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Liquid−Liquid and Liquid−Solid Equilibria of Systems Containing Water and Selected Chlorophenols

M. Jaoui,[†] M. Luszczyk,[‡] and M. Rogalski*[,†]

Laboratoire de Thermodynamique et d'Analyze Chimique, Université de Metz, 57045 Metz, France, and Instytut Chemii Fizycznej PAN, Kasprzaka 44, 01-224 Warszawa, Poland

The solubilities of phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol in water were determined in the temperature range between 270 K and 423 K. Dynamic thermal analysis and a visual static method were used to establish the phase diagrams. Results obtained over a wide temperature and concentration range were used to model the liquid−liquid coexistence curve of the systems studied.

Introduction

Chlorinated phenols are extensively used as fungicides, herbicides, algicides, insecticides, and ovicides. They are present in effluents of oil refinery, coal mining, plastic, leather, paint, and pharmaceutical industrial plants.

Aqueous solubility is a particularly important parameter for assessing environmental partitioning of different compounds. Recently, Ma et al. (1993) determined the aqueous solubility of 16 chlorophenols at 298 K, using high-performance liquid chromatography. Numerous data concerning chlorophenols published in the literature were reviewed recently by Shiu et al. (1994). However, the majority of results on aqueous solubilities were obtained only for temperatures close to 298 K. These data are useful for environmental studies, but they are not sufficient for establishing the thermodynamic properties of these solutes.

In the present work, binary diagrams of aqueous solutions of phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol over a wide range of temperatures and concentrations were studied. Experimental data reported here and those taken from the literature (Campbell et al., 1937; Sidgwick et al., 1915; Sidgwick and Turner, 1922) were used to determine the phase behavior in a series of mixtures formed by chlorophenols and water. Analytical expressions were established, allowing us to estimate of the liquid−liquid equilibria over a wide temperature range and also to perform thermodynamic modeling of these systems.

Experimental Section

Materials. Water was deionized and its purity was checked by measuring the electrical conductivity, which was found to be between 1 and 1.8 μS cm^{-1}. 2-Chlorophenol, 3-chlorophenol, and 4-chlorophenol were from Merck; the other chemicals were from Aldrich and were more than 99% pure. Their purity was checked by cryometry in benzene. All were used as purchased without further purification.

Apparatus and Procedures. Solubility data were obtained using two experimental techniques, namely dynamic thermal analysis (DTA) and a static visual method (SVM) over the temperature range 273 K to 423 K.

Dynamic Thermal Analysis. This method was used to determine the solid−liquid diagram of diluted chlorophenol in water or water in chlorophenol solutions. Mixtures were prepared by mass, using an OHAUS AS 120 balance with an accuracy of ±0.0001 g. Samples of known composition (volume 25 mL) were placed in a Pyrex cell equipped with a magnetic stirrer. The cell was closed with a Swagelok fitting. A platinum resistance Pt-100 probe connected to a Hewlett-Packard digital multimeter 34401A was introduced directly into the cell. It was calibrated according to the ITS-90 scale at the water triple-point temperature. The accuracy of the temperature determination was ±0.1 K, and the precision was ±0.01 K. The cell was immersed in the glass vessel thermostated with an ethylene glycol + water mixture or thermal oil, selected depending on the temperature range. At first, the temperature of the cell was increased above the melting temperature of the sample. Then, the sample was slowly cooled by decreasing the temperature of the circulating liquid. The variations of the sample temperature versus time were followed with a personal computer. The temperature of the liquid−solid transition was established from the cooling plot in the usual way, using a graphical construction to obtain an intersection point of the extrapolated liquid and solid curves. Three determinations were performed for each sample. The scattering of the results was <±0.1 K.

Static Visual Method. This method was used to determine liquid−liquid equilibria. The upper temperature limit was fixed at 423 K to avoid possible decomposition of the chlorophenols. The measurements were carried out using an experimental setup similar to that described in the previous section (dynamic thermal analysis). The equilibrium cell was thermostated using either water (low temperatures) or thermal oil (high temperatures), circulating through the glass jacket. A window in the external insulating part enabled a direct visual observation of the phases present in the cell. The stability of the temperature was about ±0.1 K between 273 K and 353 K but decreased with temperature above 353 K. The estimated accuracy at 420 K was about ±0.2 K. The vessel was tightly closed with a stopper fitted out with a Swagelok fitting. A platinum resistance Pt-100 probe connected to a Hewlett-Packard digital multimeter 34401A was inserted in the stopper.

