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Activity Coefficients of Chlorophenols in Water at Infinite Dilution

S. Tabai and M. Rogalski*

Laboratoire de Thermodynamique et d'Analyse Chimique, Université de Metz, 57045 Metz, France

R. Solimando

Laboratoire de Thermodynamique Chimique Appliquée, INPL-ENSIC, BP 421, 54001 Nancy, France

S. K. Malanowski

Instytut Chemii Fizycznej PAN, Kasprzaka 44, 01-224 Warszawa, Poland

The total pressure of aqueous solutions of chlorophenols was determined by a ebulliometric total pressure method for the aqueous solutions of phenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol in the temperature range from 40 to 90 °C. The activity coefficients at infinite dilution and the Henry constants were derived.

1. Introduction

Chlorinated phenols are used as disinfectants and in forest industries. They are chemicals that were widely produced and widespread in our environment and have a long half-life. The physicochemical properties depend on the electron donor−acceptor behavior of the hydroxyl group in solution. The pK_A values of chlorinated phenols indicate that they partially dissociate in aqueous solutions. The value of pK_A depends on the number and position of chlorine atoms. An excellent review of environmentally relevant properties of chlorophenols was given by Shiu et al. (1994).

A property enabling the prediction of the solubility behavior of chemicals in the environment is the activity coefficient in dilute aqueous solutions. The data for phenol were measured by several authors (Moore et al., 1995; Dohnal and Fenclova, 1995; Hakuta, 1975; Abd-el-Bary et al., 1986). There is a lack of measurements for the activity coefficients of chlorinated phenols in aqueous solutions.

The purpose of this work was to determine the activity coefficients of chlorinated phenols using the ebulliometric method.

2. Experimental Section

2.1. Chemicals. *Phenol* (CASRN 108-95-2) was Purchased from Fluka. A purity of better than 99.5% by mass was found by GLC. *2-Chlorophenol* (CASRN 95-57-8) was purchased from Aldrich-Chemie GmbH & Co. KG, as better than 99% pure, and was used as delivered. *3-Chlorophenol* (CASRN 108-43-0) was purchased from Janssen Chimica, as better than 99% pure, and was used as delivered. *4-Chlorophenol* (CASRN 106-48-9) was purchased from Fluka, as better than 99% pure, and was used as delivered. *2,4-Dichlorophenol* (CASRN 120-83-2) was purchased from Janssen Chimica, as better than 99% pure, and was used as delivered. *Water* (CASRN 7732-18-5) was double distilled and organic matter was removed by oxidation with potassium permanganate. The purity was checked by determination of the vapor pressure curve and computation of enthalpy of vaporization. At normal conditions the deviation from recommended enthalpy values was about 0.1%.

2.2. Measurements. The vapor pressure measurements of pure substances and mixtures were performed in a modified Swietoslawski's ebulliometer for total pressure measurements. The ebulliometer and procedures of determination of vapor pressure as a function of temperature and composition were described previously (Rogalski and Malanowski, 1980).

The ebulliometer was connected to the pressure-stabilizing system, which consisted of a 0.6 m^3 buffer vessel, kept in a constant temperature air bath and coupled through the system of valves with a vacuum pump and pressurized argon container. The pressure in the buffer vessel was manually adjusted using the system of valves and a pressurized rubber balloon until the boiling temperature of the sample in the ebulliometer had achieved the desired constant temperature within ±0.005 K.

The equilibrium temperature was measured with a SYSTEMTEKNIK AB S1228 thermometer with a platinum resistance probe (resolution: ±0.001 K). The temperature fluctuation during runs lasting several hours was within ±0.005 K: no systematic deviations of the temperature measurements were observed.

The pressure was determined by the Texas Instruments Precision Pressure Gauge type 144-01 with a Fused Quartz Bourdon Capsule No. 8 type 2, enabling the pressure determination in the range of (1−137) kPa with the resolution of ±0.5 Pa.

