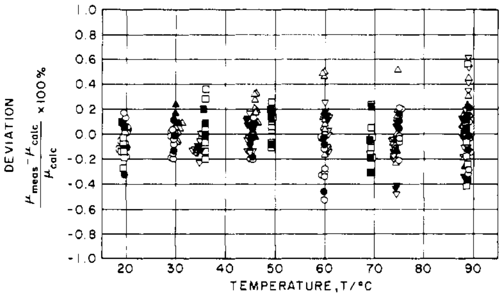

Figure 5. Comparison between our viscosity measurements and correlations for K_2CO_3 solutions: □, solution no. 1, $m = 0.495$ (■ at $P = 0$); ○, solution no. 2, $m = 0.982$ (● at $P = 0$); △, solution no. 3, $m = 1.831$ (▲ at $P = 0$); ▽, solution no. 4, $m = 2.448$ (▼ at $P = 0$).

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

	j		
i	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

	j		
i	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 (*8*). 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.

Acknowledgment

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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 Chen[4] 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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Table I. Melting Properties of Me_2SO: Thermodynamic Molar Data

T/K	P/MPa	(dP/dT)/ MPa K^{-1}	ΔH_m/ cal	ΔS_m/ cal K^{-1}	ΔV_m/ cm^3	K_m
291.6	0.1	5.91	3434[c]	11.78	8.34[a]	3.84[d]
293.6	11.9	6.10	3401	11.58	8.02[b]	3.89
301.9	66.5	6.98	3328	11.02	6.60[b]	4.12
308.4	114.0	7.73	3421	11.09	6.00[b]	4.30

[a] Calculated through the Clapeyron equation by taking into account the value given in footnote c. [b] The high rigidity of the solid phase makes these values only approximate. [c] From ref 3. [d] From ref 1 and 2.

at all temperatures and pressures. It appeared to us rather surprising that an organic liquid whose melting point was known to lie around 18 °C at atmospheric pressure would remain liquid at 1360 atm and 20 °C.

In order to clear up these points, we undertook a *PVT* study of Me_2SO in the corresponding pressure and temperature range.

Experimental Section

A 0.2115-mol sample of Me_2SO was enclosed in a stainless steel bellows. The length of the bellows was measured as a function of temperature and pressure by means of a zero-point method using linear differential transformers coupled to "step by step" (0.1 μm) micrometric devices (Micro Controle MT 50). Corrections for thermal expansion and compressibility of metallic parts of the apparatus are automatically obtained thanks to a symmetrical attachement submitted to the same pressure and temperature conditions. The apparatus, which will be described in detail elsewhere, allows an internal consistency of better than 0.1%.

Temperature inside the high-pressure vessel wall is known thanks to a platinum resistance thermometer, and pressure is measured by means of an Intersonde pressure strain gauge regularly checked against a Budenberg dead weight gauge. Four isothermal runs were performed. Pressure was first increased step by step up to 150 MPa and then decreased down to 0.1 MPa. Volume was measured at each step ($\approx$5 MPa) after thermal equilibrium has been reached.

The consistency of data determined at increasing and decreasing pressures is excellent as no hysteresis effects appear in our experiments.

Results

(*a*) ***Melting Curve.*** The discontinuities observed on the *PV* curves allowed us to determine both the melting point coordinates and the volume increments ΔV_m at fusion. From these results and use of the Clapeyron equation, melting enthalpies ΔH_m and entropies ΔS_m as functions of temperature and pressure were computed. Our experimental points fit the following Simon equation

$$\ln (P + 297) = -27.217 + 5.7989 \ln T$$

where P is given in MPa and T in K.

The correlation coefficient of the fitting process was found to be $r^2 = 0.9999$. All melting features are summarized in Table I where K_m is the molal depression of freezing. Figure 1 shows the melting curve (full line) together with the location in the *PT* diagram of the conditions (stars) in which the kinetic experiments of ref 4 were performed. But the latter experiments were carried out in Me_2SO solutions containing 0.6 mol of reactants/1000 g of solvent. Applying the regular solution approximation, one obtains the corresponding molal depression of freezing points (see Table I) and hence the solution melting curve as represented in Figure 1 by the dashed line. Furthermore, our experiments have shown that Me_2SO may easily be superpressed but that the superpressed domain does not exceed 30 MPa. Accordingly, even taking into account both phenomena, the effect of which is to increase the liquid-phase domain, we may conclude that some of the kinetic experiments of ref 4 seem to have been carried out well in the solid-phase range. This might add to the difficulties of understanding some of their results.

