Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous Mixtures of Potassium Chloride and Magnesium Sulfate up to High Concentrations at 25 °C

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The osmotic coefficients of aqueous mixtures of KCl and $MgSO_4$ have been measured by the isopiestic method at 25 °C. These measurements extend from moderate concentrations to the crystallization limits of the mixtures. Single electrolyte values for $MgSO_4$ are in good agreement with available literature data. Both Pitzer's equations and Scatchard's neutral electrolyte equations represent well the experimental data over the entire concentration range. Also, with these equations mean molal activity coefficients for KCl and $MgSO_4$ were calculated and compared.

Introduction

The thermodynamic properties of concentrated mixed electrolyte solutions are of great importance for industrial, geochemical, as well as chemical applications. Especially the activity coefficients are of interest in understanding chemical reactions and dissolution behavior or in testing of thermodynamic solution models.

Activity data are available for a great number of mixed electrolyte solutions (*1*, *2*). However, the concentration range is mostly limited to ionic strengths for which data of the constituent binary solutions exist, because standard methods for treating experimental values require these binary data. But the ionic strength of the mixtures can become much higher than that of the least soluble component in its binary solution. Therefore, only few reliable measurements at higher concentrations up to the solubility limits of the mixed solutions are available (*3*, *4*). However, for modeling the solubility behavior or other important processes activity coefficients are required up to saturation.

Recently Rard and Miller (*3*) published activity data for NaCl–$SrCl_2$ mixtures of ionic strengths from 6.7 to 11.2 mol·kg^{-1}. It was shown that Scatchard's neutral electrolyte treatment well represents the experimental data over the entire concentration range. On the other hand, Harvie and Weare (*5*) developed a thermodynamic model of the seawater systems for predicting mineral solubilities from zero to high ionic strengths. This model utilizes the activity coefficient equations of Pitzer (*1*). The calculated solubilities and phase diagrams are in excellent agreement with published experimental results. In addition, de Lima and Pitzer (*6*, *7*) calculated activity coefficients of NaCl in mixtures with KCl, CsCl, and Na_2SO_4 at saturation on the basis of Pitzer's equations. They also found reasonable agreement between calculated values and activity coefficients evaluated from solubility data.

This paper deals with isopiestic measurements performed for the ternary system KCl–$MgSO_4$–H_2O from moderate concentrations up to the solubility limits to test Scatchard's and Pitzer's equations for reliability at high concentrations in a mixture without a common ion (reciprocal salt pair) and with relatively complex and strong interactions.

Experimental Section

The isopiestic apparatus used in this work consists of glass vacuum desiccators. Each contains a stainless steel block and a copper disk, 10 cm in diameter and 0.8 cm thick. The dishes are made from chemical resistant stainless steel and have smoothly finished bottoms providing good thermal contact to the copper disk. Tightly fitting plastic caps were added, when the cups were removed from the desiccator for weighing. The measuring procedure was the same as described in the literature (*8*). Duplicate samples of the mixtures and the KCl reference solution were equilibrated at 25.00 ± 0.02 °C (in the thermostated bath) for 7 days to 2 weeks. The molalities at isopiestic equilibrium agreed to better than ±0.06% of the average of both solutions. Vacuum corrections were made for all masses.

The KCl reference solutions were prepared by direct weighing of oven-dried, recrystallized, analytical-grade KCl and deionized distilled water. Doubly recrystallized analytical-grade $MgSO_4 \cdot 7H_2O$ was used for the preparation of the $MgSO_4$ stock solution. The concentration was determined by dehydration analysis yielding 2.6060 ± 0.0013 mol·kg^{-1}. The cited uncertainty is the average deviation for triplicate analyses. The mixed solutions were prepared from weighed amounts of $MgSO_4$ stock solution, KCl, and water. The highest concentrations investigated were obtained by removal of water from the samples during evacuating air from the desiccators. After each high-concentration run the samples were examined for crystals, because $MgSO_4$ has a tendency to form supersaturated solutions. Results from samples with crystallization are not considered.

