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Osmotic and Activity Coefficients of Aqueous K_2SO_4 - $MgSO_4$ and KCl - $MgCl_2$ at 25 °C

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The osmotic coefficients of the two aqueous mixtures K_2SO_4 - $MgSO_4$ and KCl - $MgCl_2$ were determined by isopiestic measurements at 25 °C. The measurements have been carried out over an ionic strength range of 1.1–12.4 mol·kg⁻¹ (K_2SO_4 - $MgSO_4$) and 1.1–12.8 mol·kg⁻¹ (KCl - $MgCl_2$). The experimental data were treated by three different methods (Pitzer, Scatchard, Schönert). With both Pitzer's equations and Scatchard's neutral electrolyte equations the agreement between calculated and experimental osmotic coefficients is very good over the entire ionic strength range up to saturation. To examine the mean molal activity coefficients calculated by the different model equations, the solubility curves have been calculated and compared.

Introduction

The osmotic and activity coefficients of aqueous KCl - $MgSO_4$ mixtures within the ionic strength range of 0.8–11.7 mol·kg⁻¹ have recently been reported (1). Although it was necessary to extrapolate the data of the binary KCl solutions to concentrations far away from the saturation limit, both Pitzer's treatment and Scatchard's neutral electrolyte equations well represented the experimental data over the entire concentration range. Because of the necessity to apply reliable activity coefficients for modeling the thermodynamic properties of more complex multicomponent systems, especially natural saline brines, we extended our measurements and calculations to two further ternary systems of practical interest.

In this report isopiestic data are presented for H_2O - K_2SO_4 - $MgSO_4$ and H_2O - KCl - $MgCl_2$ from moderately low concentrations to nearly saturated solutions at 25 °C. Besides the well-known Scatchard and Pitzer formalisms, we tested also a method described by Schönert (2) to calculate the mean activity coefficients without consideration of the corresponding binary data. Furthermore, using Scatchard's parameters we calculated the excess Gibbs energies of mixing $\Delta_M G^E$ (referred to 1 kg solvent) characterizing the interactions of the two electrolytes in the ternary solutions at several constant total ionic strengths.

A detailed study of the activity coefficients in K_2SO_4 - $MgSO_4$ mixtures was made by Ninkovic and Radovanovic (3) using the isopiestic technique, but only up to an ionic strength of 5.5 mol·kg⁻¹.

Examination of the available osmotic coefficients and activity data for aqueous KCl - $MgCl_2$ (4–7) measured with solutions of total ionic strengths less than 6 mol·kg⁻¹ indicated remarkable discrepancies. Three of these data sets are in reasonably good agreement (4, 6, 7), while the fourth study (5) gives deviating osmotic coefficients. From this arose our intention for reinvestigation to get accurate data within an extended ionic strength range.

Experimental Section

The isopiestic apparatus is the same as previously described (1) with KCl , $MgCl_2$, and $MgSO_4$ as the reference electrolytes. For KCl reference solutions, the osmotic coefficients at isopiestic equilibrium were taken from Hamer and Wu (8) and corrected by the procedure of Rard et al. (9). The osmotic coefficients for $MgCl_2$ and $MgSO_4$ reference solutions have been calculated by means of equations given by Rard and Miller (10, 11) considering newest experimental data.

The preparation and analyses of the KCl and $MgSO_4$ solutions have been described elsewhere (1). Doubly recrystallized analytical grade $MgCl_2 \cdot 6H_2O$ was used for the preparation of a $MgCl_2$ stock solution. Concentration of this $MgCl_2$ stock was determined by mass titration with $AgNO_3$ yielding 5.4860 ± 0.0015 mol·kg⁻¹. The cited uncertainty is the average deviation of 10 independent titrations. Recrystallized analytical grade K_2SO_4 was dried in an oven at 200 °C before preparation of solutions by weight. All weights were converted to mass.

Samples of K_2SO_4 and $MgCl_2$ solutions were analyzed for impurities by using atomic absorption spectrometry (Mg, Ca) and flame photometry (Na, K, Ba). The impurities found in $MgCl_2$ were less than 5 ppm by weight for all four elements. K_2SO_4 had ca. 56 ppm Mg, 10 ppm Na, 6 ppm Ca, and less than 5 ppm Ba.

Duplicate samples of constant ionic strength fraction have been prepared by dilution or evaporation of weighted amounts of stock solutions. All water used in this study was first deionized and then distilled. A few measurements were made on pure aqueous $MgCl_2$ and $MgSO_4$ using KCl reference solutions to confirm our technique.