The calibration of both devices was made with the ice point of water for the thermometer and a vacuum better than 10^{-2} Pa for the pressure meter. In addition the saturation vapor pressure as a function of temperature was measured for pure hexane. The same accuracy was obtained.

The estimated accuracy of the pressure measurement is ±10 Pa. The estimated accuracy of the temperature measurement is ±0.01 K.

As the readings of the Bourdon Capsule were subject to drift, in order to obtain the absolute values of pressure, they were frequently recalibrated by the determination of

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* To whom correspondence should be addressed.

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Table 1. Vapor Pressure of Water Measured by the Ebulliometric Method

T/K	P/kPa	$(P_{\mathrm{exp}} - P_{\mathrm{TRC}})$/Pa	T/K	P/kPa	$(P_{\mathrm{exp}} - P_{\mathrm{TRC}})$/Pa
313.21	7.382	−19	343.14	31.166	13
318.18	9.581	−18	348.15	38.552	0
323.16	12.338	−6	353.16	47.372	−9
328.16	15.745	−7	358.14	57.805	23
333.15	19.924	0	363.13	70.109	53
338.16	25.013	0	368.13	84.524	62

Table 2. Vapor Pressures of Pure Components (Literature Data)

	constants of Antoine equation					
compound	A	B	C	temp range/K	T_{m}/K	ref
phenol	6.579 57	1710.29	−80.27	314−395	314.06	*a*
2-chlorophenol	5.786 93	1314.9	−101.05	333−449	282.0	*a*
2,4-chlorophenol	6.026 543	1636.201	−83.97	323−382	316.2	*b*

	constants of DIPPR equation							
compound	A	B	C	D	E	temp range/K	T_{m}/K	ref
3-chlorophenol	54.71	−7449.6	−4.6016	2.4798×10^{-6}	2	306−729	306.0	*c*
4-chlorophenol	45.222	−7350.4	−3.0341	1.5347×10^{-18}	6	316−738	316.0	*c*

[a] Stephenson and Malanowski (1987). [b] Calculated from Mokbel et al. (1994). [c] Daubert and Danner (1995).

the vapor pressure of water as a function of temperature. For this purpose H. Tinsley and Co. Mueller Bridge, type 4772 with a Platinum Resistance Thermometer type 5187SA, calibrated by NPL to class I, was used. The measurements were made in the same ebulliometer connected to the same pressure-stabilizing system additionally equipped with the mercury manometer, thermostated within ±0.03K, and the mercury height was measured with a cathetometer with readings to ±0.01 mm.

The results of the measurements of vapor pressure of water are given in Table 1. The comparison with the vapor pressure of water as given by Zwolinski and Wilhoit (1971) is satisfactory. Both calibration and data were given with ITS-48. The enthalpy of vaporization at T/K = 298.15 calculated from our measurements was 43.94 J/mol, which compares favorably with the value of 43.991 J/mol recommended by Zwolinski and Wilhoit and confirms the accuracy of the measurements.

The total pressure (P) measurements were made by starting with the ebulliometer containing a known mass of pure water. The pressure was adjusted until the boiling temperature was stable to within ±0.003 K, and the pressure was read. The pressure was changed, and after temperature stabilization the next reading was taken. Composition changes were made by introducing to the ebulliometer a known mass of the phenol. The procedure was repeated for all desired compositions and temperatures, always without interrupting the boiling.