Both KCl and $MgSO_4$ were analyzed for impurities by using atomic absorption spectrometry (Mg, Ca) and flame photometry (Na, K, Ba). The KCl contained by weight ~20 ppm Na, ~20 ppm Mg, <3 ppm Ca, and Ba was below its 20 ppm detection limit. For $MgSO_4$ there was found <4 ppm Na, <3 ppm Ca, ~30 ppm K, and the content of Ba was also below its detection limit.

Experimental results are reported in Table I. Index A denotes KCl and B $MgSO_4$. The ionic strength fraction of KCl is given by

$$y_A = m_A/(m_A + 4m_B) \tag{1}$$

and the total ionic strength I is calculated by

$$I = m_A + 4m_B \tag{2}$$

The corresponding equilibrium ionic strengths of the KCl-reference solutions are also listed in Table I, and the osmotic coefficients were taken from Hamer and Wu (*9*) taking into consideration the corrections by Rard et al. (*10*).

Table I. Isopiestic Ionic Strengths of $MgSO_4$ and KCl (A)–$MgSO_4$ (B) Mixtures in Relation to the Ionic Strengths and Osmotic Coefficients of the KCl Reference Solutions at 25 °C

$I/(\mathrm{mol{\cdot}kg^{-1}})$							
$y_A = 0$	$y_A = 0.04870$	$y_A = 0.09623$	$y_A = 0.25270$	$y_A = 0.46361$	$y_A = 0.75046$	$I^*_{KCl}/(\mathrm{mol{\cdot}kg^{-1}})$	Φ^*_{KCl}
	11.6873	10.5950			4.2137	3.4154	0.9465
	11.6548	10.5636			4.1869	3.3943	0.9462
11.9404	10.6503	9.5473			3.6145	2.9272	0.9331
11.8084	10.5099	9.4179			3.5408	2.8647	0.9314
11.3020			6.4009	4.5534	3.2749	2.6411	0.9258
11.1392			6.2572	4.4393	3.1870	2.5704	0.9240
	9.3000	8.2216	5.7992			2.3560	0.9190
10.4644				4.0015	2.8551	2.2982	0.9177
	8.4963	7.4391	5.1540			2.0521	0.9124
9.6932				3.5344	2.5084	2.0122	0.9116
	6.8867	5.9175			1.9044	1.5201	0.9029
7.7368			3.6434	2.4889		1.3931	0.9011
6.4188				1.9183	1.3390	1.0651	0.8978
	5.2218	4.3883	2.8315			1.0621	0.8978
5.9176	4.7745	3.9899	2.5548			0.95273	0.8971
				1.2035	0.83576	0.66160	0.8973

Table II. Pitzer's Single Electrolyte Parameters for KCl, $MgSO_4$, K_2SO_4, and $MgCl_2$

	KCl[a]	KCl[b]	K_2SO_4[a]	$MgSO_4$[a]	$MgCl_2$[a]
$\beta^{(0)}$	0.04835	0.04626	0.04995	0.221	0.35235
$\beta^{(1)}$	0.2122	0.21844	0.7793	3.343	1.6815
$\beta^{(2)}$	0	0	0	−37.25	0
C^{Φ}[c]	−0.00084	−0.000398	0	0.025	0.00519
α_1	2.0	2.0	2.0	1.4	2.0
α_2	0	0	0	12	0
b	1.2	1.2	1.2	1.2	1.2

[a] These parameters were taken from Harvie and Weare (*5*). [b] The constants listed in this column were recalculated from the latest standard data (*9, 10*) by using the value of 0.3920 for the Debye–Hückel constant A^{Φ}. [c] The binary coefficient B^{Φ} depends on the ionic strength and can be calculated from the tabulated α and β parameters (*1*).

