Literature Cited

(1) Hamer, W. J.; Wu, Y. C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047.
(2) Bräuer, K.; Strehlow, H. *Z. Phys. Chem. (Frankfurt am Main)* **1958**, *17*, 346.
(3) Åkerlöf, G. *J. Am. Chem. Soc.* **1930**, *52*, 2353.
(4) Åkerlöf, G.; Turck, H. E. *J. Am. Chem. Soc.* **1935**, *57*, 1746.
(5) Bates, R. G.; Robinson, R. A. "Chemical Physics of Ionic Solutions"; Wiley: New York, 1966; Chapter 12.
(6) Hills, G. J.; Ives, D. J. G. "Reference Electrodes Theory and Practice"; Academic Press: New York, 1961; Chapter 3.
(7) Bates, R. G. "Determination of pH"; Wiley: New York, 1964; Chapter 9.
(8) Sen, B.; Johnson, D. A.; Roy, R. N. *J. Phys. Chem.* **1967**, *71*, 1523.
(9) Dill, A. J.; Itzkowitz, L. M.; Popovych, O. *J. Phys. Chem.* **1968**, *72*, 4580.
(10) Dill, A. J.; Popovych, O. *J. Chem. Eng. Data* **1969**, *14*, 240.
(11) Berne, D. H.; Popovych, O. *J. Chem. Eng. Data* **1972**, *17*, 178.
(12) LaBrocca, P. J.; Phillips, R.; Goldberg, S. S.; Popovych, O. *J. Chem. Eng. Data* **1979**, *24*, 215.
(13) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions"; Butterworth: London, 1955; p 494.
(14) Feakins, D.; Voice, P. J. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1390.

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Densities and Molar Volumes of the $PbCl_2$–KCl–NaCl and $PbCl_2$–KCl–LiCl Ternary Systems

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Densities of the molten $PbCl_2$–KCl–NaCl and $PbCl_2$–KCl–LiCl systems have been measured by a bottom-balance Archimedean technique using a twin molybdenum cylinder density bob. From the measured densities, over a temperature range of 723–1131 K, molar volumes were calculated. The densities of these melts increase with increasing $PbCl_2$ content. The ternary molar volumes were found to obey approximately a simple additivity expression of the binary molar volumes of $PbCl_2$–KCl and $PbCl_2$–NaCl for the ternary $PbCl_2$–KCl–NaCl system and $PbCl_2$–KCl and $PbCl_2$–LiCl for the ternary $PbCl_2$–KCl–LiCl system.

Introduction

The introduction of strict legislation controlling the emissions of sulfur oxides and heavy metals has resulted in a number of innovative metallurgical processes. In the case of lead production from sulfides, a hydrometallurgical process has been developed by Wong and co-workers in which lead is recovered as lead chloride (*1–3*). This is then electrolyzed in a fused salt cell to obtain molten lead metal.

However, lead chloride alone is not a good electrolyte because of excessive fuming, high melting point, low conductivity, and a high solubility for lead. Marked improvement in these properties is obtained on addition of alkali chlorides. The ternary systems $PbCl_2$–KCl–LiCl and $PbCl_2$–KCl–NaCl have been suggested as possible electrolytes. Unfortunately, many of the physical properties of these ternary systems are not available. The phase diagrams of the ternary systems clearly indicate the depression of the melting point of lead chloride (501 °C) by the addition of the alkali halides (*4*). Although the densities of the respective binary systems are known, knowledge of this property within the ternary is not available (*5*). For this reason, the present study was undertaken to determine the densities of melts in the $PbCl_2$–KCl–LiCl and $PbCl_2$–KCl–NaCl systems.

Experimental Section

Apparatus. The apparatus used to measure the densities of the molten salts is similar to that described previously by Kaiura and Toguri (*6*). The method is based on Archimede's principle whereby the density of the fluid was determined by measuring the buoyant force of the liquid on twin molybdenum bobs of known volumes. This method differs from the conventional technique in that a balance is placed at the bottom to weigh the molten salt and bob.