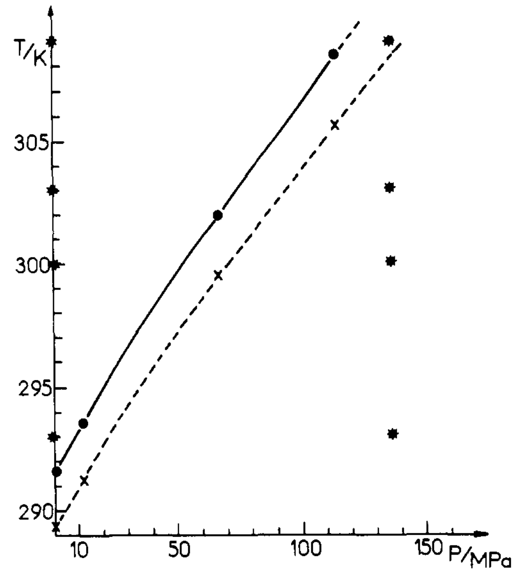

Figure 1. Melting curves of Me_2SO: full line, pure Me_2SO; dashed line, calculated melting curve for 0.6 *m* Me_2SO solution through regular solution approximations; stars, location of thermodynamic conditions for the kinetic experiments of ref 4.

Table II. Coefficients of the Parabola $V(P) = V_0(T) + a(T)P + b(T)P^2$, Fitted to the Experimentally Determined Molar Volumes of Liquid Me_2SO

T/K	V_0/cm^3	10^2a/ cm^3 MPa^{-1}	10^5b/ cm^3 MPa^{-2}
293.6	70.945	−3.470	5.719
301.9	71.366	−3.616	6.731
308.4	71.893	−3.822	6.383
323.0	72.671	−3.976	6.596

(*b*) ***PVT Data of Liquid*** Me_2SO. *PVT* data are important for the high-pressure chemist not only for estimating molar concentrations but also, when correlated to dielectric permittivity measurements under pressure, for understanding the modifications of the solvent properties with pressure and hence the change in chemical reactivity.

Molar volume data in the liquid phase were measured isothermally and fitted to a quadratic form with respect to pressure. This kind of isothermal equation of state has no physical meaning but may be easily used for direct computations of density data or for isothermal compressibility calculations. We choose to use a relationship of the structure

$$V(P) = V_0(T) + a(T)P + b(T)P^2$$

where $V(P)$ is given in cm^3 mol^{-1}.

Table II summarizes the values of v_0, a, and b as functions of temperature. The mean deviations of the fits are less than the uncertainties of the experimental volume measurements, i.e., less than 0.1%. The mean thermal expansion coefficient of Me_2SO at 0.1 MPa obtained in our experiment is $\alpha = 8.4 \times 10^{-4}$ K^{-1} that compares quite well to the previously published value of $\alpha = 8.8 \times 10^{-4}$ K^{-1} and gives an estimate of the accuracy of our results.

Conclusion

The melting curve and *PVT* data in the liquid phase of Me_2SO have been measured up to 150 MPa. We have shown that some previous kinetic experiments in Me_2SO under pressure were probably carried out within the solid-phase range of this compound and have to be carefully reconsidered. Finally, the dearth of high-pressure thermodynamic data for organic solvents should be emphasized, as the field of high-pressure chemistry is rapidly expanding.

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Transfer Activity Coefficients of Alkali, Silver, Thallium(I), Chloride, and Picrate Ions between Methanol and Propylene Carbonate

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Solubility products of various salts in propylene carbonate (PC) have been determined in order to obtain transfer activity coefficients, ${}^{S_1}\gamma^{S_2}(M^+)$, of the ions mentioned in the title between methanol and PC. Values of log ${}^{M}\gamma^{PC}(M^+)$ are reported in Table III. A critical study of literature values of solubility products in PC has been made.

