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Viscosity and Density of Aqueous Na_2SO_4 and K_2SO_4 Solutions in the Temperature Range 20–90 °C and the Pressure Range 0–30 MPa

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This paper presents experimental data of the viscosity of aqueous Na_2SO_4 and K_2SO_4 solutions. The viscosity was measured by the oscillating-disk method in the pressure range 0–30 MPa and the temperature range 20–90 °C. The measurements cover the concentration range 0–1.1 *m* for the first salt and 0–0.6 *m* for the second. The experimental results have an estimated uncertainty of ±1.0%. The effect of pressure on the density of these solutions has also been measured. These measurements constitute the first study of the viscosity and the density of Na_2SO_4 and K_2SO_4 solutions over an extended range of pressure, temperature, and concentration. The viscosity and density data have been correlated in terms of pressure, temperature, and concentration. The correlations reproduce the original data to within the quoted uncertainty. The paper includes comparisons between our correlations and the experimental results of other investigators.

Introduction

This paper is the seventh in a series (*1–3*, *6–8*) that is intended to provide data on the viscosity of the prevalent constituents in geothermal brines. The previous publications included measurements of the viscosity of distilled water (*8*) and aqueous solutions of NaCl (*6*, *7*), KCl (*3*), NaCl-KCl mixtures (*1*), and Na_2CO_3 and K_2CO_3 (*2*). In this paper we present measurements of the viscosity of aqueous Na_2SO_4 and K_2SO_4 solutions in the temperature range 20–90 °C and a pressure range of 0–30 MPa. The concentration range extends from 0 to 1.1 *m* for aqueous Na_2SO_4 solutions and from 0 to 0.6 *m* for aqueous K_2SO_4 solutions. These measurements are believed to be the only ones covering a range of pressure, temperature, and concentration corresponding to liquid-dominated geothermal reservoirs.

A careful search of the available literature (*16*) revealed the viscosity measurements on Na_2SO_4 solutions by Korosi and Fabuss (*13*) to be the only data available for comparison. Since it was also shown that only inadequate data on the density as a function of pressure exist for these solutions, it was decided to measure this effect as well. The viscosity and density are used to develop correlations valid over the entire range of temperature, pressure, and concentration covered by the measurements.

Experimental Procedure

The measurements of viscosity were performed in an oscillating-disk viscometer which has been described in detail in our previous publications (*4*, *8*, *10*). The theory of the instrument and the experimental procedure were also given there. The characteristics of the oscillating system are the same as those given in ref *1*.

The viscometer was calibrated with respect to distilled water in the manner described in ref *6* and *8*. The edge-correction factor *C* (*9*, *12*) for the viscometer is described as a function of the boundary-layer thickness, δ (*8*, *11*), defined as

$$\delta \equiv (\nu T_0/2\pi)^{1/2} \quad (1)$$

Here, ν is the kinematic viscosity of the fluid and T_0 is the period of oscillation in vacuo. Figure 1 depicts the results of the calibration where the solid line represents the least-squares fit of the experimental data given by eq 2. The original calibration

$$C(\delta) = 1.000 + 0.04085(\delta/\text{mm}) + 0.09365(\delta/\text{mm})^2 - 0.03767(\delta/\text{mm})^3 \quad (2)$$

points are shown as open symbols while the solid ones are check measurements which were taken after each cleaning and realignment of the oscillating system. It can be seen that the check points deviate from the line represented by eq 2 by less than ±0.2%.

The solutions were prepared by mixing reagent-purity salts with distilled, deaerated water. The K_2SO_4 solutions were prepared gravimetrically by means of a high-precision, high-

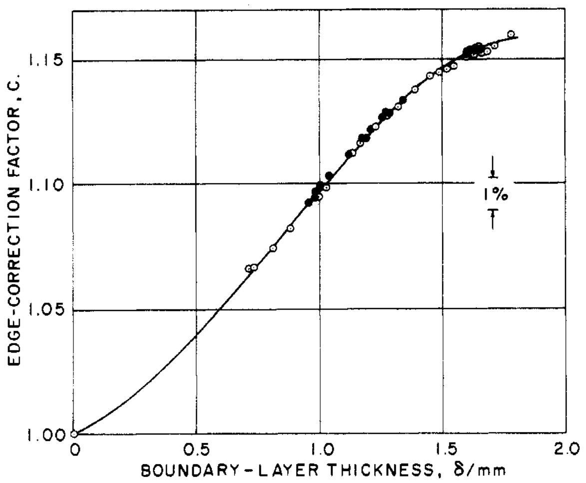

Figure 1. Calibration curve: (—) eq 2; (○) calibration points; (●) check points.

capacity balance. Because of the hygroscopic nature of Na_2SO_4, the additional precaution of drying this salt before weighing it in a dry atmosphere was taken.