Samples (40 mL) of a known composition were placed in the Pyrex cell equipped with a magnetic stirrer. The

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* Corresponding author. E-mail: rogalski@ipc.sciences.univ-metz.fr.
[†] Université de Metz.
[‡] Instytut Chemii Fizycznej PAN.

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Table 1. Experimental Liquid−Liquid Equilibrium Data of Chlorophenol (1) + Water (2) Obtained Using the Static Visual Method

phenol		4-chlorophenol		2,4-chlorophenol		2,4,6-trichlorophenol		pentachlorophenol	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	$x_1{}^b$	T/K
0.3610	278.2	0.0025	282.2	0.7310	306.6	1.0432^a	314.2	69	333.2
0.3390	290.2	0.0029	284.2	0.0007	310.5	1.2540^a	334.3	80	342.7
0.0018	298.5	0.4310	305.3	0.7100	317.6	1.2549^a	335.3	95	353.2
0.3110	299.6	0.0039	308.3	0.0008	327.1	1.5796^a	334.3	106	361.2
0.0019	307.5	0.0041	311.2	0.7000	327.3	1.5796^a	337.6	117	372.0
0.2930	308.4	0.4040	323.4	0.6800	334.2	1.9286^a	334.3	132	386.0
0.0020	313.4	0.0045	324.2	0.0009	338.1	1.9286^a	342.3	143	402.0
0.0275	313.7	0.3880	329.6	0.6710	339.0	2.1666^a	334.5	157	407.0
0.0226	319.8	0.3690	338.7	0.0010	347.2	2.1666^a	345.3	171	422.3
0.0258	324.8	0.0050	341.9	0.6570	350.2	2.5819^a	352.2		
0.2310	325.8	0.3570	342.6	0.0011	355.1	3.0869^a	334.4		
0.0290	331.5	0.3360	354.4	0.6290	359.4	2.5808^a	334.2		
0.2051	334.0	0.0058	354.7	0.0012	363.5	3.0964^a	334.4		
0.0350	336.7	0.3340	355.4	0.6120	372.7	3.0914^a	369.0		
0.1501	338.8	0.0062	359.9	0.0012	373.7	5.7605^a	334.3		
		0.3150	362.4	0.6010	376.6	4.9400^a	383.8		
		0.0068	362.7	0.0013	382.1	5.8645^a	399.7		
		0.3090	362.8	0.0014	393.5	6.4600^a	408.1		
		0.0074	364.4	0.5560	395.7	7.0900^a	420.6		
		0.0076	365.7	0.0015	401.5	0.8128	335.0		
		0.0081	366.7	0.5350	404.6	0.5608	334.6		
		0.2980	367.7	0.0016	408.4	0.7677	334.6		
		0.2850	369.7	0.5020	419.8	0.6538	334.6		
		0.2410	380.4	0.0017	423.2	0.8286	342.3		
		0.0164	386.1			0.7914	346.4		
		0.2070	387.7			0.7632	367.3		
		0.1750	396.6			0.7314	386.2		
		0.0349	397.1			0.7012	402.1		
		0.1430	397.5			0.6783	421.2		
		0.0545	402.4						
		0.1080	402.9						

^{a} $\times 10^{-4}$. ^{b} $\times 10^{5}$.

Table 2. Experimental Liquid−Solid Equilibrium Data of Chlorophenol (1) + Water (2) Obtained Using Dynamic Thermal Analysis

4-chlorophenol		2,4-chlorophenol		2,4,6-trichlorophenol	
x_1	T/K	x_1	T/K	x_1	T/K
1.16×10^{-4}	273.1	1.0000	315.2	1.0000	339.3
1.01×10^{-3}	272.9	0.9976	315.0	0.9887	338.7
2.85×10^{-3}	272.8	0.9934	314.7	0.9834	338.2
1.0000	315.5	0.9855	314.1	0.9721	337.4
0.9865	313.4	0.9783	313.5	0.9685	337.0
0.9560	309.2	0.9692	313.0	0.9643	336.3
0.9110	303.2	0.9652	312.8	0.9517	335.7
0.8700	298.1	0.9540	312.1		
		0.9412	311.7		

temperature was increased up to the complete dissolution of the solute. Then the cell was cooled until the appearance of the second liquid phase. The saturation temperature was determined by a cyclic cooling and heating of the system, using a decreasing temperature amplitude. The appearing and vanishing of the new phase was observed visually.

