Vapor-Liquid Equilibria for C_3 Hydrocarbons

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In calculating vapor-liquid equilibria for simple hydrocarbon systems ideal behavior is frequently assumed. The vaporization equilibrium ratios K's are taken to be independent of composition at a given temperature and pressure.

Studies of certain systems such as paraffin-aromatic mixtures however have shown large changes in K with composition. A small effect of composition has even been observed for the system propane-propylene (*8, 15*). Greater deviations might be expected for systems with greater differences in the degree of unsaturation such as the propane-propadiene and propane-propyne systems. An experimental program was therefore undertaken to determine the magnitude of composition effects on relative volatility for the system propane-propylene-propadiene-propyne.

There are three principal difficulties in the study of the equilibrium compositions of any close-boiling, multicomponent system: the concentration differences between the two phases are small, and very accurate analytical techniques are required; the most important concentrations from a thermodynamic and practical standpoint are the dilute regions, where unfortunately the relative analytical errors are most pronounced (*5, 20*); and study of a large number of mixtures of different composition would be required to fully characterize a multicomponent system.

In the present study these difficulties were minimized by the development of a highly efficient six-stage equilibrium unit to minimize the effects of analytical uncertainties; the use of gas chromatographic analyses which had very good relative accuracy even at the 1% concentration level; and the simultaneous study of two or three solutes at dilute concentration in a given mixture with the Hildebrand-Scatchard equation for regular solutions. In recent years this approach has found increasing acceptance as a means for correlating, extrapolating, and interpreting equilibrium data (*10, 11, 14*).

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THEORY

Vapor-liquid equilibria in hydrocarbon systems are usually correlated through the use of the vaporization equilibrium ratio K and the relative volatility. For arbitrary components i and j these quantities are defined as

$$K_i \equiv y_i/x_i = \frac{P_i^\circ}{P\theta_i}\,\frac{\gamma_i^L}{\gamma_i^V} \qquad (1)$$

$$\alpha_{ij} \equiv (y_i/x_i)/(y_j/x_j) = K_i/K_j = \frac{P_i^\circ}{P_j^\circ}\cdot\frac{\theta_j}{\theta_i}\cdot\frac{\gamma_i^L}{\gamma_j^L}\cdot\frac{\gamma_j^V}{\gamma_i^V} \qquad (2)$$

The so-called *imperfection-pressure* coefficient θ_i is defined by

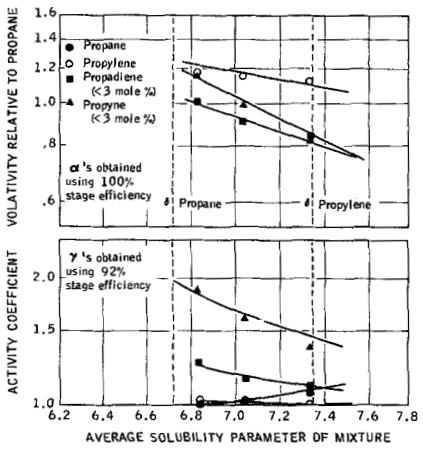

Fig. 1. Comparison of experimental volatilities and activity coefficients at 50°F. with calculated lines obtained with regular solution theory.

$$\theta_i = (f_i^V/P)_P/(f_i^L/P_i^\circ)_P \qquad (3)$$

This accounts for deviations of the vapor from perfect gas behavior and for the effect of system pressure on liquid fugacity. The pure component fugacities for ideal solutions are related to pressure by the expressions

$$\mathrm{Ln}(f_i^V/P)_P = (1/RT)\int_0^P (V_i^V - RT/P)\,dP \qquad (3a)$$

$$\mathrm{Ln}(f_i^L/P_i^\circ)_P = \mathrm{Ln}(f_i^V/P)_{P_i^\circ} + (1/RT)\int_{P_i^\circ}^P V_i^L\,dP \qquad (3b)$$

If the change of liquid volume with pressure is neglected, and if the vapor volume is expressed by a virial equation of state

$$PV_i^V = RT + B_iP + C_iP^2 + D_iP^3 + \ldots \qquad (3c)$$

then θ_i may be expressed analytically by

$$\mathrm{Ln}\theta_i = \Big[(B_i - V_i^L)(P - P_i^\circ) + \frac{C_i}{2}(P^2 - P_i^{\circ 2}) + \frac{D_i}{3}(P^3 - P_i^{\circ 3}) + \ldots\Big]/RT \qquad (4)$$

Although θ accounts for the effects of temperature and total pressure on K and α, activity coefficients must be defined to include the effects of composition (*2, 14*). By definition γ's are equal to unity for a system in which both the liquid and vapor behave as ideal solutions. Strictly speaking separate gammas are needed for the liquid and vapor phases.

