behavior, but the quantitative agreement with the data was poorer. This suggests, however, that further developments in calculating the activity coefficients in the VSM could lead to improved quantitative results. The SSTM assumes that the only interactions between adsorbed molecules are those due to molecular size difference. Since this difference is not dependent on composition, one would not expect that the SSTM could predict azeotropic behavior. The ideality assumptions inherent in the IASM also preclude it from predicting azeotropes.

Glossary

N_a	amount adsorbed (kmol/kg)
P	adsorption equilibrium pressure (kPa)
P°	vapor pressure at the adsorption temperature (kPa)
X_i	mole fraction of component i in the adsorbed phase
Y_i	mole fraction of component i in the bulk gas phase

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Received for review April 24, 1981. Accepted January 15, 1982. Financial support from Air Products and Chemicals, Inc., is gratefully acknowledged.

Densities and Viscosities of Solutions of $Cd(NO_3)_2$ in a Solvent $(Ag,Tl)NO_3$

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Densities and viscosities of the mixed liquid melt $AgNO_3$ + $TlNO_3$ + $Cd(NO_3)_2$ have been measured in the temperature range 353–393 K. The Ag/Tl mole ratio was fixed at 1.06, and the mole fraction X_{Cd} of $Cd(NO_3)_2$ in the solution was varied between 0 and 0.1. The molar volume of the solution is a linear function of both the temperature and X_{Cd}. The viscosity of the solution follows an Arrhenius relation $\eta = A\exp(E/RT)$ in which both ln A and E were found to be linear functions of X_{Cd}: $\ln A(\text{cP}) = -13.30X_{Cd} - 5.67$; $E = 59.680X_{Cd} + 27.142$ kJ mol^{-1}.

Introduction

The viscosity of fused salts is not usually, if ever, measured with great precision, simply because of the experimental difficulties associated with high temperatures. When practical application requires the use of certain salts rather than others, the operating temperature cannot be chosen arbitrarily. This is not the case, however, when one wishes to test physicochemical models or theories (*1*, *2*); one can then choose systems allowing lower operating temperatures, with consequently greater precision. With this in mind, certain low-melting nitrate mixtures lend themselves to systematic investigation by experimental methods most often used at ordinary temperatures. An example is the mixed melt $AgNO_3$ + $TlNO_3$ + $Cd(NO_3)_2$ in certain concentration ranges (*3*), and in this article we present the results of measurements of the viscosity and the density of this system under the following conditions:

$$X_{Cd(NO_3)_2} \leq 0.1$$

$$X_{AgNO_3}/X_{TlNO_3} = 1.06$$

in the temperature range 95–130 °C.

Experimental Section

$AgNO_3$ (A.C.S., Johnson Mathey) was used as received. $TlNO_3$ (Alfa) was recrystallized 3 times in water, filtered, and dried at 120 °C in vacuo. $Cd(NO_3)_2$ was introduced into the mixture as $Cd(NO_3)_2\cdot 4H_2O$ (Fisher Certified). The fused nitrates were heated in vacuo to 200 °C, to drive off water without decomposition, and then filtered through sintered glass. The mixtures were kept, for periods never exceeding 2 weeks, in a hot air oven at 150 ° in the absence of light.

The densities were measured with a 25-cm^3 Pyrex volumetric flask, calibrated twice with bromobenzene (Fisher Scientific Co., Certified) (*4*) at each experimental temperature. The uncertainty of this calibration was ±0.005 cm^3. The flask was placed in a thermostated oil bath regulated to ±0.05 °C. The level of liquid in the flask was observed horizontally with a magnifying glass through the glass wall of the bath and adjusted at each experimental temperature by means of liquid from a preheated pipet. Temperature was measured with ERTCO certified thermometers (Ever Ready Thermometer Co.). To check this pycnometric method, measurements were made on water between 80 and 100 °C, the density being known with particular precision (*5*). The results were within 0.03% of the published values, which indicates that the method is entirely satisfactory for the fused salt systems of the present work.