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Table I. Osmotic Coefficients for MgCl₂ with KCl Reference Solutions at 25 °C

$m_{\text{KCl}}^*/\text{mol}\cdot\text{kg}^{-1}$	Φ_{KCl}^*	$m_{\text{MgCl}_2}^*/\text{mol}\cdot\text{kg}^{-1}$	Φ_{exptl}	Φ^a
1.2748	0.8997	0.7479	1.0223	1.0216
2.7890	0.9295	1.3787	1.2535	1.2558
2.6067	0.9249	1.3092	1.2277	1.2278
3.5553	0.9507	1.6466	1.3685	1.3686
3.8163	0.9584	1.7353	1.4051	1.4075
4.2391	0.9715	1.8690	1.4690	1.4675

^a Computed from Rard and Miller's polynomials (10).**Table II. Osmotic Coefficients for MgSO₄ with KCl Reference Solutions at 25 °C**

$m_{\text{KCl}}^*/\text{mol}\cdot\text{kg}^{-1}$	Φ_{KCl}^*	$m_{\text{MgSO}_4}^*/\text{mol}\cdot\text{kg}^{-1}$	Φ_{exptl}	Φ^a
0.9527	0.8971	1.4794	0.5777	0.5763
1.0651	0.8978	1.6047	0.5959	0.5939
1.3931	0.9011	1.9342	0.6490	0.6491
2.0122	0.9116	2.4233	0.7569	0.7553
2.2982	0.9177	2.6161	0.8062	0.8053
2.5704	0.9240	2.7848	0.8529	0.8530
2.6411	0.9258	2.8255	0.8654	0.8651
2.8647	0.9314	2.9521	0.9038	0.9040
2.9272	0.9331	2.9851	0.9150	0.9145

^a Computed from Rard and Miller's polynomials (11).

More than 100 measuring points per ternary system taken at constant ionic strength fractions and variable total ionic strength were distributed within the whole region of stable solutions. Only such runs have been accepted where the molalities of duplicate samples at isopiestic equilibrium agreed to better than 0.06% of the average.

Results

The results for pure MgCl₂ and MgSO₄ solutions were calculated by using the equation for isopiestic equilibrium

Table III. Isopiestic Ionic Strengths and Vapor Pressures of H₂O (1)–K₂SO₄ (2)–MgSO₄ (3) Mixtures and Reference Solutions at 25 °C

$I/\text{mol}\cdot\text{kg}^{-1}$					$I_{\text{KCl}}^*/\text{mol}\cdot\text{kg}^{-1}$	Φ^*	$P_{\text{H}_2\text{O}}/\text{Pa}$
$y_2 = 0.02793$	$y_2 = 0.06685$	$y_2 = 0.09929$	$y_2 = 0.14931$	$y_2 = 0.19890$			
2.7032	2.5748	2.4607	2.3066	2.1787	2.8064 ^a	0.5182 ^a	3127
3.2344	3.0937	2.9701	2.7936	2.6462	3.3460 ^a	0.5210 ^a	3119
4.7593	4.6068	4.4791	4.2933	4.0830	0.7411	0.8969	3094
5.5082	5.3715	5.2492	5.0534	4.8451	0.8851	0.8969	3079
6.6127	6.5049	6.3985	6.2289	6.0317	1.1248	0.8982	3055
7.3493	7.2640	7.1730	7.0282	6.8486	1.3036	0.9000	3037
8.2924	8.2397	8.1851	8.0758	7.9176	1.5593	0.9035	3012
8.6422	8.6066	8.5617	8.4680	8.3236	1.6631	0.9052	3001
9.5623	9.5599	9.5405	9.4794		1.9549	0.9103	2972
10.0079	10.0186	10.0152	9.9863		2.1102	0.9136	2956
10.7264	10.7717	10.7862			2.3789	0.9195	2929
11.2782	11.3487	11.3857			2.6010	0.9248	2906
12.3234	12.4354				3.0579	0.9366	2858

$I/\text{mol}\cdot\text{kg}^{-1}$					$I_{\text{KCl}}^*/\text{mol}\cdot\text{kg}^{-1}$	Φ^*	$P_{\text{H}_2\text{O}}/\text{Pa}$
$y_2 = 0.29859$	$y_2 = 0.40049$	$y_2 = 0.49744$	$y_2 = 0.65075$	$y_2 = 0.79933$			
1.7757	1.5836	1.4321	1.2430	1.1009	2.6108 ^a	0.5182 ^a	3130
1.9456	1.7362	1.5700	1.3661	1.2149	2.8323 ^a	0.5183 ^a	3127
2.7547	2.4464	2.2271	1.9371	1.7037	0.5597	0.8983	3112
2.9571	2.6500	2.4052	2.0827	1.8411	0.6009	0.8978	3108
3.4096	3.0637	2.7857	2.4163	2.1273	0.6880	0.8972	3099
3.7436	3.3742	3.0690	2.6653	2.3473	0.7521	0.8968	3093
4.0315	3.6465	3.3152	2.8823	2.5389	0.8096	0.8968	3087
4.5695	4.1526	3.7899	3.2983		0.9155	0.8969	3076
4.8637	4.4347	4.0522	3.5312		0.9714	0.8972	3071
5.2137	4.7723	4.3741			1.0430	0.8976	3064
5.5233	5.0701	4.6606			1.1063	0.8981	3057
6.1288	5.6602				1.2350	0.8993	3044

^a MgSO₄ reference solution.

$$\Phi_{\text{exptl}} = \frac{2m^*\Phi^*}{\nu m} \quad (1)$$

where the symbols with asterisks refer to KCl isopiestic standard. Our results and corresponding values computed from polynomials given by Rard and Miller (10, 11) are reported in Tables I and II. The data agreed within ± 0.0025 in Φ .