Density

The viscosity and the density of a liquid are closely coupled in the working equations of the oscillating-disk viscometer (*9*, *12*). To a first-order approximation

$$\Delta \sim (\rho\mu)^{1/2} \tag{3}$$

where Δ is the logarithmic decrement of the damped oscillation of the disk. This shows that we must have access to reasonably accurate density values over the desired pressure–temperature–concentration range in which we want to determine the viscosity. Accurate values of the density of aqueous Na_2SO_4 and K_2SO_4 solutions are not available over the range of our interest (*16*). Specifically, a recent search of the literature failed to uncover any data on the density of these solutions over our pressure range. However, this search by Potter et al. (*14*, *15*) revealed the existence of limited information on the low-pressure density and presented an extensive compilation of them.

At elevated pressures the viscometer was used to determine the relative effect of pressure on the density at a given solution at a particular temperature. An account of this method was given earlier (*2*). The density was determined relative to water as correlated by Kell and Whalley (*5*).

The pressure effect was determined and applied to the low-pressure data compiled by Potter et al. (*14*, *15*) as a linear factor:

$$\rho(P,t,c) = \rho^0(t,c)[1 + \alpha(t,c)P/\mathrm{MPa}] \tag{4}$$

Here $\rho^0(t,c)$ is a hypothetical zero-pressure density represented by

$$\rho^0(t,c) = \sum_{i=0}^{2}\sum_{j=0}^{2} d_{ij}(c/m)^{i/2}(t/°\mathrm{C})^j \tag{5}$$

for K_2SO_4 solutions, and by

$$\rho^0(t,c) = \frac{1000\rho_w(t) + M_2c\rho_w(t)}{1000 + \phi_v(t,c)c\rho_w(t)} \tag{6}$$

for Na_2SO_4 solutions. Here m = 1 mol/kg, M_2 is the formula weight of Na_2SO_4, and

$$\phi_v(t,c) = \sum_{i=0}^{2}\sum_{j=0}^{2} d_{ij}(c/m)^{i/2}(t/°\mathrm{C})^j \tag{7}$$

Table I. Coefficients d_{ij} in Eq 7 for Na_2SO_4 Solutions

i \ *j*	0	1	2
0	0.71330	0.452 84	$-0.357\,76 \times 10^{-2}$
1	18.494	−0.127 06	$-0.600\,00 \times 10^{-4}$
2	−1.0057	−0.056 111	$0.126\,29 \times 10^{-2}$

Table II. Coefficients a_{ij} in Eq 8 for Na_2SO_4 Solutions

i \ *j*	0	1	2
0	0.5196	−0.2011	0.1101
1	-0.4136×10^{-2}	0.7622×10^{-2}	-0.5244×10^{-2}
2	0.4286×10^{-4}	-0.8874×10^{-4}	0.6051×10^{-3}

Table III. Coefficients d_{ij} in Eq 5 for K_2SO_4 Solutions

i \ *j*	0	1	2
0	1.0026	$-0.148\,17 \times 10^{-3}$	$-0.292\,94 \times 10^{-5}$
1	$0.875\,58 \times 10^{-2}$	$-0.122\,88 \times 10^{-3}$	$0.116\,66 \times 10^{-5}$
2	0.121 21	$0.849\,13 \times 10^{-5}$	$-0.400\,46 \times 10^{-6}$

Table IV. Coefficients a_{ij} in Eq 8 for K_2SO_4 Solutions

i \ *j*	0	1	2
0	0.5556	−0.4986	0.8083
1	-0.2615×10^{-2}	0.3051×10^{-3}	-0.9532×10^{-2}
2	0.1962×10^{-4}	-0.1566×10^{-4}	0.6679×10^{-4}

Table V. Viscosity of Na_2SO_4 Solution No. 1 (c = 0.2746 m)

