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Thermochimica Acta 352–353 (2000) 1–10

thermochimica acta

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Thermodynamic studies of mixed aqueous solutions of binary electrolytes of Na_2SO_4 and K_2SO_4

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Received 2 June 1999; received in revised form 12 October 1999; accepted 8 November 1999

Abstract

The thermodynamic study of Na_2SO_4 and K_2SO_4 binary and ternary aqueous solutions is materialized in obtaining both average ionic activity coefficients and excess Gibbs energies, from cryometric data. Differential cryometric method utilized for obtaining experimental data has permitted the measurement of cryometric effect with a precision of $\pm 2\times 10^{-4}$ K. The experimental data process has been obtained using a specific calculation program. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Excess Gibbs energy; Ionic activity coefficient; $NaSO_4/K_2SO_4$ binary aqueous solution; Ternary aqueous solution

1. Introduction

Many systems, biological or geological as well as chemical, involve the interest of mixed aqueous electrolytes. The representation of excess Gibbs energy and activity coefficients for aqueous electrolyte systems is a fundamental problem in the design and operation of many industrial processes.

The thermodynamic properties of aqueous electrolytes have been extensively investigated both experimentally and theoretically in works by authors like Harned and Owen [1], Robinson and Stokes [2], and others [3–5].

The numerous works which study the binary solutions represent a rich source of data for the calculation of the thermodynamic activities of the components of various systems.

The differential cryoscopy, considered a very accurate method, was extended to the investigation of the multicomponent systems [6], representing a way to make evident the behaviour of mixed electrolytes in aqueous solutions at temperatures close to the freezing point of the pure solvent.

2. General equations from cryometric data

The Harned law [7] and the Brönsted–Guggenheim equations [8] allow to express the activity coefficient of a solute from a ternary mixture with total constant molality, depending on the other solute, in dilute solutions.

We could thus correlate thermodynamic magnitudes specific to the components of ternary systems. The established equations are based on numerous experimental data, elaborated especially by measurements of electromotive forces and solubility measurements. We tried to study by colligative method the interionic actions of electrolytes in mixture.

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PII: S0040-6031(99)00429-3

The activity coefficients of the solutes of the binary systems γ_2, γ_3, and the activity coefficients γ_{23} of the mixed electrolytes of ternary systems, are calculated according to the equation deduced by Lewis and Randall [3]:

$$\log \gamma_i^1 = \log\,(\gamma_i^1)_0 - \int_{m_0}^{m} j\,\mathrm{d}\log m - \frac{j_\vartheta - j_0}{2.303} + \frac{2.5\times 10^{-4}}{\nu}\int_{m_0}^{\vartheta(m)} \frac{\vartheta}{m}\,\mathrm{d}\vartheta \tag{1}$$

The subscript i shows the nature of the solute.

Eq. (1) is illustrated by the results of cryoscopic measurements, which allow to determine directly the decrease of the freezing point of the solution with respect to the solvent, ϑ. The deviation factor of the solutions from the ideal behaviour is expressed in the form:

$$j = 1 - \frac{\vartheta}{\nu K_{\mathrm{c}} m} \tag{2}$$

K_{c} being the cryoscopic constant of solvent:

$$K_{\mathrm{c}} = \frac{R(T_0)^2}{55.51\Delta^{\mathrm{s}}H_1^0} \quad \text{and} \quad \frac{\vartheta}{\nu K_{\mathrm{c}} m} = \Phi$$

the osmotic coefficient become:

$$\Phi = 1 - j \tag{3}$$

The same equation was also applied to the calculation of the activity coefficients of the electrolyte mixture in the ternary system, owing to the colligative characteristics of the experimental method, the mixture was considered as a single substance with the $m=m_2+m_3$ molality. But we could show for activity coefficients of the electrolyte mixture in the ternary system:

$$(\gamma_{23})^m = (\gamma_2)_{23}^{m_2}(\gamma_3)_{23}^{m_3} \tag{4}$$

The values of the standard activity coefficients $(\gamma_i)_{\mathrm{ref}}$ could be calculated based on the values at freezing points $(\gamma_i)_{\mathrm{cryo}}$, with the Eq. (5):

$$\log\,(\gamma_{ii})_{\mathrm{ref}} = \log\,(\gamma_i)_{\mathrm{cryo}} - \frac{1}{\nu}[\bar{L}_2 Y - z\bar{J}_2] \tag{5}$$

in which

$$Y = \frac{298.16 - T_{\mathrm{cryo}}}{2.303R\times 298.16\times T_{\mathrm{cryo}}} \quad \text{and}$$

$$Z = 298.16Y - \frac{1}{R}\log\frac{298.16}{T'_{\mathrm{cryo}}} \tag{6}$$

The thermochemical magnitudes of Eq. (5) are represented by the partial molal relative heat content of the solute component $\bar{L}_2$ and the relative partial molal heat capacities of the solute, $\bar{J}_2$.