Viscosities were measured with an Ostwald-Ubbelhode viscometer (Cannon Instrument Co.). Its constant, C, was approximately 0.01 cSt s^{-1}. The flow times, t, lay in the range 300–1000 s, and the measured viscosities in the range 10–40 cP. The kinetic energy correction thus was negligible, and the kinematic viscosity ν was given by

$$\nu = Ct \tag{1}$$

The absolute viscosity is given by

$$\eta = \nu\rho \tag{2}$$

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Table I. Densities and Molar Volumes of Fused Salt Mixtures ($AgNO_3$ + $TlNO_3$ + $Cd(NO_3)_2$) as a Function of Temperature and Mole Fraction of $Cd(NO_3)_2$, at Mole Ratio Ag/Tl = 1.06

X_{Cd}	θ, °C	ρ, g cm^{-3}	V, cm^3 mol^{-1}
0	80.0	4.708	46.02
	85.0	4.700	46.10
	85.0	4.700	46.10
	90.0	4.691	46.19
	98.5	4.680	46.30
	98.5	4.679	46.31
	107.0	4.666	46.44
	116.0	4.651	46.59
0.025	85.0	4.640	46.80
	92.6	4.627	47.93
	100.6	4.615	47.06
	108.8	4.601	47.20
	114.2	4.592	47.29
0.050	82.0	4.585	47.47
	90.0	4.573	47.60
	98.5	4.562	47.71
	104.0	4.554	47.80
	110.0	4.546	47.88
	115.0	4.540	47.94
	121.0	4.532	48.03
0.075	80.0	4.536	48.09
	87.0	4.526	48.20
	94.5	4.514	48.32
	104.0	4.504	48.44
	113.0	4.489	48.59
	119.0	4.480	48.70
0.100	85.0	4.473	48.88
	85.0	4.474	48.87
	91.0	4.464	48.98
	94.5	4.461	49.01
	98.5	4.454	49.09
	105.0	4.448	49.16
	110.0	4.441	49.23
	115.0	4.434	49.31
	120.0	4.427	49.39

The flow time for each measurement was determined between 2 and 5 times with an electronic timer (Accusplit, Siliconix Inc.). The reproducibility was better than 0.2%.

To assure true perpendicularity of the viscometer capillary, we mounted the instrument in a rigid device whose orientation was checked with a spirit level. The viscometer was placed in a thermostated bath similar to that described earlier, and all of the active part of the viscometer was below the surface of the bath liquid.

There were no bubbles or visible solid particles in the melt under measurement, as long as the melt was prepared as explained above and the viscometer washed carefully.

The viscometer constant was determined with water, aniline, and aqueous glycerine solutions whose densities (*4*-*6*) and viscosities (*4*, *7*, *8*) are known at several temperatures between 25 and 60 °C. One of these liquids was taken as standard, and the viscosities of the others were reproduced within 0.1-0.7%. In this work, viscosities of nitrate melts were measured relative to the viscosity of water at 30 °C.

Results and Discussion

Experimental values of density as well as the molar volume of the solutions studied are given in Table I and are related by

$$V = (X_{Ag}M_{Ag} + X_{Tl}M_{Tl} + X_{Cd}M_{Cd})/\rho \qquad (3)$$

Figure 1 shows that, for each composition, V is a linear function of the temperature in the range studied

$$V = aT + b \qquad (4)$$

and values of the empirical parameters a and b are given in Table II, together with the coefficient of correlation r.

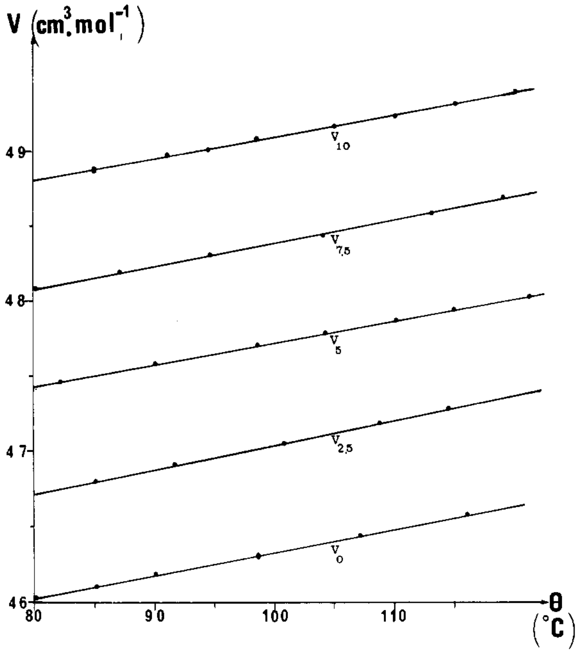

Figure 1. Molar volumes of the fused salt mixtures as a function of temperature (eq 4). The subscripts to V indicate the percent mole fraction of cadmium in the melt.

