

Figure 1. B as a function of the number of carbon atoms.

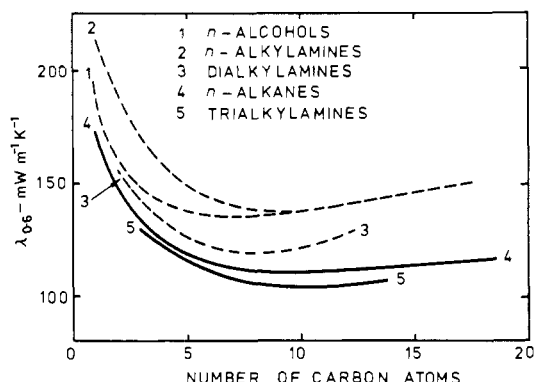


Figure 2. $\lambda_{0.6}$ as a function of the number of carbon atoms.

mental uncertainty. Tables I and II give the percentage deviation of eq 2 from the new experimental data presented in this paper.

The trialkylamines are not represented by eq 2 since they are tertiary amines and as such are polar but nonassociating. This means that they should be represented by eq 1a. Figures 1 and 2 show how the terms B and $\lambda_{0.6}$ compare with those from other

series of nonassociating liquids and Table III gives the individual percentage deviation of each measurement from that predicted by eq 1a.

Detailed tabulations using eq 1a and 2 have been prepared by the authors under the sponsorship of ESDU and may be found in ref 4 and 5 for 30 alcohols, 20 primary alkylamines, 5 secondary alkylamines, and 5 tertiary alkylamines. The necessary critical temperature data were taken from ref 6 and 7.

Conclusion

Experimental thermal conductivity data are presented for series of alcohols and primary and secondary amines. All of these fluids associate by the formation of hydrogen bonds. Experimental values are also presented for a series of tertiary amines which, while polar, do not form hydrogen bonds and so are classed as nonassociating.

An equation developed previously (1) to correlate the thermal conductivity of nonassociating liquids has been modified, and an alternative form is presented which correlates the thermal conductivity data for these associated liquids.

Acknowledgment

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Viscosity and Density of Aqueous Na_2CO_3 and K_2CO_3 Solutions in the Temperature Range 20-90 °C and the Pressure Range 0-30 MPa

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The paper presents new experimental measurements of the viscosity of aqueous Na_2CO_3 and K_2CO_3 solutions in the temperature range 20-90 °C and the pressure range 0-30 MPa. The measurements cover the concentration range 0-1.7 m for the first salt and 0-2.5 m for the second and are believed to be accurate to $\pm 1\%$. The effect of pressure on the density of these solutions has also been measured. The paper contains correlations of the density and viscosity of Na_2CO_3 and K_2CO_3 in terms of temperature, pressure, and concentration. The correlations reproduce the experimental results to within their quoted accuracy.

1. Introduction

In a number of earlier publications (2, 3, 6) we reported the viscosity of the aqueous solutions of NaCl and KCl and their mixtures over the temperature range extending to 150 °C, pressure range extending to 30 MPa, and composition range extending from zero to near saturation. These measurements are believed to be the only ones covering ranges of pressure, temperature, and concentration which correspond to those prevalent in liquid-dominated geothermal reservoirs. The present paper is the sixth in a series (2, 3, 6-8) that is intended to provide data on the viscosity of the most important constituents of geothermal fluids and, together with the other papers in this

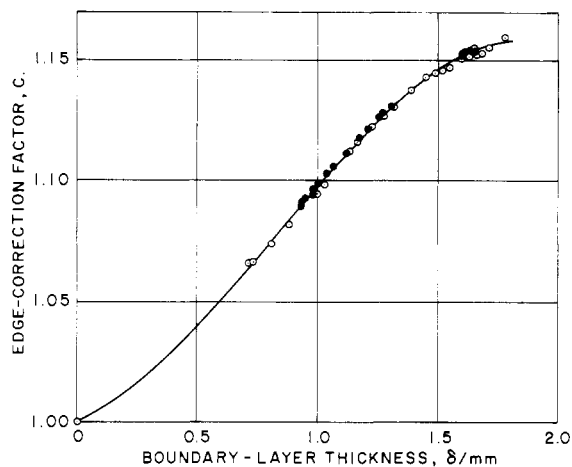


Figure 1. Calibration curve and checkpoints for the viscometer: \circ , original calibration points; \bullet , check points.

series, to complement the continuing effort of the United States Geological Survey toward the establishment of a data base for the equilibrium and transport properties of a selected number of aqueous salt solutions.