Results and Discussion

The experimental values of the liquid−liquid and liquid−solid equilibria of binary systems of phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol with water are listed in Tables 1 and 2 and shown in Figures 1 and 2. Data taken from literature are presented also in these figures, together with our previous results concerning aqueous solubility of chlorophenols (Achard et al., 1996; Jaoui, 1998). As can be seen in parts a and b of Figure 1, the solubility data of phenol and 4-chlorophenol are in good agreement with the results of Campbell et al. (1937) and Sidgwick et al. (1922). The solubilities of pentachlorophenol in water between 298 K and 423 K are presented in Figure 2. The high melting temperature of this compound (T_f = 461.4 K) made it impossible to perform the measurements of water solubility in concentrated pentachlorophenol. As can be observed in

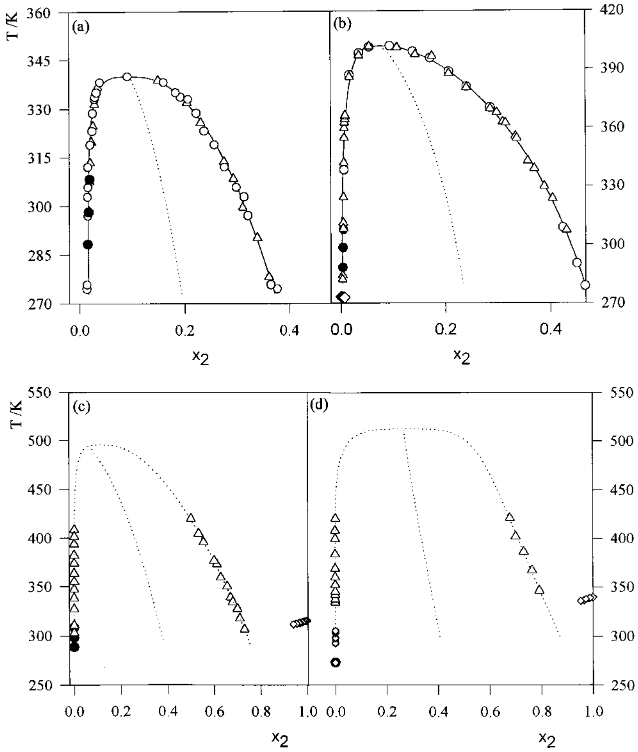

Figure 1. Liquid−liquid coexistence curves of systems formed by water (1) + chlorophenol (2): (a) phenol; (b) 4-chlorophenol; (c) 2,4-dichlorophenol; (d) 2,4,6-trichlorophenol. Experimental data obtained by: (●) conductometric method; (△) static visual method; (◇) dynamic thermal analysis; (○) literatures data. Full lines correspond to modeling using eq 3.

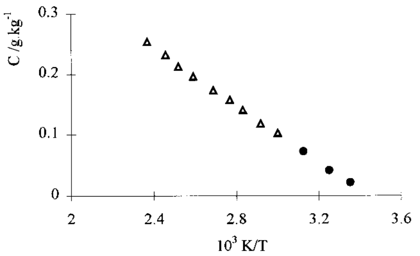

Figure 2. Aqueous solubility of pentachlorophenol as a function of T^{-1}. Experimental data obtained by: (●) conductometric method; (△) static visual method.

