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SOLUBILITY PARAMETERS OF ALKYL DERIVATIVES OF PHENOL AND RESORCINOL*

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SUMMARY

On the basis of saturated vapour pressure data, the values of solubility parameters and their temperature dependence in the range 25–200°C for about 50 alkyl derivatives of phenol and resorcinol were calculated and a rough estimation of their dispersion, polar and hydrogen bond components was made.

A comparison was made with the data obtained by using the distribution coefficient of phenols in apolar solvent–water systems and gas chromatographic retention data, the relationship with the phenol structure was investigated and calculation methods were carried out.

INTRODUCTION

Hildebrand's[1] solubility parameter in terms of the cohesive energy density and its breakdown into its various components[2,3] offers a basis for the general treatment of chromatographic retention[4]. However, in practice, the determination of solubility parameter values from the equilibrium data and *vice versa* is often difficult. This difficulty is caused by the restrictions of regular solution theory, whereas in real solutions forces other than dispersion forces play an important role (owing to the presence of polar groups and, exceptionally, $-CH_2-$ chains also. In the liquid phase, these difficulties have often been circumvented by the use of empirical solubility parameter values[5–8], but in the gaseous phase they have mostly been ignored (by taking the compressibility factor as equal to unity). In phenols, the intermolecular interaction is complicated and these simplifications may be effective to different extents. As solubility parameter data for phenols are scarce[2,3,8–10], it was our aim to calculate them by making use of various methods and, by comparing all of the results, to draw some conclusions about their general usefulness.

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THEORETICAL

Basic relationships[1,2,7]

$$\delta = \left(-\frac{E}{v}\right)^{\frac{1}{2}} = \left(\frac{(\Delta H_v - RT)z}{v}\right)^{\frac{1}{2}} \tag{1}$$

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{2}$$

$$RT \ln k_x = v_x \left[(\delta_x - \delta_M)^2 - (\delta_S - \delta_x)^2\right] \tag{3}$$

$$RT \ln (t_x/t_{st}) = (v_{st} - v_x)\,\delta_S^2 - 2\,(v_{st}\cdot\delta_{st} - v_x\cdot\delta_x)\,\delta_S \tag{4}$$

where

δ = solubility parameter, (cal/cm^3)$^{\frac{1}{2}}$;
E = energy of vaporization, cal/mole;
ΔH_v = heat of vaporization, cal/mole;
v = molar volume, cm^3;
z = compressibility factor (taken as unity);
R = universal gas constant, cal/deg·mole;
T = temperature, °K;
k = molar distribution coefficient;
t = gas chromatographic retention time.

Subscripts T, d, p, h are total value and its dispersion, and polar and hydrogen bonding components, respectively; x and st = the partitioned substances; M and S = mobile and stationary phases, respectively; w and c = water and critical, respectively.

The dispersion component was calculated from a homomorph plot for cycloparaffin hydrocarbons[11] and that of the hydrogen bond from the value of bond energy of 4300 cal per bond[12]; the values of δ_p were found from the difference. As error analysis for eqns. 1, 3 and 4 has shown, the relative errors in the values of E, t_x and k_x may not exceed 2, 30 and 50%, respectively, when calculating the values of δ or δ_x with an absolute error of less than 0.1 unit. It seems that calculations from eqns 3 and 4 are more precise. In fact, however, the latter relationships are good enough only for regular solutions.

Initial data

The heats of vaporization given in Table I were calculated from the saturated vapour pressures[13,14] by using the Douglas–Avakyan differentiation method[15].

All non-available ΔH_v values of phenols that contain up to 14 carbon atoms per molecule were calculated in the temperature range 20–200°C by the method of linear interpolation and extrapolation (with an error of about ± 700 cal/mole). The remainder of the data were obtained from the following relationships.