P, MPa	*μ*, *μ*Pa s	*P*, MPa	*μ*, *μ*Pa s
	at 20.0 °C		
0.4	1124	21.0	1120
7.0	1122	31.2	1120
14.0	1122	0.1	1125
	at 35.5 °C		
0.7	804	20.9	805
7.2	805	31.2	807
14.1	805	0.1	803
	at 50.0 °C		
1.1	620	20.9	624
7.2	621	30.8	626
14.1	623	1.1	620
	at 69.5 °C		
1.2	463	20.9	467
7.0	463	30.9	470
13.8	465	1.3	461
	at 88.5 °C		
0.6	362	20.9	369
7.3	364	30.6	371
13.9	367	1.4	364

The pressure coefficient $\alpha(t,c)$ in both cases is expressed in terms of t and c as

$$\alpha(t,c) = \sum_{i=0}^{2}\sum_{j=0}^{2} a_{ij}(c/m)^i(t/°\mathrm{C})^j \tag{8}$$

Tables I and II list the coefficients d_{ij} and a_{ij} for Na_2SO_4, and Tables III and IV for K_2SO_4, respectively. The correlations represented by eq 4–8 describe the density of the solutions to within the uncertainty of the compiled data of Potter et al. (*14*, *15*), i.e., to ±0.1%.

The density of the solutions at room temperature and atmospheric pressure was measured in a precision pycnometer both before and after each experimental run. These measurements agree with the correlations represented by eq 5–7 to within the estimated uncertainty of the latter. Furthermore, the density of a sample taken from the viscometer after an experimental run differed negligibly from the value obtained before the run. This is indicative of the absence of measurable

Table VI. Viscosity of Na_2SO_4 Solution No. 2 ($c = 0.5600$ m)

P, MPa	μ, μPa s	P, MPa	μ, μPa s
at 19.0 °C			
0.4	1290	21.0	1286
7.1	1287	31.2	1287
14.0	1290	0.4	1288
at 35.0 °C			
0.6	909	21.1	913
7.1	909	31.0	915
14.0	912	0.8	908
at 50.5 °C			
1.1	686	21.1	692
7.4	689	30.8	695
13.9	688	0.9	688
at 70.0 °C			
0.5	513	20.9	520
7.2	516	30.6	523
14.0	517	1.1	514
at 87.0 °C			
1.6	414	20.8	420
7.4	415	30.6	422
13.8	418	1.6	414

Table VII. Viscosity of Na_2SO_4 Solution No. 3 ($c = 0.8439$ m)

P, MPa	μ, μPa s	P, MPa	μ, μPa s
at 19.5 °C			
0.4	1463	21.1	1465
7.1	1462	31.2	1466
14.1	1461	0.4	1463
at 34.5 °C			
0.7	1043	21.1	1047
7.1	1043	31.1	1051
14.1	1044	0.6	1041
at 50.5 °C			
0.9	779	21.2	785
7.4	782	31.2	789
14.0	784	0.9	779
at 69.5 °C			
1.3	585	21.1	592
7.1	587	31.0	595
14.0	590	0.7	585
at 88.5 °C			
1.4	460	21.0	465
7.1	461	30.8	468
14.1	463	1.8	458

Table VIII. Viscosity of Na_2SO_4 Solution No. 4 ($c = 1.1036$ m)

P, MPa	μ, μPa s	P, MPa	μ, μPa s
at 30.5 °C			
0.4	1271	20.9	1278
7.1	1270	31.1	1283
14.0	1274	0.6	1272
at 40.5 °C			
0.5	1034	21.2	1041
7.2	1037	31.1	1046
14.1	1039	0.6	1034
at 52.0 °C			
0.9	844	21.1	851
7.3	846	31.0	857
14.1	848	0.8	842
at 69.5 °C			
1.0	646	21.0	654
7.1	650	31.1	658
14.0	652	1.2	646
at 88.5 °C			
1.4	507	20.8	513
7.1	509	30.8	518
14.0	511	1.3	507

Table IX. Viscosity of K_2SO_4 Solution No. 1 ($c = 0.1491$ m)

P, MPa	μ, μPa s	P, MPa	μ, μPa s
at 19.5 °C			
0.4	1048	21.1	1044
7.1	1047	31.0	1042
14.3	1045	0.4	1049
at 35.0 °C			
7.1	752	20.9	754
14.0	753	31.0	757
		1.0	751
at 50.0 °C			
1.0	579	20.9	584
7.3	579	31.1	585
14.0	580	1.1	579
at 69.0 °C			
0.5	435	21.1	439
6.9	436	31.0	442
14.0	436	0.6	435
at 89.5 °C			
1.6	333	21.1	338
7.8	334	30.6	340
14.0	335	2.6	333

Table X. Viscosity of K_2SO_4 Solution No. 2 ($c = 0.3000$ m)

