Compressibility Measurements of the Liquid Binary Systems KNO_3–$Ca(NO_3)_2$ and $ZnCl_2$–$C_5H_5N \cdot HCl$

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The variation of the isothermal compressibilities over a range of temperatures has been measured for two liquid binary systems. These were KNO_3 (38.1 mole %)–$Ca(NO_3)_2$ and $ZnCl_2$ (76 mole %)–$C_5H_5N \cdot HCl$ (pyridine hydrochloride).

As part of an extensive study of transport properties of molten salts, and, in particular, of glass forming molten salts near their glass transition temperature (*1*), it was necessary to obtain accurate knowledge of the compressibility of molten salt mixtures over a range of temperatures. While the compressibility of pure molten alkali nitrates and silver nitrate up to 500° C has been determined (*5, 7*), no compressibilities of molten nitrate and chloride mixtures have been reported.

EXPERIMENTAL

Of the different methods available for measuring compressibilities in liquids (*3-6*), the use of tag electrodes in a capillary is the most suitable for molten salts. Earlier measurements involved the use of an inert gas in contact with the salt under pressure, but even inert gases dissolve in molten salts, leading to errors in measured compressibility. In the present experiments the temperature range permitted the use of an inert liquid (silicone oil), which was wholly immiscible with the salt, as the pressurizing fluid.

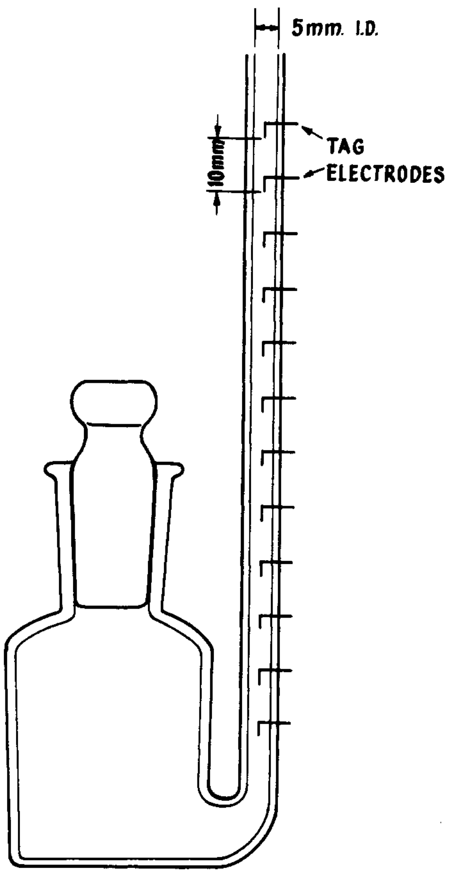

Figure 1. Compressibility cell

The compressibility cell (Figure 1) consisted of a borosilicate glass bulb fitted with a stopper for introducing the salt, and a side arm attached at the base of the bulb. The volumes of the cells used varied between 28 and 35 ml. The side arm, which was approximately 5 mm id and 140 mm long, had 12 platinum electrodes sealed through the tube at approximately 10-mm intervals, giving a volume change of 0.5 to 0.7% between electrodes. The electrodes were bent downward for sharp contact and were coated with platinum black. Carbon resistors (0.5 W) were connected between the electrodes. The cell was placed in a supporting frame, and the electrodes were connected to a terminal block of compressed asbestos.

The pressure vessels, the aluminum block heaters, electrical leads, and the instruments for measurement and control are described elsewhere (*1, 9*).

Volume measurements were made at constant temperature rather than at constant pressure, since, with the large volume within the pressure vessel and within the cell, the salt would not have been at a uniform temperature during heating and cooling. However, providing that the salt has a relatively low viscosity, changes in pressure are readily transmitted through the salt. The movement of the salt-oil interface was followed by observing the changes in resistance of the side arm chain.

Before commencing a run, the approximate position of the salt in the side arm was located using the tag electrodes. The conductance bridge was then connected between the two most suitable leads, and the pressure on the system was increased, until a sudden change in resistance was observed, corresponding to the salt beginning to break away from the electrode. This pressure was noted, and the pressure was then increased again, until there was no further rapid increase in resistance. This second pressure, which was about 200 bars greater than when the first sudden resistance change was noted, corresponds to the point at which the salt breaks away completely from the electrode. The pressure was then reduced to about 50 bars above the initial breakaway, and the system was allowed to regain thermal equilibrium. The pressure was then reduced in 10-bar steps, with thermal equilibrium being reestablished at each step. Renewed contact by the electrode with the salt was indicated by a sudden change of resistance, to a value close to the initial value. This technique, although tedious, avoided any uncertainty owing to salt clinging to the electrode and enabled points to be reproduced to within 10 bars. The process was repeated, locating points at pressures up to the maximum.