Calculations and Discussion

The osmotic coefficients of the mixed solutions can be calculated from the equation

$$\Phi = \nu^* m^* \Phi^* / (\textstyle\sum \nu_i m_i) \tag{3}$$

This equation is only valid at isopiestic equilibrium. The asterisks refer to the reference solution, ν is the number of ions formed from one molecule of solute, and Φ is the molal osmotic coefficient. For KCl–$MgSO_4$ solutions the so-called osmolality is given by

$$\textstyle\sum \nu_i m_i = 2m_A + 2m_B \tag{4}$$

The reported total ionic strengths (Table I) of the mixtures are related to the osmolality by

$$\textstyle\sum \nu_i m_i = \frac{1}{2}(3y_A + 1)I \tag{5}$$

The osmotic coefficients calculated from isopiestic ionic strengths of pure $MgSO_4$ solutions given in Table I are in excellent agreement with the latest values recently published by Rard and Miller (*11*). The maximum deviation from data calculated with their osmotic coefficient equation is 0.003, whereas the standard deviation of their fit is 0.0032.

First Scatchard's neutral electrolyte treatment (*12*, *13*) was applied to the KCl–$MgSO_4$–Φ data. The equation for the osmotic coefficient in a mixture of a 1–1 type electrolyte with a 2–2 type electrolyte can be written in the form

$$(2y_A + \tfrac{1}{2}y_B)\Phi = 2y_A\Phi_A{}^{\circ} + \tfrac{1}{2}y_B\Phi_B{}^{\circ} + \Delta \tag{6}$$

with

$$\Delta = y_A y_B I(b_{01} + b_{02}I + b_{03}I^2) + y_A y_B(y_A - y_B)I^2(b_{12} + b_{12}I) \tag{7}$$

Here $\Phi_i{}^{\circ}$ is the osmotic coefficient of the pure electrolyte i in a solution at the total ionic strength of the mixed electrolyte solution. The b_{ij} parameters represent symmetrical and asymmetrical mixing effects and were evaluated from all measured osmotic coefficients by a least-squares method applied to eq 6 and 7 using $\Phi_B{}^{\circ}$ from Rard and Miller (*11*). The $\Phi_A{}^{\circ}$ values were calculated by using the single electrolyte equation of Pitzer (*1*). The Pitzer parameters for pure KCl solutions were recalculated from standard data of Hamer and Wu (*9*) and Rard et al. (*10*) (see Table II). Hamer and Wu's equation for the osmotic coefficient of KCl could not be used beyond the solubility limit because of its maximum near I = 10 mol·kg^{-1}. The results based in isopiestic data for $I \leq 11.7$ mol·kg^{-1} are listed in Table III for the prediction of the osmotic coefficients without mixing parameters (b_{ij} = 0) and for the best fit including the term Δ, respectively. The uncertainties in the fitting parameters

Table III. Parameters for Scatchard's Neutral Electrolyte Treatment of Aqueous KCl–$MgSO_4$ Mixtures at 25 °C

$10^2 b_{01}$	$10^2 b_{02}$	$10^2 b_{03}$	$\sigma(\Phi)$
0	0	0	0.0143
4.03 ± 0.24	−0.729 ± 0.088	0.0470 ± 0.0065	0.0020

Table IV. Adjustable Mixing Parameters for Pitzer's Equations (*5*)

${}^s\theta_{K,Mg}$	${}^s\theta_{Cl,SO_4}$	$\psi_{K,Mg,Cl}$	ψ_{K,Mg,SO_4}	ψ_{K,Cl,SO_4}	ψ_{Mg,Cl,SO_4}	$\sigma(\Phi)$
0	0	0	0	0	0	0.0444
0	0.02	−0.022	−0.048	0	−0.004	0.0045

Table V. Mean Molal Activity Coefficients $\gamma_{\pm}$ of KCl in KCl–$MgSO_4$ Mixtures at 25 °C

