

52 K, his experimental heat capacity values differ by +0.92% to -0.56% from our smoothed values.

Theory regarding the overall magnetic entropy contribution,  $S_{\text{mag}}$ , indicates that it should be simply related to the net spin,  $s$ , of a compound by

$$S_{\text{mag}} = R \ln(2s + 1) \quad (\text{see Gopal (5)})$$

Our calculated magnetic entropy contribution of  $R \ln(1.7)$  is close to  $R \ln(2)$  in agreement with a spin of  $1/2$ .

A crystal field analysis of magnetic susceptibility data for  $\alpha\text{-CoSO}_4$  (7) supports this result indicating that an isolated ground Kramer's doublet occurs in this compound.

#### Acknowledgment

We thank Dr. Hollis Wickman of the Oregon State University Chemistry Department for assisting us in our research of the

magnetic behavior of cobaltous compounds.

Registry No.  $\alpha\text{-CoSO}_4$ , 10124-43-3.

#### Literature Cited

- (1) Weller, W. W. *U.S. Bur. Mines, Rep. Invest.* **1965**, 6669.
- (2) Adami, L. H.; King, E. G. *U.S. Bur. Mines, Rep. Invest.* **1965**, 6617.
- (3) Beyer, R. P.; Ferrante, M. J.; Mrazek, R. V. *J. Chem. Thermodyn.* **1983**, *15*, 827-834.
- (4) Justice, B. H. FITAB Program, University of Michigan, Ann Arbor, MI, 1969; COO-1149-143.
- (5) Gopal, E. S. R. *Specific Heats at Low Temperatures*; Plenum: New York, 1966; p 98.
- (6) Chuang, Y.; Schmid, R.; Chuang, Y. A. *Metall. Trans. A* **1985**, *16A*, 153-165.
- (7) Silvera, I. F.; Thornley, J. H. M.; Tinkham, M. *Phys. Rev.* **1964**, *136*, *3A*, A695-A710.

Received for review March 22, 1985. Accepted May 12, 1986.

## Wetting Behavior of Molten $\text{PbCl}_2$ -Alkali-Metal Chloride Mixtures

Torstein A. Utigard, Ding-Chen Mo,<sup>†</sup> and James M. Toguri\*

Department of Metallurgy and Materials Science, University of Toronto, Toronto, Canada M5S-1A4

**Contact angles formed on different materials by liquid  $\text{PbCl}_2$ -KCl-NaCl mixtures were measured by using the sessile drop technique. Drop images were obtained on X-ray films by using a high temperature X-ray fluoroscopy unit. Under an argon atmosphere, all chloride mixtures studied formed contact angles less than  $40^\circ$  on substrates of polycrystalline alumina, quartz, and Inconel. Graphite and amorphous carbon substrates were the least wetted, with contact angles between  $90$  and  $150^\circ$ . Contact angles formed on graphite substrates did not change when the argon atmosphere was replaced with chlorine gas. However, when air was introduced, complete wetting on graphite occurred, probably due to interactions between  $\text{O}^{2-}$  ions and the graphite substrate.**

#### Introduction

Recently, we determined densities and surface tensions of melts in the  $\text{PbCl}_2$ -KCl-LiCl and  $\text{PbCl}_2$ -KCl-NaCl ternary systems (1-3) since these melts were potential electrolytes for the production of metallic lead by electrolysis (4-6). During this study, we noted that alkali-metal chloride melts containing  $\text{PbCl}_2$  tended to creep up the walls of the alumina and silica crucibles. Such an observation suggests that the surface properties of these melts could give rise to problems during electrolysis of  $\text{PbCl}_2$ . In the present note, the contact angles formed by molten lead chloride containing electrolytes on various solid substrates are reported.

#### Experimental Section

The sessile drop method combined with a high-temperature X-ray fluoroscopy unit was used for contact angle measurements. In this method the image of a liquid drop resting on a horizontal plane surface is required.