The activity of the solvent $(a_1)_2$, $(a_1)_3$ and $(a_1)_{23}$, of the binary and ternary solutions is calculated by means of Eq. (7):

$$\log\,(a_1)_i = \frac{1}{2.303\nu R(T_0)^2}\left\{(\Delta^{\mathrm{s}}H_1^0)_{T_0}\vartheta_i + \left[\frac{(\Delta^{\mathrm{s}}H_1^0)_{T_0}}{T_0} - \frac{\Delta^{\mathrm{s}}C_{\mathrm{P}}}{2}\right]\vartheta_i^2 + \dots\right\} \tag{7}$$

After substituting constant quantities for the solvent water, the freezing point of the pure solvent ϑ, the molar heat of solidification $(\Delta^{\mathrm{s}}H_1^0)_{T_0}$ and the difference between the molar heat capacity of the solid and liquid states of the pure solvent $\Delta^{\mathrm{s}}C_{\mathrm{P}}$, Eq. (7) changes into the simplified form for water, Eq. (7′):

$$\log\,(a_1)_i = 4.211\times 10^{-3}\,\vartheta - 2.2\times 10 - 6\vartheta^2 \tag{7′}$$

this equation is easily evaluated by the substitution of the measured cryometric elements.

The experimental results, comprised in the values of the total activity coefficients of mixed electrolytes γ_{23} become conclusive only in correlation with the activity coefficients of the isolated electrolytes, in binary systems (γ_2 and γ_3). In these conditions the ionic interactions which appear in solutions of mixed electrolytes, are comprised in a deviation function $\log \delta_{23}$ [9,10]:

$$\log \delta_{23} = m_2\log\gamma_2 + m_3\log\gamma_3 - m\log\gamma_{23} \tag{8}$$

Analogously to the deviation $\log \delta_{23}$ we can define the rate of the interaction changes between the solvent and the solute electrolytes at the transfer from their binary solutions to their mixed solution $\log \delta_1$ [9,10]:

$$\log \delta_1 = m_2\log\,(\gamma_1)_2 + m_3\log\,(\gamma_1)_3 - m\log\,(\gamma_1)_{23} \tag{8′}$$

the summation of Eqs. (8) and (8′) leads to the total function of deviation, expressed in a logarithmic form, $\log \Delta$, [10]:

$$\log \Delta = \frac{m_1}{m}\log\delta_1 + \log\delta_{23} \tag{9}$$

The deviations from the additivity in the ternary system in regard to the associated binaries were brought into relief with the Harned coefficients, calculated with the help of deviations functions, [9,10]:

$$a_2 = \frac{\log \delta_{23}}{2m_2m_3} + \frac{\Phi_2 - \Phi_3}{2.303(m_2 + m_3)} \tag{10}$$

$$a_3 = \frac{\log \delta_{23}}{2m_2m_3} + \frac{\Phi_3 - \Phi_2}{2.303(m_2 + m_3)} \tag{11}$$

For the excess Gibbs energy the equations particularization for the most usual thermodynamic functions of an i components system, leads to expressions as [10]:

$$G^{\mathrm{E}} = RT\sum_i x_i \ln \gamma_i \tag{12}$$

For a binary solutions, at liquid–solid equilibrium we could calculate the excess Gibbs energy with the Eq. (13):

$$G^{\mathrm{E}} = RTm(1 - \Phi + \ln \gamma_{\pm}) \tag{13}$$

For the ternary solution we use the deviation function $\log \delta_{23}$ for the calculation the mixed excess Gibbs energy with the Eq. (14):

$$\Delta_m G^{\mathrm{E}} = -\frac{2.303RTm^2}{4}\frac{\log \delta_{23}}{m_2m_3} \tag{14}$$

3. Experimental part

Cryometric method, like other methods such as calorimetry, is based on temperature measurements at diverse molalities of solutions. The diminution of solution's freezing point in comparison with pure solvent at liquid–solid equilibrium represents the freezing-point depression.

The cryometric effects were determined on binary solutions of Na_2SO_4–H_2O, K_2SO_4–H_2O and on ternary solutions that contain the two mixed-electrolytes: Na_2SO_4–K_2SO_4–H_2O.

The samples were realized from high-purity compounds produced by MERK company, dissolved in bidistillated water.

The concentration range of solutions is wide, providing the acquisition of curves, which set of the behavior of these electrolytes (from 0.2 mol/kg solvent until 4.0 mol/kg solvent for Na_2SO_4–H_2O, from 0.1 mol/kg solvent until 0.65 mol/kg solvent for K_2SO_4–H_2O and from 0.2 mol/kg solvent until 1.2 mol/kg solvent for Na_2SO_4–K_2SO_4–H_2O).

The apparel consisted in an ensemble compound of a calorimeter with the freezing agent in which it is introduced the cell with the solutions to study and a differential cast to measure the freezing temperatures. The cryometric effects measurements have been obtained by using a differential cryometry assemblage. To still maintain the differential system, in the advantage of the method sensibility and precision, as well, in the Wheatstone bridge a transformation has been made: the Wheatstone bridge branch destined to the solvent (water) cell having at certain measurements the some freezing point and, therefore, the some strength (in our case — 100 Ω at 273.16 K), has been replaced by a fixed strength (standard) from manganin, and the branch containing the solution cell, equipped with a Pt (platinum) caliber (Heraeus–Degussa thermometer) of 100 Ω at 273.16 K, perfectly calibrated and a strength thermic coefficient of 0.039 Ω/K [11]. On this way, there has been able to maintain for ϑ a slight and also practically easy accessible real difference.