In this paper we present measurements of the viscosity of aqueous solutions of Na_2CO_3 and K_2CO_3 in the temperature range 20–90 °C and the pressure range 0–30 MPa. The concentration range extends from 0 to 1.7 *m* for the first solution and from 0 to 2.5 *m* for the second. The present measurements constitute the first effort to cover a wide range of pressures, temperatures, and concentrations simultaneously. It is worth mentioning that, with the exception of a few isolated measurements at low temperature and atmospheric pressure, no data could be located on the viscosity of Na_2CO_3 and K_2CO_3 solutions.

2. Experimental Technique

The measurements were carried out in an oscillating-disk viscometer which was described in detail in our previous publications (5, 8, 10). The characteristics of the oscillating system are essentially the same as those given in ref 2. The edge-correction factor (9, 12) for the viscometer was obtained by calibrating the viscometer using distilled water as a reference fluid. Figure 1 depicts the results of the calibration. The solid line represents a least-squares fit of the experimental data

$$C = 1.000 + 0.04085\delta + 0.09365\delta^2 - 0.03767\delta^3 \quad (1)$$

in which δ is the boundary-layer thickness (8, 11) defined by

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

Here ν is the kinematic viscosity of the fluid and T_0 is the period of oscillation under vacuum. The solid points are check-measurements which were taken during the course of this investigation after each cleaning and realignment. Neither the original calibration points nor the checkpoints deviate from the line represented by eq 1 by more than 0.2%.

The solutions were prepared by mixing reagent quality salts with triple-distilled, deaerated water. The hygroscopic nature of Na_2CO_3 and K_2CO_3 precluded the determination of the concentration by the gravimetric method as we did with NaCl and KCl. Instead, the concentration of the solutions was determined by titration. It is believed that the values of the concentration thus determined are accurate to within 0.001 *m*, which is adequate for our purposes.

3. Density

Because of the strong link that exists between the viscosity and density in the working equations of the oscillating-disk vis-

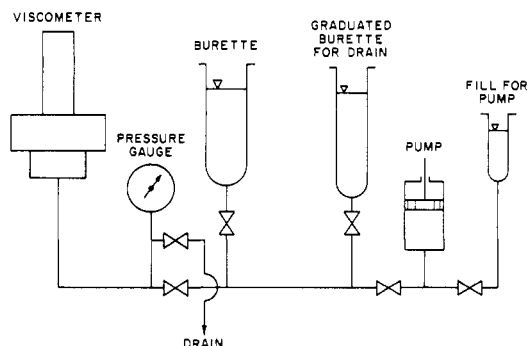


Figure 2. The pressurizing system for the viscometer.

cometer (9, 12), it is imperative to have reasonably accurate density data over the desired pressure–temperature–concentration range. Unfortunately, accurate values of the density of Na_2CO_3 and K_2CO_3 solutions are not available over the pressure–temperature–concentration range of interest in the present work (13). More specifically, an extensive search of available literature has failed to uncover any data on the density of these solutions at high pressure, even though limited data on the low-pressure density could be found in the extensive compilation of Brown et al. (7). Faced with this situation we developed a technique by which the viscometer vessel was used for the determination of the relative effect of pressure on the density of a given solution. An account of the method employed for determining this effect is given later.

The experimental setup is shown in Figure 2. At a given temperature T the viscometer is pressurized from ambient pressure P_0 to a higher pressure P (~ 30 MPa). At thermal equilibrium, the pressure is reduced slowly to P_0 while collecting the overflow fluid in the graduated buret which is maintained at the ambient conditions P_0 and T_0 . The mass of the liquid released is given by

$$\Delta m = \rho(P_0, T_0)(\Delta V) = V(T)[\rho(P, T) - \rho(P_0, T)] \quad (3)$$

Here ΔV is the volume of liquid collected in the graduated buret and $V(T)$ is the volume of the viscometer at temperature T . If the same experiment were carried out with pure water, w , we would obtain

$$\Delta m/\Delta m_w = \rho(P_0, T_0)(\Delta V)/\rho_w(P_0, T_0)(\Delta V_w) = [\rho(P, T) - \rho(P_0, T)]/[\rho_w(P, T) - \rho_w(P_0, T)] \quad (4)$$