The experimental assembly has been described in detail previously (7); thus only a brief outline is given. The X-ray

beam was generated by a medical-type tube (Picker PX-2A) with a tungsten anode which was rigidly mounted to the furnace bench to avoid changes in alignment. A split graphite resistor furnace containing molybdenum and Inconel radiation shields was used. This furnace assembly was flushed with argon gas which was purified with copper chips at  $450^\circ\text{C}$  to remove oxygen and dried with anhydrous  $\text{CaSO}_4$ . A sessile drop was formed on a horizontal base constructed from the material under study. This sample holder could be rotated up to  $90^\circ$  to allow investigation of the drop symmetry.

Graphite with a density of  $1.87\text{ g/cm}^3$  and an average pore size of approximately  $3\ \mu\text{m}$  was used for the present study. Graphite plaques, 3-5 mm thickness, were polished with  $1\text{-}\mu\text{m}$  alumina powder to a mirrorlike finish. The  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  plaques were polished with  $1\text{-}\mu\text{m}$  alumina powder. The average alumina grain size was found to be  $7\ \mu\text{m}$ . The surface of the  $\text{ZrO}_2$  showed presence of small cracks. These cracks were on average 2-3 mm long and about 0.1 mm wide.

The required amounts of reagent-grade salts were mixed together and heated to  $150^\circ\text{C}$  under vacuum (1 kPa) for 20 h to remove moisture. The salt mixture was then melted under a chlorine atmosphere. After chlorine gas bubbling, purified argon gas was bubbled through the melt for 1-2 h to remove any dissolved chlorine. A polished plaque was placed inside the sample holder and the purified premelted salt mixture was placed on the center part of the plaque. The sample holder was placed inside the reaction tube which was evacuated and flushed with argon. The sample assembly was then heated to the required temperature. As shown in Figure 1, one thermocouple was placed above the sessile drop and another below. The temperature difference between these thermocouples was 5 K.

#### Results and Discussion

The results of the contact angle measurements are summarized in Tables I and II. Substrates made of polycrystalline alumina ( $\text{Al}_2\text{O}_3$ ), quartz ( $\text{SiO}_2$ ), and Inconel were all wetted with contact angles less than  $40^\circ$  by all the liquids investigated as shown in Table I. The measurements were carried out under an argon atmosphere and up to about 100 K above the melting

<sup>†</sup> Present address: Central-South Institute of Mining and Metallurgy, Changsha, Hunan, China.

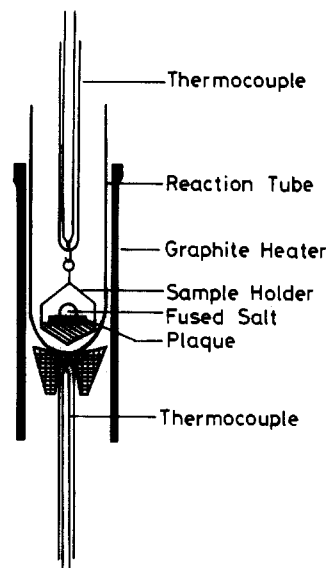


Figure 1. Sample holder.

Table I. Contact Angle of Liquid PbCl<sub>2</sub>-Alkali-Metal Chloride Mixtures on Various Solid Substrates under an Argon Atmosphere

composition, mol %				solid plaque	average	
PbCl <sub>2</sub>	KCl	NaCl	LiCl		contact angle, <sup>a</sup> deg	temp, K
100	0	0	0	Al <sub>2</sub> O <sub>3</sub>	15	823
0	100	0	0	Al <sub>2</sub> O <sub>3</sub>	15	1073
0	0	100	0	Al <sub>2</sub> O <sub>3</sub>	15	1093
0	0	0	100	Al <sub>2</sub> O <sub>3</sub>	15	923
100	0	0	0	SiO <sub>2</sub>	15	823
0	100	0	0	SiO <sub>2</sub>	15	1073
0	0	100	0	SiO <sub>2</sub>	15	1093
0	0	0	100	SiO <sub>2</sub>	15	923
40	30	0	30	SiO <sub>2</sub>	15	673
40	30	0	30	SiO <sub>2</sub>	40	693
40	30	30	0	SiO <sub>2</sub>	30	793
100	0	0	0	ZrO <sub>2</sub>	81	823
0	0	0	100	ZrO <sub>2</sub>	27	923
0	100	0	0	Inconel	15	1073
0	0	100	0	Inconel	15	1093
0	0	0	100	Inconel	22	923
100	0	0	0	BN	73	823
0	50	50	0	BN	105	953
0	50	0	50	BN	84	793
40	30	30	0	BN	130	793

