Molecular Diffusion of Inorganic Nitrate Species and Ketones in Subcritical and Supercritical Water[1]

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ABSTRACT

Limiting molecular diffusion coefficients of acetone and benzophenone in subcritical water at 300 bar were obtained with the Taylor dispersion method. Diffusion coefficients increased more than 40 fold between 25°C and 350°C. The laser-induced grating method was used to determine the molecular diffusion of lithium-, cesium-, and calcium nitrate in 1.0 m hydrothermal solutions at 450°C. At near-critical conditions, the molecular diffusion coefficients decreased to their values at ambient conditions. Subsequently, the diffusion coefficients increased with increasing density (pressure) to reach a plateau-value at high density supercritical conditions. Critical effects were observed at reduced pressures between 1 and 1.6 corresponding to reduced solution densities between 1 and 1.4.

The Stokes-Einstein equation correlated well with the experimental results for the molecular diffusion coefficients if reasonable estimates for the effective radii could be obtained. The effective radius for electrolytes could be estimated from hydration numbers, association constants, and geometric considerations.

KEYWORDS: high temperature and pressure; hydrothermal solutions; ketones; molecular diffusion; inorganic nitrates; Stokes-Einstein.

1. INTRODUCTION

This work was part of a larger effort at Los Alamos National Laboratory to elucidate the physical properties of hydrothermal solutions [1,2,3,4,5,6,7]. The results were to be used as input for engineering design equations and proces control models for hydrothermal processing of military wastes.

Two experimental techniques were evaluated for the determination of molecular diffusion coefficients at hydrothermal conditions: the laser-induced grating technique and the Taylor dispersion technique [6,7]. In this publication we report additional results to further validate both experimental techniques as well as the proposed interpretation of the results.

2. EXPERIMENTAL

Two experimental techniques were used: the laser-induced grating and the Taylor dispersion technique. Both techniques are complementary to each other as the Taylor dispersion technique performs optimally in dilute solutions sufficiently far away from the critical point, while the laser induced grating technique performs optimally in concentrated solutions near the critical point.

The experimental apparatus and validation of the experimental methods are described in detail elsewhere [6,7,8]. The molecular diffusion coefficients for acetone and benzophenone in subcritical water were determined with the Taylor dispersion technique. The molecular diffusion coefficients for $LiNO_3$, $CsNO_3$, and $Ca(NO_3)_2$ in 1.0 m hydrothermal solutions were determined with the laser-induced grating technique.

3. RESULT

3.1. Diffusion of Acetone and Benzophenone

Molecular diffusion coefficients of acetone and benzophenone in water at a nominal pressure of 300 bar are presented in Fig. 1 and Table I. The diffusion coefficients increase about 40 fold between 25°C and 350°C (P = 300 bar). These data are about 30% lower than diffusion coefficients in water up to 100°C at saturation pressure [9],

which "should be considered rough approximations". The observed trends for acetone and benzophenone are comparable to the trends observed for hydroquinone [10].

Experiments at supercritical conditions were attempted, but no data were obtained. The experimental dispersion profiles at 400°C and 490 bar suggested that two absorbing species (both ketones) were diffusing. Due to the relatively long residence times (≈ 20-40 min.), and the absence of dissolved oxygen, hydrolysis reactions probably explain the observed dispersion profiles.

3.2. Diffusion of $LiNO_3$, $CsNO_3$, and $Ca(NO_3)_2$

Molecular diffusion coefficients of $LiNO_3$, $CsNO_3$, and $Ca(NO_3)_2$ in 1.0 m hydrothermal solutions at 450°C were obtained, simultaneously with thermal diffusivities [6]. Results are shown in Fig. 2 and Table II. The molecular diffusion coefficient is at a minimum near the phase-separation pressure - due to the critical slowing down of the diffusion process - and appears to plateau at higher pressures. Plateau-values are on the order of 10^{-8} m^2s^{-1}. The minimum values of the diffusion coefficients near the critical point are comparable to the values at ambient conditions. The critical slowing down is significant as far as 300 bar from the phase-separation pressure (or at reduced pressures between 1 and 1.6), and solution densities ranging from the phase-separation density to about 500 kgm^{-3} (or $1 \leq \rho_r \leq 1.4$). Finally, contrary to the diffusion behavior at subcritical conditions [7,8], the diffusion coefficients for alkali nitrates increase with decreasing cation-radii: $D_{LiNO3} > D_{NaNO3} > D_{CsNO3}$. This result suggests that (hydrated) ion-pairs are diffusing instead of (hydrated) ions.