The apparatus is shown in Figure 1. An alumina reaction tube was placed in a furnace with a constant-temperature zone of 8 cm at 800 ± 3 °C. The reaction tube was sealed at the top by a water-cooled brass end cap with a single gas outlet. A pair of brass plates and a neoprene O-ring seal combined to permit a relatively free, vertical rotational movement of the alumina thermocouple shaft supporting the density bob.

Sufficient free play was designed into the seal to allow the thermocouple shaft to act as a limited pendulum. This feature was important in detecting any contact between the wall of the crucible, which contained the fused salt, and the density bob.

The bottom of the reaction tube was fitted to a water-cooled brass assembly which also served to seal the Plexiglas balance case housing the Mettler balance. Two argon gas inlets were installed in this apparatus. The one located in the lower part of the Plexiglas case served for flushing this case and for keeping the balance at constant temperature. The other gas inlet located in the brass connection between the alumina reaction tube and the balance case was directed through an alumina tube to a position close to the sample location. Dry, purified argon gas was injected continuously through both inlets, providing a dry, oxygen-free atmosphere throughout the whole system.

An alumina sheath, containing a Pt—Pt-13% Rh thermocouple was positioned parallel to the gas inlet tube. Cast onto both of these tubes was a series of alumina radiation baffles.

The crucible platform was connected to the Mettler balance by a 10-mm diameter alumina tube which in turn was supported by a brass platform.

The heart of the density apparatus was the Mettler PL 1200 electronic top-loading balance with a rated precision of ±0.005 g and with a readability of 0.01 g. The instrument provided a new weight reading every 0.4 s, which was adequate for these experiments.

Typical dimensions of the twin molybdenum density bob are given in Figure 2. The density bob was constructed from two sections of 1.27 cm in diameter, solid molybdenum rod, with a length of 1.5 ± 0.002 cm. A chromel wire 0.025 cm in diam-

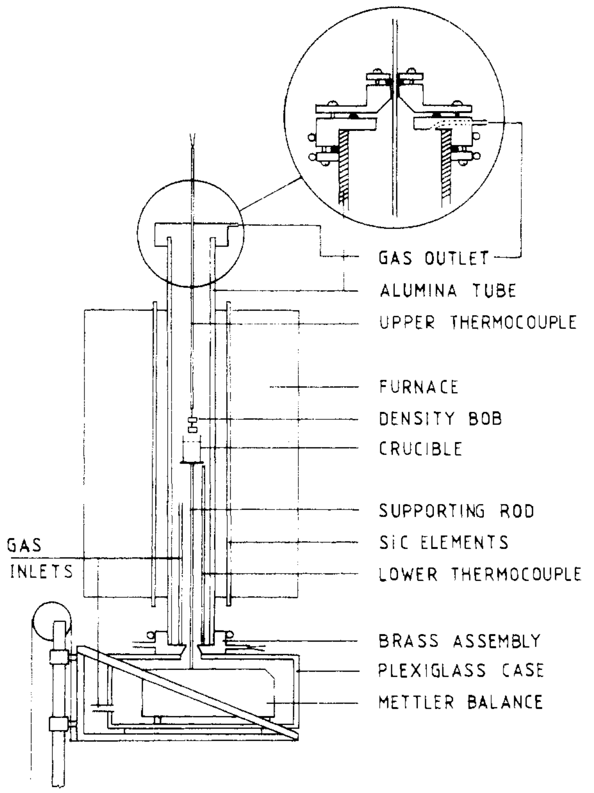

Figure 1. Density-measuring apparatus.