<sup>a</sup> Uncertainty ±5°.

point of the salt. The surface roughness of the substrates made of ZrO<sub>2</sub> and BN caused poor reproducibility resulting in contact angles varying between 27 and 130°. Graphite substrates were the least wetted and all the liquids studied formed contact angles between 90 and 150° under an argon atmosphere. The wetting behavior was similar both on amorphous carbon and on graphite. These measurements are summarized in Table II.

The change in the contact angle with time is shown in Figure 2 for pure PbCl<sub>2</sub>, KCl, NaCl, and LiCl. In all cases, the substrate was graphite with a density of 1.87 g/cm<sup>3</sup> and the measurements were carried out under an argon atmosphere. The measurements were recorded as soon as the salt mixture was completely molten at which point the time was set at zero. The uncertainty in the contact angle measurements was ±5°.

The contact angle formed shortly after melting of the different salt mixtures was between 130 and 150° for all the chloride mixtures tested on graphite substrates. Additions of other salts such as 0.5 mol % of ZnCl<sub>2</sub> or MgCl<sub>2</sub> to a mixture of PbCl<sub>2</sub>-KCl-NaCl in the molar ratio 4/3/3 had no effect on the wetting

Table II. Contact Angle of Liquid PbCl<sub>2</sub>-Alkali-Metal Chloride Mixtures on Graphite Substrates under an Argon Atmosphere

composition, mol %				contact angle, <sup>a</sup> deg		av temp, K
PbCl <sub>2</sub>	KCl	NaCl	LiCl	max	min	
100	0	0	0	122	70	823
100	0	0	0	130	103	823
100	0	0	0	138	98	848
100	0	0	0	134	80	800
0	100	0	0	135	135	1073
0	100	0	0	132	103	1073
0	0	100	0	118	119	1093
0	0	100	0	142	133	1093
0	0	0	100	140	135	923
40	60	0	0	138	132	803
40	60	0	0	148	144	826
40	0	60	0	135	114	923
0	50	50	0	138	136	953
0	50	0	50	140	140	793
40	30	0	30	147	133	698
40	30	30	0	148	138	840
40	30	30	0	139	130	793

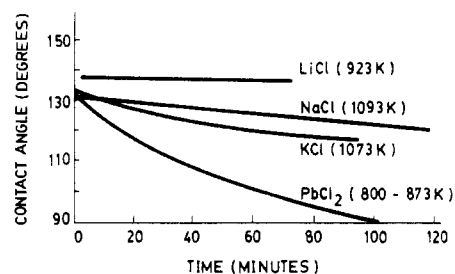
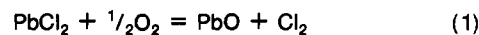
<sup>a</sup> Uncertainty ±5°.

Figure 2. Contact angle formed on graphite substrates by pure salts under an argon atmosphere.

behavior on a graphite substrate. When 1 mol % PbO was added to the chloride mixture, a strongly X-ray absorbing fluid wetted the graphite substrate at approximately 623 K while the rest of the salt mixture remained partly unmelted. This fluid was analyzed by means of X-ray diffraction and found to contain metallic lead, presumably formed by the reduction of PbO by the graphite. On further heating to 800 K, the graphite substrate was completely wetted.

