Surface Tension of $TlNO_3$ and the Binary Mixtures $TlNO_3$–$LiNO_3$ and $TlNO_3$–KNO_3

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The surface tension of molten $TlNO_3$ has been measured over the temperature range 220–350 °C, using the maximum bubble pressure method. We have also measured the surface tension of the binary mixtures $TlNO_3$–$LiNO_3$ and $TlNO_3$–KNO_3 at 350 °C over the entire composition range.

In an earlier paper (*10*) we showed that it was possible to calculate, with excellent agreement between the calculated and experimental values, the surface tension of binary molten salt mixtures by assuming regular solution behavior. However, it has been postulated that the assumptions of regular solution theory begin to fail in melts in which there are significant noncoulombic interactions (*4, 8*). It has been shown that there is a significant degree of noncoulombic interaction, generally attributed to covalent contributions, in molten thallium nitrate as well as in thallium halide–alkali halide mixtures (*3, 13*). The purpose of this paper is to present the experimental values of the surface tension of $TlNO_3$ from 220 to 350 °C and of the binary mixtures $TlNO_3$-$LiNO_3$ and $TlNO_3$-KNO_3 over the entire composition range at 350 °C and to assess the accuracy of the data. The theoretical implications of these data, insofar as they reflect on the regular solution model of a molten salt solution, will be discussed elsewhere.

Experimental Section

In this investigation the maximum bubble pressure method of measuring the surface tension was used. The design of the experimental apparatus, as well as the procedure for obtaining the measurements, has been thoroughly described in a prior publication (*9*). Two small changes were made in the experimental procedure, however. A thermocouple was attached directly to the gold capillary to enable us to know accurately the temperature of the capillary–melt interface. The depth of immersion of the capillary tip below the surface of the melt was determined by direct visual measurement with a cathethometer, a procedure we have found to be slightly more accurate than the resistance change method we used previously (*9*). To allow for visual observation of the melt, as well as the capillary tip, a furnace equipped with sighting ports was used. Because of the heat sink effect of the windows, they were kept closed with a shutter arrangement except for the brief time when the depth of immersion was being measured. To keep temperature gradients in the melt as small as possible, the quartz crucible which contained the melt was surrounded by a thick graphite sleeve which had two thin (5 mm) vertical slits oriented 180° apart to allow observation of the capillary. With these precautions, the vertical temperature gradient in the melt was less than 1.0 °C and the temperature fluctuations were kept less than 0.5 °C.

All of the chemicals used in these experiments were of reagent grade and were recrystallized at least once before being used. Because of the extreme sensitivity of $TlNO_3$ to traces of moisture, the purification procedure of Timidei and Janz (*11*) was used. Differential thermal analysis of recrystallized $TlNO_3$ showed a melting point of 207 °C and a boiling point of 430 °C in both air and argon (*2*).

The recrystallized salts were stored in an inert atmosphere glovebox in which the water vapor partial pressure was less than 10 ppm. All weighing and other manipulations of the purified salts were done in this glovebox to avoid contamination by water vapor and also because of the extremely toxic nature of $TlNO_3$.

Results

A total of 23 separate measurements of the surface tension of $TlNO_3$ were made over the temperature range 220–350 °C. Each measurement of the surface tension at a given temperature is itself the average of five separate measurements. Two different capillary orifices (0.0372 and 0.0830 cm in diameter) were used interchangeably. As a check on the accuracy of our measurements, we periodically remeasured the surface tension of KNO_3. In each case the agreement was well within 0.5% of the National Standard Reference Data recommended value (*6*).

A least-squares computer fit of the data shows that the surface tension of $TlNO_3$ over the temperature range 220–350 °C is given by an expression of the form

$$\gamma = 133.48 - 0.096\theta$$

for θ in °C. The correlation coefficient between the above equation and the experimental data was 0.99. The density data of Timidei and Janz (*11*) were used to calculate the surface tension.