The work cell has double void walls and is separated from the cooling medium with another isolating material partition, between the cell and this partition there is interposing air. The solutions subjected to the tests have been composed of high purity substances, reaching the solubility limit. The working procedure consists of measuring the cryometrical effects for every binary solution at all the concentration domain. Based on these effects, we used the Eqs. (1), (2) and (3) to calculate the thermodynamic activity coefficients and the osmotic coefficients. Using the entire set of Eqs. (1)–(14) we could obtain thermodynamic proprieties for these binary systems and for the ternary mixture obtained from the mixing of the respective binaries.

The ternary mixture has been obtained at electrolytes equal molalities.

4. Results

Differential cryometric method, utilized in order to obtain experimental data, has permitted the measurement of cryometric effect with a precision of $\pm 2\times 10^{-4}$ K.

Table 1
The mean activity coefficients of Na_2SO_4 at freezing points in Na_2SO_4–H_2O[a]

m mol/kg solvent	ϑ (K)	j	j/m	ϑ/m	$\int_{m_0}^{m}(j/m)\,\mathrm{d}m$	$\int_{\vartheta_0}^{\vartheta}(\vartheta/m)\,\mathrm{d}\vartheta$ $x(2.5\times10^{-4}/\nu)$	$\log\gamma_\pm$	$\gamma_\pm$[b]
0.2000	0.6998	0.3723	1.8613	3.494	1.9658	1.9495	−0.4330	0.369
0.3000	1.0095	0.3963	1.3210	3.365	3.5570	3.4625	−0.5216	0.301
0.4000	1.4568	0.3466	0.8665	3.642	4.6508	4.4805	−0.5758	0.266
0.5000	1.7555	0.3701	0.7402	3.511	5.4541	5.2565	−0.6133	0.264
0.6000	2.0950	0.3736	0.6226	3.4917	6.1355	5.9135	−0.6392	0.229(5)
0.6500	2.2445	0.3805	0.5854	3.4531	6.7397	6.4953	−0.6645	0.2165
0.8000	2.4689	0.4463	0.5579	3.0861	7.3115	7.0443	−0.7160	0.192
1.0000	3.2565	0.4158	0.4158	3.2565	7.7984	7.4784	−0.7555	0.176
1.2000	3.8995	0.4170	0.3472	3.2496	8.18	7.8437	−0.7724	0.169
1.4000	4.3362	0.4443	0.3174	3.0973	8.5124	8.1642	−0.7961	0.159(9)
1.6000	5.0335	0.4356	0.2722	3.1459	8.8073	8.4349	−0.8164	0.153
1.8000	5.5956	0.4423	0.2457	3.1087	9.0662	8.6850	−0.8283	0.148(5)
2.0000	6.4355	0.4227	0.2114	3.2177	9.2948	8.8803	−0.8529	0.140
2.5000	8.0595	0.4216	0.1686	3.2238	9.4848	9.0551	−0.8677	0.136
3.0000	10.095	0.3963	0.1321	3.365	9.6352	9.1781	−0.8841	0.131
3.5000	12.5955	0.3544	0.1012	3.5987	9.7518	9.2672	−0.8935	0.128
4.0000	15.5695	0.3017	0.0754	3.8924	9.8402	9.3293	−0.8969	0.127

[a] $J_0=-0.207$; $\log\gamma_0=-0.345$; $m_0=0.1000$.
[b] The $\gamma_\pm$ data are noted γ_2 in Na_2SO_4–H_2O.

The thermodynamic properties for Na_2SO_4–H_2O solution are presented in Tables 1, 2 and 3 and for K_2SO_4–H_2O solution are presented in Tables 4, 5 and 6. The cryometric depression ϑ, experimentally determined, at various molalities for the Na_2SO_4–H_2O and K_2SO_4–H_2O solutions are recorded in Tables 1 and 4 identically presented. Besides the primary quantities, data derived from them appear to be necessary for the

Table 2
The mean activity coefficients of Na_2SO_4at standard temperature Na_2SO_4–H_2O[a]