Solving for $\rho(P, T)/\rho(P_0, T)$, we get

$$\rho(P, T)/\rho(P_0, T) = 1 + \phi_w(P, T)\rho(P_0, T_0)(\Delta V)/\rho(P_0, T)(\Delta V_w) \quad (5)$$

in which

$$\phi_w(P, T) = [\rho_w(P, T) - \rho_w(P_0, T)]/\rho_w(P_0, T) \quad (6)$$

is an accurately known function for pure water; it can be determined, for example, from the accurate correlation of Kell (4). If measurements on pure water were performed at a different temperature T' , then

$$\rho(P, T)/\rho(P_0, T) = 1 + \rho(P_0, T_0)\phi_w(P, T')(\Delta V)\eta/\rho(P_0, T)(\Delta V_w') \quad (7)$$

in which

$$\eta = [1 + \alpha(T' - T_0)]/[1 + \alpha(T - T_0)] \quad (8)$$

is a factor to account for the volumetric thermal expansion of the viscometer vessel whose apparent volumetric thermal expansion coefficient is denoted by α . It can be shown that for stainless steel the factor η accounts for only 0.03% of the density change in the temperature range 20–100 °C and can,

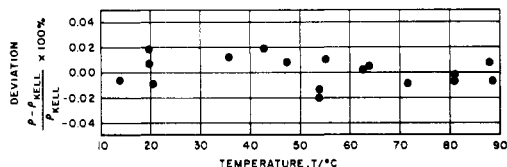


Figure 3. Comparison between the measured effect of pressure on the density of water and that of Kell.

Table I. The Coefficients d_{ij} in Equation 11 for Na_2CO_3 Solutions

i	j			
	0	1	2	3
0	0.99270	0.38432×10^{-3}	-0.13199×10^{-4}	0.53862×10^{-7}
1	0.03280	-0.11218×10^{-2}	0.20085×10^{-4}	-0.96466×10^{-7}
2	0.07910	0.45883×10^{-3}	-0.10235×10^{-4}	0.52868×10^{-7}

Table II. The Coefficients a_{ij} in Equation 14 for Na_2CO_3 Solutions

i	j		
	0	1	2
0	0.4259	0.07290	-0.06281
1	-0.1266×10^{-3}	-0.3767×10^{-2}	0.1809×10^{-2}
2	-0.2500×10^{-5}	0.4225×10^{-4}	-0.2017×10^{-4}

therefore, be neglected in the present application. Finally, eq 7 can be modified to reflect the relationship between the density of an arbitrary fluid at high pressure, given its density at low pressure (but the same temperature T), and the density of water at ambient temperature T_0 and two pressures P' and P_0 , viz.

$$\rho(P, T) = \rho(P_0, T) + \rho(P_0, T_0) \phi_w(P', T_0) (\Delta V) / (\Delta V_w) \quad (9)$$

Figure 3 contains a comparison between the measured effect of pressure on the density of water and that calculated from the correlation of Kell (4) over the temperature range 20–90 °C. It can be seen that our experimental procedure results in an error of no more than 0.02%.

The pressure effect was determined in the manner described above and applied to the low-pressure data compiled by Brown et al. (1) as a linear factor:

$$\rho(P, T, c) = \rho^0(T, c) [1 + \alpha(T, c) P / \text{MPa}] \quad (10)$$

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

$$\rho^0(T, c) = \sum_{i=0}^2 \sum_{j=0}^3 d_{ij} (c/m)^{j^2} (T/^\circ\text{C})^i \quad (11)$$

for Na_2CO_3 solutions, and

$$\rho^0(T, c) = \frac{10^3 \rho_w(T) + M_2 c \rho_w(T)}{10^3 + \phi_v c \rho_w(T)} \quad (12)$$

for K_2CO_3 solutions. Here $m = 1$ mol/kg, M_2 is the formula weight of K_2CO_3 , and

$$\phi_v(T, c) = \sum_{i=0}^2 \sum_{j=0}^2 d_{ij} (c/m)^{j^2} (T/^\circ\text{C})^i \quad (13)$$

