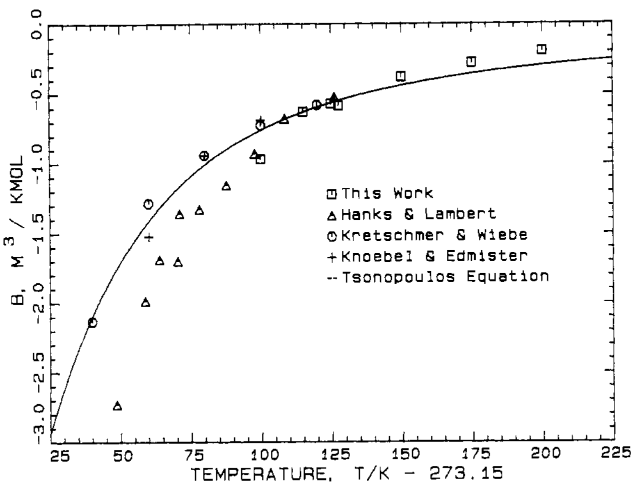

Figure 1. Second virial coefficients of ethanol. Curve is from the Tsonopoulos correlation, eq 2 and 3.

lation. His value of b for ethanol is 0.0572, and the resulting line is also shown in Figure 1. We reoptimized the constant b by using the five points of Kretschmer and Wiebe (*5*), the three points of Knoebel and Edmister (*6*), and our seven points. We found that with the latest physical constants (*1*), the value of b for ethanol should be 0.0532; this shift is not deemed significant in view of the scatter in Figure 1 and in view of the small data base.

Glossary

a	parameter in eq 3, 0.0878 for ethanol (*14*)
b	parameter in eq 3, 0.0572 for ethanol (*14*)
B	second virial coefficient, m^3 $kmol^{-1}$
$f^{(0)}$, $f^{(1)}$, $f^{(2)}$	functions of reduced temperature in eq 2 (*14*)
P	pressure, kPa
P_c	critical pressure, kPa
R	gas constant, 8.31441 kPa m^3 $kmol^{-1}$ K^{-1}
T	temperature, K
T_c	critical temperature, K
T_r	reduced temperature, T/T_c
V	volume, m^3 $kmol^{-1}$
Z	compressibility factor (PV/RT)

Registry No. Ethanol, 64-17-5; toluene, 108-88-3; tetramethylsilane, 75-76-3.

Literature Cited

(1) Ambrose, D. "Vapor-Liquid Critical Properties"; NPL Report Chem 107, NPL: Teddington, Middlesex TW11 OLW, UK, Feb 1980.
(2) Myers, J. E.; Hershey, H. C.; Kay, W. B. *J. Chem. Thermodyn.* **1979**, *11*, 1019.
(3) Dymond, J. H.; Smith, E. B. "The Virial Coefficients of Pure Gases and Mixtures"; Clarendon Press: Oxford, 1980.
(4) Hanks, P. A.; Lambert, J. D., unpublished results cited in ref *3*, 1951.
(5) Kretschmer, C. B.; Wiebe, R. *J. Am. Chem. Soc.* **1954**, *76*, 2579.
(6) Knoebel, D. H.; Edmister, W. C. *J. Chem. Eng. Data* **1968**, *13*, 312.
(7) Kay, W. B.; Rambosek, G. M. *Ind. Eng. Chem.* **1953**, *45*, 221.
(8) Chun, S. W.; Kay, W. B.; Teja, A. S. *J. Chem. Eng. Data* **1981**, *26*, 300.
(9) Barber, J. R.; Kay, W. B.; Teja, A. S. *AIChE J.* **1982**, *28*, 134, 138, 142.
(10) Lindley, D. D. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1983.
(11) Marcos, D. H.; Lindley, D. D.; Wilson, K. S.; Kay, W. B.; Hershey, H. C. *J. Chem. Thermodyn.* **1983**, *15*, 1003.
(12) Swietoslawski, W. "Ebulliometric Measurements"; Reinhold: New York, 1945.
(13) Skaates, J. M.; Kay, W. B. *Chem. Eng. Sci.* **1964**, *19*, 431.
(14) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(15) Pitzer, K. S.; Curl, R. F.; Jr. *J. Am. Chem. Soc.* **1957**, *79*, 2369.

Received for review June 3, 1983. Accepted February 10, 1984.