For alkylresorcinols (the data of Lille[16] were treated): $v^{20} = 1.202M - 44.32$, $M = 110$–376, $2s = 0.70$, $n = 9$; $dv^t/dt = 8.28\cdot10^{-4}\cdot M - 0.050$, $t = 25$–200°C, $2s = 4.2\cdot10^{-4}$, $n = 9$. At 20–22°C: for 2-isomers, $\log k = 0.4900\cdot n_C - 0.8000$, $2s = 0.49$; for 4-isomers, $\log k = 0.6128\cdot n_C - 1.1866$, $2s = 0.15$; for 5-isomers, $\log k = 0.5007\cdot n_C - 1.2473$, $2s = 0.12$. Here, M = molecular weight, k = weight distribu-

TABLE I

INITIAL VALUES OF HEATS OF VAPORIZATION (kcal/mole) AND BOILING POINTS (°C)

Alkylphenol, PhOHR				*Alkylresorcinols, Ph-1,3-(OH)$_2$R*			
R	ΔH_v^{298}	ΔH_v	t_B	*R*	ΔH_v^{298}	ΔH_v^{415}	t_B
—	13.09	11.96	182	—	21.69	17.48	273
2-C_1	13.62	11.94	191	2-C_1	16.00	20.48	264
2-C_2	13.65	12.54	207	2-C_4	19.09	27.74	—
2-C_4	16.57	13.69	237	2-C_6	20.77	28.97	324
3-C_1	—	12.37	203	4-C_1	16.94	20.96	269
3-C_2	16.06	13.45	214	4-C_5	21.56	27.71	—
3-C_3	16.33	14.66	228	4-C_6	23.41	30.98	340
3-C_4	—	14.44	249	5-C_1	22.87	18.44	289
4-C_1	—	12.62	202	5-C_2	24.48	19.79	308
4-C_2	16.52	13.48	219	5-C_7	35.50	25.72	393
4-C_3	—	13.88	232	2.5(C_1)$_2$	17.63	21.94	280
4-C_4	19.09	15.07	250	5-C_1-2-C_2	17.96	22.62	—
4-C_5	20.27	15.73	—	5-C_1-2-C_6	22.52	31.63	—
2,4-(C_1)$_2$*	—	12.59	211	4,6-(C_1)$_2$	17.49	21.00	279
2,6-(C_1)$_2$	—	12.79	212	4.5-(C_1)$_2$	17.85	—	—
3.4-(C_1)$_2$	15.51	13.85	227				
3.5-(C_1)$_2$	16.47	13.80	220				
2,3-(C_1)$_2$	—	12.12	218				

* Also for 2.5- isomer.

tion coefficient for benzene–water, t = temperature (°C), n_C-number of carbon atoms in the side-chain, s = standard error and n = number of data.

For alkylphenols (calculated from ref. 17): $v^{20} = 1.289 \cdot M - 37.36$. $M = 94$–150, $2s = 6.8$, $n = 9$; $dv^t/dt = 1.56 \cdot 10^{-3} \cdot M - 0.0777$, $t = 25$–200°C, $2s = 0.0132$.

In addition, literature data for the gas chromatographic relative retention times of alkylphenols on 60 phases were used: these data were partially summarized by Kharlamovich and Churkin[18].

RESULTS AND DISCUSSION

From the values of the solubility parameters calculated on the basis of heats of vaporization (Tables II and III), the tendencies related to the phenolic structure of the molecules can be seen. The addition of a hydroxyl group to the molecule increases the δ_T value, while the addition of a CH_2– group decreases it. Also, the influence of an alkyl chain in the *ortho* position relative to the hydroxyl group is considerably stronger than that of an alkyl chain in the *meta* or *para* position. For dibasic phenols, an increase in temperature causes a greater decrease in the δ_T value than that for monobasic phenols. This effect is connected with the lower dH_v^t/dt value for the latter compounds.

The energy density of intermolecular interactions caused by dispersion forces and hydrogen bonds shows a trend towards lower values as the length of the alkyl chain increases. At the same time. the energy density of polar interactions increases.