m mol/kg solvent	ϑ (K)	$\gamma_\pm$	Y	Z	X/ν	$\log\gamma_{\pm,\mathrm{ref.}}$	$\gamma_{\pm,\mathrm{ref.}}$[a]	$\gamma_{\pm,\mathrm{ref.}}$[b]
0.1000	0.442	0.452	1.63E-5	0.00021	−0.7969	−0.3449	0.452	0.4457
0.2000	0.6998	0.369	1.65E-5	0.00022	−0.8002	−0.4312	0.3705	0.3656
0.3000	1.0095	0.3009	1.67E-5	0.00022	−0.7952	−0.4943	0.3204	0.3212
0.4000	1.45678	0.2656	1.71E-5	0.00023	−0.8040	−0.5383	0.2895	0.2910
0.5000	1.7555	0.2636	1.73E-5	0.00024	−0.8192	−0.5756	0.2657	0.2684
0.6000	2.095	0.2295	1.75E-5	0.00024	−0.8319	−0.6024	0.2498	0.2605
0.6500	2.2445	0.2165	1.76E-5	0.00025	−0.8354	−0.6189	0.2405	–
0.8000	2.4689	0.1923	1.78E-5	0.00025	−0.8407	−0.6484	0.2247	0.2236
1.0000	3.2565	0.1756	1.83E-5	0.00027	−0.8683	−0.6927	0.2029	0.2040
1.2000	3.8995	0.1689	1.88E-5	0.00028	−0.8936	−0.7247	0.1885	0.1889
1.4000	4.3362	0.1599	1.91E-5	0.00029	−0.9117	−0.7518	0.1771	0.1774
1.6000	5.0335	0.1526	1.96E-5	0.00030	−0.9183	−0.7757	0.1676	0.1680
1.8000	5.5956	0.1485	2.00E-5	0.00032	−0.9438	−0.7953	0.1602	0.1605
2.0000	6.4355	0.1403	2.06E-5	0.00033	−0.9519	−0.8116	0.1543	0.1546
2.5000	8.0595	0.1356	2.18E-5	0.00037	−0.9772	−0.8416	0.144	0.1444
3.0000	10.095	0.1306	2.34E-5	0.00043	−0.9901	−0.8595	01382	0.1394
3.5000	12.5955	0.1278	2.35E-5	0.00049	−0.9927	−0.8649	0.1365	0.1367
4.0000	15.5695	0.1268	2.76E-5	0.00058	−0.9913	−0.8645	0.1366	0.1376

[a] The $\gamma_{\pm,\mathrm{ref.}}$ data are noted also $\gamma_{2,\mathrm{ref.}}$ in K_2SO_4–H_2O.
[b] The $\gamma_{\pm,\ \mathrm{ref.}}$ data belong to Goldberg [12].

Table 3
Thermodynamic properties of solvent in Na_2SO_4–H_2O

m mol/kg solvent	ϑ (K)	Φ	$\Phi_{ref.}$	$\Phi_{ref.}$[a]	log $(a_1)_2$	$(a_1)_2$	log $(a_1)_{2,ref.}$	$(a_1)_{2,ref}$	$(a_1)_{2,ref.}$[a]
0.1000	0.442	0.793	0.7869	0.793	−0.0019	0.9957	−0.0015	0.996	0.995
0.2000	0.6998	0.627(7)	0.7494	0.753	−0.0029	0.9932	−0.0031	0.992(8)	0.992
0.3000	1.0095	0.603(7)	0.7262	0.725	−0.0042	0.9902	−0.0047	0.989	0.988
0.4000	1.4568	0.653	0.7088	0.705	−0.0061	0.9860	−0.0062	0.985(7)	0.985
0.5000	1.7555	0.629(9)	0.6945	0.690	−0.0074	0.9831	−0.0078	0.982	0.982
0.6000	2.095	0.626	0.6824	0.678	−0.0088	0.9799	−0.0094	0.978(6)	0.978
0.6500	2.2445	0.619	–	–	−0.0095	0.9784	–	–	–
0.8000	2.4689	0.553(7)	0.6629	0.658	−0.0104	0.9763	−0.0125	0.971(6)	0.972
1.0000	3.2565	0.584	0.6481	0.642	−0.0137	0.9689	−0.0156	0.965	0.965
1.2000	3.8995	0.583	0.6289	0.631	−0.0164	0.9928	−0.0188	0.958	0.959
1.4000	4.3362	0.555(7)	0.6224	0.625	−0.0183	0.9587	−0.0219	0.919	0.953
1.6000	5.0335	0.564	0.6215	0.621	−0.0212	0.9522	−0.0250	0.944	0.947
1.8000	5.5956	0.557(7)	0.6196	0.620	−0.0236	0.9470	−0.0281	0.937	0.940
2.0000	6.4355	0.577	0.6257	0.621	−0.0272	0.9393	−0.0313	0.931	0.930
2.5000	8.0595	0.578	0.6402	0.635	−0.0341	0.9245	−0.0391	0.914	–
3.0000	10.095	0.603(7)	0.6642	0.661	−0.0427	0.9063	−0.0469	0.897	0.987
3.5000	12.595	0.645(6)	0.7015	0.696	−0.0534	0.8843	−0.0547	0.882	–
4.0000	15.569	0.698	0.7522	0.740	−0.0661	0.8588	−0.0625	0.865(9)	–

[a] The $\Phi_{ref.}$ data and $(a_1)_{2,ref.}$ data belong to Rard and Miller [13].

Table 4
The mean activity coefficients of K_2SO_4 at freezing points in K_2SO_4–H_2O[a]

m mol/kg solvent	ϑ (K)	j	j/m	ϑ/m	$\int_{m_0}^{m}(j/m)\,\mathrm{d}m$	$\int_{\vartheta_o}^{\vartheta}(\vartheta/m)\mathrm{d}\vartheta$	log $\gamma_\pm$	$\gamma_\pm$[b]
	1.9931	−0.7878	−3.9389	0.0024	0.0885	9.9806	−0.4780	0.332(6)
0.2000	2.7347	−0.6354	−2.1179	0.0686	0.0728	19.5209	−0.5293	0.295(6)
0.3000	3.6502	−0.6372	−1.5929	0.0678	0.1125	28.6415	−0.5689	0.269(8)
0.4000	4.4654	−0.6022	−1.2045	0.0830	0.1367	32.7004	−0.6087	0.246(2)
0.5000	5.2756	−0.5774	−0.9624	0.0937	0.1752	39.8802	−0.6586	0.219(5)
0.6000	5.6696	−0.5649	−0.8690	0.0992	0.1968	43.3307	−0.6859	0.206(1)
0.6500								

[a] j_0=−0.793; log γ_0=−0.386; m_0=0.1000.