Viscosity of Molten Sodium Salt Hydrates

S. K. Sharma,* C. K. Jotshi, and Amrao Singh

Department of Chemical Engineering and Technology, Panjab University, Chandigarh—160 014, India

Viscosity of molten sodium salt hydrates, $NaOH \cdot H_2O$, $Na(CH_3COO) \cdot 3H_2O$, $Na_2S_2O_3 \cdot 5H_2O$, $Na_2CO_3 \cdot 10H_2O$, and $Na_2HPO_4 \cdot 12H_2O$, suitable for energy storage applications has been determined with a modified Ubbelhode viscometer. The temperature dependence shows an Arrhenius behavior which can be represented by an equation $\eta = A \exp(E_v/RT)$, above the melting points of the salt hydrates studied. The values of activation energy (E_v) of viscous flow are reported.

Hydrated salts (*1*–*3*) have been extensively investigated for thermal energy storage applications due to their high energy storage densities and low cost. Some of the salts recommended for this purpose show great supercooling as well as glass-forming tendencies which are undesirable. In the case of tabular crystals, such as those of sodium acetate trihydrate, supercooling is considerable. Viscosity is an important parameter (*4*), as it influences the crystallization of such salts. Both the viscosity data as well as a generalized empirical corresponding states relationship which could be used to calculate the viscosities of a given class of melts outside the existing experimental range are lacking in the literature. The present investigation has been designed to determine the viscosity of the most commonly recommended salt hydrates suitable for energy storage applications, so that the utility of each can be properly assessed.

Theoretical and Experimental Section

A modified Ubbelhode viscometer (*5*) has been used in the present investigation. The salient feature of this design is that the flow of melt through the capillary is caused by its hydrostatic pressure only.

Poiseuille's equation applicable to the capillary flow is

$$\nu = \eta/\rho = at - b/t \qquad (1)$$

Values of the constants a and b have been calculated by using standard values of the density and the viscosity of carbon tetrachloride and benzene, available in the literature (*6*). With the least-squares method of curve fitting, new constants A and B for the instrument are calculated. These constants have been used to define a new correlation between viscosity and time, which can be represented as follows:

$$\eta = A + Bt \qquad (2)$$

For the viscometer used, the values of constants A and B are −0.363 and 0.0075, respectively. The accuracy of this

Table I. Viscosity (η) of Molten Hydrated Sodium Salts

temp, °C	η, cP	temp, °C	η, cP
	$NaOH\cdot H_2O$ (mp 64 °C)		
64.2	10.542	75.0	7.212
67.0	9.657	80.0	6.057
70.0	8.541		
	$Na(CH_3COO)\cdot 3H_2O$ (mp 58 °C)		
58.0	5.813	70.2	4.111
60.5	5.315	73.5	3.608
65.8	4.535	75.0	3.455
	$Na_2S_2O_3\cdot 5H_2O$ (mp 48 °C)		
48.5	9.368	60.0	6.269
50.0	8.877	65.0	5.377
55.0	7.260		
	$Na_2CO_3\cdot 10H_2O$ (mp 33.9 °C)		
35.0	7.925	45.0	5.371
40.0	6.466	50.0	4.429
	$Na_2HPO_4\cdot 12H_2O$ (mp 36.1 °C)		
37.0	4.478	45.0	3.927
40.0	4.410	50.0	3.300

Table II. Derived Values of E_v

salt hydrate	E_v, kJ/mol
$NaOH\cdot H_2O$	34.73
$NaCH_3COO\cdot 3H_2O$	28.98
$Na_2S_2O_3\cdot 5H_2O$	30.65
$Na_2CO_3\cdot 10H_2O$	32.28
$Na_2HPO_4\cdot 12H_2O$	23.43

equation has been checked by determining the viscosity of phenol. Agreement with the literature values is within ±1.5%.

Salt hydrates selected for the present studies were $NaOH\cdot H_2O$, $Na(CH_3COO)\cdot 3H_2O$, $Na_2S_2O_3\cdot 5H_2O$, $Na_2CO_3\cdot 10H_2O$, and $Na_2HPO_4\cdot 12H_2O$. All these salt hydrates were recrystallized from BDH grade samples by using double-distilled water. Melting points of the crystallized materials were evaluated from heating and cooling curves. These melting points were found to be in good agreement with those reported in the literature (*7*). After the molten salt hydrate was transferred to the viscometer, it was subjected to repeated solidification and melting cycles so as to eliminate any trapped air. The viscometer was equilibrated for 2-3 h in the thermostat before starting the experiment.

Results and Discussion

Viscosities of the selected salt hydrates at various temperatures above their melting points are reported in Table I. Figure 1 shows the plot of log η vs. reciprocal of absolute temperature. The linear nature of this plot confirms the Arrhenius behavior of these salt hydrates. The temperature interval is from the melting point to 20 °C above the melting point, which is the range generally recommended for charging the storage units. Thus, it can be inferred that the viscous flow of these melts is an activated process in which energy distribution can be represented by the equation

$$\eta = A \exp(E_v/RT) \qquad (3)$$

Energies of activation of viscous flow (E_v) of these salt hydrates are given in Table II. Contrary to this, hydrated salts of calcium nitrate, nickel nitrate, and zinc nitrate show non-Arrhenius behavior (*8*). This is most probably due to a difference in intermolecular forces between these two categories of salt melts. Results further show that the energy of activation varies with the number of moles of water of crystallization. It may be concluded that intermolecular hydrogen bonds, due to water of crystallization, play an important role in the viscous flow of these melts.