These results are in accordance with the increase in molecular polarization caused by an increase in the alkyl chain length in 2-alkylresorcinols[20]. Considering this effect, it is necessary to note that the equation of Böttcher, derived for spherical

TABLE II

SOLUBILITY PARAMETERS FOR ALKYLPHENOLS, PhOHR

R	*20 °C*		*80 °C*				$-\frac{d\delta_T}{dt}\cdot 10^2$	T_C (°K)**
	δ_T	δ_T*	δ_T	δ_d	δ_p	δ_h		
—	12.0	12.6 (ref. 8)***	11.3	8.7	2.7	6.8	1.05	695
2-C_1	11.1	11.3 (ref. 10)	10.5	8.4	0.4	6.3	1.02	693
2-C_2	10.7	—	10.1	8.0	1.6	5.8	1.12	701
2-C_3	10.4	—	9.7	7.8	1.8	5.5	1.20	707
2-C_4	10.2	—	9.4	7.6	2.1	5.1	1.26	715
2-C_5	9.9	—	9.1	7.3	2.4	4.9	1.31	724
2-C_6	9.7	—	8.9	7.1	2.7	4.6	1.36	731
3- and 4-C_1	11.7	12.2 (ref. 8)	10.9	8.3	3.3	6.3	1.22	710/709
3- and 4-C_2	11.4	11.3 (ref. 10)	10.6	8.1	3.5	5.8	1.35	711/718
3- and 4-C_3	11.2	—	10.3	7.8	3.7	5.5	1.46	717/723
3- and 4-C_4	10.9	—	10.0	7.6	3.9	5.1	1.55	732/734
3- and 4-C_5	10.7	—	9.8	7.5	4.0	4.9	1.62	742/743
3- and 4-C_6	10.5	—	9.5	7.2	4.2	4.6	1.68	740/752
2,6-$(C_1)_2$	10.7	—	10.1	8.1	1.4	5.8	1.12	708
2,4-$(C_1)_2$	11.0§,§§	11.2 (ref. 10)	10.1	8.1	1.4	5.8	1.37	707
2,3-$(C_1)_2$	10.9§	11.2 (ref. 10)	10.1	8.1	1.4	5.8	1.41	717
3,5-$(C_1)_2$	11.6§	11.3 (ref. 10)	10.6	8.1	3.5	5.8	1.41	720
3,4-$(C_1)_2$	11.3§	11.3 (ref. 10)	10.6	8.1	3.4	5.8	1.08	730

* See text.

** In the absence of boiling point data, the values of $\Delta t_B(CH_2)$ for 2-R = 14.5° and for 3- and 4-R = 15.5° were used.

*** 11.4 according to ref. 3.

§ Without smoothing of ΔH_v values over n_C.

§§ Also for the 2,5- isomer.

molecules with a dipole at the centre and used by Hansen[2], when used with alkylphenols that have long alkyl chains, gives apparent δ_p^2 values that are up to 10 times lower than the actual values (taking into account the acentric location of the dipole).

The separation of δ_p^2 and δ_h^2 is very approximate and only a rough estimate can be made. Probably an examination of the absorbances of associated hydroxyl groups in the 2.75–3.20 μm range in the IR spectra would show the order of δ_h^2 values 2-<4-<5-alkylresorcinol, in accordance with their acidities[16].

The total solubility parameters calculated from the molar distribution coefficients between an apolar solvent and water (marked with asterisk in Tables II and III) are in fair agreement with those calculated from the heats of vaporization. In previous calculations for monobasic phenols, cited in Table II, the empirical value $\delta_h = 19.0$ was mostly used[8]. The specific interaction of alkylresorcinols with water is stronger than that of alkylphenols and therefore the δ_h values must be lower. Indeed, for the latter compounds in benzene–water, the value of $\delta_h = 18.0$ is suitable. From these data, one can conclude that the degree of association of phenols in the vapour phase is negligible.

The calculation of δ_x values for phenols by using eqn. 4 is impossible owing to the lack of data for most stationary phases. However, in order to establish the predicting power of this equation in this instance, by using the known δ_x values for alkylphenols, we have calculated the δ_S values for 60 stationary phases. Some of these re-