The temperature of the molten salt was measured by Chromel-Alumel thermocouples placed immediately next to the glass cell within the pressure vessel. The thermocouples were calibrated in situ against calibrated standard thermometers, using a triple point cell as the cold junction. During pressure runs the emf output from the thermocouple

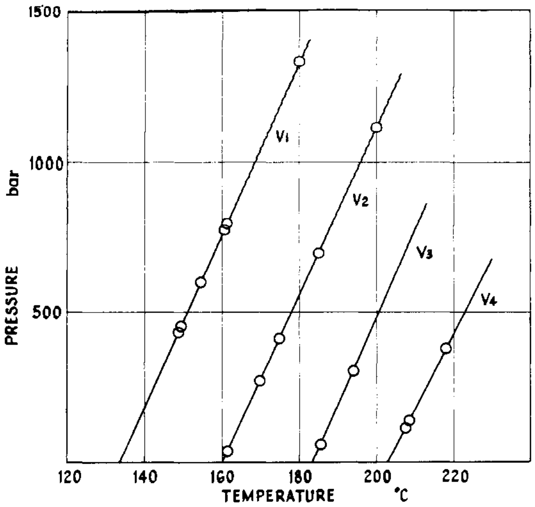

Figure 2. Typical pressure *vs.* temperature plot. Each line corresponds to the volume of a given tag electrode

was traced by a high speed, multiple range recorder, with a 1 mV full scale (12 in.) deflection. The recorder was calibrated at frequent intervals using a vernier potentiometer, and temperatures could be measured to 0.05° C.

The arrangement of the bomb within an aluminum block heater enabled the temperature to be maintained to ±0.2° C for several hours, while closer control to ±0.1° C was possible for periods of 20 min, suitable for establishing the thermal equilibrium of the sample in cell.

Pressures were measured with calibrated Bourdon tube pressure gauges, and their precision was better than ±5 bars. The salt mixtures were prepared from analytical reagent grade materials. Final traces of water were removed from the mixtures by heating to 48 hr: the nitrate mixture at 320° C and the chloride mixture at 180° C.

RESULTS

The PVT data for the salt mixtures were measured at pressures up to 1200 bars and at temperatures between 120° and 210° C.

The results were obtained in a series of pressures and temperatures equivalent to the volumes corresponding to each electrode spacing. These volumes have been corrected to allow for the compressibility and thermal expansion characteristics of the cell. When plotted on temperature *vs.* pressure curves the points for each electrode volume, Vn, fall on a smooth curve permitting interpolation of the data. Figure 2 shows a typical plot.

The approximate volume corresponding to each electrode spacing was obtained from a volumetric calibration, which was precise to ±0.01 ml. The cell was finally calibrated using the atmospheric expansivity data of Dietzel and Poegel (*3*) for the nitrate salt.

Plots of the variation of salt volume with temperature at constant pressure were obtained by taking isobars from plots similar to Figure 2. By taking isotherms from these plots the variations of volume with pressure at constant temperature were obtained.

The slope of the constant pressure plots represents the thermal expansion coefficient of the salt, α_p, since

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{1}$$

Since α_p is approximately independent of temperature over a small temperature range these plots are effectively linear. The isothermal compressibility, β_T, can be found from the slope of the constant temperature plots, since

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{2}$$

The gradients calculated from these plots were smoothed using the experimental fact that although β_T varies rapidly with pressure, the variation with temperature is approximately linear. The values obtained from the compressibility were smoothed by plotting β_T as a function of T at constant pressure. The final plots of compressibility as a function of pressures for different temperatures are shown in Figures 3 and 4.

DISCUSSION

Accuracy. The accuracy of the PVT data is limited by a number of factors. These include the calibration of the cells and the accuracy of the temperature determination of the salts.

It is estimated that the temperature of the salt was within 0.2% of that indicated by the thermocouple, while the constant temperature fixed volumes were reproducible to ±10 bars.

As mentioned above the value taken for ΔV, the interelectrode volume, was adjusted to bring the present experimental results into agreement with Dietzel and

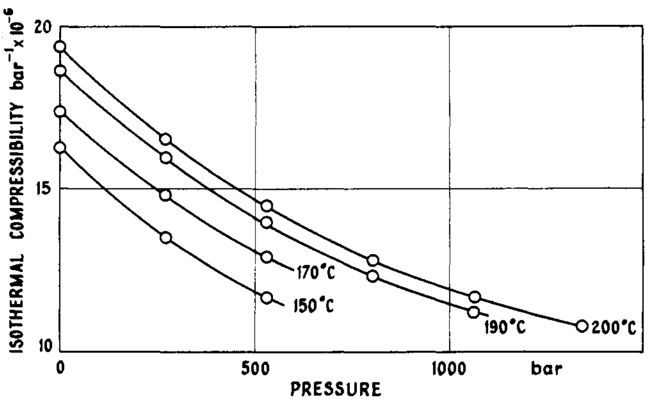

Figure 3. The isothermal compressibility of KNO_3 (38.1 mole %)-$Ca(NO_3)_2$

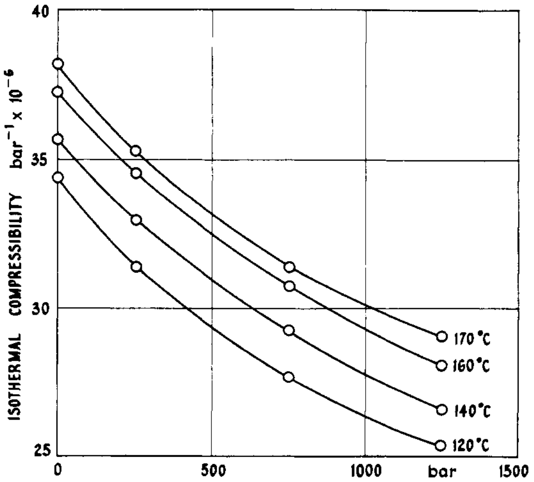

Figure 4. The isothermal compressibility of $ZnCl_2$ (76 mole %)-$C_5H_5N \cdot HCl$