The 450°C isotherm was postulated to be near the critical temperature for the 1.0 m $LiNO_3$ and $CsNO_3$ solutions. Critical temperatures of hydrothermal alkali halidesolutions were observed to be virtually independent of the cation [11]. Critical temperatures for 0.6 m and 0.8 m $CsNO_3$ solutions were 407°C and 415°C, respectively. Consequently, the critical temperature for 1.0 m alkali metal nitrate solutions was estimated to be 423±4°C. Diffusion in 1.0 m solutions of $LiNO_3$ and $CsNO_3$ at 450°C followed the trends for $NaNO_3$ at 450°C [6], since these data were taken at near identical

T/T_c. Comparison of the diffusion coefficients for the 1.0 m $Ca(NO_3)_2$ solution with the 3.0 m $NaNO_3$ data suggested that these data were obtained at $T_r < 1$ [8].

4. DISCUSSION

The molecular diffusion data were interpreted in terms of hydrodynamic theory. Diffusion coefficients were compared with predictions from the Stokes-Einstein expression in both the slip and no-slip limit, and the Wilke-Chang, Scheibel, Reddy-Doraiswamy, and Lusis-Ratcliff equations [6,7]. To evaluate these expressions, estimates needed to be obtained for the molecular radii and for the solution viscosity.

4.1. Acetone and Benzophenone

Because the molecular diffusion of acetone and benzophenone were determined at dilute conditions, the viscosity of the solution could be approximated by the viscosity of water [7,8].

To determine the effective radii, the importance of changes in the hydrogen bonded character of the solvent on the diffusion coefficient was evaluated. The Stokes-Einstein radii of acetone and benzophenone were calculated from experimental diffusion data by solving the Stokes-Einstein equation in the no-slip limit. Because both acetone and benzophenone are large compared to a solvent molecule, selection of the no-slip limit seemed more appropriate than the slip limit. A first evaluation of the importance of hydrogen bonding on the nature of the diffusing species was obtained by correlating the experimental radii with the static dielectric constant of water. Fig. 3 shows a near-linear decrease of the effective radius with decreasing static dielectric constant, especially at elevated (T > 200°C) temperatures. This trend has also been documented in the literature; e.g. Balbuena and co-workers [12] reported decreasing hydration numbers for HCl molecules with decreasing densities and increasing temperatures. Consequently, acetone and benzophenone were represented as molecules surrounded by one hydration sphere at ambient conditions, and were assumed to gradually become less hydrated as the dielectric constant decreased with increasing temperature. At near-critical subcritical temperatures,

both molecules were considered non-hydrated, as suggested for benzene dimers by Gao [13].

The estimated effective radii and volumes of the clusters are reported in Table III. The effective radii of acetone and benzophenone were obtained from the bond-length between the atoms in the hydrated molecules and structural information. Acetone was approximated as a prolate ellipsoid with dimensions a = 2.65 Å , b = 1.22 Å, and c = 1.09 Å, while a benzophenone molecule was approximated as a prolate ellipsoid with dimensions a = 5.98 Å b = 2.07 Å, and c = 1.22 Å. Because benzophenone is an elongated molecule, its orientation relative to the direction of motion should be addressed. The quality and quantity of the diffusion data did not warrant such an extensive treatment.

The ratios of the calculated over the experimental diffusion coefficient are listed in Table IV. Of the tested hydrodynamic expressions, the Stokes-Einstein equation is the most promising. The Stokes-Einstein equation in the no-slip limit yielded predicitions within 5% of the experimental results. The other expressions systematically over predicted the diffusion coefficient. However, the number of assumptions included in estimating the radii, and the complexity of the benzophenone molecule, imply that the ratios reported in Table 4 should be viewed with caution.

4.2. $LiNO_3$, $CsNO_3$, and $Ca(NO_3)_2$

A. Plateau Region:

The viscosity of the 1.0 m metal nitrate solutions was approximated by the viscosity of water taken at the mass density for water that correspond to the solution density [6,8]. Unfortunately, densities for 1.0 m solutions of $LiNO_3$, $CsNO_3$, and $Ca(NO_3)_2$ were not available in the literature. Consequently, these densities were determined by the refractive index technique and apparatus developed by Anderson [2], and are included in the appendix.

Estimates for the effective radii for the nitrate salts were determined as described in Butenhoff et al. [6]. The diffusing species were postulated to be hydrated contact ion-pairs around the cation [14]. Hydration numbers were estimated from solubility

experiments [4]. The configuration, and estimated effective radii and molar volumes are listed in Table V.

