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A New Set of Gas/Water Partition Coefficients for the Chloromethanes

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Summary. In the literature, there is a considerable number of articles and reviews providing data and information on the solubility of chloromethanes in water. However, the substantial difference between the numerical values given by various authors hinders their practical application. In the current work we present the harmonized results of experimentally determined gas/water partition coefficients of CH_2Cl_2, $CHCl_3$, and CCl_4, in the temperature range from 278 to 343 K, and with on uncertainty limit of less than 10%.

Keywords. Aqueous solution; Chloromethanes; Partition coefficients.

Introduction

Studies to measure the solubility of chloromethanes in water have been conducted for about one hundred years. Data have been compiled in two essential reviews – those of *Sander* [1] and *Horvath* and *Getzen* [2]. *Sander*'s data [1] are presented in Fig. 1 as *Tukey*'s *Box-Whisker* plots [3, 4], one of the main graphical tools in exploratory data analysis. For its realization package R was used [5, 6]. In the figure, we presented a box with the limits within the 1st and 3rd quantiles of the variable, which includes 50% of all values. The small horizontal dashes, above and below the box, mark the 1.5 interquantiles range. The results outside this range are presented as dots.

The difference of the results, obtained by different authors, considerably exceeds the experimental error (see Table 1); in addition, these results are distributed asymmetrically (Fig. 1).

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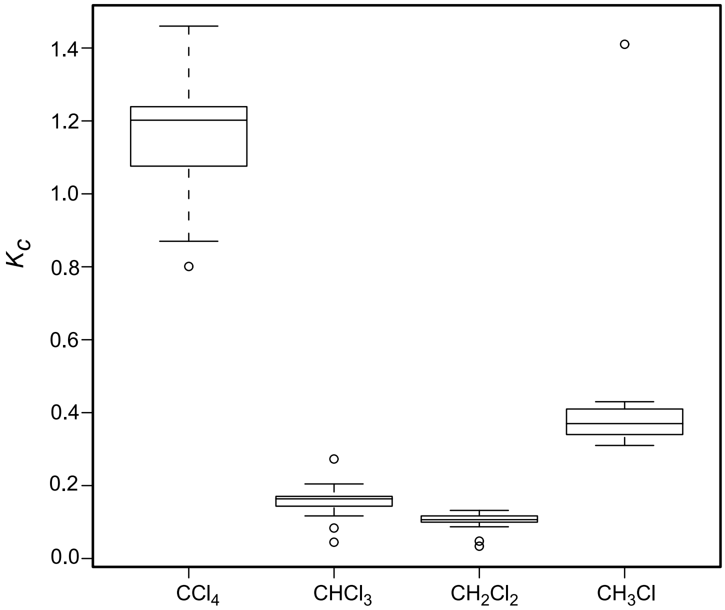

Fig. 1. Partition coefficients K_c, calulated from Ref. [1], in the set of methane chloroderivatives

Table 1. Median, mean, and maximum/minimum ratio for partition coefficients calculated from *Sander*'s data [1], 298.15 K

Compound	K_c		
	Median	Mean	Maximum/Minimum
CCl_4	1.20	1.16	1.82
$CHCl_3$	0.164	0.157	6.07
CH_2Cl_2	0.105	0.102	3.88

Results and Discussions

The purpose of the present study is to obtain a set of data on the gas/water partition of chloromethane derivatives at different temperatures, with a validity (within ±10%) and precision, which will be acceptable in most cases of application.

Although the choice of units describing solubility presents a great degree of difficulty, we adhere to the viewpoint of *Ben-Naim* [7] that partition coefficient has advantages over the other units because of a clear thermodynamic interpretation.

