J. Chem. Eng. Data **1982**, *27*, 105-109

Activity Coefficients and Transfer Free Energies of Potassium Chloride in Methanol-Water Solvents at 25 °C[†]

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Activity coefficients of potassium chloride were determined at 25 °C in water, methanol, and methanol-water mixtures containing 10.2, 20.6, 30.0, 40.3, 50.6, 60.3, 70.3, 80.3, and 90.2 wt % methanol from emf measurements using an ion-selective potassium electrode and a calomel electrode. The determinations were carried out at 10 or more KCl molalities varying from 10^{-3}-10^{-2} to saturation in each of the solvent media. The solubility of KCl in each of the above solvents was determined by evaporation and weighing, and the corresponding solubility (ion-activity) products were calculated. Transfer activity coefficients and transfer free energies of KCl were calculated from its solubility products and from the standard electrode potentials in water and the nonaqueous solvents.

In the study of ion-solvent interactions in methanol-water media, the activity coefficients and transfer free energies of potassium chloride are data of both fundamental and practical significance. For example, the activity coefficients of KCl may find application in the preparation of standards for the calibration of ion-selective potassium electrodes in methanol-water media. The transfer free energies of KCl represent key data required for the estimation of single-ion transfer free energies in the same solvent media. Before this work, the activity coefficients of KCl were known for aqueous solutions over a wide concentration range. The literature data were compiled and critically evaluated by Hamer and Wu (*1*). For anhydrous methanol solutions, the activity coefficients of KCl were available at 7 concentrations, ranging from 10^{-3} M to the saturated solution of 5.6×10^{-2} M (*2*). However, for water-methanol mixtures, the corresponding literature data were not satisfactory. In a 1930 article, Åkerlöf (*3*) reported activity coefficients of KCl at four molatities (0.02, 0.05, 0.10, and 0.50 *m*) in 10, 20, 30, 40, 50, and 60 wt % methanol and at the three lower molalities at 70, 80, and 90 wt % methanol. They were derived from the emf measurements of amalgam double cells, which yield ratios of activity coefficients in two half-cells. Unfortunately, the article failed to explain how the individual activity coefficients were evaluated from such ratios. Considering this uncertainty, the paucity of data, and the fact that no activity coefficients were reported for the saturated solutions, in which we were primarily interested, our first objective became the determination of the activity coefficients of KCl over the entire range of methanol-water solvents at a minimum of 10 KCl concentrations, including the saturated solution, in each solvent medium. By employing an ion-selective potassium electrode, we hoped to avoid the errors associated with the amalgam electrodes. Water and anhydrous methanol were included so as to check our results against existing literature data, particularly since ion-selective electrodes have been little tested for this type of work.

In the present study, the activity coefficients were derived from the emf measurements on a galvanic cell composed of an ion-selective potassium glass electrode and a calomel electrode in solutions covering a KCl concentration range from 10^{-3}-10^{-2} *m* through saturation. Because the compositions of the methanol-water mixtures for which KCl solubilities were available in the literature (*4*) did not correspond in general to the solvent compositions employed in this study, the solubilities were determined by us, rather than by interpolation of the literature data. Saturated solutions had to be prepared for the emf measurements anyway. The solubility (ion-activity) products of KCl in each of the methanol-water media were calculated as products of the molal solubility, m_{satd}, and $\gamma_{\pm\mathrm{satd}}$, the mean molal activity coefficient of KCl characteristic of the saturated solution:

$$K_s = (m_{\mathrm{satd}}\gamma_{\pm\mathrm{satd}})^2 \qquad (1)$$

The transfer activity coefficients (medium effects) of KCl, $\log {}_m\gamma_\pm^2$ can be calculated from the relationship

$$\log {}_m\gamma_\pm^2 = \log {}_wK_s - \log {}_sK_s \qquad (2)$$

where ${}_wK_s$ and ${}_sK_s$ are the solubility products in water and in a nonaqueous solvent, respectively. Alternatively, $\log {}_m\gamma_\pm^2$ for KCl can be determined from the $E°$'s of a galvanic cell reversible to K^+ and to Cl^- ions, such as cell I:

$$\log {}_m\gamma_\pm^2(\mathrm{KCl}) = ({}_sE° - {}_wE°)/0.05916 \qquad \text{(at 25 °C)} \qquad (3)$$