Tables I and II show the surface tensions of the binary $TlNO_3$–$LiNO_3$ and $TlNO_3$–KNO_3 mixtures at 350 °C. Here, as in the $TlNO_3$ case, each measurement of the surface tension at a given composition is itself the average of five separate measurements.

Figures 1 and 2 show plots of the surface tension for $TlNO_3$–$LiNO_3$ and $TlNO_3$–KNO_3 as a function of composition at 350 °C. For those compositions for which more than one surface tension value was available, the data point shown on the figure is the mean.

We note the very pronounced angularity of these curves which is in decided contrast to more typical surface tension–composition curves. These tend, in general, to be smooth functions of the composition in those molten salt mixtures in which there appear to be no significant noncoulombic interactions (*10*).

The densities for the $TlNO_3$–$LiNO_3$ and $TlNO_3$–KNO_3 mixtures were taken from the data compilation of Janz (*7*).

As in our previous work (*9*), the equation

$$\gamma = (rg/2)(hd_1 - id_2) - (r^2 d_2 g/3) \qquad (1)$$

where r is the radius of the capillary bore, g is the gravitational constant, h is the height of the column of manometric fluid (dibutyl phthalate) whose density is d_1, i is the depth of immersion of the capillary tip, and d_2 is the density of the liquid under investigation, was used to calculate the surface tension.

Discussion

To our knowledge, no previous surface tension measurements have been made on either the $TlNO_3$–$LiNO_3$ or the $TlNO_3$–KNO_3 systems.

Our results for the surface tension of $TlNO_3$ are significantly different from those of Addison and Coldrey (*1*) and in fair agreement with those of Jaeger (5). This difference is shown in Table III for a temperature of 300 °C.

Table I. Surface Tension Values for $TlNO_3$-$LiNO_3$ at 350 °C

Composition (mol % $TlNO_3$)	γ, dyn/cm	Composition (mol % $TlNO_3$)	γ, dyn/cm
9.1	106.8	38.0	101.1
	105.4		101.3
	105.2		101.2
17.0	103.9	50.0	101.4
	103.6		101.5
19.6	102.5		101.3
	102.0	70.0	99.9
29.0	102.4		99.9
	102.4	90	99.7
	101.9		99.7
	101.1		

Table II. Surface Tension Values for $TlNO_3$-KNO_3 at 350 °C

Compn (mol % $TlNO_3$)	γ, dyn/cm	Compn (mol % $TlNO_3$)	γ, dyn/cm
9.1	107.6	37.4	102.4
	106.9		102.0
	106.6		102.1
16.7	105.0		102.8
	104.8		102.4
	106.0	47.4	100.5
	105.0		101.4
	106.2	50.0	99.7
28.6	104.2		101.7
	104.1	55.4	99.8
	104.0		99.6
33.0	103.2	70.0	100.5
			99.3
		90.0	100.3
			100.1

Table III. Comparison of Surface Tension Values for $TlNO_3$ at 300 °C

Author	γ, dyn/cm	$d\gamma/dt$, dyn/(cm deg)
Addison and Coldrey (*1*)	87.5	−0.078
Jaeger (*5*)	110.4	−0.084
This work	104.7	−0.096

We are unable to offer a reason for this discrepancy except to note that Addison and Coldrey (1) claim to have measured the surface tension of $TlNO_3$ up to 458 °C. This is rather surprising considering the fact that $TlNO_3$ boils at 430 °C (*2, 3*). Jaeger (*5*) carried his investigation up to the boiling point of $TlNO_3$. Our data (*2*) indicate that there is appreciable volatilization of $TlNO_3$ at temperatures as low as 400 °C. This could conceivably have an adverse effect on the results, a point that has previously been noted (*6*).

Although molten $TlNO_3$ had a very pale yellow color, the solidified salt was pure white. Thermal analysis of samples of recrystallized $TlNO_3$ showed that the material was thermally stable up to and beyond its boiling point (*2*). Within the limits of our experimental accuracy (1%), there was no evidence whatever of irreproducibility of measurements of the surface tension, even for samples that had been in the molten state for up to 5 days.