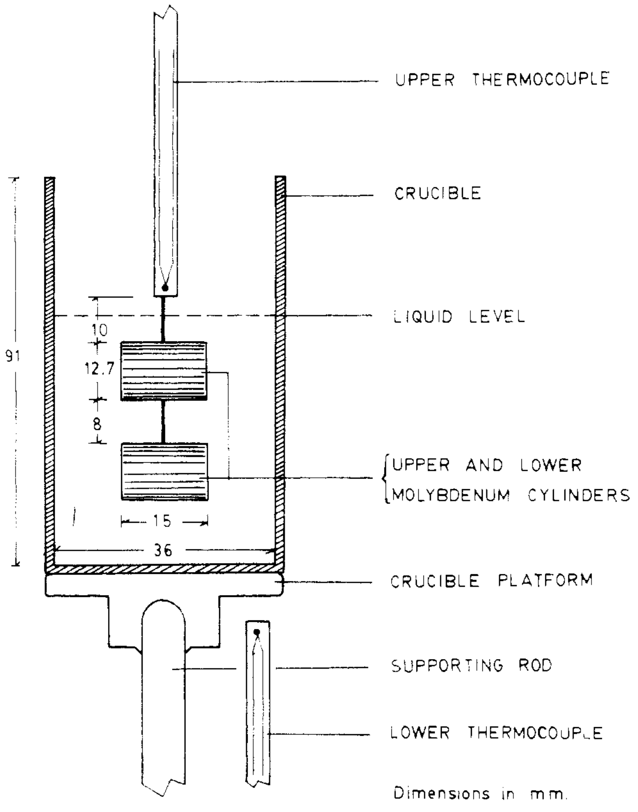

Figure 2. Density bob and crucible.

eter was used to join the bobs. The wire separated the bobs by a distance of 0.8 cm.

When both bobs were fully immersed, as shown in Figure 2, the distance separating the thermocouple junction from the liquid surface was at the most 4 mm.

Alumina, McDanel 998 ACN 100, cylindrical crucibles of 9-cm height and 100-mL capacity were used to contain the salt. A minimum liquid depth of 4.0 cm was aimed for in all cases.

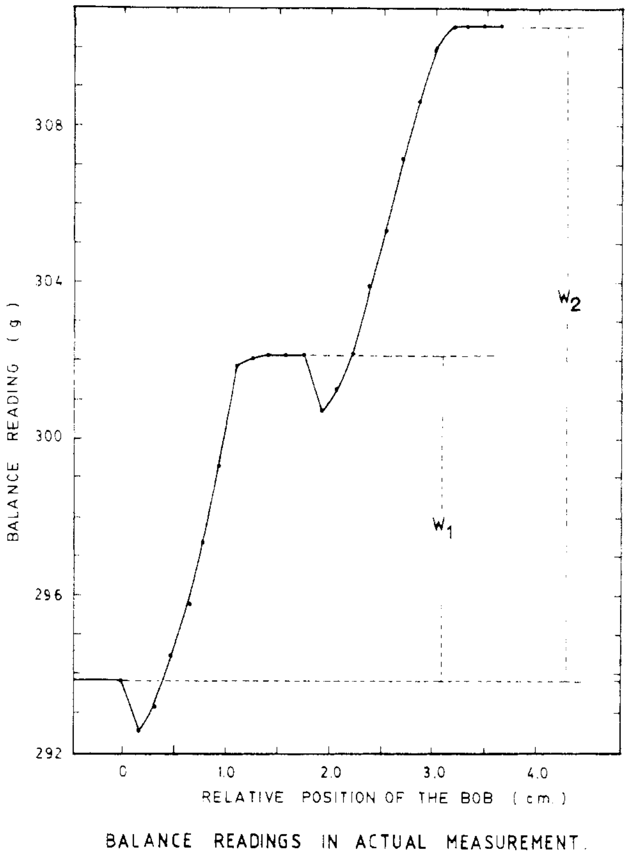

Figure 3. Density measurements.

Operating Procedure. The following procedure was adopted. The bottom balance supporting the crucible with the salt was kept in a dry atmosphere until the temperature was stabilized. Then weight recordings were obtained for the following sequence of positions of the calibrated bob: both cylinders of the density bob out, lower cylinder immersed, W_1, and both cylinders immersed, W_2. A typical balance reading vs. bob position with respect to the crucible is shown in Figure 3. A plateau occurred when the wire connecting the two bobs was at the liquid surface. W_1 and W_2 can be defined by the following relations:

$$W_1 = V_1\rho + \text{surface tension effect on wire} \qquad (1)$$

$$W_2 = (V_1 + V_2 + v)\rho + \text{surface tension effect on wire} \qquad (2)$$

where V_1 and V_2 are the volumes of the lower and upper cylinders, v is the volume of the wire joining both cylinders, and ρ is the density of the liquid.