where ${}_wE°$ and ${}_sE°$ are the standard potentials in water and the nonaqueous solvents, respectively. Since the $E°$ of a potassium glass electrode varies for different electrodes, it is possible to apply eq 3 only if the identical glass electrode was used for both measurements. At 25 °C, the standard free energy for the transfer of KCl from water to a nonaqueous medium, $\Delta G_t°$, is given in kcal mol^{-1} by

$$\Delta G_t° = 1.364 \log {}_m\gamma_\pm^2 \qquad (4)$$

Experimental Section

Materials. Potassium chloride (ACS reagent grade from Hall Laboratories Reagents) was recrystallized from deionized water and dried for 24 h in a vacuum oven at 100 °C. For the preparation of methanol-water mixtures, certified ACS spectranalyzed methanol (Fisher Scientific Co.) was used without further purification. At 25 °C, it had a density of 0.7865 g/mL, which agreed well with the literature value of 0.7866 g/mL (*5*). To prepare anhydrous methanol, we refluxed the above commercial solvent over aluminum amalgam for 25 h and then distilled it through a 30-cm Vigreux column, collecting the middle 3 L of a 4-L charge. The portion collected had a density of 0.7862 g/mL at 25 °C.

Methanol-water mixtures were prepared by combining appropriate volumes of the methanol and deionized water. The densities of the mixtures were determined gravimetrically in quadruplicate by using class A 100-mL volumetric flasks. The precise weight-percent composition of each mixed solvent was interpolated from a large-scale plot of density vs. weight percent methanol prepared from literature data (*5*).

Electrodes. The potassium ion-selective electrode was a K/NH_4 Selectro-Mark Electrode No. 1018 from Markson Science, Inc. The calomel electrode was homemade according

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[†] Taken in part from the dissertation submitted by Lillian Malahias in partial fulfillment of the requirements for the degree of Master of Arts at Brooklyn College of the City University of New York.

0021-9568/82/1727-0105$01.25/0

Table I. Molality-Emf Data for KCl at 25 °C

m	E_{I},[a,b] V	E_{II},[a,b] V	m	E_{I},[a] V	m	E_{I},[a,b] V	E_{II},[a,b] V	m	E_{I},[a] V
Water									
0.02082	−0.1308	−0.0854	0.02239	−0.1920	1.7974	+0.0761	+0.1219	4.683	+0.0607
0.05184	−0.0868	−0.0421	0.05005	−0.1535	2.0538	+0.0830	+0.1281	4.788	+0.0622
0.1050	−0.0542[c]	−0.0084[c]	0.1096	−0.1172	2.4900	+0.0923	+0.1373		
0.3620	+0.0012	+0.0012	0.2056	−0.0873	3.0419	+0.1021	+0.1472		
0.5104	+0.0182[c]	+0.0639	0.5223	−0.0457	3.5165	+0.1099	+0.1545		
0.6459	+0.0282	+0.0748	1.0420	−0.0016	4.0075	+0.1175	+0.1626		
0.7981	+0.0380	+0.0848	1.3866	+0.0117	4.3632	+0.1219	+0.1661		
1.0296	+0.0500	+0.0961	1.8208	+0.0292	4.6998	+0.1260	+0.1710		
1.2597	+0.0470[c]	+0.1051	2.5873	+0.0407	4.788	+0.1272	+0.1721		
1.4133	+0.0652	+0.1108	4.0563	+0.0532					