We consider that the situation can be changed through obtaining in the framework of one study a set of data on chloromethanes solubility in terms of partition coefficients, which, instead of the stated high precision, would be in good agreement and would possess high validity. For this purpose, we choose rather to use the partition method. This method was well tested by previous research [8]. The method is used for measuring the studied substance in equal volumes of gaseous and aqueous phases in a system at equilibrium (Eq. (1)) where K_c [17] is a partition coefficient for gas/liquid, and C_g and C_l are the concentrations of the studied substance in gaseous and aqueous phases, n_g and n_l – are the amount of the studied substance in equal volumes of the phases. $K_c = (k_H^{cc})^{-1}$, where (k_H^{cc}) is the dimensionless *Henry*'s law constant from *Sander* [1].

$$K_c = \frac{C_g}{C_l} = \frac{n_g}{n_l} \tag{1}$$

The method has been described in detail previously [9] and the limitations are discussed in Ref. [8]. The use of the method allows us to avoid the different problems, *e.g.*, saturation, solvent degassing, *etc.*, inherent in other methods. We would like to emphasize the fact that the measurements are conducted under the condition of infinite dilution, and the partition coefficient K_c is in full agreement with the measuring method, and does not require complex calculations and extra corrections.

Usually, to detect chloroderivatives by gas chromatography (GC) a very specific and highly sensitive electron capture detector is used. However, it is limited in its dynamic range; therefore, our preference was to use the flame ionization detector (FID), the range of which is 100 times greater. For conducting this study, FID's sensitivity to chloromethanes appeared to be sufficient. We made from 3 to 5 measurements for each case, where overall errors did not exceed 10%. The experimental data obtained are presented in Table 2.

The data for 298 K are in good agreement (in the range of 10%) with the median of *Sander*'s data [1] (Table 1) and are in satisfactory agreement with the mean value.

In Fig. 2, we compared the results of measurements of tetrachloromethane in this study and *Bullister*'s data [10]. For comparison, we selected this particular work, out of the number of similar ones, due to the very high degree of precision (error of less than ±1%) stated. It is evident, that all the data and their precision are in satisfactory agreement.

The obtained set of data for all compounds in the range (Table 2), with the temperatures ranging from 278 to 343 K, gives us a general idea of the influence of

Table 2. Obtained experimental data on CH_4, CH_2Cl_2, $CHCl_3$, and CCl_4 partition coefficients

T/K	$K_c \pm s$			
	CH_4	CH_2Cl_2	$CHCl_3$	CCl_4
278		0.040 ± 0.002	0.044 ± 0.005	0.47 ± 0.030
283	22.0 ± 0.9	0.054 ± 0.004	0.068 ± 0.002	0.58 ± 0.010
288		0.067 ± 0.005	0.094 ± 0.005	0.82 ± 0.020
293		0.073 ± 0.006	0.11 ± 0.008	1.0 ± 0.040
298	30.0 ± 1.0	0.095 ± 0.005	0.17 ± 0.014	1.2 ± 0.094
303		0.12 ± 0.003	0.20 ± 0.011	1.5 ± 0.067
308		0.14 ± 0.005	0.23 ± 0.013	1.9 ± 0.14
313	36.0 ± 2.4	0.15 ± 0.013	0.30 ± 0.022	2.3 ± 0.18
323		0.21 ± 0.012	0.47 ± 0.029	3.0 ± 0.21
333		0.27 ± 0.008	0.59 ± 0.033	4.0 ± 0.33
343		0.40 ± 0.020	0.87 ± 0.035	5.0 ± 0.38