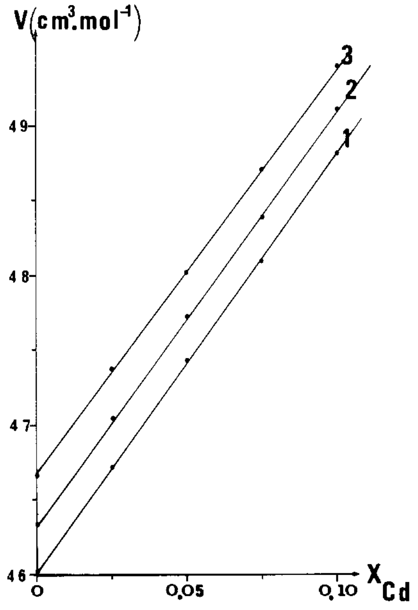

Figure 2. Molar volumes of the fused salt mixtures as a function of cadmium mole fraction (eq 5): (1) 80, (2) 100, and (3) 120 °C.

Table II. Parameters of Eq 4, $V = aT + b$, for the Molten Salt Mixtures Specified in Table I, in the Temperature Range 80-120 °C

X_{Cd}	100a, cm^3 mol^{-1} K^{-1}	b, cm^3 mol^{-1}	r
0	1.563	40.50	0.9994
0.025	1.675	40.80	1.0000
0.050	1.420	42.43	0.9994
0.075	1.533	42.67	0.9989
0.100	1.439	43.73	0.9986

Figure 2 shows that, at a given temperature and fixed Ag/Tl ratio, V varies linearly also with X_{Cd}

$$V = pX_{Cd} + q \qquad (5)$$

and Table III gives values of the fitting parameters p and q at three representative temperatures, covering the range, represented in Table I, together with the coefficient of correlation

Table III. Parameters of Eq 5, $V = pX_{Cd} + q$, for the Molten Salt Mixtures Specified in Table I

θ, °C	p, cm^3 mol^{-1}	q, cm^3 mol^{-1}	r
80	27.80	46.03	0.9998
100	27.52	46.34	0.9999
120	27.18	46.67	0.9998

Table IV. Viscosities of the Molten Salt Mixtures Specified in Table I, as Functions of Temperature and Cadmium Mole Fraction

θ, °C	η, cP	θ, °C	η, cP
	$X_{Cd} = 0$		
98.7	22.74	113.6	15.96
100.4	21.71	114.8	15.52
101.3	21.19	116.0	15.08
102.5	20.44	118.9	14.25
105.3	19.28	120.7	13.71
107.3	18.43	122.7	13.26
107.4	18.42	123.6	12.98
109.4	17.53	125.9	12.40
112.0	16.46	129.1	11.68
	$X_{Cd} = 0.025$		
98.9	25.96	117.5	16.49
98.9	25.87	119.2	15.85
100.6	24.82	119.3	15.79
102.2	23.74	121.0	15.26
104.2	22.55	122.5	14.76
106.6	21.28	123.4	14.49
108.4	20.35	125.5	13.87
110.1	19.47	126.3	13.74
110.6	19.29	128.2	13.17
113.4	18.01	129.2	12.95
115.3	17.29		
	$X_{Cd} = 0.050$		
97.7	31.26	116.0	19.49
98.8	29.83	116.0	19.26
100.8	28.16	118.4	18.22
102.4	27.06	120.4	17.52
102.5	27.21	120.4	17.42
106.3	24.58	122.4	16.64
107.9	23.52	124.3	15.98
110.4	22.08	126.0	15.41
112.7	20.82	127.2	15.05
113.6	20.52	129.4	14.37
113.6	20.39		
	$X_{Cd} = 0.075$		
99.2	34.81	117.1	21.29
101.5	32.33	119.2	20.29
103.3	30.60	120.6	19.60
104.6	29.44	122.6	18.71
106.6	28.19	124.0	18.13
107.9	27.22	125.2	17.61
109.7	25.87	126.6	17.10
111.8	24.44	127.6	16.71
112.5	23.97	129.1	16.18
114.8	22.62		
	$X_{Cd} = 0.100$		
99.1	41.04	116.9	24.69
102.1	37.38	118.0	24.11
104.2	35.33	120.4	22.70
106.0	33.67	121.3	22.06
108.3	31.37	122.8	21.38
110.8	29.30	125.7	19.99
112.2	28.02	127.0	19.41
114.0	26.65	128.1	18.89
114.7	26.18	129.5	18.27