$I/$ (mol·kg^{-1})	y_A					
	0.0	0.1	0.3	0.6	0.9	1.0
	Pitzer's Equation					
1	0.615	0.613	0.608	0.604	0.603	0.603
2	0.576	0.574	0.571	0.570	0.571	0.572
3	0.563	0.562	0.561	0.562	0.566	0.568
4	0.562	0.560	0.562	0.565	0.573	0.576
5	0.569	0.569	0.570		0.586	0.591
6	0.582	0.581				
8	0.620	0.617				
10	0.671	0.663				
	Scatchard's Equation					
1	0.608	0.608	0.607	0.605	0.604	0.604
2	0.575	0.574	0.573	0.573	0.573	0.573
3	0.563	0.563	0.563	0.564	0.567	0.568
4	0.560	0.560	0.562	0.566	0.572	0.574
5	0.566	0.567	0.570		0.587	0.591
6	0.575	0.577				
8	0.605	0.609				
10	0.649	0.656				

$$\begin{aligned}\Phi = 1 &+ \frac{m_A + 4m_B}{m_A + m_B}\left(-\frac{A^{\Phi}I^{1/2}}{1 + bI^{1/2}}\right) \\ &+ \frac{m_A^2}{m_A + m_B}\left(B^{\Phi}{}_{KCl} + (m_A + 2m_B)C^{\Phi}{}_{KCl}\right) \\ &+ \frac{m_B^2}{m_A + m_B}\left(B^{\Phi}{}_{MgSO_4} + \frac{m_A + 2m_B}{2}C^{\Phi}{}_{MgSO_4}\right) \\ &+ \frac{m_A m_B}{m_A + m_B}\left(B^{\Phi}{}_{K_2SO_4} + B^{\Phi}{}_{MgCl_2} + \frac{m_A + 2m_B}{2^{1/2}}\left(C^{\Phi}{}_{K_2SO_4} + C^{\Phi}{}_{MgCl_2}\right)\right) \\ &+ \frac{m_A m_B}{m_A + m_B}\left(\theta_{K,Mg} + I\,{}^{e}\theta'_{K,Mg} + \theta_{Cl,SO_4} + I\,{}^{e}\theta'_{Cl,SO_4}\right) \\ &+ \frac{m_A m_B}{m_A + m_B}\left(m_A\left(\psi_{K,Mg,Cl} + \psi_{K,Cl,SO_4}\right) + m_B\left(\psi_{K,Mg,SO_4} + \psi_{Mg,Cl,SO_4}\right)\right)\end{aligned} \tag{8}$$

$$\theta_{K,Mg} = {}^{e}\theta_{K,Mg} + {}^{s}\theta_{K,Mg} \tag{9}$$

$$\theta_{Cl,SO_4} = {}^{e}\theta_{Cl,SO_4} + {}^{s}\theta_{Cl,SO_4} \tag{10}$$

are also given in Table III. Our calculations have shown that the effect of the asymmetrical mixing parameters is insignificant. It is obvious that Scatchard's equation represents the experimental data up to the highest concentrations accurately within the experimental error.