The precision of our experiments was good (0.5%), but we estimate an overall accuracy in the data of about 1%. We are unable to account precisely for the relatively large error in this particular series of experiments. Our earlier studies on the LiCl-KCl system (*9*) showed this method of measuring surface tension is capable of much higher accuracy (at least 0.5%).

One possible source of error is poor wetting of the capillary by the liquid in which it is immersed. In this case the bubble displaces the liquid from a part or, in the most extreme case, all of the capillary wall. Then *r* is no longer equal to the radius of the capillary bore but takes on some other, indeterminate value. Careful observation of the capillary tip through a cathetometer, as bubbles were being formed, showed that there was complete wetting of the tip and that the bubbles were all formed on the inner radius.

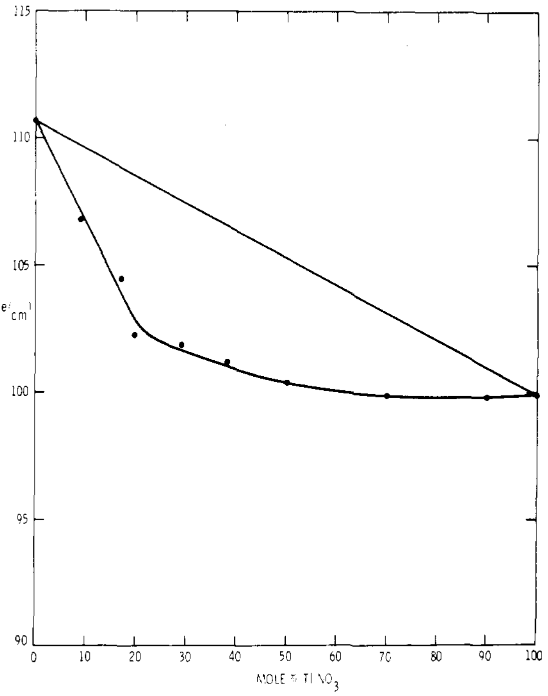

Figure 1. Isothermal surface tension of the system $TlNO_3$-$LiNO_3$ as a function of composition (T = 350 °C).

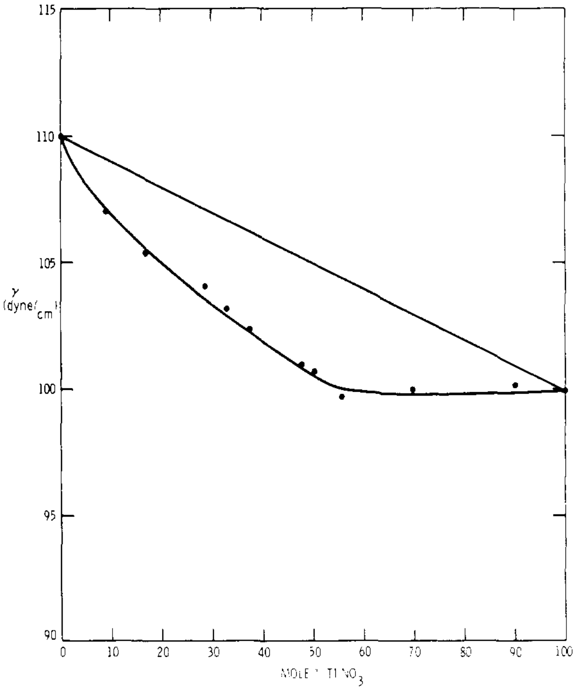

Figure 2. Isothermal surface tension of the system $TlNO_3$-KNO_3 as a function of composition (T = 350 °C).