In this work the excess free energy of the vapor phase is neglected as suggested by Yu and Coull (*24*) and as commonly assumed in equilibrium studies, and γ_i^V is assumed to be unity. All deviations from ideal solution behavior are thus attributed to the excess free energy of the liquid phase as expressed by γ_i^L.

In the past a number of thermodynamically consistent approaches have been used extensively to express the relationship between liquid phase activity coefficients and composition (*6, 23*). The activity coefficients are expressed as empirical or semitheoretical functions of composition, and most of the approaches have been fairly successful in correlating data for binary mixtures and a few ternary and quaternary systems. As the number of components increases however, the equations become unwieldy because two binary constants are usually required for each binary pair, in addition to ternary and perhaps even quaternary constants.

The simplest approach to expressing activity coefficients for multicomponent mixtures is a modified form of the

TABLE 1. EQUILIBRIUM DATA AT 50°F.

Sample used†	Average liquid composition, mole %* Propane	Propylene	Propadiene	Total pressure, lb./sq. in. abs.	Relative volatility, (component/propane) Propylene	Propadiene	Propyne	Average solubility parameter
B_1-D_6	4.0	93.5	1.3	110	1.105	0.839	0.819	7.344
B_1-D_6	4.1	94.1	0.9	110	1.100	0.828	0.822	7.337
B_1-D_6	49.2	47.0	1.9	104	1.159	0.929	1.005	7.042
B_1-D_6	47.7	48.8	1.8	100	1.156	0.905	0.984	7.042
B_1-D_6	82.2	12.5	2.8	95	1.162	1.000	1.137	6.841
B_1-D_6	83.4	12.0	2.4	—	1.189	1.004	1.167	6.827

* Average of samples used to determine relative volatility.
† B_1 is the liquid from Still 1, D_1 is the vapor from Still 1, etc.

Hildebrand (9) and Scatchard (*18*) relationship originally derived for so-called *regular* binary solutions. A regular solution is defined as one in which the entropy of mixing is equal to that of an ideal solution throughout the concentration range, that is no excess entropy of mixing. For multicomponent regular solutions whose components all have closely similar molar volumes the liquid phase activity coefficient is given by

$$\ln \gamma_i^L = V_i^L (\delta_i - \bar{\delta})^2/RT \qquad (5)$$

where

$$\bar{\delta} = \Sigma \phi_i \delta_i \qquad (5a)$$

The pure component solubility parameters δ_i's for regular solutions are defined as the square root of the cohesive energy per unit volume (*18*). The simplicity of Equation (5) is evident in that a single parameter δ_i for each component is sufficient to calculate the activity coefficient for every component in a given mixture.

Experimental data already available in the literature for many different systems have proven that Equation (5) is entirely too simple to be of completely general use. For example activity coefficients less than unity have been observed in a few special systems, and these are not permitted by Equation (5). The compounds investigated in this study however are very similar in structure and behavior, and no negative deviations are expected. In addition these compounds are of sufficient commercial importance to merit simplified treatment provided that such simplification does not compromise the accuracy of the experimental results.

EXPERIMENTAL APPARATUS AND PROCEDURE

A complete description of the construction details and operating procedure for the six-stage equilibrium unit was given in a recent paper (*13*). The lowest stage was designated No. 1 and the highest No. 6.

The complete equilibrium assembly was mounted in an insulated box equipped with a heating and cooling system capable of controlling the box temperature to within a few degrees of the still temperature. The average range of still temperatures over which relative volatilities were measured in a given run was 2° to 3°F. In this study the temperature level was varied from 50° to 140°F.