[b] The $\gamma_\pm$ data are noted also γ_3 in K_2SO_4–H_2O.

Table 5
The mean activity coefficients of K_2SO_4 at standard temperature K_2SO_4–H_2O

m mol/kg solvent	ϑ (K)	$\gamma_\pm$	Y	Z	X/v	log $\gamma_{\pm,ref.}$	$\gamma_{\pm,ref.}$[a]	$\gamma_{\pm,ref.}$[b]
0.1000	0.9996	0.411	1.67E–5	0.00022	−0.0259	−0.3603	0.436	0.441
0.2000	1.9931	0.333	1.74E–5	0.00024	−0.0294	−0.4487	0.356	0.361
0.3000	2.7347	0.295(6)	1.79E–5	0.00025	−0.0246	−0.5047	0.313	0.317
0.4000	3.6502	0.269(8)	1.86E–5	0.00027	−0.0204	−0.5485	0.283	0.283
0.5000	4.4654	0.246	1.92E–5	0.00029	−0.0252	−0.5835	0.261	0.264
0.6000	5.2756	0.219(5)	1.98E–5	0.00031	−0.0441	−0.6144	0.243	0.246
0.6500	5.6696	0.206	2.01E–5	0.00032	−0.0454	−0.6405	0.228(8)	0.229

[a] The $\gamma_{\pm,ref.}$ data are noted also $\gamma_{3,ref.}$ in K_2SO_4–H_2O.

[b] The $\gamma_{\pm,ref.}$ belong to Robinson and Stokes [2].

Table 6
The thermodynamic properties of solvent in K_2SO_4–H_2O

m mol/kg solvent	ϑ (K)	Φ	$\Phi_{ref.}$	$\Phi_{ref.}{}^{a}$	log $(a_1)_3$	$(a_1)_3$	log $(a_1)_{3\ ref.}$	$(a_1)_{3,ref.}$
0.1000	0.9996	1.793(3)	0.768(7)	0.779	−0.0042	0.990(3)	−0.0023	0.994(6)
0.2000	1.9931	1.787(8)	0.730(4)	0.742	−0.0084	0.980(8)	−0.0047	0.989(2)
0.3000	2.7347	1.635(4)	0.710(2)	0.721	−0.0115	0.973(8)	−0.0070	0.983(9)
0.4000	3.6502	1.637(2)	0.697(1)	0.703	−0.0154	0.965(2)	−0.0094	0.978(6)
0.5000	4.4654	1.602(2)	0.687(5)	0.691	−0.0188	0.957(5)	−0.0117	0.973(4)
0.6000	5.2756	1.577(4)	0.680(9)	0.679	−0.0223	0.950	−0.0141	0.968(1)
0.6500	5.6696	1.564(8)	0.680	–	−0.0239	0.946(3)	−0.0152	0.965(5)

[a] The $\Phi_{ref.}$ data belong to Goldberg [12].

computations and have the usual significances. The integrals in Eq. (1) were graphically solved, by using as γ_0, the values obtained by Goldberg [12], Robinson and Stokes [2], for the low concentrations. The computation was made step by step, considering as reference values the above mentioned quantities, at concentrations near the solubility of salts. We may find an analogous behaviour for the values of the activity coefficients of these electrolytes at standard temperatures in binary solutions (Tables 2 and 5), using the Eqs. (5) and (6). For binary solutions of these electrilytes we calculated the thermodynamic properties of solvent: the thermodynamic activities and the osmotic coefficients of water, presented in Tables 3 and 6, respectively. The data pertaining to the ternary mixture Na_2SO_4–K_2SO_4–H_2O, for thermodynamic properties are listed in Tables 7, 8 and 9. In ternary solution, are the thermodynamical magnitudes of Na_2SO_4 are noted with index 2, the thermodynamical magnitudes of K_2SO_4 are noted with index 3 and the thermodynamical magnitudes of Na_2SO_4–K_2SO_4–H_2O are noted with index 23. The mean activity coefficients of ternary system are in Table 7. In Table 8, the log δ_{23} deviation function and the Harned

Table 7
The mean activity coefficients at freezing points in Na_2SO_4–K_2SO_4–H_2O[a]

m mol/kg solvent	ϑ (K)	j	j/m	ϑ/m	$-\int_{m_0}^{m}(j/m)\,dm$	$\int_{\vartheta_0}^{\vartheta}(\vartheta/m)\,d\vartheta$	log γ_{23}	$\gamma_{23}{}^{b}$
0.4000	1.4609	0.3448	0.8620	3.6522	0.0850	6.7904	−0.4505	0.354(4)
0.6000	2.4072	0.2802	0.4671	4.0119	0.1872	8.5036	−0.5246	0.298(8)
0.8000	3.0363	0.3191	0.3989	3.7954	0.2163	0.9597	−0.5703	0.268(9)
1.0000	3.2588	0.4153	0.4153	3.2588	0.2141	11.7444	−0.6099	0.245(5)
1.2000	5.2895	0.2092	0.1743	4.4079	0.3455	21.8867	−0.6509	0.223(4)

[a] $j_0=-0.343$; log $\gamma_0=-0.365$; $m_0=0.2000$.
[b] The γ_{23} data are experimental data.