The correlation between the experimental results and the hydrodynamic diffusion equations are shown in Tables VI as ratios of the predicted to the measured plateau diffusion coefficients. The Stokes-Einstein equation in the no-slip limit, the Wilke-Chang correlation (except for 1.0 m $CsNO_3$) and the Reddy-Doraiswamy correlation (except for 1.0 m $Ca(NO_3)_2$) predicted the background diffusion coefficient within about 15%. Because the solute sizes were probably overestimated - resulting in underestimated diffusion coefficients - the Stokes-Einstein or Wilke-Change relationships yielded more reliable predictions. Because a hydrated associated metal nitrate molecule is significantly larger and heavier than a water molecule, the no-slip limit for the Stokes-Einstein equation is reasonable. The Stokes-Einstein equation predicted the diffusion coefficient within 10% if the diffusing species was assumed to be a combination of hydrated contact ion pairs, anions, and hydrated cations. The fraction of each was determined from NaCl ionization constants [15]. If the diffusing species were assumed to be non-hydrated associated ion pairs (Table V), the model predictions were significantly higher than the measured plateau values.

B. Critical Phenomena

The critical behavior of the diffusion coefficient was further investigated as described for $NaNO_3$ elsewhere [6]. The diffusion coefficients were plotted on a log-log plot versus P/P_c-1 (where the critical pressure P_c was taken to be the observed phase-separation pressure). The mass diffusion coefficient approached zero as $D_{12} \sim (P/P_c-1)^{\nu}$ as the pressure approached the phase-separation pressure. Critical exponents of ν = 0.49, 0.68, and 0.81 were obtained for $LiNO_3$, $CsNO_3$, and $Ca(NO_3)_2$, respectively. Although not as remarkable as for $NaNO_3$ ($\nu = 0.60 \pm 0.02$ [6]), these values are still in reasonable agreement with the theoretically expected asymptotic critical exponent ν = 0.63 [16,17], and are also similar to measured critical exponents at consolute points [19,20]. This power law behavior was observed at reduced pressures between 1 and

1.4-1.6 or reduced densities between 1 and 1.2-1.4. These values for the reduced pressure or density are normally not considered asymptotically close to the critical point, nor were the data obtained on the critical isotherm. However, similar behavior was observed for diffusion in concentrated hydrothermal $NaNO_3$ solutions [6], and for diffusion of various alkali nitrates and nitrites in supercritical water [7]. Whether these results are due to the particular properties of the salt-water system should be further investigated.

4.3. Estimation of Diffusion in Concentrated Hydrothermal Solutions

Based on the available diffusion data for diffusion of $NaNO_3$ [6] and $LiNO_3$, $CsNO_3$, and $Ca(NO_3)_2$ in concentrated hydrothermal solutions, an empirical fit was developed. In the absence of experimental data - or validated theoretical models for diffusion in hydrothermal electrolyte solutions - this equation might be useful to obtain estimates for diffusion of electrolytes other than inorganic nitrates.

The molecular diffusion coefficient can be separated in a background and a critical contribution [21], or $D_{12} = D_{12,b} + \Delta D_{12,c}$. Very far away from the critical point - the plateau region - the transport properties are described by their background values, such as those obtained from the Stokes-Einstein equation. Asymptotically close to the critical point, the transport properties are dominated by the critical enhancements, which satisfy power laws with universal critical exponents. In between these two limiting regions, transport properties are described by cross-over functions.

It was demonstrated that the background contributions satisfy the Stokes-Einstein equation, $D_{12,b} = kT/6\pi\eta_2 r_1$. In addition, the analysis of the previous paragraphs suggest that power law behavior is observed over larger regions than commonly acknowledged. Mistura [18,22] predicted that the critical contributions should satisfy Stokes-Einstein behavior asymptotically close to the critical point. Luettmer-Strathmann and Sengers [21] derived cross-over functions so that the critical enhancements could be written as

$$\Delta D_{12,c} = \frac{AkT}{6\pi\eta_{2c}\xi}\,\Omega(\xi,...)$$

(1)