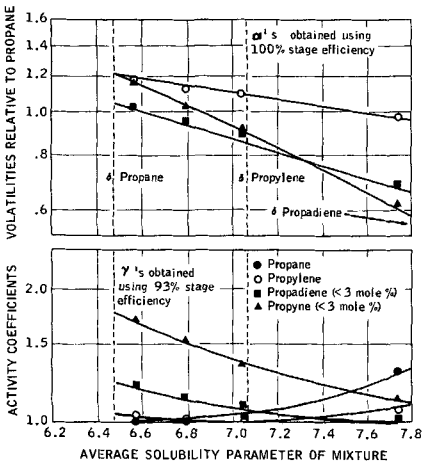

Fig. 2. Comparison of experimental relative volatilities and activity coefficients at 90°F. with calculated lines obtained with regular solution theory.

To insure good mixing of the liquid and vapors each still was fitted with a small bucket pump which was magnetically operated. Each still also had a separate heat control.

The unit was operated at total reflux, and when equilibrium was reached, samples were withdrawn at various points and analyzed with a vapor fractometer. The lowest concentration level which could be measured with sufficient accuracy for these relative volatility studies was about 0.5 mole %. Duplicate analyses were made on each sample, and the average values were used to calculate alphas. The precision or repeatability of the analyses ranged from 0.5 to 7% of the concentration present, with the poorer precision corresponding to very low concentration levels.

RESULTS

The equilibrium data obtained at 50°, 90°, and 140°F. are summarized in Tables 1, 2, and 3 respectively. The α's reported in these tables were calculated directly from the measured compositions. Four distinct feed compositions were studied, and each composition contained either one or two major components with the other components present at the 1 to 3% concentration level.

Relative Volatilities

All α's were calculated relative to propane with Equation (6) which had been derived by Fenske (3) for total reflux operation:

$$\text{Ln } \alpha_{ij} = \frac{1}{NE} \text{Ln} \frac{(Y_i/Y_j)\ N\text{th stage}}{(X_i/X_j)\ 1\text{st stage}} \qquad (6)$$

An apparent overall stage efficiency of the equilibrium unit was found by comparing the experimental- and ideal-solution alphas for propylene to propane in a 50/50 mixture by volume of the two. At this concentration the two alphas are theoretically identical for a perfect contacting stage because the activity coefficients for each component are equal, as calculated by Equation (5), and their ratio is then unity

TABLE 2. EQUILIBRIUM DATA AT 90°F.

Samples used*	Average liquid composition, mole % Propane	Propylene	Propadiene	Total pressure, lb./sq. in. abs.	Relative volatility, (component/propane) Propylene	Propadiene	Propyne	Average solubility parameter
D_1-D_5	9.3	86.5	2.0	193	1.083	0.896	0.912	7.044
B_1-D_6	9.5	86.2	2.0	193	1.097	0.884	0.900	7.049
B_1-D_5	46.5	53.5	—	185	1.136	—	—	6.795
D_1-D_5	51.6	47.0	0.7	183	1.127	0.948	1.025	6.785
D_1-D_6	48.2	49.4	1.2	183	1.129	0.966	1.051	6.795
B_1-D_6	54.0	40.0	2.8	180	1.130	0.945	1.015	6.798
B_1-D_6	91.2	5.8	1.3	169	1.171	1.025	1.181	6.552
B_1-D_6	92.4	4.7	1.4	168	1.152	1.028	1.148	6.550
D_1-D_6	87.1	8.4	2.1	170	1.179	1.022	1.161	6.597
D_2-D_5†	2.6	2.7	93.5	141	0.969	0.694	0.605	7.749
D_1-D_6†	1.2	3.7	93.3	141	0.963	0.683	0.654	7.745
D_1-D_6†	1.0	3.6	94.1	142	0.968	0.683	0.616	7.743

* See second footnote of Table 1.
† The average concentration of 2-chloropropene in these samples was 0.2 to 0.4 vol. %. 2-chloropropene was present in the propadiene used.

TABLE 3. EQUILIBRIUM DATA AT 140°F.