The measured ionic strengths of ternary mixtures at different ionic strength fractions together with the ionic strengths and osmotic coefficients of reference solutions are summarized in Tables III and IV. Molal osmotic coefficients of the mixed solutions were calculated by using the equation

$$\Phi_{\text{exptl}} = \frac{r\Phi^*I^*}{(1+y_2)I} \quad (2)$$

with $r = 4$ (KCl reference solution) or $r = 1$ (MgSO₄ reference solution) for H₂O (1)–K₂SO₄ (2)–MgSO₄ (3) and $r = 2$ (reference electrolyte KCl) or $r = 1$ (reference electrolyte MgCl₂) for H₂O (1)–KCl (2)–MgCl₂ (3). The corresponding vapor pressures of solutions at 25 °C referred to 3168.7 Pa for pure water (12) are also listed in Tables III and IV.

Calculations and Discussion

The results reported in this paper were analyzed by three methods. The first method used is Scatchard's neutral electrolyte treatment (13) in the general form

$$\Phi = \frac{1}{\frac{\nu_2}{k_2}y_2 + \frac{\nu_3}{k_3}y_3} \left[\frac{\nu_2}{k_2}\gamma_2\Phi_2^0 + \frac{\nu_3}{k_3}\gamma_3\Phi_3^0 + y_2y_3I\text{Fu}(I) \right] \quad (3)$$

with

$$\text{Fu}(I) = b_{01} + b_{02}I + b_{03}I^2 + (y_2 - y_3)I(b_{12} + b_{13}I) \quad (4)$$

and

$$k_i = \frac{1}{2}\nu_i|z_i^+z_i^-| \quad (i = 2, 3) \quad (5)$$

Table IV. Isoopiestic Ionic Strengths and Vapor Pressures of H₂O (1)-KCl (2)-MgCl₂ (3) Mixtures and Reference Solutions at 25 °C

<i>I</i> /mol·kg ⁻¹					<i>I</i> * _{MgCl₂} /mol·kg ⁻¹	Φ*	<i>P</i> _{H₂O} /Pa
<i>y</i> ₂ = 0.02436	<i>y</i> ₂ = 0.05076	<i>y</i> ₂ = 0.10199	<i>y</i> ₂ = 0.20065	<i>y</i> ₂ = 0.29228			
2.2104	2.1701	2.0986	1.9675	1.8572	2.2437	1.0218	3041
3.7014	3.6612	3.5786	3.4272	3.2919	3.7347	1.2023	2922
4.8260	4.7948	4.7223	4.5737	4.4471	4.8606	1.3572	2814
5.2367	5.2106	5.1445	5.0054	4.8754	5.2698	1.4170	2770
5.7568	5.7293	5.6774	5.5522	5.4307	5.7861	1.4949	2711
6.3447	6.3180	6.2747	6.1724	6.0581	6.3630	1.5849	2642
6.8549	6.8374	6.8027	6.7174	6.6314	6.8691	1.6660	2578
7.4665	7.4577	7.4429	7.3883	7.3193	7.4730	1.7650	2499
7.5258	7.5169	7.4959	7.4417		7.5258	1.7736	2491
7.7423	7.7378	7.7255	7.6823		7.7436	1.8100	2462
8.5361	8.5484	8.5569	8.5624		8.5251	1.9420	2351
10.0454	10.0849	10.1557			10.0056	2.1965	2133
10.6529	10.7035				10.6017	2.2998	2042
11.3030	11.3715				11.2362	2.4098	1945
11.4119	11.4818				11.3430	2.4283	1929
12.0201	12.1068				11.9364		1839
12.6172	12.7178				12.5160	2.5374	1750