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

$$\alpha = \sum_{i=0}^2 \sum_{j=0}^2 a_{ij} (c/m)^{j^2} (T/^\circ\text{C})^i \quad (14)$$

Tables I and II contain the coefficients d_{ij} and a_{ij} for Na_2CO_3 and Tables III and IV the coefficients for K_2CO_3 , respectively. The correlations represented by eq 10–14 describe the density

Table III. The Coefficients d_{ij} in Equation 13 for K_2CO_3 Solutions

i	j		
	0	1	2
0	-0.81670	0.43265	-0.33343×10^{-2}
1	21.889	-0.26285	0.18678×10^{-2}
2	-2.4998	0.46176	-0.30161×10^{-3}

Table IV. The Coefficients a_{ij} in Equation 14 for K_2CO_3 Solutions

i	j		
	0	1	2
0	0.4847	-0.07534	0.2366×10^{-2}
1	-0.1857×10^{-2}	-0.1634×10^{-2}	0.1009×10^{-2}
2	0.1371×10^{-4}	0.2133×10^{-4}	-0.1168×10^{-4}

Table V. Viscosity of Na_2CO_3 Solution No. 1 ($c = 0.280$ m)

P , MPa	μ , $\mu\text{Pa s}$	P , MPa	μ , $\mu\text{Pa s}$
at 20.5 °C		at 35.5 °C	
0.1	1145	0.1	825
7.2	1143	7.3	824
14.0	1142	14.2	825
21.2	1143	20.9	826
31.2	1141	31.3	828
0.1	1145	0.1	825
at 53.5 °C		at 69.5 °C	
0.7	597	1.0	470
7.1	601	7.7	472
14.1	601	13.9	474
21.0	606	20.6	477
31.3	606	31.2	478
0.9	597	1.0	469
at 87.0 °C			
0.6	376		
7.3	376		
13.9	379		
20.7	381		
34.1	384		
1.1	376		

of the solutions to within the uncertainty of the compiled data of Brown et al. (1), that is, $\pm 0.1\%$.

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 11–13 to within the estimated uncertainty of the latter. Furthermore, the density of a sample taken from the viscometer after an experimental run (about 2 weeks) differed negligibly from the density of a fresh sample. This is indicative of the absence of measurable changes in the composition of the solution due to interactions with the internal surfaces of the viscometer.

4. Viscosity

The experimental values of the viscosity of Na_2CO_3 and K_2CO_3 solutions are presented in Tables V–XIII. Each entry in these tables is an average of at least two independent measurements taken at the specified P , T , c point. Checkpoints taken during decompression and cooling are included in the tables. The reported values have been adjusted to nominal temperatures by means of a small linear correction based on an Arrhenius-type interpolation of our experimental results, i.e.

$$\mu \approx A \exp(B/T) \quad (15)$$

Table VI. Viscosity of Na₂CO₃ Solution No. 2 (*c* = 0.565 *m*)

<i>P</i> , MPa	μ , $\mu\text{Pa s}$	<i>P</i> , MPa	μ , $\mu\text{Pa s}$
at 28.0 °C		at 33.5 °C	
0.1	1115	0.1	987
7.5	1117	7.2	990
14.4	1118	14.1	994
21.0	1119	21.0	996
31.1	1123	31.3	1000
0.1	1117	0.3	992
at 38.0 °C		at 45.0 °C	
0.7	903	0.3	799
7.2	904	7.4	802
14.2	906	14.4	805
20.9	907	20.9	806
31.3	912	31.1	810
0.4	904	1.4	798
at 51.5 °C		at 71.0 °C	
0.8	709	0.6	528
7.1	711	7.2	529
14.0	714	14.0	532
20.9	716	20.8	532
30.9	718	31.2	536
0.7	709	1.7	526
at 90 °C			
0.8	413		
7.2	414		
13.9	416		
20.6	418		
31.0	422		
2.0	414		

Table VII. Viscosity of Na₂CO₃ Solution No. 3 (*c* = 0.946 *m*)