If V_1, V_2, and v are known, the density is obtainable without knowledge of the surface tension effect on the wire, since

$$\rho = \frac{W_2 - W_1}{(V_1 + V_2 + v) - V_1} = \frac{W_2 - W_1}{V_2 + v} \qquad (3)$$

The linear thermal expansion coefficient of molybdenum is 5×10^{-6} cm/(cm deg) (*7*). Thus, the room-temperature bob volume, V_{RT}, was converted to that at the density-measuring temperature, V_T, according to the equation

$$V_T = V_{RT}[1 + (5 \times 10^{-6})\Delta T]^3 \qquad (4)$$

Error Analysis. Calibration Error. The error introduced during the calibration of the density bobs was due to the readability of the balance. The error was estimated from the average fluctuation between calibration using water and mer-

Table I. Densities (g/cm^3) of KCl-NaCl (50-50 mol %)

temp, K	this work	ref *8*	difference, %
1040	1.548	1.542	0.41
1100	1.509	1.509	0.00

cury and was found to be ±0.35%. The densities of both calibrating fluids have been well established (*7*) and were not considered as significant error sources.

Temperature Error. The difference between the temperature measured by the bob thermocouple and that of the lower thermocouple positioned below the crucible platform corresponded to ±0.3% error in the recorded sample temperature.

Balance Error. The balance readability of 0.01 g in combination with the manual recording of the weight changes during immersion of the bob translated to an error of ±0.25%.

Compositional Error. The main source of compositional error was due to the volatilization of $PbCl_2$. However, this loss was monitored by the weight loss of the sample, assuming $PbCl_2$ to be the only volatile species. The maximum compositional error due to volatilization was ±1%, as determined experimentally.

Total Error. The total estimated error in the present study is ±1.90%.

Sample Preparation. The mixing and the weighing of all salts was carried out in a drybox under an argon atmosphere. The source of the salts used was as follows.

Potassium Chloride and Sodium Chloride. Fisher ACS and USP grades were used for potassium chloride and sodium chloride, respectively. These materials were dried for 3 days under vacuum at a temperature of 130 °C and then kept in the drybox.

Lithium Chloride. 99.8% LiCl obtained from CERAC was used. The lithium chloride which was packed in an argon atmosphere was opened inside the drybox and used without further purification.

Lead Chloride. Reagent-grade $PbCl_2$ obtained from BDH was used. This material was always handled in a dry atmosphere of the drybox.

Preliminary Experiments. The density apparatus was tested by measuring the density of a 50 mol % mixture of NaCl-KCl. The results of this study are shown in Table I. Agreement with the results of Van Artsdalen and Yaffe (*8*) using the Archimedean method was excellent, the difference being 0.41% at 1040 K.

Results

The compositions of the ternary systems are expressed by the parameters *y* and *t* (*9*), as shown in Figure 4, where

$$y = 1 - X_{PbCl_2} \tag{5}$$

and

$$t = X_{MCl}/X_{MCl} + X_{KCl} \tag{6}$$

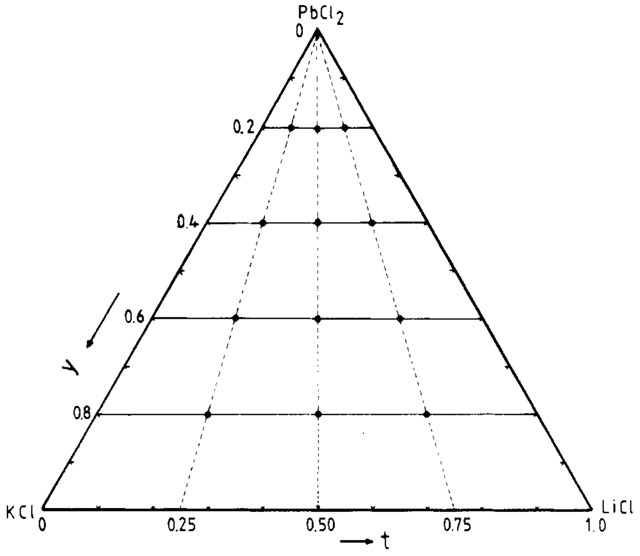

Figure 4. Pattern used for selection of composition.