where s is the standard deviation of K_c

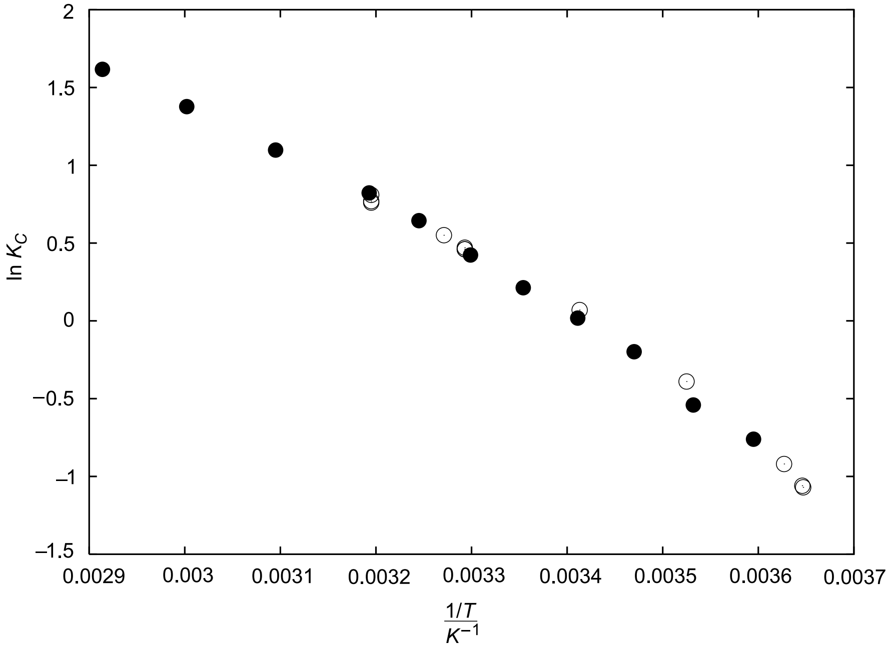

Fig. 2. Comparison of CCl4 partition; *Bullister*'s data [10] (white circles) and present work (black circles)

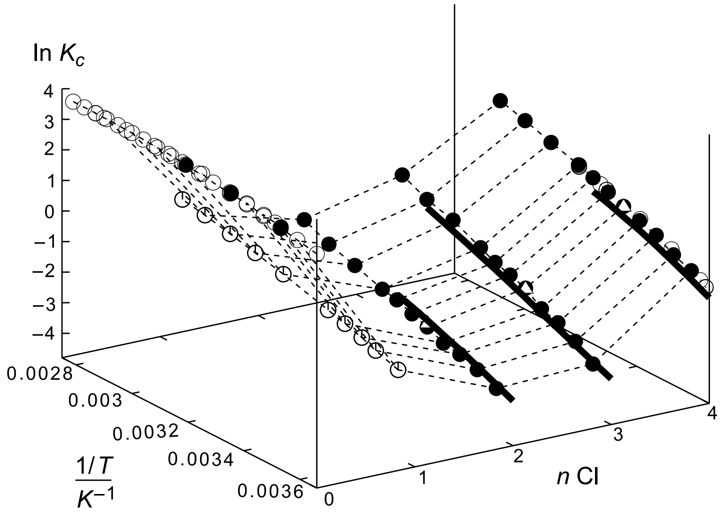

Fig. 3. The influence of the methane chloroderivatives structure on their partitioning in a gas/water system at the temperature range from 278 to 323 K

the compound structure upon their partition between gas and water (see Fig. 3). In Fig. 3, the white circles represent *Bullister*'s [10] and other researchers data (CH_4 – *Morrison* [11], CH_3Cl – *Glew* [12]). The triangles show the median of *Sander*'s data [1]. Continuous bold lines represent *Horvath* and *Clever*'s data [2].

Our attention was drawn to the presence of an extremum in the dependence of energy of transfer on the volume of the molecule, which could be observed in the whole range of temperatures studied. The extremum was observed for calculated molecule volumes of 200 to 250 Å^3. It should be noted that a similar effect had been discussed before for linear alkanes [13]. In that case the respective volume equalled 220 Å^3.

In our point of view, the studied system, which is simple enough in its chemical structure, possesses a peculiar feature – an obvious discrepancy between the model of additivity for atomic contributions and the experimental results revealing on extremum.

We consider the nonlinearity of the temperature dependence to be one of the reasons for the considerable scatter for the derived thermodynamic functions of transference of these compounds from the gaseous phase into water (*Sander* [1]). In the examined temperature range ΔH varies at least by a factor of 1.5.