<i>P</i> , MPa	μ , $\mu\text{Pa s}$	<i>P</i> , MPa	μ , $\mu\text{Pa s}$
at 33.5 °C		at 38 °C	
0.6	1213	0.1	1100
7.6	1214	7.2	1103
14.2	1215	14.2	1106
21.1	1218	21.1	1107
31.3	1221	31.2	1103
0.7	1209	0.3	1099
at 45.0 °C		at 53.0 °C	
0.7	964	0.6	834
7.4	967	7.4	838
14.1	968	14.2	840
21.1	971	20.8	846
31.2	975	31.2	849
1.3	964	1.5	835
at 70.0 °C		at 89.5 °C	
0.7	638	1.7	492
7.2	641	7.2	495
14.0	643	14.0	498
21.1	646	20.7	501
31.1	650	31.0	504
1.7	637	2.0	494

The estimated uncertainty of the reported results is $\pm 1\%$. Part of this uncertainty is attributed to the inferior quality of the available density data for these solutions relative to those of water and sodium chloride solutions.

5. Correlation of Viscosity

Due to the weak dependence of the viscosity of liquids on pressure, it is sufficient to express the pressure dependence by a linear factor. Thus we write

$$\mu(P, T, c) = \mu^0(T, c)[1 + \beta(T, c)P/\text{MPa}] \quad (16)$$

The hypothetical zero-pressure viscosity, μ^0 , was correlated in

Table VIII. Viscosity of Na₂CO₃ Solution No. 4 (*c* = 1.306 *m*)

<i>P</i> , MPa	μ , $\mu\text{Pa s}$	<i>P</i> , MPa	μ , $\mu\text{Pa s}$
at 38.0 °C		at 46.0 °C	
0.1	1331	0.5	1133
7.3	1334	7.2	1135
14.2	1339	14.2	1141
21.2	1343	20.7	1142
31.2	1349	31.2	1151
0.1	1332	0.9	1132
at 55.0 °C		at 70.5 °C	
0.9	959	1.3	748
7.3	960	7.2	753
14.1	963	14.2	756
21.0	968	20.9	760
31.3	976	31.0	762
1.1	959	1.3	749
at 89.0 °C			
0.7	580		
7.3	583		
14.2	588		
30.8	596		
1.9	578		

Table IX. Viscosity of Na₂CO₃ Solution No. 5 (*c* = 1.672 *m*)

<i>P</i> , MPa	μ , $\mu\text{Pa s}$	<i>P</i> , MPa	μ , $\mu\text{Pa s}$
at 46.0 °C		at 52.0 °C	
1.7	1379	1.0	1225
7.4	1385	7.4	1229
14.4	1389	14.3	1237
21.2	1399	21.0	1239
31.3	1406	31.1	1250
1.3	1379	1.8	1226
at 60.0 °C		at 73.0 °C	
1.3	1052	1.3	859
7.4	1058	7.4	863
14.3	1062	14.2	866
21.0	1070	21.2	869
30.9	1079	31.0	877
		1.8	860
at 89.5 °C			
1.2	682		
14.1	689		
21.0	693		
31.1	698		
0.7	683		

terms of temperature and concentration by means of an expression of the form

$$\mu^0(T, c) = \mu^0(T, 0)[1 + \sum_{i=0}^2 \sum_{j=0}^2 f_{ij}(T/^\circ\text{C})(c/m)^{j+1}] \quad (17)$$

in which $\mu^0(T, 0)$ is the zero-pressure viscosity of water at *T*. The values of the viscosity of water can be obtained from the accurate correlation of Kestin et al. (11), which is based on a critical evaluation of the viscosity of pure water in the temperature range -8 to $+150$ °C. The coefficients f_{ij} which appear in eq 17 are given in Table XIV for Na₂CO₃ and Table XV for K₂CO₃. Equation 17 reproduces the experimental values to within a standard deviation of 0.3% for Na₂CO₃ and 0.2% for K₂CO₃ with random dispersion as shown by the solid symbols in Figures 4 and 5 for Na₂CO₃ and K₂CO₃, respectively.