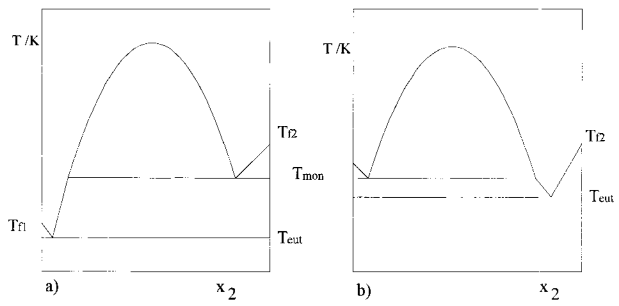

Figure 3. General pattern of phase diagrams of the systems formed by water (1) and chlorophenol (2): T_{f1}, melting temperature of water; T_{f2}, melting temperature of chlorophenols; T_{mon}, temperature of the monotectic point; T_{eut}, temperature of the eutectic point; a, $T_{mon} > T_{eut}$; b, $T_{eut} > T_{mon}$.

Table 3. Coordinates of the Triple Points Observed in Phase Diagrams of Chlorophenols with Water: $(H_2O)_S$, Ice; $(CP)_S$, Chlorophenol Solid; S_I, Solution Rich in Chlorophenol; S_{II}, Diluted Solution of Chlorophenol

compound	T/K	triple point	S/g kg^{-1}
4-chlorophenol	272.8	$(H_2O)_s-(CP)_s-S_I$	20.000
	273.9[a]	$(H_2O)_s-(CP)_s-S_I$[a]	86.5[a]
2-chlorophenol	263.9[a]	$(H_2O)_s-(CP)_s-S_{II}$[a]	91.2[a]
3-chlorophenol	276.4[a]	$(H_2O)_s-(CP)_s-S_I$[a]	82.3[a]
2,4-dichlorophenol	273.09	$(H_2O)_s-(CP)_s-S_I$	2.000
2,4,6-trichlorophenol	273.11	$(H_2O)_s-(CP)_s-S_I$	0.040
pentachlorophenol	273.12	$(H_2O)_s-(CP)_s-S_I$	0.013

[a] Experimental data by Sidgwick and Turner (1922).

Figure 2, the aqueous solubility of pentachlorophenol is a linear function of T^{-1} over a large temperature range. Good agreement of our results with literature data (Sidgwick et al., 1915; Sidgwick and Turner, 1922; Campbell et al., 1937) was noted.

Schematic patterns of phase diagrams with one monotectic and one eutectic triple point are presented in Figure 3. All systems considered in the present study follow these patterns. In the case of the 2-chlorophenol + water system the eutectic composition is in the range of rich-in-chlorophenol solutions (Figure 3b). However, with all other systems this composition corresponds to diluted chlorophenol solutions (Figure 3a). The temperatures and compositions of triple points observed within the chlorophenol + water diagrams are listed in Table 3.

Only aqueous solubility data of phenol and 4-chlorophenol cover the critical solution temperature (UCST). The following expression was proposed by Cuevas et al. (1995).

$$T/\mathrm{K} = \sum A_i\left\{\left[\frac{x_1}{B} - \frac{x_2}{(1-B)}\right]\Big/\left[\left[\frac{x_1}{B} + \frac{x_2}{(1-B)}\right]\right]\right\}^{2i} \quad (1)$$

Table 4. Upper Critical Solution Temperature and Critical Composition of Systems Formed by Water with Phenol and Monochlorophenols Estimated Using the Method Proposed by Cuevas et al. (1995) and the pK_a Values According to Doedens (1967)

compound	UCST/K	x_c	Sd(T)	pK_a
phenol	339.9	0.0828	1.49	9.93
2-chlorophenol	446.6	0.0691	3.06	8.48
3-chlorophenol	404.0	0.0661	1.10	8.96
4-chlorophenol	401.0	0.0521	3.87	9.34

Equation 1 was used to interpolate their upper critical solubility temperature and their composition. The same calculation was performed with the solubility data of 2-chlorophenol and 3-chlorophenol published by Sidgwick et al. (1915) and Sidgwick and Turner (1922).