Table 8
Harned coefficients for ternary solution Na_2SO_4–K_2SO_4–H_2O

m mol/kg solvent	ϑ (K)	log δ_{23}	log γ_{23}	γ_{23}	$(\gamma_2)_{23}$	$(\gamma_3\ )_{23}$	a_2	a_3	a_2+a_3
0.2000	0.7319	−1.4E-5	−0.3655	0.431	0.274	0.678	2.1712	−2.1726	−0.0014
0.4000	1.4609	−0.0020	−0.4505	0.354	0.209	0.601	1.2345	−1.2840	−0.0495
0.6000	2.4072	−0.0005	−0.5246	0.299	0.180	0.496	0.7438	−0.7494	−0.0056
0.8000	3.0363	−0.0016	−0.5703	0.269	0.163	0.443	0.5289	−0.5390	−0.0101
1.0000	3.2588	−0.0011	−0.6099	0.246	0.150	0.401	0.4199	−0.4244	−0.0044
0.2000	5.2895	−0.6485	−0.6509	0.223	0.495	1.226	−0.5566	−1.2448	−1.8014

Table 9
The thermodynamic properties of solvent in ternary solution Na_2SO_4–K_2SO_4–H_2O at freezing points

m mol/kg solvent	ϑ (K)	Φ	$\log (a_1)_{23}$	$(a_1)_{23}$	$(a_1)_2$	$(a_1)_3$	$\log \delta_1$
0.2	0.7319	0.656(6)	−0.0031	0.992(9)	0.995(7)	0.990(3)	9.7E-6
0.4	1.4609	0.655(2)	−0.0062	0.985(9)	0.993(2)	0.980(8)	0.0002
0.6	2.4072	0.719(8)	−0.0101	0.976(9)	0.990(2)	0.973(8)	0.0045
0.8	3.0363	0.680(9)	−0.0128	0.970(9)	0.986	0.965(2)	0.0016
1.0	3.2588	0.584(6)	−0.0137	0.968(8)	0.983(1)	0.957(5)	0.0006
1.2	5.2895	0.790(8)	−0.0223	0.949(9)	0.979(8)	0.950	0.0081

coefficients at the various freezing points are presented. In ternary solution the thermodynamic activity, the osmotic coefficient and $\log \delta_0$ deviation function for water are presented in Table 9.

The values of the activity coefficients can be graphically represented as a function of the concentration for both binary solutions (Figs. 1 and 2), at freezing points and at standard temperature, and for the ternary system likeness the associated binaries (Fig. 3).

The excess Gibbs energy for Na_2SO_4–H_2O, for K_2SO_4–H_2O and for the ternary mixture Na_2SO_4–K_2SO_4–H_2O are presented in Table 10. In Figs. 4, 5 and 6 we have the variation of the excess Gibbs energy with molality of solution.

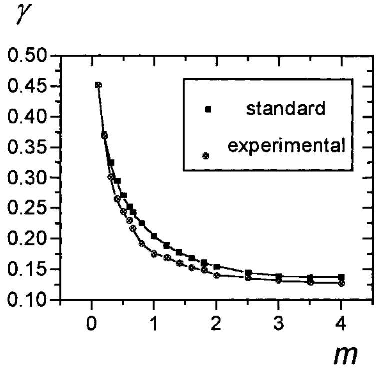

Fig. 1. The mean activity coefficients at standard temperature and at freezing points for Na_2SO_4 in binary solution Na_2SO_4–H_2O.

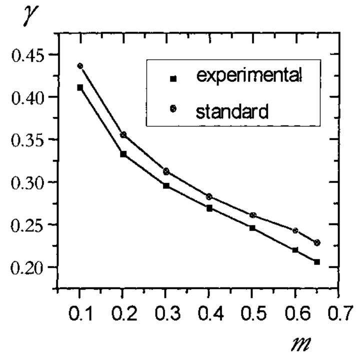

Fig. 2. The mean activity coefficients at standard temperature and at freezing points for K_2SO_4 in binary solution K_2SO_4–H_2O.

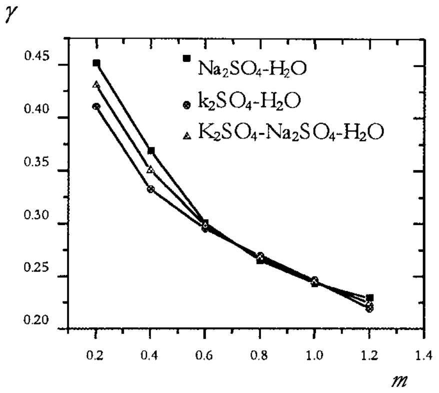

Fig. 3. The mean activity coefficients at freezing points in binary and ternary aqueous electrolytes solution of Na_2SO_4 and K_2SO_4.