where A is a constant and $\Omega(\xi,...)$ is the cross-over function which, among others, is a function of the correlation length. For practical applications, the viscosity is obtained from the steam tables and critical effects are thus accounted for, hence $\eta_{2c} = \eta_2$. To further develop the empirical fit it was postulated that the correlation length could be divided into a background value (= the effective radius used previously) and a critical enhancement according to $\xi = r_1B(P/P_c - 1)^{-0.60}$, with B an empirical constant. Finally, the diffusion data suggested an exponential-like increase of the effective radius with P/P_c-1. Since $\xi \sim (P/P_c-1)^{-0.60}$ and $\Omega = f(\xi,...)$ [21], $\exp\left[A'(P/P_c-1)^{-0.60}\right]$ was selected as empirical cross-over function. The resulting fitting equation for D_{12}, after collection of constant terms, is

$$D_{12} = \frac{kT}{6\pi\eta_2 r_1} * (1 + B'(P/P_c - 1)^{0.60} \exp\left[(P/P_c-1)^{-0.60}\right]) \qquad (2)$$

Fitting Eq. 2 to all the diffusion data for concentrated solutions yielded the empirical constant $A' = 4.8\text{x}10^{-2}$ and $B = 8.4\text{x}10^{-11}$ resulting in a pre-exponential factor of $B' = 8.8\text{x}10^{-11}$ (Goemans, 1996). Obviously, with the uncertainty surrounding the phase-separation pressure and the effective radius, Eq. 2 really uses three adjustable parameters, two of which have a physical meaning (r_1 and P_c) and can therefore be estimated a priori. If the critical exponent (=0.60) was allowed to change, the optimized value was 0.60, thus providing additional validation for Eq. 2.

As demonstrated in Fig. 4, the correlation between the data and Eq. 2 was within 20%. Predictions at pressures very near the phase separation pressure ($1 < P_r < 1.1$) were less reliable with deviations as large as 400%. As would be expected, the performance of Eq. 2 was sensitive to variations in P_c and - to a lesser degree - in r_1. Diffusion coefficients at the plateau region are smaller that those estimated from Eq. 2.

5. CONCLUSIONS

Limiting molecular diffusion coefficients of acetone and benzophenone in subcritical water at 300 bar were obtained with the Taylor dispersion method. Diffusion coefficients increased more than 40 fold between 25°C and 350°C. The laser-induced grating method was used to determine the molecular diffusion of lithium-, cesium-, and calcium nitrate in 1.0 m hydrothermal solutions at 450°C. At near-critical conditions, the molecular diffusion coefficients decreased to their values at ambient conditions. Subsequently, the diffusion coefficients increased with increasing density (pressure) to reach a plateau-value at high density supercritical conditions. Critical effects were observed at reduced pressures between 1 and 1.6 corresponding to reduced solution densities between 1 and 1.4.

The Stokes-Einstein equation correlated well with the experimental results for the molecular diffusion coefficients if reasonable estimates for the effective radii could be obtained. The effective radii could be estimated from hydration numbers, association constants, and geometric considerations. An empirical fitting equation was presented to estimate electrolyte diffusion in concentrated hydrothermal solutions.

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APPENDIX: Density of 1.0 m hydrothermal $LiNO_3$, $CsNO_3$, and $Ca(NO_3)_2$ solutions

Data obtained with the index of refraction technique developed by Anderson (1996).

$LiNO_3$		$CsNO_3$		$Ca(NO_3)_2$	
P (bar)	ρ (kg m^{-3})	P (bar)	ρ (kg m^{-3})	P (bar)	ρ (kg m^{-3})
408.8	P.S.	405.7	P.S.	466.6	P.S.
411.9	420	412.5	476	469.4	538
418.9	443	432.6	508	470.4	544
438.8	451	471.7	552	497.7	556
488.4	503	539.1	585	514.5	586
573.6	561	634.2	649	532.9	603
702.9	604	770.3	693	578.4	625
817.9	632	917.6	730	590.4	631
938.7	662	1081	754	640.4	641
				731.5	678
				773.9	697
				844.0	701
				979.7	735
				1110	744
				1234	779

P.S. = Phase separation
Experimental error estimated at ±5%

Table I. Molecular diffusion coefficients of acetone and benzophenone in water at a nominal pressure of 300 bar.

Benzophenone			Acetone		
T (°C)	P (bar)	$10^9 x D_{12}$ ($m^2 s^{-1}$)	T (°C)	P (bar)	$10^9 x D_{12}$ ($m^2 s^{-1}$)
			25.1±1.3	300.7±1.0	0.958±0.131
100.0±1.2	300.4±1.1	2.28±0.13	100.0±1.3	299.7±1.5	3.59±0.24
200.0±1.8	300.3±1.3	7.57±1.35	200.2±1.9	300.2±1.7	10.6±0.1
300.0±1.9	299.6±1.8	19.1±3.6	299.9±2.3	299.9±1.7	25.0±3.4
349.9±2.5	300.1±2.1	31.7±9.9	350.1±1.9	301.6±2.1	43.6±5.3

P, T, and D_{12}: 95% confidence interval.