<i>I</i> /mol·kg ⁻¹					<i>I</i> * _{MgCl₂} /mol·kg ⁻¹	Φ*	<i>P</i> _{H₂O} /Pa
<i>y</i> ₂ = 0.40085	<i>y</i> ₂ = 0.48470	<i>y</i> ₂ = 0.60430	<i>y</i> ₂ = 0.74660	<i>y</i> ₂ = 0.90136			
1.4071	1.3334	1.2434	1.1507	1.0621	1.0125 ^a	0.8974 ^a	3067
1.5409	1.4637	1.3671	1.2658	1.1708	1.1169 ^a	0.8981 ^a	3056
2.2883	2.1914	2.0622	1.9250	1.7930	1.7181 ^a	0.9061 ^a	2996
2.5019	2.3993	2.2630	2.1166	1.9760	1.8952 ^a	0.9093 ^a	2978
3.3281	3.2107	3.0535	2.8809	2.7073	2.6067 ^a	0.9249 ^a	2905
3.5333	3.4156	3.2522	3.0739	2.8947	2.7890 ^a	0.9295 ^a	2886
4.3708	4.2448	4.0730	3.8777	3.6741	3.5553 ^a	0.9507 ^a	2805
4.6484	4.5223	4.3500	4.1517	3.9396	3.8163 ^a	0.9584 ^a	2777
5.2150	5.0976	4.9197	4.7116	4.4921	5.7240	1.4854	2719
5.5543	5.4411	5.2628	5.0510	4.8273	6.0312	1.5328	2683
6.0361	5.9260	5.7556			6.4635	1.6008	2630
6.2775	6.1679				6.6738	1.6344	2603

^a KCl reference solution.**Table V. Pitzer's Single Electrolyte Coefficients for K₂SO₄, MgSO₄, KCl, and MgCl₂**

	K ₂ SO ₄ ^a	MgSO ₄ (11)	KCl ^b	MgCl ₂ (10)
β(0)	0.04432	0.21499	0.04626	0.35093
β(1)	0.7365	3.3646	0.21844	1.65075
β(2)		-32.743		
C ^{†c}	0.00181	0.02797	-0.000398	0.00651
α ₁	2.0	1.4	2.0	2.0
α ₂		12		
B*	1.2	1.2	1.2	1.2

^a Evaluated with extrapolated data for the supersaturated solutions according to a procedure applied by Robinson et al. (16).
^b Taken from Hamer and Wu (8) and corrected with respect to real gas behavior (9).
^c B* depends on the ionic strength and can be calculated from the tabulated α and β parameters (14).

Table VI. Scatchard's Coefficients for H₂O (1)-K₂SO₄ (2)-MgSO₄ (3) at 25 °C

10 ² <i>b</i> ₀₁	10 ² <i>b</i> ₀₂	10 ² <i>b</i> ₀₃	σ (Φ)
-0.95 ± 0.07	-0.32 ± 0.01	0	0.0018
-0.65 ± 0.12	-0.46 ± 0.05	0.011 ± 0.004	0.0014

Φ_{*i*}⁰ is the osmotic coefficient of the pure electrolyte *i* in a solution at the total ionic strength of the mixed salt solution. The *b_{ij}* parameters were calculated from the measured osmotic coefficients by using a least-squares method. Φ_{*i*}⁰ values were calculated from equations given by Rard and Miller (10, 11) (MgSO₄, MgCl₂) or with Pitzer's single electrolyte equation (14). The corresponding Pitzer parameters are available and listed in Table V. Calculated Scatchard coefficients *b_{ij}* for the two investigated systems are given in Tables VI and VII. As checked with an F test, it was found that Fu(I), eq 4, could be expressed by only three parameters leading to the tabulated standard deviations between experimental and recalculated osmotic coefficients. From these parameters, the mean activity

Table VII. Scatchard's Coefficients for H₂O (1)-KCl (2)-MgCl₂ (3) at 25 °C

10 ² <i>b</i> ₀₁	10 ² <i>b</i> ₀₂	10 ² <i>b</i> ₀₃	σ (Φ)
4.53 ± 0.08	-1.18 ± 0.01	0	0.0020
3.99 ± 0.13	-0.95 ± 0.05	-0.019 ± 0.04	0.0014

coefficients of constituent electrolytes can be calculated with equations given in Scatchard's papers.

The second method is concerned with Pitzer's treatment of mixed electrolyte solutions (14, 15) specialized to the type of the used electrolytes. For the K₂SO₄ (2)-MgSO₄ (3) mixtures we obtain

$$\Phi - 1 = \frac{6m_2 + 8m_3}{3m_2 + 2m_3} \left(-\frac{0.392I^{1/2}}{1 + 1.2I^{1/2}} \right) + \frac{4m_2(m_2 + m_3)}{3m_2 + 2m_3} [B^{\Phi}_{K_2SO_4} + 2^{1/2}(m_2 + m_3)C^{\Phi}_{K_2SO_4}] + \frac{2m_3(m_2 + m_3)}{3m_2 + 2m_3} [B^{\Phi}_{MgSO_4} + (m_2 + m_3)C^{\Phi}_{MgSO_4}] + \frac{4m_2m_3}{3m_2 + 2m_3} [\theta^{\Phi}_{K,Mg} + (m_2 + m_3)\psi_{KMgSO_4}] \quad (6)$$

and for KCl (2)-MgCl₂ (3)

$$\Phi - 1 = \frac{2m_2 + 6m_3}{2m_2 + 3m_3} \left(-\frac{0.392I^{1/2}}{1 + 1.2I^{1/2}} \right) + \frac{2m_2(m_2 + 2m_3)}{2m_2 + 3m_3} [B^{\Phi}_{KCl} + (m_2 + 2m_3)C^{\Phi}_{KCl}] + \frac{2m_3(m_2 + 2m_3)}{2m_2 + 3m_3} \left[B^{\Phi}_{MgCl_2} + \left(\frac{m_2 + 2m_3}{2^{1/2}} \right) C^{\Phi}_{MgCl_2} \right] + \frac{2m_2m_3}{2m_2 + 3m_3} [\theta^{\Phi}_{K,Mg} + (m_2 + 2m_3)\psi_{KMgCl}] \quad (7)$$