In addition, Pitzer's eqations were used to calculate the osmotic coefficients for the measured concentrations listed in Table I. The general equation for the osmotic coefficient (*1*, *14*) was specialized to a mixture of a 1–1 type electrolyte with a 2–2 type electrolyte (see eq 8–10). All symbols used have the same meaning as pointed out by Pitzer (*1*, *14*). It should be noted that the ${}^{s}\theta'_{i,j}$ terms have been omitted. Equation 8 cannot be fitted to the experimental values in a simple way. Therefore, the six adjustable mixing parameters from the appropriate four mixtures with a common ion must be used. A complete set of these parameters is only given by Harvie and Weare (*5*). They evaluated the unknown values (${}^{s}\theta_{K,Mg}$, $\psi_{K,Mg,Cl}$, ψ_{K,Mg,SO_4}) from common-ion solubility data using a graphical method. The parameters for electrostatic asymmetrical mixing effects ${}^{e}\theta_{i,j}$ and ${}^{e}\theta'_{i,j}$ only depend on the total ionic strengths and the charges of the ions. Both parameters were calculated from the appropriate equations given by Pitzer (*14*) using a numerical integration procedure. All adjustable mixing parameters required for eq 8 are reported in Table IV. The binary constants for KCl, $MgSO_4$, K_2SO_4, and $MgCl_2$ were also taken from Harvie and Weare (*5*), because of internal consistency of the data set (see Table II). The differences between experimental and calculated Φ in terms of the standard deviation are also given in Table IV. It is obvious that the consideration of mixing parameters gives a significantly better prediction of the experimental data. The calculated values are in astonishing good agreement with the experimental data considering that one-half of the mixing parameters were evaluated from solubility data. A loss of accuracy as suggested by Harvie and Weare (*5*) could not be observed in this case. The greatest deviation between experimental and calculated Φ data (0.0102) occurs at ionic strengths beyond $I = 11$ mol·kg^{-1}. This may be partly due to the inadequacy of the binary KCl and K_2SO_4 constants at such high concentrations.

For comparison, Scatchard's equation represents the KCl–$MgSO_4$ data with a standard deviation about one-half that for the Pitzer equation. This fact is not surprising, because Scatchard's equation was fitted to the experimental data by using mixing parameters as much as required for a reasonably good approach. However, it is interesting that contrary to many other systems (*1*, *3*) the binary approximation to Φ with the Scatchard equation also gives a better representation of the experimental data than Pitzer's equation without adjustable mixing parameters, especially at high concentrations.

Furthermore, values of the mean molal activity coefficients $\gamma_{\pm}$ of KCl and $MgSO_4$ were calculated at various ionic strengths and ionic strength fractions by using both Scatchard's and Pitzer's equations (*1*, *12–14*) and the mixing parameters listed in Tables III and IV. Results are reported in Table V for KCl and in Table VI for $MgSO_4$. The values of $y_i = 1$ are the pure-component values while $y_i = 0$ are the trace activity coefficients. Activity coefficients are also listed at concentrations above the KCl binary crystallization limit. These values are of somewhat lower accuracy, because of the unknown uncertainty of an extrapolation to ionic strengths beyond the KCl solubility limit. Nevertheless, they should be realistic as recently pointed out by Harvie and Weare (*5*) and de Lima and Pitzer (*6*, *7*). Another reason for this assumption is the comparatively good agreement between the activity coefficient values in Tables V and VI calculated with the two different functions (maximum deviation only 0.022 for the trace value of KCl at $I = 10$ mol·kg^{-1}). The binary equation for $MgSO_4$ is valid for higher ionic strengths than reported in Table VI so there is no extrapolation problem. Summarizing, the conclusion can be drawn that both Scatchard's neutral electrolyte treatment and

Table VI. Mean Molal Activity Coefficients $\gamma_{\pm}$ of $MgSO_4$ in KCl–$MgSO_4$ Mixtures at 25 °C.

I/(mol·kg^{-1})	y_B					
	0.0	0.1	0.4	0.7	0.9	1.0
			Pitzer's Equation			
1	0.128	0.125	0.117	0.112	0.109	0.109
2	0.100	0.097	0.088	0.082	0.078	0.077
3	0.093	0.089	0.079	0.070	0.065	0.063
4	0.093	0.088	0.075	0.065	0.058	0.055
5	0.095	0.090		0.062	0.054	0.051
6					0.052	0.048
8					0.052	0.047
10					0.056	0.050
			Scatchard's Equation			
1	0.116	0.114	0.110	0.106	0.104	0.103
2	0.095	0.092	0.085	0.079	0.075	0.073
3	0.090	0.086	0.076	0.067	0.062	0.060
4	0.092	0.087	0.072	0.062	0.056	0.053
5	0.098	0.090		0.059	0.052	0.049
6					0.050	0.047
8					0.050	0.045
10					0.053	0.047

Pitzer's equation are useful approaches for modeling activity data of aqueous KCl–$MgSO_4$ mixtures from low to high concentrations.