m	E_{I}, V	m	E_{I}, V	m	E_{I}, V	m	E_{I}, V
10.2 wt % MeOH							
1.590×10^{-3}	−0.3103	0.06083	−0.1337	1.2044	+0.0049	2.9294	+0.0492
5.688×10^{-3}	−0.2453	0.1288	−0.0989	1.8881	+0.0273	3.6052	+0.0604
9.792×10^{-3}	−0.2204	0.6488	−0.0239	2.5068	+0.0409	3.8748	+0.0642
0.02008	−0.1867						
20.6 wt % MeOH							
0.01850	−0.1776	0.2521	−0.0553	1.4650	+0.0349	2.5651	+0.0512
0.06286	−0.1191	0.4923	−0.0250	1.9699	+0.0383	2.7231	+0.0542
0.09859	−0.0981	0.9758	+0.0069	2.2448	+0.0446	2.8642	+0.0567
30.0 wt % MeOH							
5.473×10^{-3}	−0.2109	0.09862	−0.0748	1.2347	+0.0379	1.9085	+0.0580
0.01084	−0.1771	0.2515	−0.0331	1.5001	+0.0471	2.0683	+0.0618
0.02407	−0.1398	0.4915	−0.0030	1.7278	+0.0537	2.1294	+0.0621
0.05062	−0.1049	0.9494	+0.0256				
40.3 wt % MeOH							
3.915×10^{-3}	−0.2098	0.05078	−0.0885	0.4995	+0.0129	1.3371	+0.0563
5.994×10^{-3}	−0.1898	0.1009	−0.0585	0.991	+0.0431	1.4036	+0.0586
0.01059	−0.1612[c]	0.2569	+0.0159	1.2527	+0.0531	1.5109	+0.0621
0.02047	−0.1304						
50.6 wt % MeOH							
1.769×10^{-3}[c]	−0.2278	0.01921	−0.1109	0.2475	+0.0019	0.8925	+0.0568
6.710×10^{-3}[c]	−0.1622	0.05374	−0.0652	0.4985	+0.0321	0.9512	−0.0599
9.858×10^{-3}	−0.1430	0.1005	−0.0372	0.7561	+0.0499	1.0062	+0.0620
60.3 wt % MeOH							
1.960×10^{-3}	−0.1981	0.02135	−0.0852	0.09865	−0.0186	0.5503	+0.0549
5.008×10^{-3}	−0.1552[c]	0.05395	−0.0446	0.2586	+0.0231	0.6097	+0.0592
1.192×10^{-2}	−0.1106	0.07456	−0.0305	0.4705	+0.0486	0.6457	+0.0618
70.3 wt % MeOH							
1.996×10^{-3}	−0.1728	0.02142	−0.0604	0.09863	+0.0060	0.3054	+0.5038
4.943×10^{-3}	−0.1292[c]	0.05107	−0.0221	0.1821	+0.0318	0.3517	+0.0589
8.794×10^{-3}	−0.1020	0.07528	−0.0425	0.2551	+0.0461	0.3728	+0.0618
0.01006	−0.0954						
80.3 wt % MeOH							
2.087×10^{-3}	−0.1436	0.01173	−0.0621	0.09914	+0.0311	0.1726	+0.0536
6.159×10^{-3}	−0.0918	0.01966	−0.0387	0.1202	+0.0391	0.1894	+0.0580
9.339×10^{-3}	−0.0725	0.05134	+0.0031	0.1517	+0.0489	0.2106	+0.0621
90.2 wt % MeOH							
2.130×10^{-3}	−0.1131	9.810×10^{-3}	−0.0427	0.06157	+0.0371	0.1011	+0.0578
4.971×10^{-3}	−0.0736	0.02034	−0.0100	0.07483	+0.0452	0.1159	+0.0618
9.810×10^{-3}	−0.0460	0.04136	+0.0203	0.09118	+0.0529		
100% MeOH							
2.117×10^{-3}	−0.0629	0.01267	0.0170	0.05151	0.0761	0.6710	0.0868
4.908×10^{-3}	−0.0248	0.02007	0.0379	0.6166	0.0829	0.0707	0.0879
7.427×10^{-3}	−0.0058	0.03613	0.0621				

[a] I and II denote galvanic cells I and II. [b] Corresponds to the use of a K^+ electrode from Thomas Technological Services vs. the K^+ electrode from Markson Science, Inc., used to obtain the remaining measurements. [c] Values have been omitted from polynomial curve-fitting program.

to a method similar to that described by Hills and Ives (*6*). It was constructed from a piece of borosilicate glass tubing with an S12/18 male joint on one end and a sealed base on the other, with a platinum wire 2 mm in diameter and about 3 mm in length sealed into the base to make contact with the solution. The paste of mercury mixed with mercurous chloride placed at the bottom of the electrode was exposed to the solution through two openings 8 mm in diameter located on opposite sides of each other 1.5 cm from the base. The glass tubing was filled with mercury and the external connection was made by means of a platinum wire. The silver-silver chloride electrodes were prepared by the thermal-electrolytic method as described by Bates (*7*). All electrodes were fitted tightly into the glass joints with the aid of vinyl adapters.