TABLE III

SOLUBILITY PARAMETERS FOR ALKYLRESORCINOLS. Ph-1,3-$(OH)_2R$

R	*20 °C*		*80 °C*				$-\frac{d\delta_T}{dt}\cdot 10^2$	T_c (°K)[**]
	δ_T	δ_T[*]	δ_T	δ_d	δ_p	δ_h		
—	15.4	14.7[***]	14.4	9.0	5.5	9.8	1.65	804
2-C_1	13.6	13.8	12.7	8.6	2.8	8.9	1.55	775
2-C_2	13.3	13.5	12.3	8.3	3.8	8.3	1.69	777
2-C_3	13.0	13.2	11.9	8.1	4.0	7.7	1.80	779
2-C_4	12.8	13.0	11.7	7.9	4.6	7.3	1.89	783
2-C_5	12.6	12.9	11.4	7.6	4.9	6.9	1.97	787
2-C_6	12.5	12.8	11.2	7.4	5.2	6.6	2.04	792
2-C_7	12.4	12.6	11.1	7.2	5.6	6.4	2.10	798
2-C_8	12.2	—	11.0	7.0	5.9	6.1	2.15	804
4-C_1	13.9[§]	14.0	12.9	8.6	3.6	8.9	1.65	782
4-C_2	13.5	13.6	12.5	8.4	4.2	8.3	1.68	786
4-C_3	13.2	13.3	12.2	8.1	4.8	7.7	1.71	792
4-C_4	13.0	13.0	11.9	8.0	4.9	7.3	1.73	798
4-C_5	12.8	12.8	11.7	7.8	5.3	6.9	1.75	805
4-C_6	12.6	12.6	11.6	7.5	5.9	6.6	1.77	813
4-C_7	12.5	12.5	11.4	7.3	6.0	6.4	1.78	823
4-C_8	12.4	—	11.3	7.1	6.3	6.1	1.79	830
5-C_1	14.7[§§]	14.2	13.6	8.8	5.3	8.9	1.73	811
5-C_2	14.2	13.8	13.2	8.5	5.8	8.3	1.81	822
5-C_3	13.9	13.5	12.8	8.3	5.9	7.7	1.87	831
5-C_4	13.6	13.2	12.5	8.1	6.1	7.3	1.92	837
5-C_5	13.4	13.1	12.2	7.9	6.2	6.9	1.96	848
5-C_6	13.2	12.9	12.0	7.7	6.4	6.6	2.00	858
5-C_7	13.2	12.8	11.8	7.5	6.5	6.4	2.33	870
5-C_8	12.9	—	11.7	7.3	6.8	6.1	2.06	882

[*] See text.

[**] In the absence of boiling point data the values of $\Delta t_g(CH_2)$ for 2-R = 12°, 4-R = 14° and 5-R = 17° were used.

[***] Calculated as 14.9 according to ref. 19.

[§] Without smoothing of ΔH_v values over n_C for R = 4.6 − $(C_1)_2$ and 4.5 − $(C_1)_2$, 13.0 and 14.4, respectively.

[§§] See [§], for R = 2.5 − $(C_1)_2$, 5-C_1 − 2-C_2 and 5-C_1 − 2-C_6, 13.3, 12.7 and 12.4, respectively

sults are shown in Table IV. On 59 phases (sodium dodecylbenzenesulphonate being the only exception), the calculated δ_S values were distributed into two groups in accordance with the structure of the phenol. The values, calculated from the data for *meta-* and *para-*substituted alkylphenols, are as a rule higher than those calculated from the data for *ortho-*substituted alkylphenols. For example, the δ_S values obtained for glycerine are 13.6 ± 0.2 and 11.8 ± 0.3, respectively (at 160 °C). For this phase, some vapour pressure data are known[21,22] and from these data δ_S values of 13.6–15.4 were estimated at the same temperature.

For *ortho-*substituted alkylphenols, the relative retention times are higher than those calculated from the Rohrschneider equation (exceptionally, 2.6-dimethylphenol often behaves in the same manner as the 3,4- and 3,5- isomers). Sometimes, the relative retention is so high that eqn. 4 has an imaginary solution, particularly

TABLE IV

TOTAL SOLUBILITY PARAMETERS FOR SOME GROUPS OF LIQUID PHASES, CALCULATED BY USING EQN. 4 ON THE BASIS OF RETENTION DATA FOR ALKYLPHENOLS ($M \leqslant 122$)