r. The simultaneous effects of T and X_{Cd} on V can be represented by the single equation

$$V = 40.38 + 33.28X_{Cd} + 0.0160T - 0.0155X_{Cd}T \text{ cm}^3 \text{ mol}^{-1} \quad (6)$$

Experimental η values are given in Table IV. Whenever the data allow it, it is convenient to represent η by an exponential function of inverse temperature (*9*). This representation offers the possibility of an interesting (*10*) though by no means unique (*11*) theoretical interpretation. In figure 3 is shown a ln η vs. $1/T$ plot. The viscosity is seen to conform quite closely to a relation of the form

$$\eta = A \exp(E/RT) \quad (7)$$

where both A and E vary with the composition of the solution. Values of A and E are given in Table V, together with those of r for the straight-line correlation ln $\eta = f(T^{-1})$. It is seen that an increase in X_{Cd} entails an increase in E but a decrease in A. That E increases with X_{Cd} is understandable, since the effect is to replace singly charged with doubly charged ionic species, thus increasing the energy of cation–cation and cation–anion electrostatic interaction. The simultaneous decrease of A with X_{Cd} is not so readily rationalized, although absolute reaction rate theory (*10*) postulates that A is proportional to the quantity $[\exp(-\Delta S/R)]/V$, where ΔS is the entropy of activa-

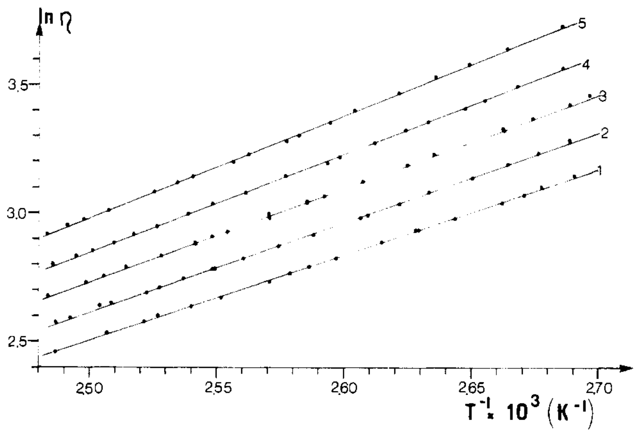

Figure 3. Arrhenius-type plot (eq 6) for the viscosity of the fused salt mixtures for various cadmium mole fractions (X_{Cd}): (1) 0, (2) 0.025, (3) 0.050, (4) 0.075, (5) 0.100.

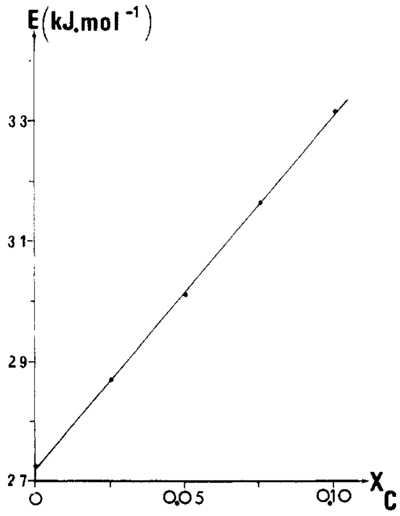

Figure 4. Viscosity Arrhenius parameter E as a function of X_{Cd} (eq 7).