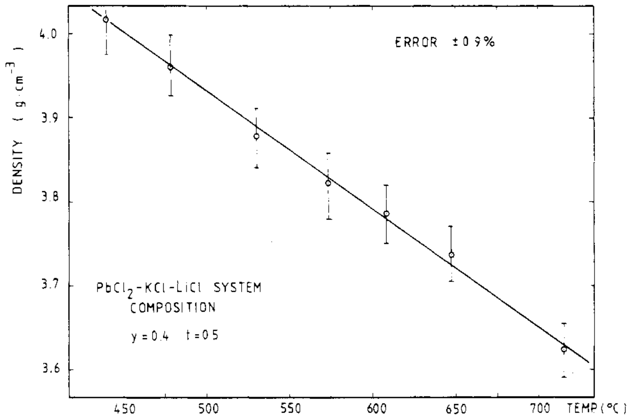

Figure 5. Typical results of density change with temperature.

where M = Li or Na. In these equations, X_i is the mole fraction of component i.

Eleven compositions in the $PbCl_2$-KCl-LiCl system were studied. Typical results are shown in Figure 5 for a composition corresponding to $y = 0.4$ and $t = 0.5$. Using a least-squares technique, we fitted the density results to a straight-line equation of the form

$$\rho = A + BT \tag{7}$$

where *A* and *B* are constants and *T* is the absolute temperature (K).

The tabulation of the constants *A* and *B*, the temperature range of the measurements, and density values predicted for certain temperatures are shown for each experimental composition in the $PbCl_2$-KCl-LiCl and $PbCl_2$-KCl-NaCl systems in

Table II. Densities for the $PbCl_2$-KCl-LiCl Ternary System

compn, mol %						density, g/cm^3							
$PbCl_2$	KCl	LiCl	*A*	10^4B	temp, °C	673 K	723 K	773 K	823 K	873 K	923 K	973 K	1073 K
80	5	15	5.578	−14.0	527–675	4.636	4.566	4.496	4.426	4.356	4.290	4.216	4.076
80	10	10	5.296	−11.0	475–622	4.556	4.501	4.446	4.391	4.336	4.281	4.226	4.116
80	15	5	5.574	−15.0	464–547	4.564	4.984	4.414	4.339	4.264	4.189	4.114	3.964
60	10	30	4.957	−12.2	527–675	4.136	4.075	4.014	3.953	3.892	3.831	3.770	3.648
60	20	20	5.015	−14.0	440–716	4.073	4.003	3.933	3.863	3.793	3.723	3.653	3.513
60	30	10	4.814	−12.5	452–683	3.972	3.909	3.847	3.784	3.722	3.659	3.597	3.472
40	45	15	4.060	−10.6	445–726	3.346	3.294	3.241	3.188	3.135	3.081	3.028	2.922
40	30	30	4.066	−9.8	502–780	3.406	3.357	3.308	3.260	3.210	3.161	3.112	3.015
40	15	45	4.195	−10.4	474–719	3.501	3.450	3.398	3.347	3.296	3.244	3.193	3.089
20	20	60	3.471	−10.9	607–735	2.737	2.683	2.628	2.514	2.519	2.465	2.411	2.302
20	40	40	2.932	−7.5	485–712	2.427	2.389	2.352	2.315	2.277	2.240	2.202	2.127

Table III. Densities for the $PbCl_2$-KCl-NaCl Ternary System

compn, mol %						density, g/cm³							
$PbCl_2$	KCl	NaCl	*A*	10^4B	temp, °C	673 K	723 K	773 K	823 K	873 K	923 K	973 K	1073 K
20	20	60	3.219	−8.2	727–852	2.667	2.626	2.585	2.544	2.503	2.462	2.421	2.339
20	40	40	3.105	−7.4	702–857	2.607	2.570	2.533	2.496	2.439	2.422	2.385	2.311
20	60	20	3.219	−10.1	717–845	2.539	2.488	2.438	2.387	2.337	2.286	2.236	2.135
42.85	14.30	42.85	4.235	−10.4	647–795	3.535	3.483	3.431	3.379	3.327	3.275	3.223	3.119
42.85	42.85	14.30	4.098	−10.5	617–795	3.391	3.338	3.286	3.233	3.181	3.128	3.076	2.971
40	30	30	3.969	−9.4	582–747	3.336	3.289	3.242	3.195	3.148	3.101	3.054	2.960
60	20	20	4.920	−13.7	487–785	3.997	3.929	3.860	3.792	3.723	3.655	3.586	3.449