P, MPa	μ, μPa s	P, MPa	μ, μPa s
at 21.0 °C			
0.3	1042	21.1	1038
7.2	1040	31.3	1038
14.4	1038	0.1	1042
at 38.0 °C			
0.6	732	21.1	736
7.2	733	31.2	737
14.2	735	0.8	734
at 52.5 °C			
1.4	575	21.0	578
7.2	576	30.9	581
14.1	577	1.3	575
at 70.0 °C			
0.4	445	21.3	451
6.9	447	31.2	453
14.2	449	1.1	445
at 87.5 °C			
0.5	357	22.0	363
7.5	359	31.1	366
12.5	361	1.9	359

Table XI. Viscosity of K_2SO_4 Solution No. 3 ($c = 0.4495$ m)

P, MPa	μ, μPa s	P, MPa	μ, μPa s
at 20.5 °C			
0.1	1089	21.1	1085
7.8	1085	31.3	1085
14.1	1084	0.6	1088
at 36.0 °C			
1.0	792	21.0	794
7.2	793	31.1	795
14.2	794		
at 49.0 °C			
1.0	632	21.0	635
7.2	633	31.0	638
14.0	634	1.1	631
at 70.0 °C			
0.7	465	14.1	470
1.4	467	20.7	472
7.1	468	31.1	464
at 88.5 °C			
0.5	370	20.9	375
6.9	371	31.0	377
13.9	373	1.6	370

Table XII. Viscosity of K_2SO_4 Solution No. 4 ($c = 0.5998$ m)

P, MPa	μ, μPa s	P, MPa	μ, μPa s
	at 21.0 °C		
0.1	1109	21.1	1111
7.1	1112	31.1	1110
14.0	1112	0.1	1108
	at 35.0 °C		
0.9	830	21.2	834
7.3	832	31.3	836
14.0	831	0.5	831
	at 50.5 °C		
1.0	640	21.0	643
7.2	641	31.1	646
14.0	643	0.9	638
	at 71.0 °C		
1.1	476	21.0	482
7.2	478	31.1	485
13.8	480	1.1	476
	at 88.5 °C		
1.3	386	20.8	391
7.1	387	30.9	394
14.1	389	1.6	386

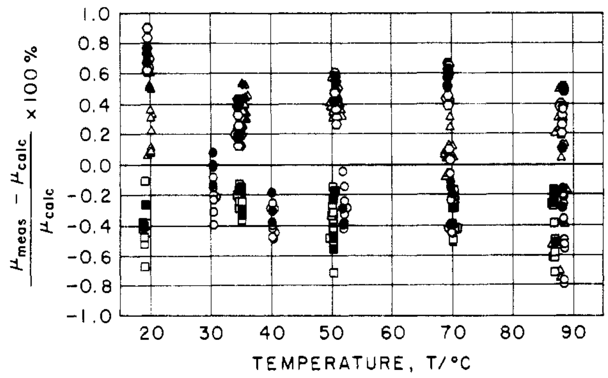

Figure 2. Deviation of measurements from calculations for aqueous Na_2SO_4 solutions: (△) solution no. 1, $c = 0.2746$ m ((▲) at $P \simeq 0$); (□) solution no. 2, $c = 0.5600$ m ((■) at $P \simeq 0$); (□) solution no. 3, $c = 0.8439$ m ((■) at $P \simeq 0$); (○) solution no. 4, $c = 1.1036$ m ((●) at $P \simeq 0$).

changes in the composition of the solution due to interactions with the viscometer.

Viscosity

Tables V–VIII contain the experimental values of the viscosity for the four Na_2SO_4 solutions and Tables IX–XII for the four K_2SO_4 solutions. Each entry in these tables is an average of at least two independent measurements taken at the specified pressure, temperature, and concentration. Check points taken during decompression and cooling are included in the tables. The reported values for all viscosity measurements have been adjusted to a nominal temperature by means of a small linear correction based on our original results (eq 9). The

$$\mu(t_{nom}) = \mu(t) + (t_{nom} - t)(\partial\mu/\partial t)_{P,c} \qquad (9)$$

estimated uncertainty of the reported results is ±1.0%. A part of this uncertainty is due to the uncertainty in the density.