Table VIII. Pitzer's Mixing Parameters (25 °C)

parameters	K ₂ SO ₄ (2)-MgSO ₄ (3)	KCl (2)-MgCl ₂ (3)
${}^{\circ}\theta_{K,Mg}$	-0.031 ± 0.002	0.0371 ± 0.0019
${}^{\circ}\theta'_{K,Mg}$	-0.0048 ± 0.0002	-0.0113 ± 0.0002
$\psi_{K,Mg,anion}$	0	0
$\sigma(\Phi)$	0.0025	0.0032

Table IX. Coefficients for the Ionic Strength Fraction Polynomials

coeff	K ₂ SO ₄ (2)-MgSO ₄ (3)	KCl (2)-MgCl ₂ (3)
b_1	-0.0952 ± 0.0026	-0.0019 ± 0.0008
b_2	0.031 ± 0.011	0.048 ± 0.014
b_3	0.013 ± 0.010	0.070 ± 0.060
b_4		-0.129 ± 0.093
b_5		0.076 ± 0.046
c_1	-0.0276 ± 0.0019	0.0065 ± 0.0002
c_2	-0.0367 ± 0.0081	-0.0052 ± 0.0042
c_3	0.0165 ± 0.0073	-0.013 ± 0.018
c_4		0.043 ± 0.028
c_5		-0.021 ± 0.013
d_1	-0.0034 ± 0.0003	-0.00047 ± 0.00002
d_2	0.0062 ± 0.0014	0.0006 ± 0.0003
d_3	0.0030 ± 0.0013	0.0010 ± 0.0015
d_4		-0.0037 ± 0.0023
d_5		0.0023 ± 0.0011

The parameters B^{Φ} and C^{Φ} were calculated from published or recommended coefficients for binary solutions by using the known Pitzer formalism. These coefficients are summarized in Table V. Assuming a linear ionic strength dependence of the ${}^{\circ}\theta_{i,j}(I)$ interaction parameter, the interaction parameter $\theta^{\Phi}_{i,j}$ can be divided into the following terms

$$\theta^{\Phi}_{i,j} = {}^{\circ}\theta_{i,j} + 2I{}^{\circ}\theta'_{i,j} + {}^{\circ}\theta_{i,j}(I) + I{}^{\circ}\theta''_{i,j}(I) \quad (8)$$

Both electrostatic contributions, ${}^{\circ}\theta_{i,j}$ and ${}^{\circ}\theta'_{i,j}$, were calculated with appropriate expressions (15) by numerical integration. The adjustable mixing parameters and their standard deviations for the best fits of osmotic coefficients are given in Table VIII. For both systems there was no improvement in fitting by inclusion of ψ parameters. The values of Tables V and VIII were used to obtain the mean activity coefficients with expressions given also in Pitzer's papers.

Furthermore, we applied a procedure proposed by Schönert (2) to evaluate the activity coefficients. This method consists of a suitable integration of the Gibbs-Duhem equation yielding for ternary solutions

$$\Phi = 1 - A_m / \left[\left(\frac{y_2}{|z_2+z_2|} + \frac{y_3}{|z_3+z_3|} \right) B^* I \right] \left[(1 + B^* I^{1/2}) - 2 \ln(1 + B^* I^{1/2}) - 1/(1 + B^* I^{1/2}) \right] + B(y_3)I + C(y_3)I^2 + D(y_3)I^3 \quad (9)$$

B , C , and D are functions of the ionic strength fractions. This dependence may be expressed by polynomials of the following type (2)

$$B(y_i) = b_1 + b_2 y_i + b_3 y_i^2 + \dots \quad (10)$$

$$C(y_i) = c_1 + c_2 y_i + c_3 y_i^2 + \dots$$

$$D(y_i) = d_1 + d_2 y_i + d_3 y_i^2 + \dots$$

with $i = 2, 3$. The calculated values of coefficients in eq 10 are listed in Table IX. From the empirical parameters B , C , and D calculated by the least-squares method, the activity coefficients can be obtained with appropriate expressions (2).