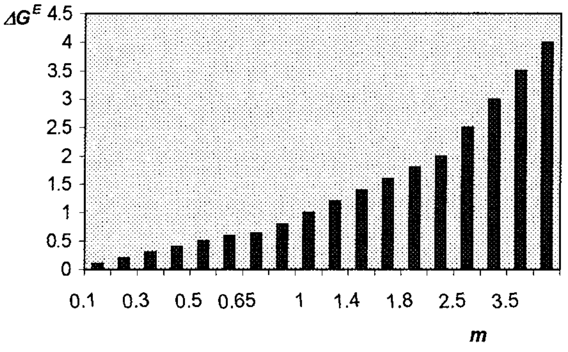

Fig. 4. Excess Gibbs energy in binary solution Na_2SO_4–H_2O at freezing points K_2SO_4.

Table 10
Excess Gibbs free energy for binary and ternary aqueous solutions of Na_2SO_4 and K_2SO_4

Na_2SO_4–H_2O			K_2SO_4–H_2O			Na_2SO_4–K_2SO_4–H_2O		
m mol/kg solvent	ϑ (K)	G^E (kJ/mol)	m mol/kg solvent	ϑ (K)	G^E (kJ/mol)	m total mol/kg solvent	ϑ (K)	$\Delta_m G^E$ (kJ/mol)
0.1000	0.442	−0.062(5)	0.1000	0.9996	–	0.2000	0.7319	7.303E-5
0.2000	0.6998	−0.055	0.2000	1.9931	1.142(4)	0.4000	1.4609	0.001(3)
0.3000	1.0095	−0.170(1)	0.3000	2.7347	–	0.6000	2.4072	0.002(6)
0.4000	1.4568	−0.414(2)	0.4000	3.6502	2.554(9)	0.8000	3.0363	0.008(3)
0.5000	1.7555	−0.548(8)	0.5000	4.4654	–	1.0000	3.2588	0.005(7)
0.6000	2.095	−0.718(4)	0.6000	5.2756	3.752(5)	1.2000	5.2895	0.004(3)
0.6500	2.2445	−0.831(7)	0.6500	5.6696	–	–	–	–
0.8000	2.4689	−0.971(1)	–	–	5.235(7)	–	–	–
1.0000	3.2565	−1.524(7)	–	–	–	–	–	–
1.2000	3.8995	−1.909(3)	–	–	6.715(8)	–	–	–
1.4000	4.3362	−2.716(8)	–	–	–	–	–	–
1.6000	5.0335	−2.091(3)	–	–	8.395(6)	–	–	–
1.8000	5.5956	−3.091(3)	–	–	–	–	–	–
2.0000	6.4355	−3.816(3)	–	–	9.300(5)	–	–	–
2.5000	8.0595	−4.916(4)	–	–	–	–	–	–
3.0000	10.095	−6.401(1)	–	–	–	–	–	–
3.5000	12.5955	−8.175(5)	–	–	–	–	–	–
4.0000	15.5695	−10.197(8)	–	–	–	–	–	–

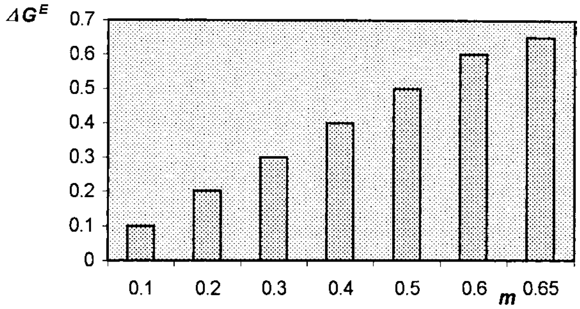

Fig. 5. Excess Gibbs energy in binary solution K_2SO_4–H_2O at freezing points K_2SO_4.

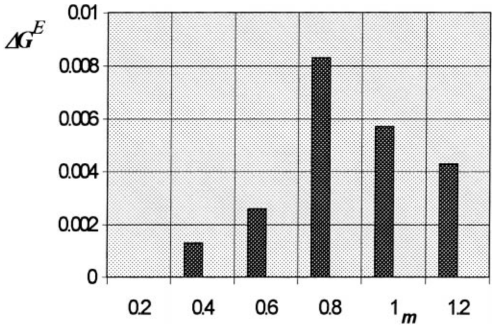

Fig. 6. Excess Gibbs energy in ternary solution Na_2SO_4–K_2SO_4–H_2O at freezing points K_2SO_4.

5. Discussions

We find that for binary aqueous solutions of Na_2SO_4 and K_2SO_4 at freezing points the mean thermodynanic activity coefficients decrease at the same time with the concentration increasing (Tables 1 and 4 or Figs. 1 and 2). We may find an analogous behaviour for the values of the activity coefficients of these electrolytes at standard temperatures in binary solutions like in Figs. 1 and 2. The experimental data at freezing points are always below the standard data at 298.16 K. (Figs. 1 and 2).

In Tables 2 and 5 we find that the experimental data we have obtained are in accordance with the literature data belong to R.N. Golbderg [12] for Na_2SO_4–H_2O and to R.A. Robinson and R.H. Stokes [2] for K_2SO_4–H_2O. This fact proves the accuracy of the method we use in order to obtain data at freezing points as well the exactness of the calculation program. In Tables 3 and 6 we present the results obtained for the thermodynamic activity and for osmotic coefficients of water as a solvent. We find also the experimental data we have obtained are in a good accordance with the literature data belong to J.A. Rard and D.G. Miller [13] for Na_2SO_4–H_2O and R.N. Golbderg [12] for K_2SO_4–H_2O. From the examination of results obtained for the thermodynamic activity of water as a solvent in all binary solutions the solvent activity values decreases at the same time with the increasing of the solution molality.