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Glossary

A	symbols subscripted A refer to KCl
B	symbols subscripted B refer to $MgSO_4$
*	symbols with asterisks refer to KCl isopiestic standard
m_i	molal concentration of electrolyte i, mol·kg^{-1}
y_i	ionic strength fraction of electrolyte i
I	total ionic strength, mol·kg^{-1}
Φ	molal osmotic coefficient
ν_i	number of ions formed by the complete dissociation of one molecule of electrolyte i
b, α_1, α_2, $B^{\Phi}{}_i$, $C^{\Phi}{}_i$, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$	parameters in Pitzer's equations for single electrolytes
${}^s\theta_{i,j}$, ${}^e\theta_{i,j}$, ${}^s\theta'_{i,j}$, ${}^e\theta'_{i,j}$, $\psi_{i,j,k}$	parameters in Pitzer's equations for mixed electrolytes
$\Phi_i{}^o$	molal osmotic coefficient of a solution containing electrolyte i only at the total ionic strength of the mixed solution
b_{01}, b_{02}, b_{03}, b_{12}, b_{13}	mixing parameters for Scatchard's neutral electrolyte treatment
$\sigma(\Phi)$	standard deviation of osmotic coefficients
$\gamma_{\pm}$	mean molal activity coefficient

Registry No. KCl, 7447-40-7; $MgSO_4$, 7487-88-9.

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Osmotic Coefficients of Low-Equivalent-Weight Organic Salts. 2

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The osmotic coefficients of aqueous solutions of sodium benzoate, sodium salicylate, sodium 3-methylsalicylate, and sodium 3,5-diisopropylsalicylate by isopiestic measurements at 25 °C are reported. The osmotic coefficients decline with increasing molality of these salts except sodium benzoate. With sodium benzoate, the osmotic coefficients of the aqueous solution increase at low molality (>0.2 *m*), reach a maximum at ca. 1.2 *m*, and then descend slowly. Activity coefficients of these salts were computed from least-squares fits to the water activities.

Introduction

We have reported the isopiestic results of four two-component systems composed of sodium alkylbenzenesulfonate and water, and one three-component system containing sodium *p*-cymenesulfonate/NaCl/H_2O at 25 °C (*1*). Although we found some indication in these low-equivalent-weight sulfonate systems of the presence of either small aggregates or strong interactions between the ions, there appeared to be no evidence for micelles, commonly encountered with surfactants.

In this paper we present isopiestic measurements of sodium benzoate and three alkyl-substituted sodium salicylates. The salicylates are sodium salicylate (S_{AC} = 0), 3-methylsalicylate (S_{AC} = 1), and 3,5-diisopropylsalicylate (S_{AC} = 6). S_{AC} is the number of alkyl carbons on the benzene ring of the salicylates. These salts are also recognized as hydrotropes; that is, their aqueous solutions can solubilize substantial quantities of hydrocarbons (*2–5*). Among all the groups of low-equivalent-weight organic salts (protosurfactants) we have studied, salicylates show the most pronounced increases in solubilization in comparison with the analogous benzenesulfonates or benzoates (*4*). Sodium benzoate has about the same hydrotropic ability as benzenesulfonate (*3*). The solubilizing effect of the organic hydrotropic salts depends heavily on the average degree of alkyl substitution, but the un-ionized *o*-hydroxy group appears also to have a substantial effect on the hydrotropic property. The highest alkyl-substituted salicylate in this paper, sodium 3,5-diisopropylsalicylate, has not only the strongest hydrotropic properties among the protosurfactants we have studied (*4*), but also mimics most closely surfactants in chemical and phase behavior of multicomponent systems (*6*). Free energy studies of the aqueous solutions of these organic salts may help in understanding their hydrotropic properties and the role they play in solubilization.

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