Thus, we obtained a set of experimental data for partition coefficients of gas/liquid for methane (CH_4), carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), and dichloromethane (CH_2Cl_2) in water at temperatures ranging from 278 to 343 K, with a validity and precision within ±10%. We discovered that in the studied temperature interval the dependence of *Gibbs*' energy transfer (from the gaseous into the aqueous phase) on the molar volume has an extreme character. Also, we studied the possible applicability of the linear model of atomic contributions to describe the resolution of transfer energy for the chloromethanes.

Conclusion

In this paper, we presented the experimentally evaluated harmonized set of partition coefficients for chloroderivatives of methane at temperatures ranging from 278 to 343 K. We came to the conclusion that the validity of the obtained set of data is within ±10%, and that the data can be used as an experimental basis for creating new solubility models and analyzing existing ones. We also showed experimentally a nonlinear dependence of transfer energy from the gaseous into the aqueous phases on the molecular volume (number of chlorine atoms in chloromethanes) for the temperature interval studied.

Experimental

In this work, chemically pure CH_4, CCl_4, $CHCl_3$, and CH_2Cl_2 (containing no less than 99.8% of the main substance), and also distilled water were used. The chloromethanes were purified in accordance with the methodologies described in *Gordon*'s work [14].

The analysis of the chloromethanes after their purification (GC, SUPELCOWAX $30\,\text{m} * 0.32\,\text{mm} * 0.25\,\mu\text{m}$ column, carrier – helium, 20 cm/s, temperature program from 318 to 393 K, FID) indicated that the total content of volatile admixtures did not exceed 0.01%. After purification, the amount of ethanol in liquid chloroform did not exceed 0.005%. In the vapor, no traces of ethanol were observed. The amount of water in the chloromethanes was not tested.

The detailed description of the measuring method is presented in Refs. [9, 8].

The measurements were conducted in a thermostated cell with 60–120 cm^3 working capacity. For this purpose, an outer liquid thermostat was used, which kept the temperature fluctuations in the cell ≤ 0.2 K. Sampling was made with the help of a handmade syringe with constant volume (0.1–0.2 cm^3). The studied substance is introduced into the cell as vapor with the help of another syringe, containing 2–10 cm^3 vapor of the compound. The reagents' temperature is 278 K, which exclude their possible

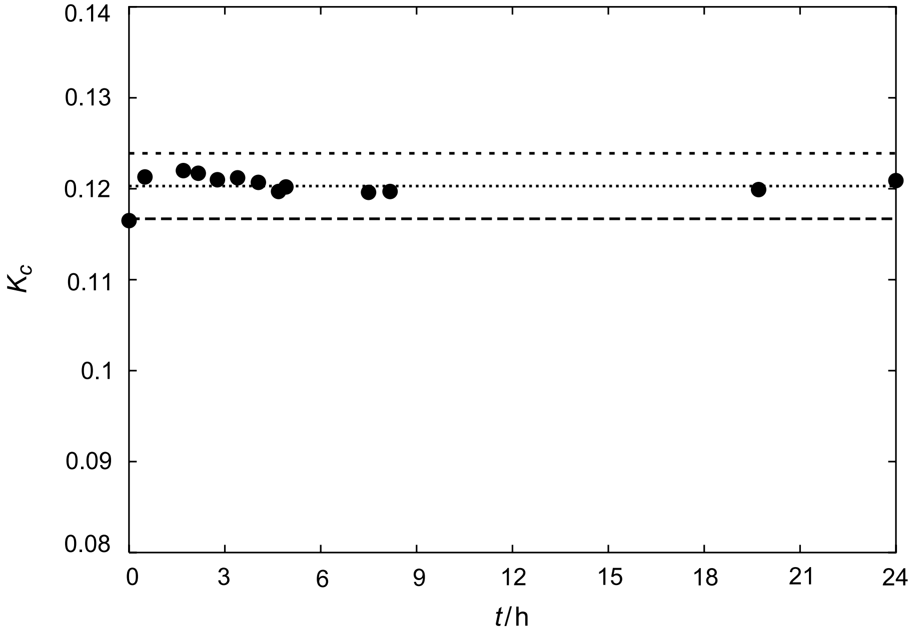

Fig. 4. Time stability of CH_2Cl_2 partition coefficient K_c (303 K); lines represents $K_c + s$, K_c, $K_c - s$