Table II. Molecular Diffusion Coefficients of $LiNO_3$, $CsNO_3$, and $Ca(NO_3)_2$ in 1.0 m Hydrothermal Solutions at 450°C

$LiNO_3$		$CsNO_3$		$Ca(NO_3)_2$	
P (bar)	$10^9 D_{12}$ ($m^2 s^{-1}$)	P (bar)	$10^9 D_{12}$ ($m^2 s^{-1}$)	P (bar)	$10^9 D_{12}$ ($m^2 s^{-1}$)
422.9	7.3±0.4	422.9	5.0±0.4	476.2	1.2±0.2
450.1	12.3±1.4	450.1	10.1±1.0	500.0	4.2±0.4
500.1	18.1±1.2	500.0	15.8±2.0	550.1	8.0±0.4
600.0	25.2±2.2	600.0	19.9±2.2	600.0	10.1±1.4
700.1	25.2±3.2	700.0	20.4±2.6	700.0	12.5±2.0
		800.0	21.8±2.4	800.0	13.6±3.0
		899.6	22.4±3.8	900.0	14.9±2.8

Table III. Estimated radii for acetone and benzophenone as a function of temperature.

Species	T (°C)	n_h	Configuration	Effective Radius (Å)	Molar Volume (cm^3mol^{-1})
Acetone	25	2	Oblate Ellipsoid[a]	2.41	43.3
	100	2	Oblate Ellipsoid[a]	2.41	43.3
	200	2	Oblate Ellipsoid[b]	2.29	28.5
	300	1	Oblate Ellipsoid	1.98	29.5
	350	0	Prolate Ellipsoid	1.57	13.1
Benzophenone	100	4	Prolate Ellipsoid	3.98	233
	200	2	Oblate Ellipsoid	3.56	99.1
	300	1	Ellipsoid[c]	1.95	53.4
	350	0	Ellipsoid[c]	1.95	53.4

[a] Hydration water attached to shortest axis.

[b] Hydration water attached to longest axis.

[c] Molecule postulated to move with longest axis parallel with flow. The effective radius is the average of the two shortest axis. The molar volume is the volume of non-hydrated benzophenone (prolate ellipsoid).

Table IV. Ratios[a] between predicted and measured[b] diffusion coefficients for acetone and benzophenone in subcritical water.

Species	Stokes-Einstein (no-slip)	Stokes-Einstein (slip)	Wilke-Chang	Reddy-Doraiswamy	Lusis-Ratcliff	Scheibel
Acetone	0.97 ±0.18	1.46 ±0.28	1.19 ±0.28	1.38 ±0.27	1.82 ±0.24	2.21 ±1.04
Benzo-phenone	1.03 ±0.26	1.55 ±0.19	0.81 ±0.24	1.29 ±0.48	1.33 ±0.13	1.32 ±0.42

[a] The ratios are the average of the calculated values for all diffusion coefficients between 100°C and 350°C at 300 bar. The errors refer to the 95% confidence interval.

[b] The data at 25°C were not included for the reasons outlined in Section 4.4.1.

Table V. Estimated radii of hydrated and non-hydrated contact ion pairs.

Species	Comments	Configuration	Effective Radius (Å)	Molar Volume (cm^3mol^{-1})
$LiNO_3 \cdot 5H_2O$	Hydrated Contact Ion-Pairs	Prolate Ellipsoid	3.40	98.3
$CsNO_3 \cdot 3H_2O$	Hydrated Contact Ion-Pairs	Oblate Ellipsoid	3.70	127
$Ca(NO_3)_2.4H_2O$	Hydrated Contact Ion-Pairs	Prolate Ellipsoid	3.84	139
$LiNO_3$	Contact Ion-Pairs	Prolate Ellipsoid	2.04	20.8
$CsNO_3$	Contact Ion-Pairs	Prolate Ellipsoid	2.37	30.1
$Ca(NO_3)_2$	Contact Ion-Pairs	Prolate Ellipsoid	2.72	40.1

Table VI. Ratios between predicted and measured diffusion coefficients in concentrated hydrothermal electrolyte solutions.[a]