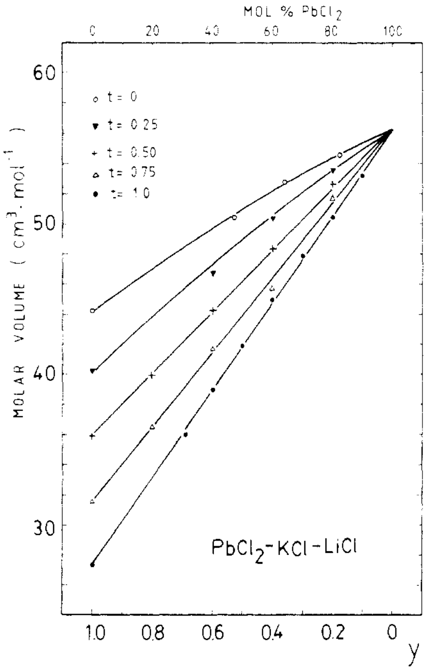

Figure 6. Molar volumes as a function of *y* at constant *t* and at 773 K.

Table IV. Molar Volumes in the $PbCl_2$-KCl-LiCl System

compn, mol %			$V = C + DT$,[a] cm³/mol	
$PbCl_2$	KCl	LiCl	*C*	*D*
80	5	15	38.500	0.0171
80	10	10	42.346	0.0134
80	15	5	39.040	0.0187
60	10	30	34.574	0.0143
60	20	20	34.614	0.0179
60	30	10	37.277	0.0169
40	15	45	31.602	0.0130
40	30	30	33.466	0.0140
40	45	15	34.423	0.0159
20	20	60	24.306	0.0159
20	40	40	32.538	0.0142

[a] *T* in K.

Table V. Molar Volumes in the $PbCl_2$-KCl-NaCl System

compn, mol %			$V = C + DT$,[a] cm³/mol	
$PbCl_2$	KCl	NaCl	*C*	*D*
60	20	20	35.876	0.0185
42.85	14.30	42.85	34.225	0.0142
40	30	30	36.186	0.0135
42.85	42.85	14.30	36.386	0.0158
20	20	60	30.656	0.0132
20	40	40	32.987	0.0129
20	60	20	30.633	0.0199

[a] *T* in K.

Tables II and III, respectively.

Discussion

From the density data, the molar volumes of the ternary mixtures were evaluated. The molar volume of the mixture, *V*, is defined by

$$V = \frac{\sum_{i}^{j} X_i M_i}{\rho} \qquad (8)$$

where M_i = molecular weight of component i.

Typical calculated molar volumes for the ternary mixtures $PbCl_2$-KCl-LiCl are shown in Figures 6 and 7 for temperatures of 773 and 973 K, respectively. In Figure 6, the molar volumes are shown as a function of *y* at constant *t*. The curves for $t = 0$ and $t = 1$ correspond to the binary systems $PbCl_2$-KCl and $PbCl_2$-LiCl, respectively, and were evaluated from the data reported by Boardman et al. (*10*) and Shevlyakova and Lantratov (*11*). In the case of the binary $PbCl_2$-alkali chloride systems, increasing positive deviations are observed with an increase in the ionic radius of the alkali cation. This positive deviation can be attributed to the stabilization of the anionic complex $PbCl_4^{2-}$ as the alkali cation radius is increased from Li^+ to Cs^+.

In both the $PbCl_2$-KCl-LiCl and $PbCl_2$-KCl-NaCl ternary systems, a linear change in molar volume with *t* was observed at constant *y*, within experimental error, as shown in Figure 7 for the case of the $PbCl_2$-KCl-LiCl system at a temperature of 973 K. The molar volumes in the KCl-LiCl binary system reported by Van Artsdalen and Yaffe (*8*) are represented by $y = 1.0$ and show an ideal behavior. Atomistically, the exchange of alkali cations K^+ for Li^+ or K^+ for Na^+ results in a linear change in molar volume, at a constant Pb^{2+} content. This can be expressed by a simple additivity relationship

$$V_{123(y)} = tV_{12(y)} + (1 - t)V_{13(y)} \qquad (9)$$

where

$V_{123(y)}$ = molar volume in the ternary system at *y*

$V_{12(y)}$ = molar volume in the 1–2 binary system at *y*

$V_{13(y)}$ = molar volume in the 1–3 binary system at *y*

A similar equation was derived by Carmichael and Flengas (*12*).