condensation while introducing them into the cell. Thus, the vapor pressure of the measured components constitutes a small part of the saturated vapor pressure. The cell is shaken at the frequency of 5–7 $\sec^{-1}$ during 20 minutes. Before the beginning of the measurements, the settling of the cell's contents is recommended for no less than 3 hours.

This kind of installation is widely used for conducting kinetic research, where the speed of reactions is up to 10^{-3} $\sec^{-1}$ (*Rudakov* [15]). Thus, the speed of mass transfer in this system allows to obtain the gas concentration at equilibrium in liquid, where vapor is introduced, in less than 1 minute. However, it is a well-known fact that the sedimentation of gas bubbles in an aqueous phase requires a much longer period of time (*Eganhouse* [16]). In a number of experiments, we showed that after 20–30 minutes of settling, the measured values of K_c become stable (Fig. 4). A three-hour settling guarantees 100% sedimentation. After the settling was completed, the samples of gaseous and aqueous phases of equal volume were taken and analyzed by GC. This allowed us to define the absolute quantity of the studied substance in equal volumes of gaseous and aqueous phases. To introduce the liquid sample into the GC line, a section for stripping of volatile components was installed. The section allows to remove the dissolved components in a fast and effective way (*Battino* [17]).

K_c was obtained through dividing the average value for the gas phase by the average value for the liquid phase. The results were distributed symmetrically, with standard deviations not exceeding ±10%. The relatively low precision is related to the use of low concentrations of the studied substances, and consequently, the maximum GC sensitivity.

References

[1] Sander R (2001) In: NIST Chemistry Webbook, Standard Reference Database Number 69, July 2001 release, http://www.nist.gov/srd

[2] Horvath AL, Getzen FW (eds) (1995) Solubility Data Series Volume 60, Halogenated Methanes with Water. Oxford University Press, Oxford, UK

[3] Tukey J (1977) Exploratory Data Analysis. Addison-Wesley

[4] Esty WW, Banfield JD (2003) J Stat Soft **8**(17): 1

[5] Ihaka R, Gentleman R (1996) J Comput Graph Stat **5**: 299

[6] Schwartz M (2003) R News **3/2**: 2

[7] Ben-Naim A, Mazo R (1997) J Phys Chem B **101**: 11221

[8] Suykov SYu (1987) PhD Thesis. Institute of Physical Organic and Coal Chemistry, Donetsk

[9] Lutsyk AI, Rudakov ES, Tretjakov VP, Suykov SYu, Galenin AA (1978) Dopov Akad Nauk UkrRSR Ser B **6**: 528

[10] Bullister JL, Wisegarver DP (1998) Deep-Sea Research **45**: 1285

[11] Morrison B (1952) J Chem Soc **10**: 3819

[12] Glew DN, Moelwyn-Hughes EA (1953) Disc Faraday Soc **15**: 150

[13] Rudakov ES, Lutsyk AI (1983) In: Titov EV (ed) Mezhmolekularnye vzaimodeistviya i reaktsionnaya sposobnost' organicheskikh soedinenii (Intermolecular interactions and reactivity of organic compounds). Kiev, Naukova Dumka, p 3

[14] Gordon AJ, Ford RA (1976) Sputnik Khimika. Moskow, Mir, p 437

[15] Rudakov ES, Lobachev VL, Geletij YuV (2001) Chem Res Toxicol **14**: 1232

[16] Eganhouse RP, Calder JA (1976) Geochim Cosmochim Acta **40**: 555

[17] Battino R, Clever HL (1966) Chem Rev **66**: 395