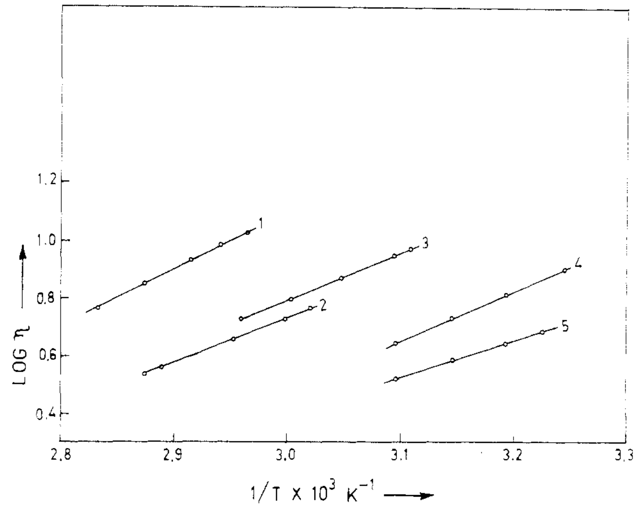

Figure 1. Plot of log (viscosity) vs. T^{-1} for (1) $NaOH\cdot H_2O$, (2) $NaCH_3COO\cdot 3H_2O$, (3) $Na_2S_2O_3\cdot 5H_2O$, (4) $Na_2CO_3\cdot 10H_2O$, and (5) $Na_2HPO_4\cdot 12H_2O$.

From the results of this study the temperature dependence of the viscosity of sodium salt hydrates such as $NaOH\cdot H_2O$, $CH_3COONa\cdot 3H_2O$, $Na_2S_2O_3\cdot 5H_2O$, $Na_2CO_3\cdot 10H_2O$, and $Na_2HPO_4\cdot 12H_2O$ may be expressed by the following exponential equations: $\eta = (3.715 \times 10^{-5}) \exp(34732/RT)$ cP, $\eta = (1.549 \times 10^{-4}) \exp(28988/RT)$ cP, $\eta = (9.77 \times 10^{-5}) \exp(30654/RT)$ cP, $\eta = (2.63 \times 10^{-5}) \exp(32282/RT)$ cP, and $\eta = (5.37 \times 10^{-4}) \exp(23436/RT)$ cP, respectively. The deviation from the experimental values is ±0.14%.

Glossary

a, *b*	constants, eq 1
A, *B*	constants, eq 2
t	time of flow, s
T	temperature, K
E_v	activation energy of viscous flow, kJ/mol

Greek Letters

η	viscosity, cP
ν	kinematic viscosity, cm^2/s

Registry No. $NaOH\cdot H_2O$, 12200-64-5; $Na(CH_3COO)\cdot 3H_2O$, 6131-90-4; $Na_2S_2O_3\cdot 5H_2O$, 10102-17-7; $Na_2CO_3\cdot 10H_2O$, 6132-02-1; $Na_2HPO_4\cdot 12H_2O$, 10039-32-4.

Literature Cited

(1) Sharma, S. K.; Jotshi, C. K. "Proceedings of the First National Workshop on Solar Energy Storage"; Department of Chemical Engineering, Panjab University: Chandigarh, India, 1979; p 309.
(2) Lorsch, H. G.; Kauffman, K. W.; Denton, J. C. *Energy Convers*. **1975**, *15*, 1.
(3) Telkes, M. "Solar Heat Storage"; American Society of Mechanical Engineers: New York, 1964; paper 64-LA/SOL-9.
(4) Andrew, V. H. *Ind. Eng. Chem.* **1945**, *37*, 782.
(5) Mohan, Chander. M.Sc. Thesis, Panjab University, Chandigarh, India, 1983, p 30.
(6) Timmerman, J. "Physico-chemical Data of Pure Organic Compounds"; Elsevier: New York, 1950.
(7) Weast, Robert C. "Handbook of Chemistry and Physics", 50th ed.; The Chemical Rubber Publishing Co.: Cleveland, OH, 1969-70.
(8) Jain, S. K. *J. Chem. Eng. Data* **1978**, *23*, 171.

Received for review June 29, 1983. Accepted January 31, 1984. This work has been financially supported by Tata Energy Research Institute, Bombay (India).