The pressure coefficients $\beta(T, c)$ have been correlated by means of the expression

$$\beta(T, c) = \beta_w(T) + 10^{-3} \sum_{i=0}^3 \sum_{j=0}^2 g_{ij}(T/^\circ\text{C})(c/m)^{j+1} \quad (18)$$

Table X. Viscosity of K₂CO₃ Solution No. 1 (c = 0.495 m)

P, MPa	μ, μPa s	P, MPa	μ, μPa s
at 19.0 °C			
0.4	1189	1.0	831
7.1	1186	7.3	831
14.2	1185	14.1	833
21.0	1185	21.1	837
31.2	1186	31.2	838
0.4	1189	1.1	831
at 36.0 °C			
1.1	663	1.4	492
7.3	664	7.2	495
14.3	666	13.7	496
21.0	668	21.0	499
31.3	670	31.0	501
1.1	662	1.6	493
at 49.0 °C			
0.7	384		
7.0	386		
13.8	388		
20.7	390		
30.7	393		
2.2	384		
at 69.0 °C			
at 89.0 °C			

Table XI. Viscosity of K₂CO₃ Solution No. 2 (c = 0.982 m)

P, MPa	μ, μPa s	P, MPa	μ, μPa s
at 19.5 °C			
0.2	1359	0.7	1086
7.1	1362	7.1	1089
14.2	1366	14.1	1089
21.1	1365	21.3	1093
31.1	1368	31.5	1096
0.3	1364	0.2	1089
at 30.0 °C			
at 45.5 °C			
0.7	821	0.8	656
7.3	822	7.3	659
14.1	825	14.1	659
20.9	828	20.9	662
31.3	830	31.0	666
0.3	820	0.9	657
at 60.0 °C			
at 75.0 °C			
0.4	539	0.9	455
7.2	540	7.2	457
14.0	542	13.9	459
20.8	544	20.9	462
30.9	549	31.1	466
0.9	538	0.4	455
at 89.0 °C			

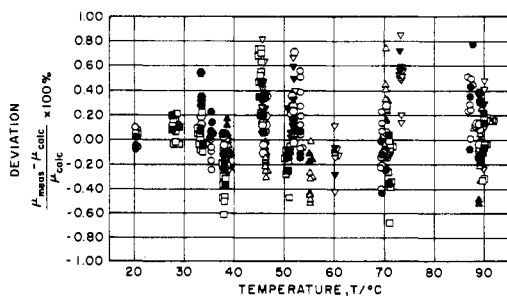


Figure 4. Comparison between our viscosity measurements and correlations for Na₂CO₃ solutions: O, solution no. 1, m = 0.280 (● at P = 0); □, solution no. 2, m = 0.565 (■ at P = 0); ○, solution no. 3, m = 0.946 (● at P = 0); △, solution no. 4, m = 1.306 (▲ at P = 0); ▽, solution no. 5, m = 1.672 (▼ at P = 0).

Table XII. Viscosity of K₂CO₃ Solution No. 3 (c = 1.831 m)

P, MPa	μ, μPa s	P, MPa	μ, μPa s
at 30.0 °C			
0.7	1419	0.8	1068
7.2	1422	7.2	1071
14.3	1425	14.1	1074
21.2	1430	21.0	1078
31.4	1436	31.3	1082
0.6	1421	0.7	1067
at 45.5 °C			
at 60.0 °C			
1.4	858	1.3	705
7.2	857	7.3	707
14.0	861	14.2	712
21.2	864	21.1	714
31.3	867	31.0	718
1.3	856	1.2	705
at 74.5 °C			
at 89.0 °C			
1.8	598		
7.2	598		
14.0	604		
20.9	605		
30.9	610		
1.3	597		

Table XIII. Viscosity of K₂CO₃ Solution No. 4 (c = 2.448 m)

P, MPa	μ, μPa s	P, MPa	μ, μPa s
at 35.5 °C			
0.5	1540	0.6	1285
7.3	1545	7.4	1286
14.2	1549	14.1	1291
20.9	1555	20.6	1294
31.2	1561	31.0	1302
0.4	1540	0.8	1285
at 45.5 °C			
at 60.0 °C			
0.7	1025	1.3	835
7.3	1028	7.2	842
14.1	1032	14.1	844
21.2	1035	21.0	849
31.3	1043	31.0	857
0.6	1025	1.1	837
at 75.0 °C			
at 89.0 °C			
1.6	715		
7.4	718		
14.1	720		
20.9	721		
31.0	722		
1.8	713		

Table XIV. The Coefficients f_{ij} in Equation 17 for Na₂CO₃ Solutions

i	j		
	0	1	2
0	0.5165	0.07321	0.1575
1	0.1013 × 10 ⁻²	-0.5218 × 10 ⁻³	-0.2793 × 10 ⁻²
2	-0.1024 × 10 ⁻⁴	-0.1025 × 10 ⁻⁵	0.1736 × 10 ⁻⁴