The results were calculated following the “total-pressure method” described earlier (Malanowski, 1982). This procedure involves correction for the change of liquid-phase composition due to partial evaporation of the liquid introduced to the ebulliometer. For each mole of the sample in ebulliometer the amounts of liquid (L) and vapor together with condensate (V) satisfy the equation

$$V + L = 1 \tag{1}$$

The mole fraction (q_i) of the component i in the ebulliometer is related to the mole fractions of the component i in the liquid (x_i) and in the vapor and vapor condensate (y_i) streams by the mass balance equation

$$q_i = Vy_i + L\,x_i \tag{2}$$

This enables the definition of the characteristic constant ($f = V/L$) of an ebulliometer. This constant should be determined in a separate procedure (Rogalski and Malanowski, 1980), and in this work it was equal to 0.04. On this assumption, the liquid-phase composition (y_i) and consequently activity coefficients of phenol in water at infinite dilution γ_1^∞ were calculated, by means of an iterative procedure involving integration of the Gibbs−Duhem equation, according to formula given by Rogalski and Gierycz (1980)

$$\gamma_1^\infty = \frac{1}{p_1^0}\left(p_2^0 + \delta Px\,\frac{1+f}{1+f\,\gamma_1^\infty\,p_1^0/p_2^0}\right) \tag{3}$$

where

$$\delta Px = \lim_{x_1 \to 0}\left(\frac{\partial P}{\partial x_1}\right)_T \tag{4}$$

The Henry constant of phenol in water is given by the following equation:

$$H_{\mathrm{ph}} = \gamma_1^\infty \cdot p_1^0 = p_2^0 + \delta Px\,\frac{1+f}{1+f\,\gamma_1^\infty\,p_1^0/p_2^0} \tag{5}$$

The necessary vapor pressure data of chlorophenols are given in Table 2 along with constants of correlating equations. For phenol and 2-chlorophenol and 2,4-dichlorophenol the Antoine equation

$$\log_{10}(P/\mathrm{kPa}) = A - \frac{B}{C + (T/\mathrm{K})} \tag{6}$$

was used. The parameters for 2,4-dichlorophenol were calculated from data by Mokbel et al. (1994). Only these for the temperature range 323−383 were used. For 3- and 4-chlorophenols the equation

$$P/\mathrm{Pa} = \exp\left(A + \frac{B}{T/\mathrm{K}} + C\ln(T/\mathrm{K}) + D(T/\mathrm{K})^{\mathrm{E}}\right) \tag{7}$$

with parameters recommended by Daubert and Danner (1995) was used.

3. Results

The results of total pressure measurements are given in Table 3. The calculated Henry constants and activity

Table 3. Vapor Pressure of Dilute Aqueous Solutions of Phenol and Chlorinated Phenols

Phenol

	P/kPa					
x_1	313.24 K	323.15 K	333.15 K	343.18 K	353.12 K	363.14 K
0.000 00	7.413	12.338	19.610	31.213	47.305	70.087
0.000 98	7.418	12.350	19.645	31.228	47.336	70.164
0.003 00	7.418	12.362	19.664	31.263	47.405	70.263
0.005 10	7.425	12.377	19.692	31.307	47.439	70.291
0.007 12	7.432	12.389	19.700	31.337	47.512	70.423
0.011 23	7.436	12.395	19.734	31.410	47.623	70.588
0.015 87	7.444	12.424	19.809	31.487	47.754	70.787
1.000 00	0.173	0.345	0.655	1.187	2.048	3.415
H_1/kPa	1.9	5.0	11.2	19.7	28.1	55.5
RMSD/%	0.03	0.07	0.09	0.06	0.02	0.13
γ_1^∞	54.0	50.3	47.0	42.9	36.8	33.8

2-Chlorophenol

	P/kPa				
x_1	323.15 K	333.39 K	343.09 K	353.08 K	363.09 K
0.000 35	12.338	19.887	31.117	47.309	70.084
0.000 73	12.409	19.886	31.222	47.425	70.257
0.001 44	12.422	19.955	31.282	47.637	70.580
0.002 20	12.464	20.078	31.507	47.865	70.925
0.002 95	12.536	20.163	31.597	48.092	71.266
1.000 00	0.737	1.329	2.278	3.736	5.907
H_1/kPa	66.3	114.8	191.1	300.4	453.9
RMSD/%	0.13	0.91	0.38	0.02	0.02
γ_1^∞	107.0	100.2	98.3	93.6	89.2