Schönert's treatment offers the advantage that the activity coefficients are calculable from the solvent activities without

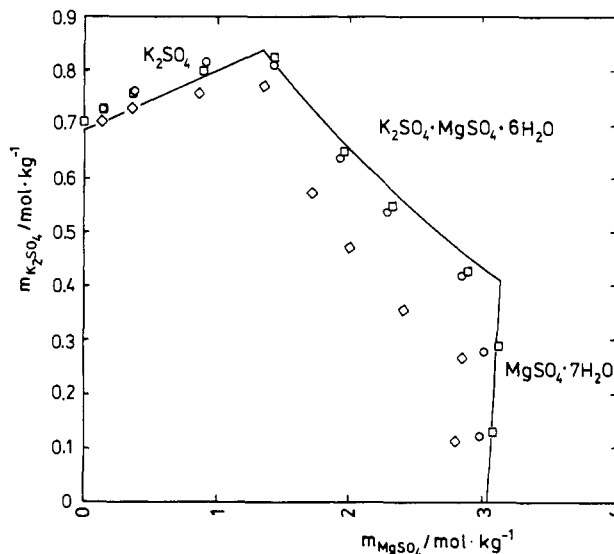


Figure 1. Experimental solubilities (—) and corresponding data calculated by using different methods for H₂O (1)-K₂SO₄ (2)-MgSO₄ (3) at 25 °C: (O) Pitzer's equations, (□) Scatchard's equations, (◇) Schönert's procedure.

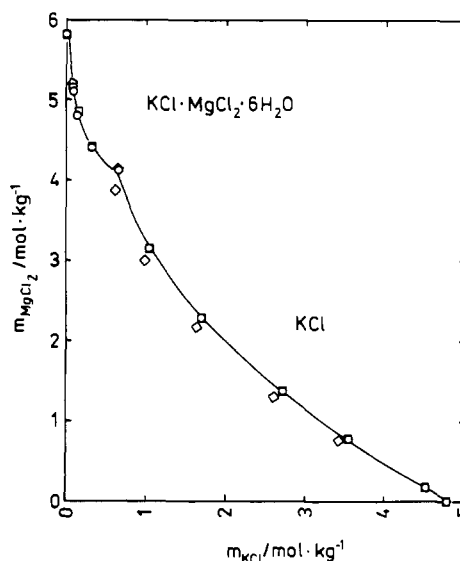


Figure 2. Experimental solubilities (—) and corresponding data calculated by using different methods for H₂O (1)-KCl (2)-MgCl₂ (3) at 25 °C: (O) Pitzer's equations, (□) Scatchard's equations, (◇) Schönert's procedure.

knowledge of the activities of the corresponding binary solutions. However, the regression of experimental data and the numerical calculation of derivatives with respect to y require an extensive set of accurate measuring points.

The comparison between empirical and calculated solubility data enables to check the reliability of the applied three models. The solubility data were evaluated from solubility constants for ternary solutions being in contact with the stable solid phases. These constants have been determined with standard chemical potentials reported by Harvie and Weare (17). From the well-known relationships between solubility constants and activity coefficients, the solubilities have been determined by an iterative method. Figures 1 and 2 reveal the very good agreement between predicted solubilities and experimental data (18) with the exception of K₂SO₄-MgSO₄ treated by the Schönert procedure. The discrepancies in the K₂SO₄-MgSO₄ system occurring especially at high ionic strengths and high MgSO₄ content are obviously due to the difficulty to calculate the coefficients of eq 10 with a sufficient precision.

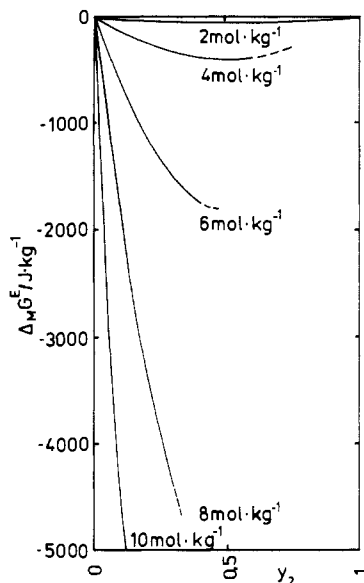


Figure 3. Excess Gibbs free energy of mixing $\Delta_M G^E$ for H₂O (1)–K₂SO₄ (2)–MgSO₄ (3) at 25 °C.

Osmotic coefficients for K₂SO₄–MgSO₄ obtained in this study and fitted by the Scatchard equation have been compared with those of Ninkovic and Radovanovic (3) ($I_{\max} = 5.5 \text{ mol}\cdot\text{kg}^{-1}$). The data are practically identical within ± 0.004 . For KCl–MgCl₂, our results are systematically lower by 0.002 up to 0.007 than osmotic coefficients given in the literature (4, 7) ($I_{\max} = 5 \text{ mol}\cdot\text{kg}^{-1}$) indicating a reasonable good agreement. Activity coefficients of KCl measured by Gieskes and Christenson (6) at $I = 1 \text{ mol}\cdot\text{kg}^{-1}$ using an ion-selective electrode are in excellent agreement with data obtained in the present work. On the other hand, the deviating data of Kirgintsev and Lukyanov (5) for the ionic strength range from 3.3 to 6 mol·kg⁻¹ are obviously not accurate. There are already considerable discrepancies between reported isopiestic molalities and generally accepted standard values for pure MgCl₂ solutions (10).