Samples used*	Average liquid composition, mole % Propane	Propylene	Propadiene	Total pressure, lb./sq. in. abs.	Relative volatility, (component/propane) Propylene	Propadiene	Propyne	Average solubility parameter
B_1-D_6	10.6	84.7	2.2	358	1.078	0.918	0.948	6.648
B_1-D_3	10.0	85.3	2.2	364	1.078	—	—	6.655
D_2-D_6	3.4	96.4	0.1	378	1.091	0.913	0.928	6.645
B_1-D_6	3.9	92.9	1.7	362	1.066	0.927	0.933	6.665
D_5-D_6	41.3	58.7	—	364	1.096	—	—	6.477
B_1-D_6	49.9	50.1	—	344	1.116	—	—	6.441
B_1-D_6	49.2	50.8	—	341	1.098	—	—	6.468
D_1-D_5	51.2	46.8	1.0	344	1.096	0.989	1.032	6.447
B_1-D_3	55.5	38.0	3.0	339	1.082	0.947	1.020	6.455
B_1-D_6	91.9	5.5	1.2	319	1.123	1.030	1.123	6.276
B_1-D_6	92.9	4.7	1.1	313	1.137	1.022	1.149	6.271
B_1-D_6	86.7	8.7	2.2	320	1.119	1.019	1.120	6.311
D_1-D_6†	1.4	1.6	95.9	260	0.988	0.777	0.715	7.188
D_1-D_6†	0.7	3.2	95.1	266	0.991	0.794	0.750	7.197

* See second footnote of Table 1.
† See second footnote of Table 2.

TABLE 4. ANTOINE CONSTANTS

	A_1	A_2	A_3	Reference
Propane	5.55654	1900.8	479.5	Reamer and Sage (*15*)
Propylene	5.56311	1852.4	477.7	Reamer and Sage (*15*)
Propadiene	5.93025	2234.3	498.1	Present study
Propyne	5.97927	2378.4	510.1	Vohr (*21*)

in Equation (2). Furthermore the analytical accuracy is greatest in this concentration region so that these runs are the most accurate.

At this composition, the apparent stage efficiency in the present six-stage study varied from 92 to 95%. The corresponding efficiencies of the single stage studies of Reamer and Sage were 100 to 112% (*15*), while the studies of Hanson showed a variation from 92 to 103% (*8*).

Previous tests on this equilibrium unit with mixtures of well-established relative volatilities (*n*-heptane:methylcyclohexane and toluene:methylcyclohexane) at atmospheric pressure showed the apparent number of theoretical plates as 6.2 with individual tests varying between 5.85 and 6.45 (13). The fact that this efficiency is higher than that found with the C_3 system can be ascribed to somewhat greater entrainment for the C_3's resulting from the higher gas densities and lower liquid densities encountered.

These apparent overall stage efficiencies include the combined limitations of the contacting stages, the sampling and analytical procedures, and the calculated values of the ideal alpha for propylene to propane.

Solubility Parameters

Equation (5) was combined with Equation (2), and values of the solubility parameter were assumed for all components except propane. The solubility parameter for propane was taken from a paper by Prausnitz, Edmister, and Chao (*14*). With the δ of propane held fixed, a digital computer continually adjusted the parameters of the other components until the calculated relative volatilities agreed with the experimental values for each experimental run.

The values of δ for each component were averaged. Slight adjustments in this value were then made so that the calculated line would fit the experimental data.

The best values of the solubility parameters for each component at each of the three temperatures are plotted on Figure 4. Because of the nature of Equation (5), the important consideration is the differences between solubility parameters of the individual components, not the absolute values.

Activity Coefficients

The experimental activity coefficients (of all components except the major) were determined from the measured volatilities relative to the major component with Equation (2). The activity coefficient of the major component in the mixture was calculated from Equation (5). This value was always very close to 1.000.

The vapor pressures at each temperature were obtained by the use of the Antoine equation form:

$$\log_{10}P^\circ = A_1 - A_2/(t + A_3) \quad (7)$$

The constants for this equation are given in Table 4. Propadiene vapor pressures were determined experimentally because only fragmentary and inconclusive data were available in the literature (*19*).

The molar liquid volumes and vapor phase virial coefficients required to calculate the imperfection pressure coefficient used in Equation (2) were found or calculated from literature data (*1, 4, 7, 12, 16, 21*). The values used in this work are tabulated in Table 5.