Measurements. A minimum of 10 KCl solutions varying in concentration from 10^{-3} m to saturation were prepared by weight, correcting for the buoyancy. Solutions in anhydrous methanol were prepared, transferred, and stored inside a drybox. Before emf measurements, the solutions were equilibrated in a constant-temperature bath controlled to 25.00 ± 0.01 °C by a Yellow Springs Instrument Co. Model 72 proportional temperature controller, and subsequently the galvanic cell was thermostated in the same bath during the measurements. The potassium glass electrode was stored overnight in the most dilute KCl solution in the solvent to be used the next day. Reproducibility studies have shown the conditioning of the electrode in different methanol–water media to be fully reversible. The emf measurements were obtained on an Instrumentation Laboratory DELTA-matic Model 135A pH/mV electrometer. Voltage readings were taken as final when they were constant to about 0.3 mV, which is the limit of precision for this instrument. More precise voltage measurements would be futile in view of the inherent uncertainties in the electrode behavior in nonaqueous media. Saturated solutions of KCl in the methanol–water solvents were prepared by shaking excess solid KCl in each solvent on a Burrel wrist-action shaker in water-jacketed flasks through which water was circulated from a bath maintained as described above at 25.00 ± 0.01 °C. Aliquots of the saturated solutions were weighed, evaporated to dryness in a vacuum oven at 60 °C, and heated until the KCl residue attained a constant weight. Generally, the reproducibility of the solubility determination was of the order of 1%. Usually, 1 week of equilibration was sufficient for saturation. In each medium, the solubilities were determined in octuplicate.

Results and Discussion

Emf Data and Activity Coefficients. In all of the solvents, emf measurements were made on cell I

$$\mathrm{Hg(l);Hg_2Cl_2(s)|Cl^-,K^+|K(glass)} \qquad \text{(I)}$$

the potential of which, E_{I}, is given in volts by

$$E_{\mathrm{I}} = E^\circ_{\mathrm{I}} + 0.1183 \log m + 0.1183 \log \gamma_\pm \qquad (5)$$

where $E^\circ_{\mathrm{I}} = E^\circ_{\mathrm{K(glass)}} - E^\circ_{\mathrm{calomel}}$, m is the molality, and $\gamma_\pm$ is the mean molal ionic activity coefficient of KCl. In aqueous solutions, the emf measurements were repeated on cell II

$$\mathrm{Ag(s);AgCl(s)|Cl^-,K^+|K(glass)} \qquad \text{(II)}$$

for which the Nernst equation is identical in form with eq 5, except that here $E^\circ_{\mathrm{II}} = E^\circ_{\mathrm{K(glass)}} - E^\circ_{\mathrm{AgCl}}$. The molality–emf data are shown in Table I. In order to evaluate the E° and $\gamma_\pm$, eq 5 is rearranged and log $\gamma_\pm$ is formulated as a polynomial in $I^{1/2}$, where I is the ionic strength:

$$E - 0.1183 \log m = E^\circ - 0.1183 A_1 I^{1/2} - 0.1183 A_2 I - 0.1183 A_3 I^{3/2} - \ldots \qquad (6)$$

This amounts to expressing the activity coefficient as

$$-\log \gamma_\pm = A_1 I^{1/2} + A_2 I + A_3 I^{3/2} + \ldots \qquad (7)$$

The above formulation of activity coefficients was applied successfully in the past in the interpretation of emf (*8*,*9*) and solubility (*10*–*12*) data. A plot of the left-hand side of eq 6 vs. $I^{1/2}$ yields the value of E° at zero ionic strength. Analyzing our data according to eq 6 by a polynomial curve-fitting program on an IBM 370-145 computer, we obtained values of the E° as well as the A coefficients characteristic of KCl in each solvent medium. First- through fourth-order polynomials were tried, and the best fit was chosen on the basis of smallest error for the E°. The results of the curve-fitting computations are listed in Table II. Duplicate determinations showed the E° to be reproducible to the order of magnitude of 0.1 mV in water, but only to 1 mV in 80.3 wt % methanol. Of course, the E°'s reported here should not be considered as "standard values" applicable to all potassium glass electrodes. The E°'s of individual potassium glass electrodes differ from each other, as do the E°'s of the more familiar pH glass electrodes. However, this represents no drawback in the determination of activity coefficients, which requires the constancy not of the E°, but of the term $E - E^\circ$ for a given solution.