The contact angles formed on melting under an argon atmosphere were between 130 and 150°. When chlorine gas was introduced, no change in the contact angle was observed. However, when air or dry air was introduced, the contact angle decreased rapidly. As shown in Figure 3, the liquid PbCl<sub>2</sub>-KCl-NaCl mixture formed a contact angle of about 130° under an argon atmosphere and as air was introduced the contact angle decreased. After about 5 min the liquid droplet had spread completely with a contact angle of about 10–20°. The most likely cause of the increased wetting is a change in the graphite substrate/melt interfacial tension due to interactions between O<sup>2-</sup> ions and the graphite substrate. The O<sup>2-</sup> ions are the result of the oxidation of PbCl<sub>2</sub> according to reaction 1, for



which the equilibrium constant is 0.023 at 800 K. Chlorine gas did not cause any change in the contact angle formed on graphite substrates which is consistent with its inertness both to graphite and to the chloride mixture.

A liquid mixture of PbCl<sub>2</sub>-KCl-NaCl with a molar ratio of 4/3/3 formed a contact angle of 130° on a BN substrate under an argon atmosphere. When dry air was introduced, only a slight decrease in the contact angle of about 15° was observed. Thus, oxygen does not significantly change the surface and

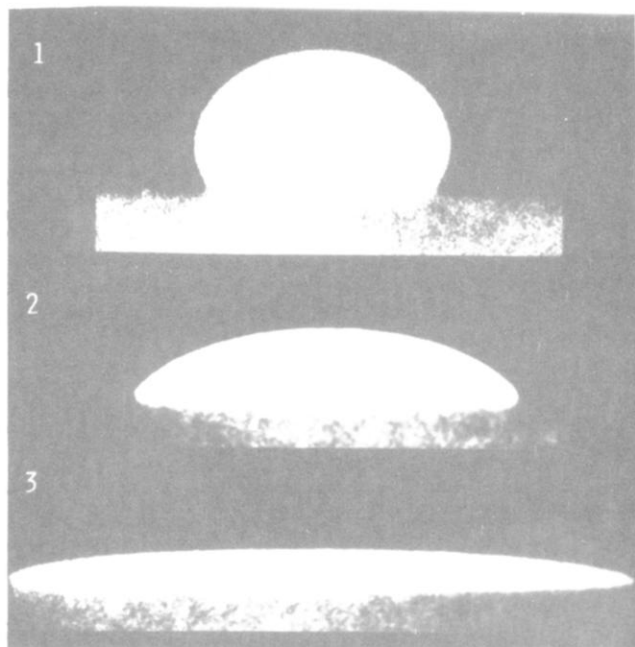


Figure 3. Sessile drop of a  $\text{PbCl}_2$ -KCl-NaCl mixture (4/3/3 molar ratio) on graphite at 793 K under (1) argon atmosphere, (2 and 3) dry air.

interfacial tensions of salt mixtures on BN substrate.

### Conclusions

1. The molten chloride mixtures studied under an argon atmosphere formed contact angles less than  $40^\circ$  on substrates made of polycrystalline alumina ( $\text{Al}_2\text{O}_3$ ), quartz ( $\text{SiO}_2$ ), and Inconel. The contact angle formed on  $\text{ZrO}_2$  varied between 27

and  $81^\circ$ , and the contact angle formed on BN varied between  $73$  and  $130^\circ$ .

2. Graphite and amorphous carbon substrates were the least wetted and under an argon atmosphere the contact angles varied between  $90$  and  $150^\circ$ .

3. The contact angles formed on graphite substrates did not change when the argon atmosphere was replaced with chlorine gas. However, when air or dry air was introduced, the contact angle decreased rapidly and complete wetting was observed after about 5 min. This effect was not observed when the graphite substrate was replaced with BN.

### Acknowledgment

We are grateful to Dr. J. E. Dutrizac for many helpful discussions.