Phenols	*Phase*	δ_t, *160 °C*	$-d\delta_T/dt \cdot 10^2$	*n*	*Temperature range (°C)*
3-, 4-, 3,4- and 3,5-substituted phenols (δ'_S)	Apiezon L (M,W)	11.05 ± 0.84	5.00 ± 0.7	41	135–200
	Phthalates	11.18 ± 0.48	5.13 ± 0.4	39	115–190
	Phosphates	11.91 ± 1.08	5.30 ± 0.4	45	110–200
	Sugars, alcohols	13.79 ± 0.80	3.67 ± 1.0	47	140–180
Ortho-substituted phenols (except 2,6-isomer (δ''_S)	Apiezon L (M,W)	7.73 ± 1.34	2.36 ± 1.1	40	135–200
	Phthalates	8.50 ± 1.02	2.84 ± 0.8	44	115–190
	Phosphates	9.47 ± 1.32	2.46 ± 0.6	48	110–200
	Sugars, alcohols	12.07 ± 0.90	1.94 ± 1.3	41	140–180

on apolar phases. Apparently, for *ortho*-substituted alkylphenols, those factors which are critical for obeying to the Rohrschneider equation (in particular the distribution in the stationary phase and the fugacity coefficient) are different from those of the standard compound (phenol). Probably, with 2,6-dimethylphenol mutual compensation of these factors takes place. It is noteworthy that such phenomena have also been noticed in extraction. For instance, for the distribution of 3-methylphenol in an apolar solvent–water system, a value of $\delta_w = 19.0$ is appropriate, but for the 2-isomer $\delta_w = 18.0$ is more suitable[8].

The interaction of sodium dodecylbenzenesulphonate with phenols is strong and the solute emerges from the column at a temperature considerably higher than its normal boiling point (methyl- and dimethylphenols at 260°C).

Thus, with a suitable standard substance, the Rohrschneider equation can be used for the estimation of the total solubility parameters (Table V) and also the heats of vaporization for compounds with any polarity.

It may also be possible for gas chromatography to be used for estimating the components of the total solubility parameter.

CONCLUSION

By means of saturated vapour pressures, distribution coefficients in an apolar solvent–water system and gas chromatographic retention data, values of the total solubility parameters for phenols have been obtained. However, the use of empirical solubility parameter values for water and suitable standard substances in these methods was necessary. The calculated values of the solubility parameters and their temperature dependance for about 50 phenols would be useful in order to choose the optimal operating conditions for their chromatographic and extractive separation.

TABLE V

COMPARISION OF TOTAL SOLUBILITY PARAMETER VALUES CALCULATED FOR SOME ALKYLPHENOLS BY USING EQNS. 1 AND 4 ON VARIOUS STATIONARY PHASES

Stationary phases: A, Apiezon L, $\delta_s' = 12.07$, $\delta_s'' = 8.90$: B, Erythrit, $\delta_s' = 14.14$, $\delta_s'' = 12.68$; C, dimenthyl phthalate, $\delta_s' = 12.27$, $\delta_s'' = 9.35$: D, tri-2,4-xylenyl phosphate, $\delta_s' = 15.03$, $\delta_s'' = 11.83$.

R	*150 °C*			*136 °C*		*120 °C*	
	Eqn. 1	*Eqn. 4, A*	*Eqn. 4, B*	*Eqn. 1*	*Eqn. 4, C*	*Eqn. 1*	*Eqn. 4, D*
2-C_1	9.7	9.82	9.78	9.9	9.95	10.1	10.17
3-C_1	10.1	10.07	10.06	10.2	10.22	10.4	10.42
4-C_1	10.1	10.07	10.04	10.2	10.20	10.4	10.42
2,3-$(C_1)_2$	9.3	9.34	9.37	9.4	9.47	9.6	9.61
2,4-$(C_1)_2$	9.3	9.29	9.28	9.4	9.40	9.6	9.61
2,5-$(C_1)_2$	9.3	9.27	9.27	9.4	9.42	9.6	9.61
2,6-$(C_1)_2$	9.3	9.25	9.10	9.4	9.24	9.6	9.58
3,4-$(C_1)_2$	9.6	9.68	9.70	9.8	9.84	10.0	10.04
3,5-$(C_1)_2$	9.6	9.63	9.63	9.8	9.81	10.0	10.04
2-C_2	9.3	9.24	9.24	9.4	9.38	—	—
3-C_2	9.6	9.63	9.62	9.8	9.80	—	—
4-C_2	—	—	9.62	9.8	9.78	—	—
5-C_2	—	—	9.26	—	—	—	—

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