Species	C (m)	T (°C)	$D_{12,pl}$	Model 1[b]	Model 2	Model 3	Model 4	Model 5	Model 6
$LiNO_3$	1.0	450	2.52 ±0.32	0.90 ±0.06	1.30 ±0.12	0.80 ±0.08	1.47 ±0.20	1.42 ±0.16	1.12 ±0.04
$CsNO_3$	1.0	450	2.21 ±0.38	0.91 ±0.18	1.21 ±0.32	0.70 ±0.18	1.23 ±0.38	1.25 ±0.36	1.06 ±0.20
CaN_2O_6	1.0	450	1.43 ±0.30	1.15 ±0.22	1.70 ±0.32	0.96 ±0.18	1.66 ±0.34	1.73 ±0.34	1.54 ±0.26

Model 1: Stokes-Einstein in the no-slip limit; Model 2: Stokes-Einstein in the slip limit; Model 3: Wilke-Chang (1955); Model 4: Scheibel (1954); Model 5: Lusis-Ratcliff(1968); Model 6: Reddy-Doraiswamy (1967)

[a] The viscosity of the solution was estimated by the viscosity of water at the same temperature and mass density as the solution.

[b] Model predictions were within 15-20% of the measured diffusion coefficients if only the diffusion of hydrated contact ion pairs was considered.

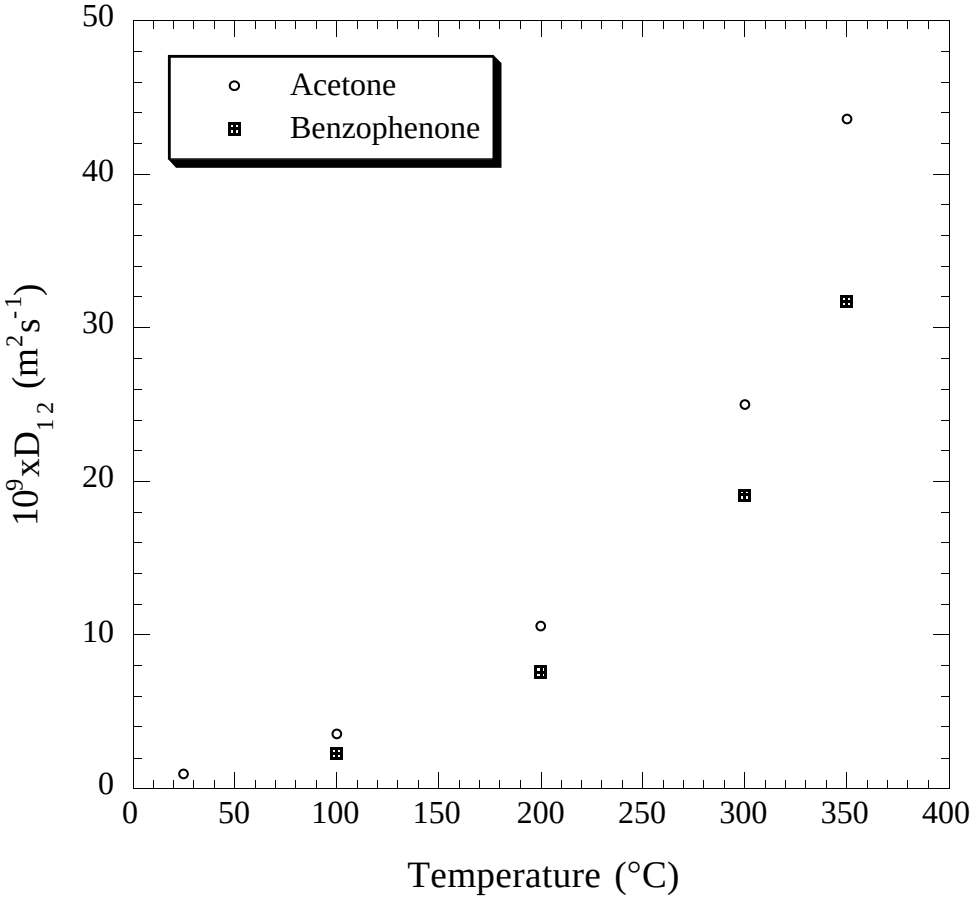

Fig. 1. Molecular diffusion coefficient of acetone and benzophenone at 300 bar as a function of temperature.