**Registry No.**  $\text{PbCl}_2$ , 7758-95-4; KCl, 7447-40-7; NaCl, 7647-14-5; LiCl, 7447-41-8;  $\text{Al}_2\text{O}_3$ , 1344-28-1; C, 7440-44-0; BN, 10043-11-5;  $\text{ZrO}_2$ , 1314-23-4; quartz, 14808-60-7; Inconel, 12606-02-9; graphite, 7782-42-5.

### Literature Cited

- (1) Gutierrez, A.; Toguri, J. M. *J. Chem. Eng. Data* **1982**, *27*, 109.
- (2) Fujisawa, T.; Utigard, T.; Toguri, J. M. *Can. J. Chem.* **1985**, *63*, 1132.
- (3) Liu, G.; Utigard, T.; Toguri, J. M. *J. Chem. Eng. Data* **1986**, *31*, 342.
- (4) Wong, M. M.; Haver, F. P. *Symposium on Molten Salt Electrolysis in Metal Production*; Institute of Mining and Metallurgy: London, 1977.
- (5) Skeaff, J. M.; Bale, C. W.; Pelton, A. D.; Thompson, W. T. "Selection of Ternary Fused Chlorides for the Electrowinning of Lead and Zinc based on Calculations of Thermodynamic Properties"; CANMET Report 79-23, 1979.
- (6) Abramov, G. A.; Zernyakov, V. S. *J. Appl. Chem. USSR* **1950**, *23*, 1123.
- (7) Utigard, T.; Toguri, J. M. *Metall. Trans. B* **1985**, *16B*, 333.

Received for review November 8, 1985. Accepted May 8, 1986. This research was carried out under contract and with the financial support of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Contract No. 05SU.23440-1-9064, Supply and Services, Canada.

## Physicochemical Properties of Mono- and Diisocyanates

Peter J. Achorn,\* William G. Haseltine, and J. K. Miller

American Cyanamid Company, Chemical Research Division, Stamford, Connecticut 06904-0060

Liquid density, viscosity, specific heat, and vapor pressure data are reported for a new class of mono- and diisocyanates.

### Introduction

Isocyanates are well established for use in the production of foams, elastomers, coatings, adhesives, and fibers. A new series of isocyanates, shown in Table I, is commercially available. The materials are 1,3-bis(1-isocyanato-1-methylethyl)benzene [*m*-TMXDI], 1,4-bis(1-isocyanato-1-methylethyl)benzene [*p*-TMXDI], 1-(1-isocyanato-1-methylethyl)-3-(1-methylethenyl)benzene [*m*-TMI], and 1-(1-isocyanato-1-methylethyl)-4-(1-methylethenyl)benzene [*p*-TMI]. Chemically these compounds contain the isopropylidene  $(\text{CH}_2)_2\text{C}<$  group which separates the isocyanate function from the aromatic ring. In this paper we report physicochemical data for these compounds.

### Experimental Section

**Materials.** All compounds are liquids at room temperature except *p*-TMXDI which is a solid (mp  $80^\circ\text{C}$ ). Purity of the compounds was not established rigorously. Estimation by gas chromatographic analysis gave contents of the desired isomers of 99%, 99%, 98%, and 91% for *m*-TMXDI, *p*-TMXDI, *m*-TMI, and *p*-TMI, respectively. For isothermometer vapor pressure measurements, materials were further purified by freeze-pump-thaw cycles to remove volatiles. All materials are American Cyanamid Research samples.

**Liquid Density.** A PAAR DMA-10 density meter (*1*) was used to measure densities every 5 deg from 25 to  $80^\circ\text{C}$ . Temperature was regulated to  $\pm 0.1^\circ\text{C}$ . No liquid densities were determined for *p*-TMXDI as it is solid in this temperature range.

**Viscosity.** Cannon-Fenske capillary viscometers were used to measure kinematic viscosities from 25 to  $180^\circ\text{C}$ . Flow times were repeatable within 1%. Temperatures were accurate to  $\pm 2^\circ\text{C}$ . For *p*-TMXDI, viscosities were measured from