On the basis of this relationship, isovolumetric lines can be constructed over the entire liquid region of the ternary diagram at constant temperature. Typical examples are shown in Figures 8 and 9 for the $PbCl_2$-KCl-LiCl and $PbCl_2$-KCl-NaCl systems at a temperature of 773 and 973 K, respectively. The experimentally obtained molar volumes are shown by solid circles. For the binary system NaCl-$PbCl_2$, the data reported by Bloom et al. (*13*) were adopted. A summary of the calculated molar volumes is given in Tables IV and V.

Although the density data indicate that these systems are relatively simple in their physical behavior, this assumption may not be completely valid. As indicated by the emf studies of Hagemark et al. (*14*), negative deviations in $G^E_{PbCl_2}$ were observed in the $PbCl_2$-KCl-NaCl system as the $PbCl_2$-KCl binary

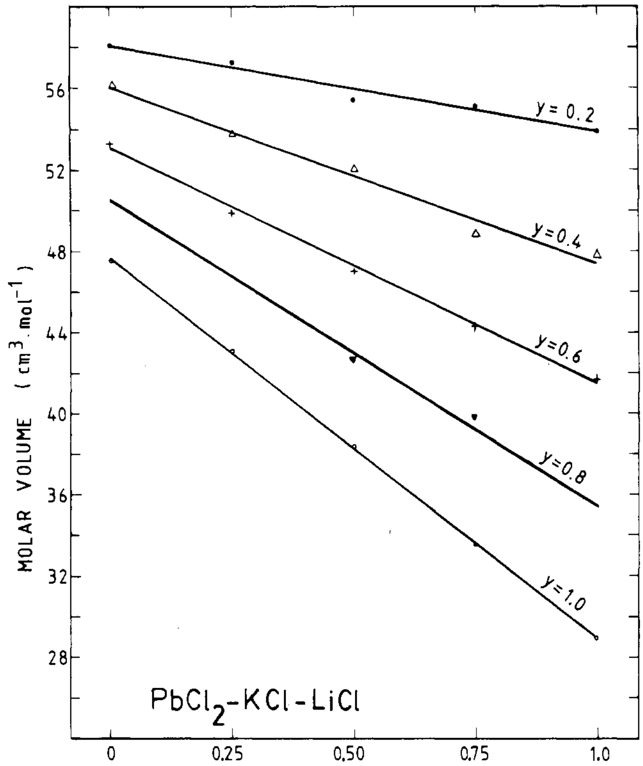

Figure 7. Molar volumes as a function of *t* at constant *y* and at 973 K.

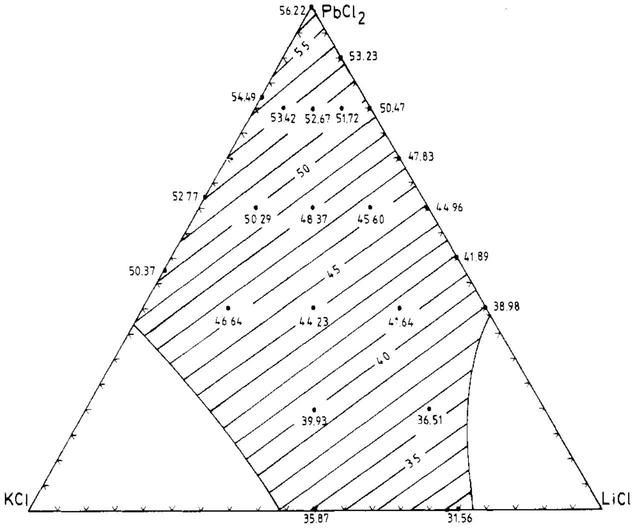

Figure 8. Isovolumetric lines in the $PbCl_2$–KCl–LiCl system at 773 K.

was approached, with the maximum deviation occurring near the 33 mol % $PbCl_2$ composition.