Table I. Comparison of Compressibility Data for Molten Salts

Salt	Temp, °C	Compressibility, $\text{bar}^{-1} \times 10^{-6}$ 1	1000	1500	5000	Reference
KNO_3	400	21.0[a]		18	13	Owens (7)
KNO_3	400	23.4[b]				Bockris and Richards (2)
	500	29.4[b]				
KNO_3	400	15.5	13.0			Fray (5)
KNO_3 (38.1 mole %)-$Ca(NO_3)_2$	200	19.0	11			Present work
$ZnCl_2$ (76 mole %)-$C_5H_5N \cdot HCl$	170	38.2	30.1			Present work
KCl	800	38.4[b]				Bockris and Richards (2)
$CdCl_2$	600	29.8[b]				

[a] Extrapolated from high pressure values. [b] From ultrasonic measurements of adiabatic compressibility.

Poegel's atmospheric expansivity data. ΔV was calculated from

$$\Delta V / V_0 \approx \alpha \Delta T \tag{3}$$

where α is the Dietzel and Poegel value for the expansion coefficient, V_0 is known to ±0.1%, T to ±0.2% (corresponding to ±0.2°C). The expansion coefficient, α, is apparently accurate to within 1%. The resulting uncertainty in ΔV after recalibration is therefore approximately 3%, compared with approximately ±10% from the initial volumetric calibration.

The relative uncertainty in the values β can be estimated from

$$\frac{\Delta\beta}{\beta} = \frac{\Delta V}{V} + \Delta\left(\frac{\partial V}{\partial p}\right) / \frac{\partial V}{\partial p} \tag{4}$$

To determine this uncertainty approximately, it is recognized that ΔV, the uncertainty in volume, is approximately ±3% of V, and furthermore $\Delta(\partial V/\partial p)$, the uncertainty in the slope $\partial V/\partial p$ is approximately ±3% of $\partial V/\partial p$. Thus $\Delta\beta/\beta = \pm 6\%$.

Comparison with Other Work. The only previously reported data for the isothermal compressibility of molten salts are by Fray (5) and Owens (7). A number of ultrasonic measurements of adiabatic compressibility have also been reported (2). These results are given, together with a comparable value from the present measurements, in Table I. The compressibilities are of same order of magnitude, although the compressibility of the mixture decreases more rapidly with pressure than for the pure salt. However, both Owens' and Fray's methods are not very reliable in the low pressure range. Fray, who worked with gas pressures, used an arbitrary correction to allow for the effect of dissolved gas, while the piston displacement technique used by Owens is subject to hysteresis effects below 1500 bars, and the quoted results have been extrapolated from work at higher pressures.

The compressibility measurements enabled constant volume activation energies for transport processes to be calculated, and so allow reasonable comparisons between experimental and predicted behavior to be made.

ACKNOWLEDGMENT

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LITERATURE CITED

(1) Angell, C. A., Pollard, L. J., Strauss, W., *J. Chem. Phys.*, **43**, 2899-900 (1965); **50**, 2694 (1969).

(2) Bockris, J. O'M., Richards, N. E., *Proc. Roy. Soc. (London)*, **241**, 44 (1957).

(3) Dietzel, A., Poegel, H. J., Proceedings of the Third International Glass Congress (Venice), Assoziazione Nazionale degli Industriali del Vetro, Roma, 1954, p 219.

(4) Eduljee, H. E., Newitt, D. M., Weale, K. E., *J. Chem. Soc.*, **1951**, p 3086.

(5) Fray, D. J., Thesis, University of London, London, England, 1965.

(6) Kuss, E., *Z. Angew. Physik*, **4**, 201 (1952).

(7) Owens, B. B., *J. Chem. Phys.*, **44**, 3919 (1966).

(8) Pearce, P. J., Strauss, W., *Aust. J. Chem.*, **21**, 1213 (1969).

(9) Pollard, L. J., Ph.D. Thesis, University of Melbourne, Melbourne, Australia, 1968.

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CORRECTION

In the article "Low-Temperature Volumetric Properties of Methane" by A. J. Vennix, T. W. Leland, and Riki Kobayashi [*J. Chem. Eng. Data* **15**, 238 (1970] in Table I on page 241 under =0.341 Gram/Cc. in the last column, the second entry under Press., Atm., should read 622.874 rather than 662.874.