We suspect that the real source of error may arise from the uncertainties in determining the depth of immersion of the capillary tip. This uncertainty, when multiplied by the extremely large densities of $TlNO_3$ or $TlNO_3$ solutions, may become appreciable; cf. eq 1. By going to smaller diameter capillaries (0.0372 vs. 0.0830 cm), it is possible to mitigate the influence of the id_2 term of eq 1. However, gold capillaries with the smaller diameter were very difficult to fabricate properly. Furthermore, it was hard to keep a constant, slow rate of bubble formation with these capillaries. Failure to maintain a constant and fairly slow rate of bubble formation (~2/min) can cause erroneous results (*12*).

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Thermodynamic Properties of the Systems Methylcyclohexane–Toluene, *n*-Heptane–Toluene, and Methylcyclohexane–Toluene–*n*-Heptane

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Enthalpy–concentration data and boiling point–composition correlations have been determined for the binary systems methylcyclohexane–toluene and *n*-heptane–toluene. New vapor–liquid equilibrium data are presented for the ternary methylcyclohexane–*n*-heptane–toluene. The system behaves almost ideally, and its activity coefficients are well correlated by the Redlich–Kister equation.

The hydrocarbon systems methylcyclohexane–toluene, *n*-heptane–toluene, and methylcyclohexane–toluene–*n*-heptane have been used normally for testing the efficiency of fractionating columns. These systems are near ideal and easy to analyze and their boiling point range is small enough to neglect the temperature effect on the activity coefficients. Extensive information is available on the vapor–liquid equilibrium of the binaries (*2–5, 7, 9, 11–13, 17, 18*), but the data on the ternary system are meager (*3, 6*). Bromiley and Quiggle (*3*) have reported the vapor–liquid equilibrium compositions at atmospheric pressure without indicating the boiling point of the mixture nor the activity coefficient of its components. Katayama et al. (*7*) have determined the isothermal activity coefficients at 25 °C. Holzhauer and Ziegler (*6*) have recently reported the heat capacity of the pure components and the excess heat capacity and excess enthalpy of the binary mixtures over a wide temperature range.

All the necessary thermodynamic information is now available to calculate the enthalpy–concentration diagram of the binaries and correlate their boiling points. These new data should increase the calibration power of the systems as well as help in the determination of point to point plate efficiencies.

Experimental Section

Purity of Materials. Analytical grade reagents (+99%) purchased from Merck and Fluka were used without further purification after gas chromatography analysis failed to show any significant impurities. Properties of the pure components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik (*1*) recirculation still was used in the equilibrium determinations. The equipment and operating techniques have been described elsewhere (*19*). All analysis were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm in diameter and was packed with OV-17 on 80–100 mesh Supelcoport and was operated isothermally at 60 °C. Injector and detector temperatures were 180 °C. Calibration analyses were carried out to convert the peak area ratio to weight composition. Concentration measurements were generally accurate to within ±0.3%.

Results and Discussion

Boiling Point Correlation. The boiling points of the binary systems were correlated with their compositions using the equation suggested by Wisniak and Tamir (*20*)

$$T = x_1T_1^0 + x_2T_2^0 + \omega + x_1x_2 \sum_{k=0}^{l} C_k(x_1 - x_2)^k \qquad (1)$$

where T_1^0 and T_2^0 are the boiling points of the pure components, l is the number of terms in the series expansion of $(x_1 - x_2)$ and

$$\omega = x_1 \ln y_1/x_1 + x_2 \ln y_2/x_2 \qquad (2)$$

The contribution of ω was found to be negligible and the term was dropped from eq 1.

The data of ref 5 and 9 were judged to be thermodynamically consistent and used to determine the constants in eq 1. The

Table I. Physical Properties of Pure Compounds

Index	Compd	Refractive index at 25 °C	Bp, °C (760 mmHg)
1	*n*-Heptane	1.38505	98.38
		1.38511[a]	98.43[a]
2	Methylcyclohexane	1.41935	100.92
		1.42058[a]	100.93[a]
3	Toluene	1.49255	110.65
		1.49413[a]	110.62[a]

[a] Reference 14.