3-Chlorophenol

	P/kPa				
x_1	323.18 K	333.52 K	343.17 K	353.22 K	363.22 K
0.00014	12.339		31.169	47.310	70.009
0.00037	12.341	19.624	31.175		70.035
0.00065	12.343	19.632	31.184		
0.00094				47.342	70.074
0.00123	12.348	19.638	31.199	47.363	70.095
1.00000	0.191	0.344	0.595	0.990	1.599
H_{Ph}/kPa	8.5	16.0	28.1	46.5	76.9
RMSD/%	0.01	0.01	0.01	0.01	0.01
γ_1^∞	108.8	103.5	99.6	94.7	91.9

4-Chlorophenol

	P/kPa				
x_1	323.12 K	333.52 K	343.21 K	353.23 K	363.15 K
0.000 42	12.338	19.620	31.168	47.309	70.012
0.000 87	12.338	19.622	31.170	47.316	70.022
0.001 76	12.339	19.624	31.177	47.328	70.050
0.002 36	12.339	19.626	31.181	47.337	70.059
0.003 07	12.340	19.627	31.183	47.343	70.077
1.000 00	0.140	0.259	0.442	0.744	1.215
H_{Ph}/kPa	0.5	2.7	6.1	12.9	24.7
RMSD/%	0.01	0.01	0.01	0.01	0.01
γ_1^∞	91.2	86.1	84.3	80.9	77.9

2,4-Dichlorophenol

	P/kPa				
x_1	323.10 K	333.48 K	343.16 K	353.18 K	363.21 K
0.000 08	12.339	19.621	31.170	47.314	70.021
0.000 17	12.339	19.623	31.172	47.321	70.030
0.000 28	12.339	19.625	31.179	47.332	70.059
0.000 39	12.339	19.627	31.183	47.341	70.067
0.000 50	12.340	19.628	31.185	47.347	70.086
1.000 00	0.153	0.294	0.517	0.889	1.469
H_{Ph}/kPa	48.2	94.0	170.3	296.6	486.9
RMSD/%	0.11	0.12	0.13	0.13	0.14
γ_1^∞	396.2	385.9	389.4	386.9	379.0

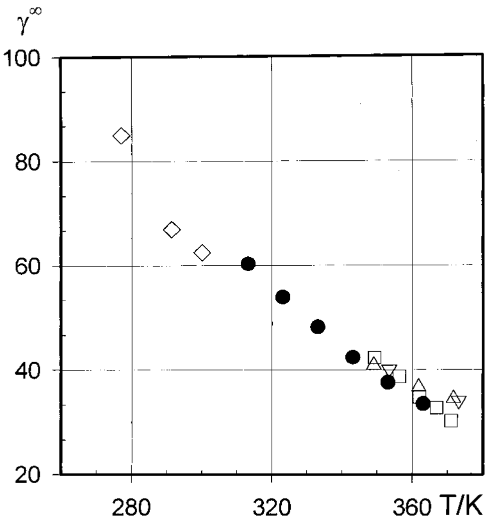

Figure 1. Comparison of the temperature dependence of the activity coefficients of phenol at infinite dilution; ○, this work; □, Moore et al. (1995); △, Dohnal and Fenclova (1995); ▽, Hakuta (1975); and ◇, Abd-el-Bary et al. (1986).

coefficients of phenols in water are also given in this table. The root-mean-square deviation (RMSD) of the computed and experimental pressure were calculated according to the formula

$$\mathrm{RMSD} = 100\sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{P_{\exp,i} - P_{\mathrm{calc},i}}{P_{\exp,i}}\right)^2} \qquad (8)$$

where $P_{\exp}$ and P_{calc} denote, respectively, the experimental and calculated total pressure and n is number of experimental points. The values obtained are listed in Table 4. In general the RMSD values are smaller than 1%.