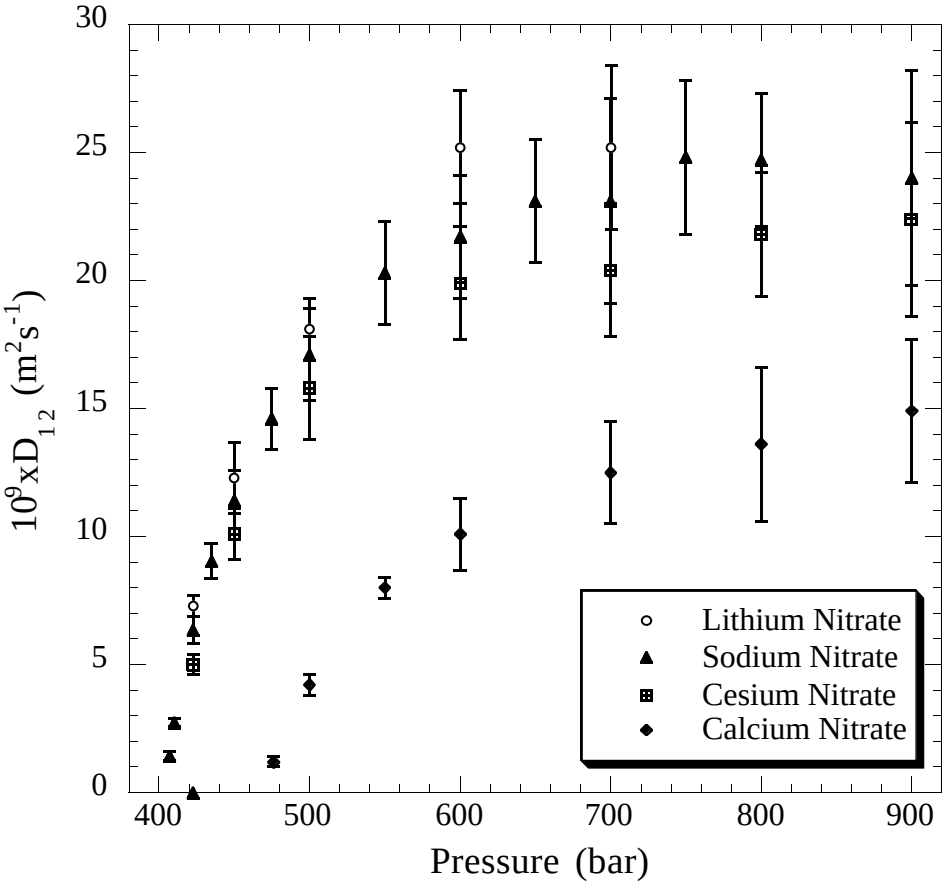

Fig. 2. Molecular diffusion coefficients of NaNO3 (Butenhoff et al., 1996), and $LiNO_3$, $CsNO_3$, $Ca(NO_3)_2$ in 1.0 m solutions at 450°C (error bars correspond to the 95% confidence interval).