The deviation from additivity of the activity coefficients of the ternary solution in regard to the corresponding binaries, grow as the concentration increases (see Fig. 3). The behaviour of the electrolytes in ternary solutions with the associated binaries is characterized also by Harned coefficients a_2 and a_3 and $\log \delta_{23}$, $\log \delta_{0s}$ functions.

Taking into account the ternary system Na_2SO_4–K_2SO_4–H_2O we find that if the values of the deviation function $\log \delta_{23}$, which is responsible for ion–ion interactions, are negative in all concentrations range in the study, the function $\log \delta_0$, responsible for ion-solvent interactions has only positive values which is understandable by the fact that the two. The negative values for function $\log \delta_{23}$, demonstrated that between the two electrolytes of the mixture the coulombian component of interaction energy prevails in comparison with the other components of energy.

The modification of the interactions of electrolytes from binary solutions to associated ternary solution can be seen also from the values $(\gamma_2)_{23}$ and $(\gamma_3)_{23}$ of electrolytes in ternary solution in comparison with the values (γ_2) and (γ_3) according to binary solutions. Comparing the values of the mean ionic activity coefficients of Na_2SO_4 and for $K_2SO_4$from Tables 1, 4 and 8 we find that for $Na_2SO_4$the mean activity coefficients in ternary system $(\gamma_2)_{23}$ — Table 8 — decrease in comparison with the values of the same electrolyte in binary solution (γ_2) — Table 1 — and vice versa for K_2SO_4 the mean activity coefficients in ternary system $(\gamma_3)_{23}$ — Table 8 — increase in comparison with the values of the same electrolyte in binary solution (γ_3) — Table 4. In the Table 10 are presented in kJ/mol the results obtained for the excess Gibbs energy in the aqueous binary and ternary solutions of Na_2SO_4 and K_2SO_4. In Fig. 4 we have represented the excess Gibbs energy in binary solution Na_2SO_4–H_2O at freezing points. In Fig. 5 we have represented also, the excess Gibbs energy in binary solution K_2SO_4–H_2O at freezing points. The values increase with the molality solution for binary solution of these electrolytes.

For the ternary Na_2SO_4–K_2SO_4–H_2O it is noticeable that the Gibbs energy values are in majority positive and have been calculated on the basis of $\log \delta_{23}$ function, which has in majority negative values. In Fig. 6 we have represented mixed excess Gibbs energy in ternary solution Na_2SO_4–K_2SO_4–H_2O at freezing points. We find that the values reach a maximum and then increase with the molality of solution.

6. Conclusions

From cryometric data we deduced the thermodynamic behaviour of the binary solutions Na_2SO_4–H_2O and K_2SO_4–H_2O and of the ternary associated solution Na_2SO_4–K_2SO_4–H_2O.

The importance of the study is based on the fact that the values of thermodynamic activity and osmotic coefficients of water are obtained at the freezing points with great accuracy. The studies performed are original; therefore, no literature data exist for Na_2SO_4–K_2SO_4–H_2O ternary solution for the values mean activity coefficients at freezing points.

We obtained in the first time the values for the excess Gibbs energy in the aqueous binary and ternary solutions of Na_2SO_4 and K_2SO_4 at their freezing points.

7. Notation

a_1	thermodynamic activity of solvent;
a_{23}	thermodynamic activity of mixed electrolytes solution (2 and 3);
G^E	excess Gibbs energy of electrolyte solution;
$\Delta_m G^E$	excess Gibbs energy of mixed electrolyte solution;
m	concentration in molality in mol/kg solvent;
T_0	freezing point temperature;
$\Delta^s H_1^0$	molal solidification heat;
j_0	corrective factor at increase dilution with molality m_0

Greek letters

γ_i	mean ionic activity coefficient;
$(\gamma_i^1)_0$	mean ionic activity coefficient at increase dilution with molality m_0;
γ_2	mean ionic activity coefficient of electrolyte 2 in a binary solution;
γ_3	mean ionic activity coefficient of electrolyte 3 in a binary solution;

γ_{23}	mean ionic activity coefficient of electrolytes 2 and 3 in a ternary solution;
$(\gamma_2)_{23}$	mean ionic activity coefficient of electrolyte 2 in a ternary solution;
$(\gamma_3)_{23}$	mean ionic activity coefficient of electrolyte 3 in a ternary solution;
$\gamma_\pm$	mean ionic activity coefficient of electrolyte in a aqueous electrolyte solution;
$\log \delta_0$	deviation function responsible for ion-solvent interactions in a ternary electrolyte solution;
$\log \delta_{23}$	deviation function responsible for ion–ion interactions in a ternary electrolyte solution;
Φ	osmotic coefficient;
ϑ	freezing-point depression in K;
v	stoichiometric coefficient

Acknowledgements

The authors acknowledge most gratefully the criticisms and encouragement's received from Professor Rodica Vilcu.

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