It follows from the detailed analysis of our results that the equation of Scatchard is quite suitable to accurately evaluate the osmotic and activity coefficients also at high concentrations. However, the higher accuracy in comparison with Pitzer's method requires a higher number of adjustable parameters leading to an increasing numerical expense in case of more complex systems. Consequently, the Pitzer procedure appears to be optimal with respect to accuracy and number of empirical parameters. Because of the relatively high sensitivity against random errors of regression coefficients, the Schönert method was found to be limited in applicability.

Finally, the values of the excess Gibbs free energy of mixing have been calculated from the Scatchard coefficients given in Tables VI and VII by using the expression

$$\Delta_M G^E = RTI^2 y_2 y_3 (b_{01} + \frac{1}{2} b_{02} I + \frac{1}{3} b_{03} I^2) \quad (11)$$

The results at round ionic strengths are shown in Figures 3 and 4. Owing to the dominating factor RTI^2 , the absolute values of $\Delta_M G^E$ are somewhat uncertain (approximately 35% at high ionic strengths). Nevertheless, the principal trend at varying ionic strength should be correct. For K₂SO₄–MgSO₄, the $\Delta_M G^E$ data are generally negative. On the contrary, in KCl–MgCl₂ mixtures occurs a change of sign at an ionic strength of about 7.5 mol·kg⁻¹. It can be assumed that the considerable difference between both systems is due to comparatively large contributions of anions (especially the SO₄ anion) to the ionic interaction in the investigated ternary solutions. The relatively

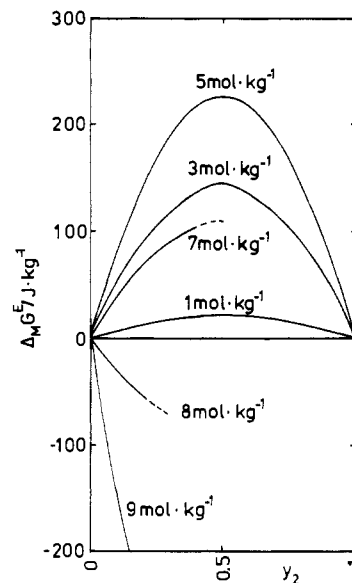


Figure 4. Excess Gibbs free energy of mixing $\Delta_M G^E$ for H₂O (1)–KCl (2)–MgCl₂ (3) at 25 °C.

large difference between the calculated ${}^{\circ}\theta_{K,Mg}$ interaction coefficients for K₂SO₄–MgSO₄ and KCl–MgCl₂ mixtures supports this interpretation.

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Glossary

Φ	molal osmotic coefficient
ν	number of ions formed by the complete dissociation of one molecule of solute
I	total ionic strength, mol·kg ⁻¹
y_i	ionic strength fraction of electrolyte i
*	asterisked symbols refer to the isopiestic reference solution
P	vapor pressure, Pa
Φ_i^0	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
$\alpha_1, \alpha_2, \beta(0), \beta(1), \beta(2)$	parameters for Pitzer's single electrolyte equation
$B_i^{\Phi}, C_i^{\Phi}, \theta_{ij}^{\Phi}, {}^{\circ}\theta_{ij}, {}^{\circ}\theta'_{ij}, {}^{\circ}\theta_{ij}, {}^{\circ}\theta'_{ij}, \psi_{ijk}$	parameters in Pitzer's equations for mixed electrolytes
A_m, B^*	constants in the extended Debye–Hückel model
B, C, D, b_i, c_i, d_i	parameters for Schönert's equation
$\Delta_M G^E$	excess Gibbs free energy of mixing, J·kg ⁻¹
$\sigma(\Phi)$	standard deviation of osmotic coefficients

Registry No. K₂SO₄, 7778-80-5; MgSO₄, 7487-88-9; KCl, 7447-40-7; MgCl₂, 7786-30-3.

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Excess Thermodynamic Properties for Acetonitrile/Water

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Heat-of-mixing data for the binary liquid system acetonitrile/water at 50 °C are reported. These data, together with H^E data at 5 and 25 °C from the literature and a previously published set of VLE data at 50 °C, are combined to provide correlations for H^E , G^E , and S^E that are functions of both composition and temperature.

Experimental heat-of-mixing data at 50 °C for the acetonitrile/water system, taken with the apparatus of Winterhalter and Van Ness (1), are listed in Table I. The acetonitrile was OmniSolv reagent from MCB Manufacturing Chemists, Inc., with an assay of 99.8 mol %; the water was doubly deionized. Boiling the reagents accomplishes partial degassing, and they are loaded into the calorimeter while hot. With this procedure, no evolution of dissolved gases occurs during a run.