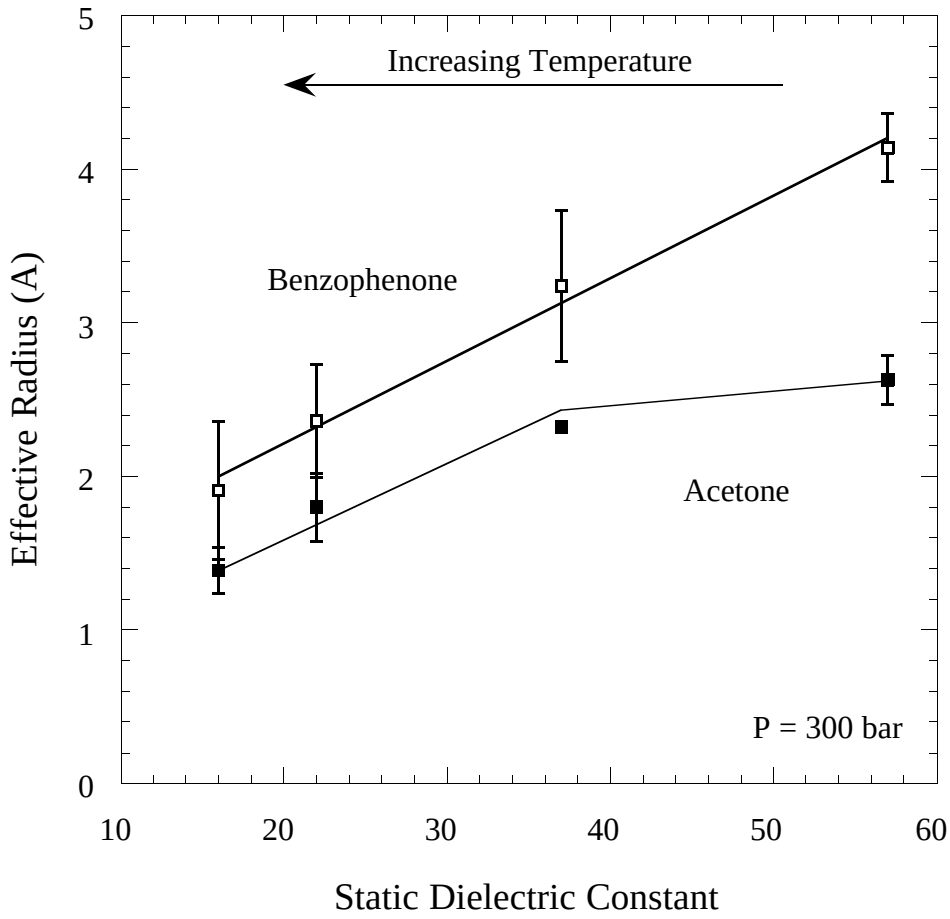

Fig. 3. Relation between the effective radius of acetone and benzophenone and the static dielectric constant of subcritical water.

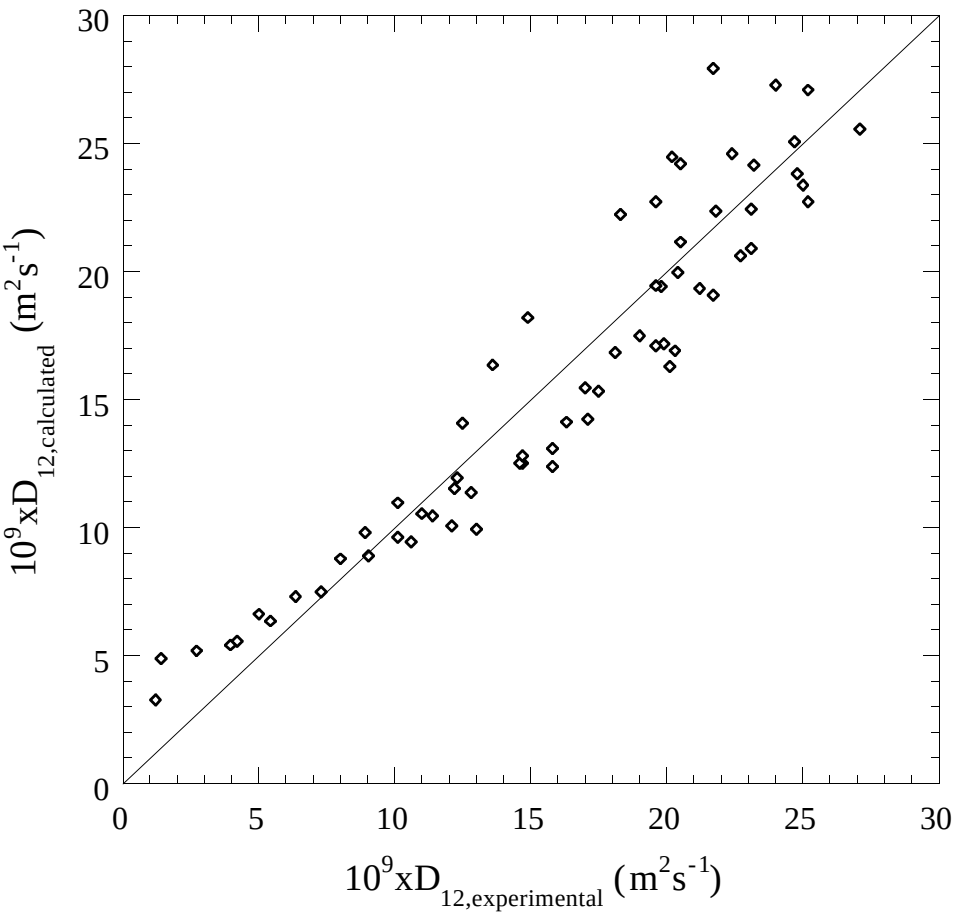

Fig. 4. Correlation between experimental diffusion coefficients in concentrated hydrothermal solutions and diffusion coefficients calculated from the semi-empirical Stokes-Einstein equation modified for critical effects.