The comparison with the data obtained for phenol by Moore et al. (1995), Dohnal and Fenclova (1995), Hakuta (1975), and Abd-el-Bary et al. (1986) is given in Figure 1. The agreement is good.

4. Conclusions

The computed values of activity coefficients are strongly dependent on the knowledge of vapor pressures of pure chlorophenols, which are not well established. The critical evaluation of experimental data available in literature leads us to the parameters values reported in Table 2.

The temperature dependence of γ_1^∞ is given by the equation

$$\ln \gamma^\infty = A_1 + \frac{A_2}{T/\mathrm{K}} + A_3 \ln(T/\mathrm{K}) \qquad (9)$$

To increase the reliability of the computed parameters, the partial molar heat of mixing of phenols at infinite dilution $\bar{H}_1^{\mathrm{E},\infty}$, determined by calorimetry (Tabai, 1997), at T/K = 323.45 were used. The parameters A_2 and A_3 are related to $\bar{H}_1^{\mathrm{E},\infty}$ by the equation

$$\bar{H}_1^{\mathrm{E},\infty} = R(A_2 - A_3 T) \qquad (10)$$

Equation 9 can be rearranged to

$$\ln \gamma^\infty = A_1 + \frac{\bar{H}_1^{\mathrm{E},\infty}}{RT/\mathrm{K}} + A_3\left(\frac{323.45}{T} + \ln(T/\mathrm{K})\right) \qquad (11)$$

The parameters A_1 and A_3 are computed by fitting to data in Table 3, while parameter A_2 is calculated directly from

Table 4. Parameters of Equations 8 and 10 Representing the Dependence of Activity Coefficients at Infinite Dilution (γ^{∞}) and the Henry Constant (*H*/KPa) on Temperature

compound	temp range/K	property	A_1	A_2	A_3	RMSD eq 12
phenol	313−363	γ^{∞}	41.1305	−1026.40	−5.89113	3.99
	313−363	H/kPa	670.117	−39274.5	−94.6679	12.36
2-chlorophenol	323−363	γ^{∞}	15.2156	−97.4516	−1.77333	1.30
	323−363	H/kPa	161.250	−12658.0	−20.4027	1.17
3-chlorophenol	323−363*	γ^{∞}	3.13414	502.446	0	0.43
	323−363	H/kPa	22.0921	−6444.46	0	1.59
4-chlorophenol	323−363*	γ^{∞}	147.618	−6684.07	−21.1833	5.09
	323−363*	H/kPa	2017.07	−110385.	−290.078	14.51
2,4-dichlorophenol	323−363	γ^{∞}	5.67929	96.1948	0	0.93
	323−363	H/kPa	24.9070	−6791.07		2.04

eq 10. The values obtained together with RMSD of the fit, calculated according to the formula

$$\mathrm{RMSD}(\gamma^{\infty}) = 100\sqrt{\frac{1}{(n-m)}\left(\sum_{i=1}^{n}\frac{\gamma^{\infty}_{i,\mathrm{exp}} - \gamma^{\infty}_{i,\mathrm{calc}}}{\gamma^{\infty}_{i,\mathrm{exp}}}\right)^{2}} \qquad (12)$$

are given in Table 4 (m denotes the number of adjustable parameters, n the number of experimental entries).

The Henry constants seem to be better determined. In eq 5 the vapor pressure of pure phenols is involved only as a small correction factor in the denominator and practically does not influence the computed values of the Henry constant. The dependence on temperature of the Henry constant (H_{Ph}/kPa) was calculated according to

$$H_{\mathrm{Ph}}/\mathrm{kPa} = A_1 + \frac{A_2}{T/\mathrm{K}} + A_3 \ln(T/\mathrm{K}) \qquad (13)$$

Results are given in Table 4 with corresponding values of RMSD(H_{Ph}) calculated with a formula analogous to eq 12.

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