Correlations for the Excess Properties

An excellent correlation of the reported H^E data is achieved by the eight-parameter Margules equation

$$H^E/(x_1x_2RT) = A' - C'x_1x_2 + D'(x_1x_2)^2 - E'(x_1x_2)^3 \quad (1)$$

where $A' \equiv A_{21}'x_1 + A_{12}'x_2$; $C' \equiv C_{21}'x_1 + C_{12}'x_2$; $D' \equiv D_{21}'x_1 + D_{12}'x_2$; $E' \equiv E_{21}'x_1 + E_{12}'x_2$. Regression of the data to minimize the sum of squares of the differences between experimental and calculated values of H^E , all points weighted equally, leads to the following values of the parameters: $A_{21}' = 3.09040$, $A_{12}' = 0.28205$; $C_{21}' = 0.49964$, $C_{12}' = -13.33587$; $D_{21}' = -14.10170$, $D_{12}' = -66.70484$; $E_{21}' = -25.87204$, $E_{12}' = -104.79037$. The rms value of the deviations is 1.1 J mol⁻¹ and the maximum deviation is 2.1 J mol⁻¹. We could find no equation with a smaller number of parameters that provided a proper correlation of the data.

A comparable set of vapor/liquid equilibrium data, also at 50 °C, was reported recently by Villamañán et al. (2). A suitable correlation of these P - x data resulted when the excess Gibbs energy of the liquid phase was represented by the six-parameter Margules equation. For present purposes, we require Margules equations for both G^E and H^E with the same number of terms. We have therefore refit the P - x data of Villamañán

Table I. H^E - x Data for Acetonitrile (1)/Water (2) at 50 °C

x_1	x_2	$H^E/\text{J mol}^{-1}$	x_1	x_2	$H^E/\text{J mol}^{-1}$
0.0194	0.9806	28.0	0.4902	0.5098	1189.3
0.0501	0.9499	113.0	0.5418	0.4582	1232.2
0.0686	0.9314	177.6	0.5989	0.4011	1255.1
0.1066	0.8934	319.3	0.6482	0.3518	1249.2
0.1507	0.8493	472.8	0.6988	0.3012	1218.8
0.1999	0.8001	626.6	0.7511	0.2489	1147.6
0.2405	0.7595	739.1	0.7981	0.2019	1049.2
0.2475	0.7525	755.4	0.8494	0.1506	891.9
0.2919	0.7081	862.1	0.9007	0.0993	661.8
0.3432	0.6568	969.8	0.9327	0.0673	484.7
0.3936	0.6064	1060.2	0.9579	0.0421	318.1
0.4457	0.5543	1137.2	0.9858	0.0142	115.3

et al. to provide parameters for the eight-parameter Margules equation, which may be written for G^E as

$$G^E/(x_1x_2RT) = A - Cx_1x_2 + D(x_1x_2)^2 - E(x_1x_2)^3 \quad (2)$$

where $A \equiv A_{21}x_1 + A_{12}x_2$; $C \equiv C_{21}x_1 + C_{12}x_2$; $D \equiv D_{21}x_1 + D_{12}x_2$; $E \equiv E_{21}x_1 + E_{12}x_2$. The resulting parameter values are $A_{21} = 2.01413$, $A_{12} = 2.51424$; $C_{21} = 1.19013$, $C_{12} = 0.51224$; $D_{21} = 1.06764$, $D_{12} = -4.51292$; $E_{21} = -0.84890$, $E_{12} = -8.86791$. The rms value of the pressure deviations is 1.0 kPa, and the maximum deviation is 1.9 kPa.

Since $S^E = (H^E - G^E)/T$, we also have

$$S^E/(x_1x_2R) = A'' - C''x_1x_2 + D''(x_1x_2)^2 - E''(x_1x_2)^3 \quad (3)$$

where $A'' \equiv A_{21}''x_1 + A_{12}''x_2$, $C'' \equiv C_{21}''x_1 + C_{12}''x_2$, $D'' \equiv D_{21}''x_1 + D_{12}''x_2$, $E'' \equiv E_{21}''x_1 + E_{12}''x_2$, with each parameter M_{ij}'' related to the corresponding parameters in eq 1 and 2 by

$$M_{ij}'' = M_{ij}' - M_{ij}$$

The resulting parameter values for 50 °C are therefore $A_{21}'' = 1.07627$, $A_{12}'' = -2.23219$; $C_{21}'' = -0.69049$, $C_{12}'' = -13.84811$; $D_{21}'' = -15.16934$, $D_{12}'' = -62.19192$; $E_{21}'' = -25.02314$, $E_{12}'' = -95.92246$. The three excess properties at 50 °C as calculated from eq 1, 2, and 3 are plotted as functions of x_1 in Figure 1.

Additional data from the literature allow development of correlations that incorporate the temperature dependence of the parameters. The assumption that H^E is linear in T and

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