Table V. Parameters of Eq 6, $\eta = A \exp(E/RT)$, for the Molten Salt Mixtures Specified in Table I

X_{Cd}	1000A, cP	E, kJ mol^{-1}	r
0	3.43	27.163	0.9997
0.025	2.43	28.668	0.9997
0.050	1.81	30.032	0.9996
0.075	1.26	31.616	0.9997
0.100	0.91	33.149	0.9997

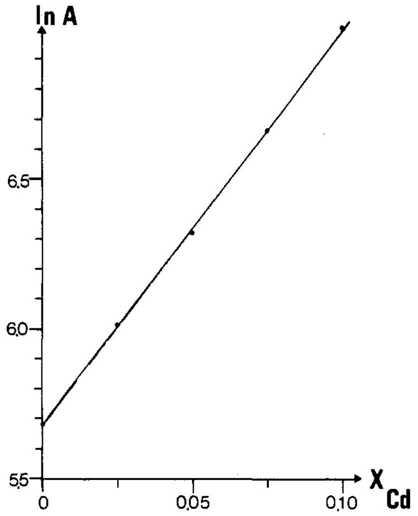

Figure 5. Viscosity Arrhenius parameter ln A of the molten salt mixtures as a function of the cadmium mole fraction (eq 8).

tion and V is again molar volume. The observed variation of V is, however, too small to account for the changes in A shown in Table V.

The variation of A and E with X_{Cd} may be expressed quantitatively by the equations (see Figures 4 and 5)

$$E = 59.680X_{Cd} + 27.142 \text{ kJ mol}^{-1} \qquad (8)$$

$$\ln A(\text{cP}) = -13.30X_{Cd} - 5.674 \qquad (9)$$

and the values of r are 0.9997 in both cases.

The simultaneous effects of T and X_{Cd} on ln η can be represented by the equation

$$\ln \eta = -5.674 - 13.30X_{Cd} + 3264T^{-1} + 7178X_{Cd}T^{-1} \qquad (10)$$

Glossary

a, b	constants in eq 4, units cm^3 mol^{-1} K^{-1} and cm^3 mol^{-1}, respectively
A	viscosity preexponential factor (eq 6), cP
C	viscometer constant (eq 1), cSt s^{-1}
E	viscosity activation energy (eq 6), kJ mol^{-1}
p, q	constants in eq 5, cm^3 mol^{-1}
r	coefficient of correlation
R	gas constant, 8.314 J mol^{-1} K^{-1}
T	temperature, K
t	flow time (eq 1), s
V	molar volume (eq 3), cm^3 mol^{-1}
X_i	mole fraction of salt i in the mixture
Greek Letters	
η	absolute viscosity, cP
ν	kinematic viscosity, cSt
ρ	density, g cm^{-3}
θ	temperature, °C

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Received for review June 6, 1981. Accepted January 21, 1982. We thank the Natural Sciences and Engineering Research Council of Canada for financial aid.

Measurements of the Specific Heat, C_v, of Ethylene

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We have measured the specific heat, C_v, of gaseous and liquid ethylene in both the single- and two-phase regions, at pressures to 30 MPa. Temperatures varied from the triple point to 338 K, and densities varied from 0.6 to 2.8 times the critical value. The specific heats of the saturated liquid, C_σ, are derived. The results are compared with values calculated via the extended Benedict–Webb–Rubin (BWR) equation of state.

Introduction

The present work is part of a joint industry–government project to determine the thermodynamic properties of ethylene. This project consisted of two parts: acquisition of new experimental results (*1–8*), and the development of a model for the equation of state which would reproduce these results and which could be used to calculate reliable thermodynamic properties (*9*) over a wide range of temperature and pressure. The reader should refer to ref *9* for a complete set of references to work on ethylene.

The equation of state, in combination with the specific heat of the ideal gas, can be used to calculate the specific heat of the dense gas and the liquid through the use of well-known thermodynamic formulas. The accuracy of the results is generally rather poor, however, because the calculation depends upon the second derivative, $(\partial^2P/\partial T^2)_\rho$, of the PVT surface. This quantity has a very small value, and it is often known with low accuracy even when high-quality PVT data are available. For calculations in the compressed liquid at low reduced temperatures, a further complication arises from the fact that the bulk of the integration (given in eq 1) required to calculate C_v must be performed inside the gas–liquid two-phase region where there are no data and where the behavior of the equation of state is thus unconstrained. As a result of these difficulties, calculated specific heats often diverge widely from the correct values in the liquid. If, however, measurements of specific heat are available, they may be combined with PVT