DISCUSSION

The experimental α's and γ's are plotted vs. the average solubility pa-

TABLE 5. PHYSICAL PROPERTY DATA

	Temperature 50°F.	90°F.	140°F.	Reference
Molar liquid volume (cu. ft./lb. mole)				
Propane	1.38	1.47	1.65	*16*
Propylene	1.27	1.37	1.56	*4*
Propadiene	1.06	1.11	1.23	*12*
Propyne	1.01	1.07	1.15	*12, 21*
Second virial coefficient (cu. ft./lb. mole)				
Propane	—7.82	—5.90	—4.80	*1, 16*
Propylene	—6.80	—5.32	—4.42	*4*
Propadiene	—6.40	—5.08	—4.22	*7*
Propyne	—8.32	—6.30	—5.16	*1*
Third virial coefficient (cu. ft./lb. mole lb./sq. in. abs.) × 10^3				
Propane	—11.6	—7.7	—4.1	*16*
Propylene	—6.2	—3.7	—1.9	*4*
Propadiene*	—8.9	—5.7	—3.2	—
Propyne	—6.4	—4.0	—2.3	*21*
Fourth virial coefficient (cu. ft./lb. mole lb./sq. in. abs.)^2 × 10^6				
Propane	—32.0	—17.0	—8.5	*16*
Propylene	—32.0	—17.0	—8.5	*4*
Propadiene*	—32.0	—17.0	—8.5	—
Propyne	—32.0	—17.0	—8.5	*21*

* Estimated.

rameter of the mixture in Figures 1, 2, and 3. The points are averages of the values for runs at roughly the same concentration and average solubility parameter. (See division of data indicated by dotted lines in Tables 1, 2, and 3.) The γ's at 50°, 90°, and 140°F. were obtained by the use of stage efficiencies of 92, 93, and 95% respectively. As previously discussed these were obtained at a 50/50 concentration of propane and propylene. These adjustments yielded experimental γ's for all compositions which were equal to or greater than 1.0 (as would be expected for a solution of this nature).

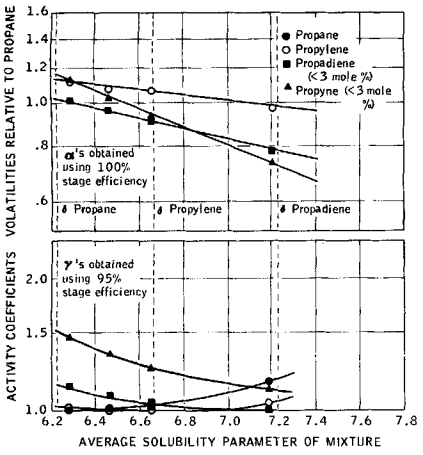

Fig. 3. Comparison of experimental relative volatilities and activity coefficients at 140°F. with calculated lines obtained with regular solution theory.

Semilogarithmic coordinates were used because the theory of regular solutions suggested such a plot of α vs. δ would be linear when the liquid volumes are similar and the range of δ is not very great. The lines on the plots are calculated values.

It may be seen that the relative volatility is linear with the average solubility parameter. The calculated lines would have shown slight curvature if they had been extended to nearly pure propyne. However experimental runs were not made in this concentration range because of safety hazards thought to be associated with pure propyne. The change in relative volatility with composition is greatest for propyne followed in order by propadiene and propylene. The effect of composition on α decreases as temperature increases.

Very good agreement between experimental and calculated γ's is seen with an average deviation of ± 0.9%. The maximum deviation is 5.9% for propyne at 50°F.

The intersections of the various alphas in the figures correspond to compositions where the components in question have equal volatility out of a mixture having a δ given by the intersection. This suggests that certain binary combinations of the four components may form azeotropes. Intersections outside the range included between the solubility parameters of the two components in question do not then correspond to binary azeotropes. No higher azeotropes are indicated.

The only binary azeotropes are the propane-propadiene and propane-propyne pairs. An experimental azeotropic composition for the propane-propyne system was reported by Walls (*22*) to be 11.4% propyne at 140.3°F. This is in fair agreement with the estimated composition of 15.4 vol.% obtained from Figure 3 at 140°F. for this pair.

COMPARISON WITH LITERATURE DATA

The results of the present study may be compared with the results of Reamer and Sage (*15*), and Hanson et al. (*8*) for propylene-propane. Their studies covered the temperature range from 10° to 190°F. and the composition range from about 15 to 85% propylene.

