly with increasing concentration of carbon tetrachloride [6].

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