The parameters of eq 1 were determined using a standard CURFIT procedure proposed by Bevington (1969). Estimated values of critical parameters of the four systems considered are given in Table 4. The upper critical point loci of water + 2,4-dichlorophenol and +2,4,6-trichlorophenol mixtures are out of the range of the present experiments and cannot be determined directly. However, we noticed that the critical temperatures reported in Table 4 can be correlated in terms of selected physical properties. The best results were obtained using pK_a data (Doedens, 1967). The resulting expression

$$\mathrm{UCST/K} = -72.11\mathrm{p}K_a + 1054.3 \quad (R^2 = 0.958) \quad (2)$$

can be used to estimate the upper critical temperatures of water + 2,4-dichlorophenol and + 2,4,6-trichlorophenol. It is difficult to justify this relationship by physical arguments. pK_a is the logarithm of the dissociation equilibrium constant. The acidity of chlorophenols increases strongly with increasing number of chlorine substitutents, attaining with pentachlorophenol a value similar to that of acetic acid. The increasing dissociation of chlorophenols should facilitate their solubilization in water. However, this effect is probably overcome by an increased hydrophobicity due to the chlorine substitutents. Consequently, good correlation of the UCSTs obtained with phenol and monochlorophenols cannot be considered as an argument that eq 2 can afford reliable estimates of the UCSTs of polychlorophenols.

However, this very rough procedure makes it possible to estimate the critical temperatures of 2,4-dichlorophenol and 2,4,6-trichlorophenol. The UCST data are necessary to correlate the liquid−liquid equilibria in terms of models based on the theory of critical phenomena. In the present work, a model proposed by Luszczyk (1988) was used. It is summarized by the following formula:

$$x = a_0 + a_1|\epsilon| + a_2|\epsilon|^{(1-\alpha)} + a_3|\epsilon|^{(1-\alpha+\Delta)} + (f/2)\sum_{i=0} b_i|\epsilon|^{(\beta+i\Delta)} \quad (3)$$

where

$$\epsilon = \frac{(T - \mathrm{UCST})}{\mathrm{UCST}}$$

The a_0 parameter in eq 3 corresponded to the critical composition. According to Luszczyk (1988), this model can be used to represent liquid−liquid solubility data over a wide temperature range. It contains two contributions. The first one corresponds to the Wegner expansion (Wegner, 1972) and takes into account the pattern of the coexistence curve in the vicinity of the critical point. The second is the analytical expression of the diameter curve of the coexist-

Table 5. Representation of Liquid−Liquid Coexistence Curves of Systems Formed by Water and Chlorophenols Using the Model Proposed by Luszczyk (1988)

compound	UCST/K	diameter curve constants	coexistence curve constants	temp range/K	10^2Sd(x)	N_T N_{Lit}
phenol	339.9	$a_0 = 0.0942 \pm 0.0007$	$b_0 = 0.2931 \pm 0.0023$	64.4	0.35	42
		$a_1 = -1.3223 \pm 0.0104$	$b_1 = 0.0176 \pm 0.0069$			24
		$a_2 = 1.5565 \pm 0.0088$				
2-chlorophenol	446.6	$a_0 = 0.0792 \pm 0.0047$	$b_0 = 0.2564 \pm 0.0188$	157.6	0.53	12
		$a_1 = -2.0235 \pm 0.6302$	$b_1 = 0.3355 \pm 0.0525$			12
		$a_2 = 2.4513 \pm 0.5521$				
3-chlorophenol	404.0	$a_0 = 0.0714 \pm 0.0040$	$b_0 = 0.3157 \pm 0.0223$	45.6	0.10	9
		$a_1 = -5.3345 \pm 0.1852$	$b_1 = -0.0061 \pm 0.1002$			9
		$a_2 = 4.9267 \pm 0.1456$				
4-chlorophenol	401.0	$a_0 = 0.0771 \pm 0.0027$	$b_0 = 0.2789 \pm 0.0063$	120.7	0.59	44
		$a_1 = -2.1052 \pm 0.2607$	$b_1 = 0.1318 \pm 0.0159$			12
		$a_2 = 2.3351 \pm 0.2316$				
2,4-dichlorophenol	500.6	$a_0 = 0.1058 \pm 0.0016$	$b_0 = 0.3664 \pm 0.0016$	134.7	0.25	27
		$a_1 = -1.8241 \pm 0.0038$	$b_1 = 0.2097 \pm 0.0028$			0
		$a_2 = 2.2695 \pm 0.0035$				
2,4,6-trichlorophenol	519.3	$a_0 = 0.2339 \pm 0.0403$	$b_0 = 0.6103 \pm 0.0111$	86.6	0.25	17
		$a_1 = -0.6526 \pm 1.3780$	$b_1 = -0.7872 \pm 0.0213$			0
		$a_2 = 1.0187 \pm 1.3420$				

ence curve. The following values of universal parameters were used in the calculations: $\alpha = 0.100$, $\beta = 0.325$, and $\Delta = 0.5$, $f = 1$ if $x > a_0$ and $f = -1$ if $x < a_0$.