Their pressure and temperature measurements were very accurate. As suggested by Redlich, Kister, and Turnquist (*17*) it is theoretically possible to determine activity coefficients and solubility parameter differences without relying on the analysis of the vapor. In fact because this mixture behaves as if it formed a regular solution, total pressure measurements for a single composition are sufficient. An equal volume mixture is the most sensitive composition for this test. The molar liquid volumes for these similar hydrocarbons can be assumed to be equal. With this assumption it may be shown that the total pressure for this composition relative to the ideal total pressure is given by

$$\mathrm{Ln}(P/P_{(\mathrm{Ideal})}) = V^L(\delta_i - \delta_j)^2/4RT \qquad (8)$$

where

$$P_{(\mathrm{Ideal})} = \sum_i X_i P_i^\circ/\theta_i \qquad (9)$$

With Equation (8) the solubility parameters for propylene were determined relative to the literature values for propane (*14*). The solubility parameters calculated from the literature data are plotted in Figure 4 as a function of temperature. The values calculated from the literature are shown to be in good agreement with values obtained for propylene here.

CONCLUSIONS

Even though substantial deviations from ideal-solution behavior were observed, these deviations were adequately correlated in terms of the theory of regular solutions.

This method enables one to obtain vapor-liquid equilibrium data on a number of systems with relatively few runs and is a simple method for handling multicomponent systems.

The measured relative volatilities are in good agreement with limited data available in the literature.

Study of other systems is needed to determine if regular solution theory is adequate for all hydrocarbon systems

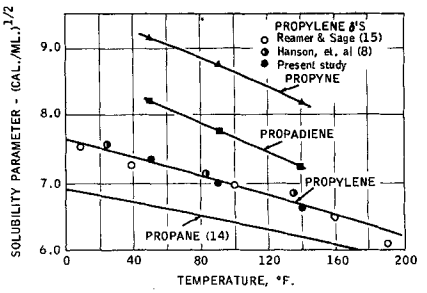

Fig. 4. Apparent solubility parameters.

and if it is possible to calculate solubility parameters for hydrocarbons from pure component properties without recourse to the study of mixtures.

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NOTATION

A_1, A_2, A_3 = Antoine constants
B, C, D = 2nd, 3rd, and 4th virial coefficients in Equation (4)
E = stage efficiency
f = fugacity
N = number of stages
P = pressure
P° = pure component vapor pressure
V = molar volume
t = °F.
x = mole fraction in liquid phase
y = mole fraction in vapor phase

Greek Letters

α = relative volatility
γ = activity coefficient
δ = solubility parameter
$\bar{\delta}$ = volume average solubility parameter for the liquid solution
ϕ = volume fraction of component in liquid
θ = imperfection-pressure coefficient

Superscripts

L = liquid phase
V = vapor phase

Subscripts

i = component i
j = component j
P = evaluated at total pressure, P
P_i° = evaluated at vapor pressure, P_i°

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Reaction Kinetics in the Absorption of Chlorine into Aqueous Media

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It was established that chlorine reacts with both water and hydroxyl ions. At a short reaction time when the pH was less than 3 the reversible reaction of chlorine and water controlled the absorption rate. From pH 3 to 10.5 the forward reaction predominated and yielded an apparent first-order rate constant of 20.9 sec.$^{-1}$ at 25°C. Between pH 10.5 and 12.5 the reaction of chlorine with hydroxyl ions occurred simultaneously with the chlorine-water reaction. Above pH 12.5 the second-order reaction between chlorine and hydroxyl ions became controlling and the reaction-rate constant was evaluated to be in the order of 10^9 liters/(mole)(sec.) at 25°C.

These ionic reactions of chlorine were further interpreted through the collision and transition state theories. Certain important quantities with regard to the reaction characteristics were derived from the experimental data.

When chlorine is dissolved in aqueous solutions, certain ionic reactions are known to occur. The kinetics of these reactions however are not yet clear, and the important reaction characteristics have never been quantitatively determined. Shilov and Solodushenkov (*1*) investigated the kinetics of the reaction of chlorine in water by the conductivity technique. They assumed that the reaction

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl \quad (1)$$

was the rate-controlling mechanism and evaluated the apparent first-order rate constants which indicated a decreasing tendency as the reaction proceeded.

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