Conclusions

(1) A twin density bob bottom balance technique was used to determine the densities of the ternary systems $PbCl_2$–KCl–NaCl and $PbCl_2$–KCl–LiCl over the temperature range 723–1130 K. The density values were fitted to a linear expression of temperature.

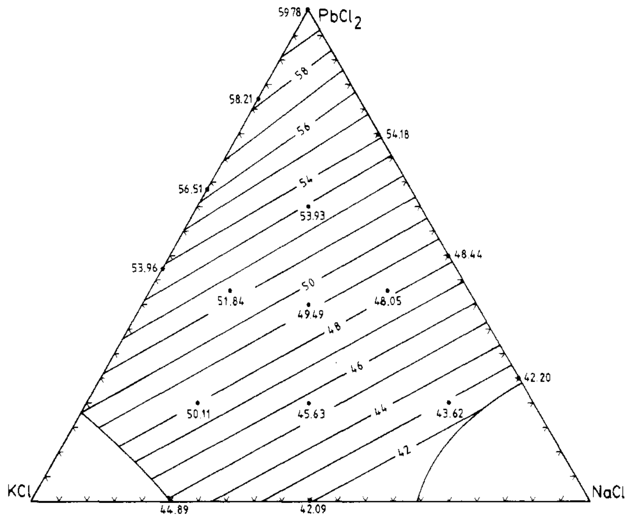

Figure 9. Isovolumetric lines in the $PbCl_2$–KCl–NaCl system at 973 K.

(2) The density data were used to calculate the molar volumes. The molar volumes were found to be additive at constant values of *y*, and their behavior could be described by the additivity rule with respect to *t*:

$$V_{123(y)} = (1 - t)V_{13(y)} + tV_{12(y)}$$

where the ternary system is designated by the subscripts 123, and the two binary systems, each containing $PbCl_2$, are denoted by the subscripts 12 and 13.

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Literature Cited

(1) Haver, F. P.; Elges, C. E.; Wong, M. M. *Rep. Invest.—U.S., Bur. Mines* **1976**, *RI 8166*.
(2) Murphy, J. E.; Haver, F. P.; Wong, M. M. *Rep. Invest.—U.S., Bur. Mines* **1974**, *RI 7913*.
(3) Wong, M. M.; Haver, F. P. "Symposium on Molten Salt Electrolysis in Metal Production"; Institute of Mining and Metallurgy: London, 1977.
(4) Levin, E. M.; Robbins, C. R.; McMurdie, H. F. "Phase Diagram for Ceramists"; American Ceramic Society, Inc.: Columbus, OH, 1964; Supplement 1969.
(5) Janz, G. J.; Tomkins, R. P. T.; Allen, C. B.; Downey, J. R.; Gardner, G. L.; Krebs, U.; Singer, S. K. *J. Phys. Chem. Ref. Data* **1975**, *4*, 871.
(6) Kalura, G. H.; Toguri, J. M. *Can. Metall. Q.* **1979**, *18*, 155.
(7) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 56th ed.; CRC Press: Cleveland, OH, 1975.
(8) Van Artsdalen, E. R.; Yaffe, I. S. *J. Phys. Chem.* **1955**, *59*, 118.
(9) Wagner, C. "Thermodynamics of Alloys"; Addison-Wesley: Reading, MA, 1952; p 15.
(10) Boardman, N. F.; Dorman, F. H.; Heymann, E. *J. Phys. Chem.* **1949**, *53*, 375.
(11) Shevlyakova, T. N.; Lantratov, M. F. *Tr. Vses. Soveshch. Fiz. Khim. Rasplavl. Solei, 2nd, 1963* **1965**, 88.
(12) Carmichael, N. R.; Flengas, S. N. *J. Electrochem. Soc.* **1979**, *126*, 2098.
(13) Bloom, H.; Boyd, P. W. O.; Laver, J. L.; Wong, J. *Aust. J. Chem.* **1966**, *19*, 1591.
(14) Hagemark, K.; Hengstenberg, D.; Blander, M. *J. Chem. Eng. Data* **1972**, *17*, 216.

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