Introduction

In a recent study (*1*) we have reported transfer activity coefficients ${}^{M}\gamma^{S}(LM^+)$ at 25 °C of complexes of alkali, silver, and thallium(I) ions with dibenzo-18-crown-6 (DB-18) between methanol (M) on the one hand and water, acetonitrile (AN), propylene carbonte (PC), and dimethyl sulfoxide (Me_2SO) on the other. The extrathermodynamic assumption of Parker (*2*) that ${}^{M}\gamma^{S}(Ph_4As^+) = {}^{M}\gamma^{S}(BPh_4^-)$ was employed. The transfer activity coefficients of the various solvated cations, ${}^{M}\gamma^{S}(M^+)$, between methanol and the above solvents were required in order to obtain values of ${}^{M}\gamma^{S}(LM^+)$ in the various solvents. Such data are available in the literature. However, some discrepancy in literature values of ${}^{M}\gamma^{PC}(M^+)$ made it desirable to make an independent study of these values of the ions mentioned in the title. For this purpose it was necessary to determine the solubility products of silver tetraphenylborate, chloride, and picrate and thallium(I) tetraphenylborate in PC and of alkali chlorides in M, AN, and PC. From these data values of ${}^{M}\gamma^{PC}(Cl^-)$ and ${}^{M}\gamma^{PC}(Pi^-)$ were also obtained.

Experimental Section

Chemicals. Methanol was Fisher Spectroquality grade, distilled once over magnesium turnings. Acetonitrile was Aldrich Co. product, distilled over phosphorus pentoxide, while propylene carbonate was from Burdick and Jackson Laboratories, used without further purification. The water content of these solvents ranged from 0.003 to 0.01%. Silver chloride (*3*), perchlorate (*1*), and tetraphenylborate (*4*) and thallium(I) tetraphenylborate (*5*) had been used previously. Silver picrate was prepared from sodium picrate and silver nitrate in aqueous solution as described by Kolthoff, Lingane, and Larson (*6*). Tetraethylammonium tetraphenylborate was prepared by metathesis in aqueous solution of equimolar amounts of sodium tetraphenylborate and tetraethylammonium bromide. It was recrystallized from water. Tetraethylammonium (*7*), sodium (*5*) and potassium chlorides (*5*), and tetraethylammonium picrate (*8*), were also used previously. Lithium chloride was Mallinckrodt Reagent grade product recrystallized from an acetonitrile–water mixture (5:1). Rubidium and cesium chlorides were Ventron Co. puriss. grade and Fisher reagent grade products, respectively, and were not purified further. All salts were dried at 50 °C in vacuo.

Techniques. Solubility Determinations at 25.0 ± 0.1 °C. Saturated solutions of the alkali chlorides in methanol, acetonitrile, and propylene carbonate were prepared by stirring the finely divided salt suspension for 2 days and filtering. Total solubilities were determined by taking aliquots of the methanol or acetonitrile solutions to dryness (but not those of propylene carbonate), flooding with 50 volumes of methanol–water mixture (10:1), and titrating the residues potentiometrically with standard aqueous silver nitrate solution using a silver wire electrode. Saturated solutions of silver tetraphenylborate and chloride in PC were prepared by slowly adding, while stirring, 0.010 M silver perchlorate solution to 1.3×10^{-3}–3×10^{-3} M tetraethylammonium tetraphenylborate or chloride. In the chloride systems the mole ratio of Cl^- to Ag^+ was kept between 1 and 2 to avoid complete dissolution of silver chloride by complexation. The mixtures were initially opalescent; upon seeding with 5 mg of solid silver tetraphenylborate or chloride they became very turbid upon being stirred for 1 h. They were then stirred for 2 days and p*a*(Ag) values measured potentiometrically with a silver wire electrode. Stable potentials (to within ±1 mV) were attained after 10 min. Under these conditions supersaturation does not occur.

For the determination of the complexation constant $K^f(AgCl_2^-)$, solutions of silver perchlorate were added to tetraethylammonium chloride as described above, but in mole ratios of Cl:Ag ranging from 2:1 to 10:1, and p*a*(Ag) values of the resulting clear solutions measured within 15 min of preparation. All silver solutions were prepared and kept in dark containers.

Solubility products of thallium(I) tetraphenylborate and silver picrate in PC were estimated from p*a*(Tl) or p*a*(Ag) measurements in 0 to 4.3×10^{-3} M tetraethylammonium tetraphenylborate or picrate solutions saturated with thallium(I) tetraphenylborate or silver picrate, respectively. Measurements of p*a*(Tl) were made with a potassium ion selective electrode (Markson Co. Cat. No. 1002) conditioned in 5×10^{-4} M thallium(I) nitrate solution in PC. Total solubilities of silver picrate in absence and presence of tetraethylammonium picrate were determined by argentometric titration with potassium bromide in a similar way as with the alkali chlorides.

Instrumentation. The potentiometric cell and 0.010 M $AgClO_4$/Ag reference electrode used for p*a*(Ag) and p*a*(Tl)

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