Table II. Results of Polynomial Curve-Fitting Computations Using Eq 5

wt % MeOH	E° [a]	A_1	A_2	A_3
0 (water)	0.0088_5 (I)	0.3498	−0.1578	0.02084
	0.0738 (I)[b]	0.3115	−0.0996	
	0.0737	0.3069	−0.1076	
	0.1185 (II)[b]	0.3381	−0.1655	0.02903
10.2	0.0218 (I)	0.4070	−0.2417	0.04846
20.6	0.0341	0.4197	−0.2465	0.05458
30.0	0.0617	0.6099	−0.4588	0.1305
40.3	0.0808	0.7405	−0.6542	0.2268
50.6	0.1038	0.8331	−0.7904	0.3132
60.3	0.1280	1.066	−1.2295	0.5957
70.3	0.1513	0.9764	−1.0828	0.6167
80.3	0.1807	1.252	−1.7751	1.294
	0.1796	1.191	−1.5667	1.0392
90.2	0.2119	1.830	−4.499	5.778
100	0.2646	2.387	−7.460	0.1248

[a] I and II denote galvanic cells I and II. [b] Corresponds to the use of K$^+$ electrode from Thomas Technological Services vs. the K$^+$ electrode from Markson Science, Inc., used to obtain the remaining measurements.

Table III. Comparison of the Activity Coefficients of KCl from This Study with Their Literature Values in Aqueous Solutions at 25 °C

	$\gamma_\pm$		
m	calcd from cell I	calcd from cell II	from ref *13*[a]
0.02082	0.896		
0.05184	0.847	0.847	
0.1050	0.789	0.806	0.770
0.3620	0.672	0.705	0.674
0.5104	0.664	0.677	0.649
0.6459	0.637	0.661	0.631
0.7981	0.624	0.650	0.617
1.0296	0.611	0.628	0.602
1.2597	0.594	0.611	0.591
1.4133	0.599	0.609	0.585
1.7974	0.582	0.595	0.576
2.0538	0.581	0.587	0.572
2.4900	0.575	0.579	0.569
3.0419	0.570	0.575	0.569
3.5165	0.574	0.573	0.572
4.0057	0.584	0.579	0.577
4.3632	0.584	0.589	0.581
4.6998	0.587	0.591	0.586
4.79	0.592	0.593	0.588

[a] Interpolated values.

Once the A coefficients characteristic of KCl in a given solvent are known, $\gamma_\pm$ values at any ionic strength can be calculated from eq 7. Alternatively, at the specific molalities for which the emf data are available, the activity coefficients can be calculated more simply from eq 5 and the known E°. Where our results could be compared with reliable literature values (i.e., for pure water and anhydrous methanol), the latter method yielded better agreement. Table III lists the activity coefficients for aqueous solutions obtained in this study from the emf of cells I and II and compares them with the literature data (*13*) interpolated at the molalities employed here. In

Table IV. Solubilities of Potassium Chloride in Methanol-Water Solvents at 25 °C from This Study

wt % MeOH	$m_{\text{satd}} \pm$ SD	$\gamma_{\pm\text{satd}}$[a]	K_s[e]
0 (water)	4.79 ± 0.02 4.826 (4)	0.591[b] 0.591[b,c] 0.596[b,c] 0.593[c,d]	8.01
10.2	3.87 ± 0.03	0.589	5.21
20.6	2.87 ± 0.02	0.542	2.41
30.0	2.13 ± 0.02	0.473	1.01
40.3	1.51 ± 0.02	0.460	0.483
50.6	1.01 ± 0.01	0.441	0.197
60.3	0.646 ± 0.007	0.427	7.60×10^{-2}
70.3	0.373 ± 0.002	0.470	3.07×10^{-2}
80.3	0.211 ± 0.001	0.472 0.482	9.88×10^{-3}
90.2	0.1168 ± 0.0005	0.465	2.95×10^{-3}
100.0	0.0707 ± 0.0006 0.0707 (4) 0.071 (2)	0.454 0.455 (2)	1.03×10^{-3}

[a] From eq 5. [b] Cell I. [c] K^+ electrode from Technological Services. [d] Cell II. [e] From eq 1.

general, the results derived from cell I (calomel electrode) agree much better with the literature values than do the results from cell II (silver-silver chloride electrode). This is not surprising, as the AgCl equilibria in chloride solutions are complicated by the formation of soluble complexes. Consequently, cell I was used exclusively for the nonaqeous solvent media.