The parameters of this model were determined using the standard CURFIT procedure of Bevington (1969). These parameters are given in Table 5 together with the corresponding standard deviations Sd(x) calculated according to the formula

$$\mathrm{Sd}(x) = 100\sqrt{-\sum_{i=1}^{N}(x_{\mathrm{exp}} - x_{cal})} \qquad (4)$$

It is difficult to determine the reliability of the calculated portions of the phase diagrams of 2,4-dichlorophenol and 2,4,6-trichlorophenol represented in Figures 1c and 1d, since it depends on the critical temperature values. Equation 2 may lead to satisfactory results only if the profile of the coexistence curve changes smoothly within a series of chlorophenols. It seems to be the case with 2,4-dichlorophenol + water, whose profile is similar to the phenol and monochlorophenol aqueous diagrams. However, with 2,4,6-trichlorophenol the solubility curve is qualitatively different. In solutions concentrated in chlorophenol, the solubility changes only slightly with an increase in temperature and two liquid phases coexist probably up to very high temperatures.

Conclusion

In this work we present measurements and a correlation of liquid−liquid coexistence curves of aqueous solutions of chlorophenols. The low solubility of chlorophenols in water decreases in a logarithmic way with increasing number of chlorine substitutents, and the relatively important water solubility in the organic phase constitutes a characteristic feature of these diagrams. Due to the complexity of the molecular interactions observed in this series of mixtures, the profile of the coexistence curve is not the same for all the systems. Consequently, our attempt to generalize the liquid−liquid solubilities in the homologous series of chlorophenols using the expression proposed by Luszczyk was only partly successful and it is difficult to estimate the reliability of the extrapolated sections of the 2,4-dichlorophenol and 2,4,6-trichlorophenol diagrams. Nevertheless, a set of liquid−liquid measured and extrapolated data concerning systems formed by chlorophenols and water is interesting from the thermodynamic modeling point of view.

Literature Cited

Achard, C.; Jaoui, M.; Schwing, M.; Rogalski, M. Aqueous Solubilities of Phenol Derivatives by Conductimetry Measurements. *J. Chem. Eng. Data* **1996**, *41*, 504−507.

Bevington, P. R. *Data Reduction and Error Analysis for the physical sciences*; McGraw-Hill: New York, 1969.

Campbell, A. N.; Campbell, J. R. *J. Am. Chem. Soc.* **1937**, *59*, 2481−2486.

Cuevas, R. M.; Eustaquio-Rincon, R.; Romero-Martinez, A.; Trejo, A. Experimental Liquid−Liquid miscibility curves for binary systems: ethanenitrile and butanenitrile with *n*-alkanes. *Fluid Phase Equil.* **1995**, *107*, 201−212.

Doedens, J. *Lang's Handbook of Chemistry*; McGraw-Hill Inc: New York, 1967.

Jaoui, M. Ph.D. Thesis, Universite de Metz, 1998.

Luszczyk, M. Volumetric behavior of (3-methoxypropionitrile + water) in the vicinity of the upper critical solution temperature. *J. Chem. Thermodyn.* **1988**, *20*, 29−38.

Ma, K. C.; Shiu, W. Y.; Mackay, D. Aqueous solubilities of chlorinated phenols at 25 °C. *J. Chem. Eng. Data* **1993**, *38*, 364−366.

Shiu, W. Y.; Ma, K. C.; Varhanickova, D.; Mackay, D. Chlorophenols and Alkylphenols: A review and Correlation of Environmentally Relevant Properties and Fate in an Evaluative Environment. *Chemosphere* **1994**, *29* (6), 1155−1224.

Sidgwick, N. V.; Spurrell, W. L.; Davies, T. E. *J. Chem. Soc.* **1915**, *107*, 1202−1209.

Sidgwick, N. V.; Turner, J. L. The Solubility of Chlorophenols. *J. Chem. Soc.* **1922**, 2256−2263.

Wegner, F. J. *Phys. Rev. B* **1972**, *5*, 4529−4535.

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