The experimental results were analyzed and correlated in three stages. Since the viscosities of liquids exhibit a weak dependence on pressure, the values are first correlated along an isotherm as a linear function of pressure:

$$\mu(P,t,c) = \mu^0(t,c)[1 + \beta(t,c)P] \qquad (10)$$

Table XIII. Coefficients f_{ij} in Eq 11 for Na_2SO_4 Solutions

i \ j	0	1	2
0	0.3160	0.2100	0.03241
1	0.4664×10^{-2}	-0.7093×10^{-2}	0.1544×10^{-2}
2	-0.3419×10^{-4}	0.5594×10^{-4}	-0.1686×10^{-4}

Table XIV. Coefficients g_{ij} in Eq 13 for Na_2SO_4 Solutions

i \ j	0	1	2
0	7506	−14.90	8.338
1	−0.3498	0.7376	−0.4186
2	0.5026×10^{-2}	−0.01085	0.6226×10^{-2}
3	-0.2117×10^{-4}	0.4490×10^{-4}	-0.2589×10^{-4}

Table XV. Coefficients f_{ij} in Eq 11 for K_2SO_4 Solutions

i \ j	0	1	2
0	−0.061 21	0.7583	−0.6681
1	0.017 65	−0.05365	0.05111
2	$-0.148\,8 \times 10^{-3}$	0.5144×10^{-3}	-0.5005×10^{-3}

Table XVI. Coefficients g_{ij} in Eq 13 for K_2SO_4 Solutions

i \ j	0	1	2
0	−3.788	25.98	−27.59
1	0.4755	−2.506	2.643
2	−0.01062	0.05239	−0.05470
3	0.6301×10^{-4}	-0.3032×10^{-3}	0.3140×10^{-3}

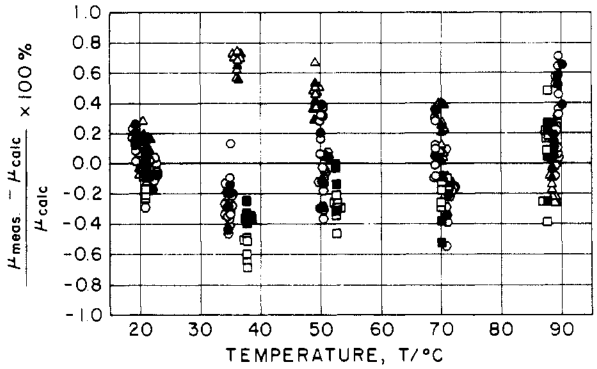

Figure 3. Deviation of measurements from calculations for aqueous K_2SO_4 solutions: (○) solution no. 1, $c = 0.1491$ m ((●) of $P \simeq 0$); (□) solution no. 2, $c = 0.3000$ m ((■) at $P \simeq 0$); (△) solution no. 3, $c = 0.4495$ m ((▲) at $P \simeq 0$); (□) solution no. 4, $c = 0.5998$ m ((■) at $P \simeq 0$).

Subsequently, the hypothetical zero-pressure viscosity, $\mu^0(t,c)$, was correlated in terms of temperature and concentration as

$$\mu^0(t,c)/\mu^0(t) = 1 + \sum_{i=0}^{2} \sum_{j=0}^{2} f_{ij}(t/{}^\circ\mathrm{C})^i(c/m)^{j+1} \qquad (11)$$

In this expression $\mu^0(t)$ represents the viscosity of pure water at low pressure which can be obtained from the correlation of Kestin, Sokolov, and Wakeham (*11*); viz.

$$\log\,[\mu_w^0(t)/1002.0\ \mu\mathrm{Pa\ s}] = (20 - t/{}^\circ\mathrm{C})\,[1.2378 - 1.303 \times 10^{-3}(20 - t/{}^\circ\mathrm{C}) + 3.06 \times 10^{-6}(20 - t/{}^\circ\mathrm{C})^2 + 2.55 \times 10^{-8}(20 - t/{}^\circ\mathrm{C})^3]/(96 + t/{}^\circ\mathrm{C}) \qquad (12)$$

Finally, the coefficients $\beta(t,c)$ have been correlated by means of an expression of the form

$$[\beta(t,c) - \beta_w(t)](\mathrm{GPa}) = \sum_{i=0}^{3} \sum_{j=0}^{2} g_{ij}(t/{}^\circ\mathrm{C})^i(c/m)^{j+1} \qquad (13)$$

The pressure coefficient for water, $\beta_w(t)$, was given in ref *8* as

$$\beta_w(t)/(\mathrm{GPa})^{-1} = -1.297 + 0.574 \times 10^{-1}(t/{}^\circ\mathrm{C}) - 0.697 \times 10^{-3}(t/{}^\circ\mathrm{C})^2 + 0.447 \times 10^{-5}(t/{}^\circ\mathrm{C})^3 - 0.105 \times 10^{-7}(t/{}^\circ\mathrm{C})^4 \qquad (14)$$