Solubility Products and Transfer Free Energies. Table IV summarizes the molal solubilities of KCl in methanol-water solvents determined in this study, the activity coefficients of KCl in the saturated solutions calculated from eq 5, and the corresponding solubility (ion-activity) products calculated from eq 1. Literature data available for water and anhydrous methanol are included for comparison. The reproducibility of the $\gamma_\pm$ values in the saturated solutions is illustrated by the results of four separate determinations in aqueous solutions involving three different electrode pairs. Similarly, two separate determinations are compared in the case of 80.3 wt % methanol.

Transfer activity coefficients of KCl calculated from the solubility products and the $E°$'s according to eq 2 and 3, respectively, and the corresponding transfer free energies calculated from eq 4 are shown in Table V for the specific solvent compositions employed here. The good agreement between the transfer free energies calculated from the $E°$'s and those obtained from the solubility products suggests that the potassium glass electrode employed here behaved in a thermodynamically consistent manner upon transfer from water to methanol-water media. In addition, we list the values interpolated from our data at other solvent compositions, to enable a comparison with the literature results (*3*, *14*). The latter were evaluated from the emf of cells with potassium-amalgam electrodes. A drawback in the literature methods is the well-known corrosion error associated with amalgam electrodes in methanol-water media (*2*). Therefore, the transfer free energies determined in this study from the solubilities and experimental values of activity coefficients as well as those obtained directly from the standard potentials are likely to be more reliable.

Glossary

A_1, A_2, A_3	coefficients of power terms of $I^{1/2}$ in eq 6
E	emf, V
$E°$	standard potential, V
${}_sE°$	standard potential in a nonaqueous solvent, V
${}_wE°$	standard potential in water, V
$\Delta G_t°$	standard free energy for the transfer (of KCl) from water to a nonaqueous medium, kcal/mol
I	ionic strength, mol/(kg of solvent)
${}_sK$	solubility product, mol²/(kg of solvent)²
${}_sK_s$	solubility product in a nonaqueous solvent, mol²/(kg of solvent)²
${}_wK_s$	solubility product in water, mol²/(kg of solvent)²
m	mol/(kg of solvent)
m_{satd}	mol/(kg of solvent) in a saturated solution (molal solubility)
M	mol/(L of solution)

Greek Letters

${}_m\gamma_\pm^2$	transfer activity coefficient (medium effect) of a 1:1 electrolyte
$\gamma_\pm$	mean ionic activity coefficient (molal scale)
$\gamma_{\pm\text{satd}}$	mean ionic activity coefficient in a saturated solution (molal scale)

Table V. Transfer Activity Coefficients and Transfer Free Energies of KCl in Methanol-Water Solvents at 25 °C

			$\Delta G_t°$, kcal/mol			
	log ${}_m\gamma_\pm^2$ (KCl) (this study)		this study			
wt % MeOH	from solubility[d]	from $E°$'s[e]	from solubility	from $E°$'s	ref *3*[b]	ref *14*
10.0			0.250[a]	0.281[a]	0.233	0.407
10.2	0.187	0.219	0.255	0.299		
20.0			0.690[a]	0.554[a]	0.470	0.855
20.6	0.521	0.427	0.711	0.583		
30.0	0.897	0.894	1.22	1.22	0.720	
40.0			1.65[a]	1.65[a]	1.00	1.72
40.3	1.22	1.22	1.66	1.66		
50.0			2.15[a]	2.15[a]	1.270	
50.6	1.61	1.61	2.20	2.19		
60.0			2.74[a]	2.74[a]	1.642	2.73
60.3	2.02	2.02	2.76	2.75		
70.0			3.26[a]	3.26[a]	2.051	
70.3	2.42	2.41	3.30	3.29		
80.0			3.98[a]	3.93[a]	2.545	3.97
80.3	2.91	2.90	3.97	3.96		
90.0			4.65[a]	4.65[a]	3.147	
90.2	3.43	3.43	4.68	4.68		
99			5.25[a]	5.75[a]		5.31
100	3.89	4.32	5.31	5.90		5.33[c]

[a] Interpolated value. [b] Calculated from the literature values of log ${}_m\gamma_\pm^2$ via eq 4. [c] Extrapolated value. [d] Equation 2. [e] Equation 3.

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Received for review June 15, 1981. Revised October 30, 1981. Accepted November 20, 1981. This research was supported in part by Grant No. 13138 from the PSC-CUNY Research Award Program of the City University of New York.

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-

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