Table XV. The Coefficients f_{ij} in Equation 17 for K₂CO₃ Solutions

i	j		
	0	1	2
0	0.2124	0.08072	0.01046
1	0.4697 × 10 ⁻²	-0.2120 × 10 ⁻²	0.6296 × 10 ⁻⁴
2	-0.3065 × 10 ⁻⁴	0.1962 × 10 ⁻⁴	-0.1955 × 10 ⁻⁵

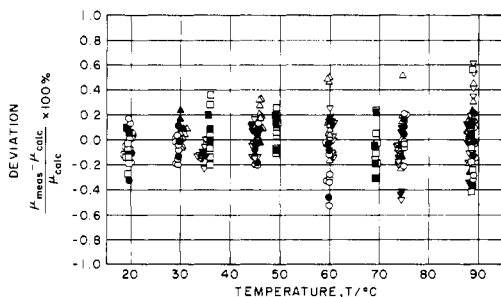


Figure 5. Comparison between our viscosity measurements and correlations for K_2CO_3 solutions: \square , solution no. 1, $m = 0.495$ (\blacksquare at $P = 0$); \circ , solution no. 2, $m = 0.982$ (\bullet at $P = 0$); \triangle , solution no. 3, $m = 1.831$ (\blacktriangle at $P = 0$); ∇ , solution no. 4, $m = 2.448$ (\blacktriangledown at $P = 0$).

Table XVI. The Coefficients g_{ij} in Equation 18 for Na_2CO_3 Solutions

i	j		
	0	1	2
0	4.026	-3.904	-0.1640
1	-0.2343	0.3310	-0.05880
2	0.4760×10^{-2}	-0.3922×10^{-2}	0.2177×10^{-2}
3	-0.3083×10^{-4}	0.5476×10^{-4}	-0.1756×10^{-4}

Table XVII. The Coefficients g_{ij} in Equation 18 for K_2CO_3 Solutions

i	j		
	0	1	2
0	2.265	-2.481	1.011
1	-0.08117	0.1227	-0.05550
2	0.1019×10^{-2}	-0.2095×10^{-2}	0.1006×10^{-2}
3	-0.4320×10^{-5}	0.1156×10^{-4}	-0.5786×10^{-5}

in which $\beta_w(T)$ is the pressure coefficient for pure water given in our earlier work (β). The coefficients g_{ij} are listed in Table XVI for Na_2CO_3 and in Table XVII for K_2CO_3 .

Figures 4 and 5 depict the deviations of the experimental results from the correlations for Na_2CO_3 and K_2CO_3 , respectively.

The correlations represent the experimental results with a maximum deviation of 0.9% for Na_2CO_3 and 0.6% for K_2CO_3 . The standard deviations are 0.3 and 0.2%, respectively, which are well within the estimated accuracy of the experimental data.

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Melting Curve and Pressure-Volume-Temperature Data of Liquid Dimethyl Sulfoxide up to 150 MPa

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The melting curve as well as PVT data of stable and superpressed liquid dimethyl sulfoxide were measured from 293 to 322 K up to 150 MPa. This study clearly indicates that some previous high-pressure chemistry work on dimethyl sulfoxide solutions must be carefully reconsidered.

Introduction

Dimethyl sulfoxide (Me_2SO) is known to be one of the most polar among the aprotic solvents and to have remarkable

chemical reactivity and interesting pharmaceutical properties.^{1,2}

Thermodynamic properties at atmospheric pressure were carefully determined,³ but, to our knowledge, no high-pressure thermodynamic data have been published. However, the privileged position occupied by Me_2SO among aprotic organic solvents favored its use in high-pressure chemistry. In particular, kinetic studies were performed by Brower, Ernst, and Chen⁴ in order to determine activation volumes for several alkylation reactions of ambident anions in Me_2SO . They carried out measurements in different systems at five temperatures (20, 27, 30, 36, and 47 °C) and at two pressures (1 and 1360 atm) for each temperature.

Their general conclusion was that pressure had no effect on the proportions of isomeric products. But they supposed implicitly that the chemical medium remained liquid and homogeneous

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