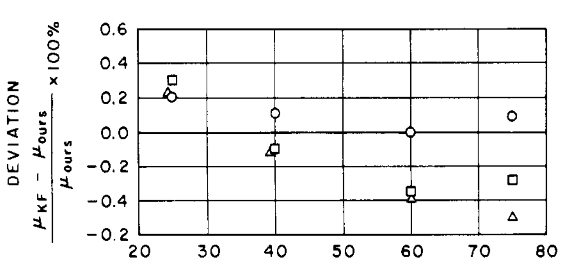

Figure 4. Deviation of the viscosity measurements of ref *13* from the calculated values via eq 10–14: (○) $c = 0.3330$ *m*; (□) $c = 0.2356$ *m*; (△) $c = 0.4712$ *m*.

The coefficients f_{ij} and g_{ij} which appear in eq 11 and 13, respectively, were calculated from the measurements presented earlier. The resulting coefficients are seen listed in Tables XIII and XIV for Na_2SO_4 solutions and Tables XV and XVI for K_2SO_4 solutions, respectively.

Figures 2 and 3 depict the deviations of the experimental results from the correlations for Na_2SO_4 and K_2SO_4, respectively. The correlations reproduce the experimental results with a maximum deviation of 0.9% for Na_2SO_4 solutions and 0.7% for K_2SO_4 solutions. The standard deviation is 0.4% for the Na_2SO_4 as well as the K_2SO_4 solutions, which is well within the estimated accuracy of the experimental data.

The only measurements of viscosity available for comparison are those by Korosi and Fabuss (*13*) for aqueous Na_2SO_4 solutions. Figure 4 depicts the deviation of these measurements from the correlations presented here. The deviations are within ±0.5% with a standard deviation of 0.26%, which is within the quoted accuracy of the measurements.

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Solubility of Solids in Supercritical Carbon Dioxide and Ethylene

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Solubility data were obtained for five different solids in both supercritical carbon dioxide and supercritical ethylene. A one-pass flow system was used to measure the equilibrium solubilities. The range in temperatures covered was 308–338 K and the range in pressures was roughly 80–280 bar.

Over the past few years, significant interest has been expressed in a separation concept wherein a condensed phase (liquid or solid) is contacted with a fluid phase that is supercritical both in the temperature and pressure sense. An often-quoted example is the German patent to remove, selectively, caffeine from green coffee beans by using supercritical carbon dioxide (*24*). Other examples would include deasphalting heavy residual oils with supercritical propane (*19*) and removing adsorbed materials from activated carbon with supercritical carbon dioxide (*8*, *9*). Supercritical water has been explored as a solvent medium to carry out chemical reactions or biological degradations without char formation (*1*, *7*).

In all of these instances, the dissolution effect appears to be related primarily to the nonideality of the supercritical fluid phase which leads to solvent behavior more representative of a liquid phase—at temperatures above what could have been attained if only a liquid had been used. Also, because of the high density of the supercritical solvent, process volumes are reduced (but the high pressure increases equipment costs) and transport properties are intermediate in value between those of a gas and a liquid; i.e., diffusion coefficients are much higher than for typical liquids.

Table I. References with Solubility of Solids in Supercritical Fluids

solid	solvent	T, K	P, bar	ref
hexachloroethane	ethylene	289.5–296.5	1–170	*22*
naphthalene	ethylene	289.5–296.5	1–170	*22*
hexachloroethane and naphthalene	ethylene	289.5–296.5	1–170	*22*
quartz	water	653–698	300–500	*23*
quartz	water	423–873	1–1000	*5*
naphthalene	ethylene	285–318	50–300	*20*
naphthalene	carbon dioxide	308–328	60–330	*20*
naphthalene	ethylene	285–308	40–100	*3*
phenanthrene	ethylene	313	138–551	*4*
phenanthrene	ethane	313	138–551	*4*
phenanthrene	carbon dioxide	313	138–551	*4*
phenanthrene	methane	313	138–551	*4*
diphenylamine	carbon dioxide	305–310	50–225	*21*

In view of the interest expressed in this technology, it is surprising that so few data exist to illustrate quantitatively the solvent effect. In Table I, we summarize those references known to us that provide equilibrium solubility data. Not shown in this table are a number of other references which relate only

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