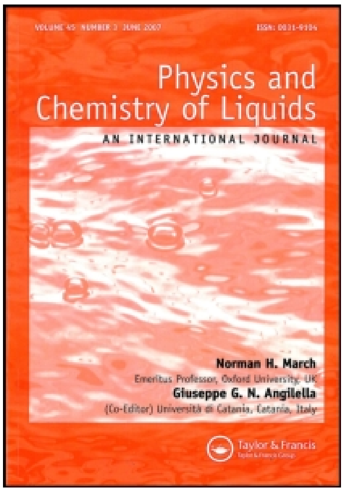

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Thermodynamic Properties of Ternary Aqueous Electrolyte Solutions

Luminita Grigore[a]; Aurelia Meghea[b]; Ovidiu Grigore[c]; Rodrigo Martins[a]
[a] CEMOP-UNINOVA, Monte de Caparica, Portugal [b] Faculty of Chemistry, POLITEHNICA University, Bucharest, Romania [c] Faculty of Electronics and Telecommunications, Bucharest, Romania

To cite this Article Grigore, Luminita , Meghea, Aurelia , Grigore, Ovidiu and Martins, Rodrigo(1999) 'Thermodynamic Properties of Ternary Aqueous Electrolyte Solutions', Physics and Chemistry of Liquids, 37: 4, 409 — 428

To link to this Article: DOI: 10.1080/00319109908031445

URL: http://dx.doi.org/10.1080/00319109908031445

Phys. Chem. Liq., 1999, Vol. 37, pp. 409-428
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

THERMODYNAMIC PROPERTIES OF TERNARY AQUEOUS ELECTROLYTE SOLUTIONS

LUMINITA GRIGORE[a,*], AURELIA MEGHEA[b],
OVIDIU GRIGORE[c] and RODRIGO MARTINS[a]

[a] *CEMOP-UNINOVA, Quinta da Torre, 2825, Monte de Caparica, Portugal;* [b] *Faculty of Chemistry, POLITEHNICA University, Calea Grivitei 132, Bucharest, Romania;*
[c] *Faculty of Electronics and Telecommunications, Bd. Iuliu Maniu 1-3, Bucharest, Romania*

(Received 1 December 1997)

In previous papers the mean excess chemical potential, μ_{I}^{E}, in ternary systems of the type I sulphate + II sulphate + H_2O, at 25°C was determined. Results obtained for systems with $CuSO_4$(I), and $ZnSO_4$(I) respectively, pointed out an obvious disparity between their behaviours. They show the existence of some important association phenomena partially accounting for the substantial deviations from ideal behaviour. The ternary sulphate systems ($CuSO_4 + Me^{\mathrm{I,II}}SO_4 + H_2O$; $ZnSO_4 + Me^{\mathrm{I,II}}SO_4 + H_2O$) studied were characterized against the binaries of the same ionic strength, experimental data being obtained using both e.m.f. and spectrophotometric methods. Deviations from the ideal behaviour were discussed in terms of thermodynamic excess functions and association constants. A comparative study between the results obtained with the two above mentioned methods is presented.

Keywords: Ternary aqueous systems; e.m.f. method; spectrophotometry; association constants

INTRODUCTION

In some previous papers [1-5] the means excess chemical potential, μ_{I}^{E}, in ternary systems of the type I sulphate + II sulphate + H_2O, at 25°C was determined. Considering a conventional model (an "ideal

---

*Corresponding author.

ternary solution" defined against a real binary solution of I sulphate in water), the studied systems were devised in three groups (see Fig. 1).

Group I: $ZnSO_4(m_1)$ + $Me^{I,II}SO_4(m_2)$ + H_2O solutions for which the mean activity coefficient depends only on the ionic strength fraction. They are quasi-independent both of the ionic strength and of the added cation charge;

Group II: $CuSO_4(m_1)$ + $(Me_{alc})_2SO_4(m_2)$ + H_2O solutions with asymmetrical cationic charge have deviations from the ideal behaviour. The shape of mean activity coefficient dependencies on ionic strength fraction has a first linear portion (till a fraction of approximately 0.5), for which negative deviations increase in the order Li, Na, K. In the second portion, for fractions greater than 0.5, this order isn't always obeyed;

Group III: $CuSO_4(m_1)$ + (Mg, Mn, Zn)$SO_4(m_2)$ + H_2O solutions with symmetrical cationic charge have very high deviations from the ideal behaviour. Curves shape in this case is very complex, with both negative and positive values.

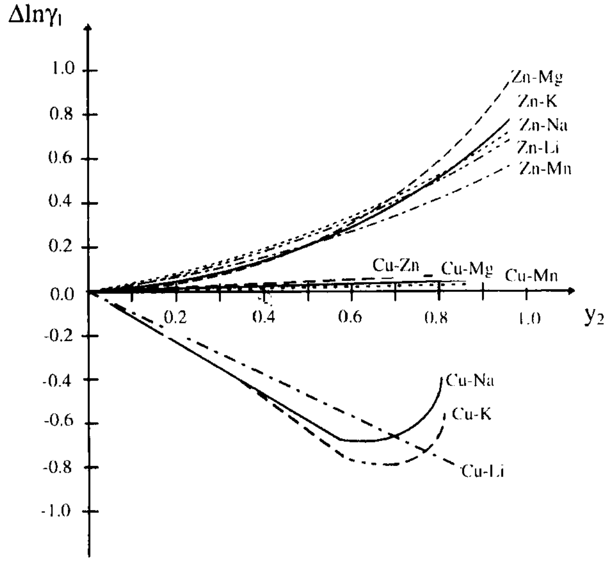

FIGURE 1 Variation of $\Delta\ln\gamma_1$ with ionic strength fraction (y_2) for all studied systems ($I = 2.4$).

The studied sulphate ternary systems (of the type $CuSO_4 + Me^{I,II}$ $SO_4 + H_2O$ or $ZnSO_4 + Me^{I,II}$ $SO_4 + H_2O$) were characterized against the binaries of the same ionic strength, experimental data being achieved using both e.m.f. and spectrophotometric methods. Systems deviations from the ideal behaviour were discussed in terms of thermodynamic excess functions and association constants.

A comparative study between the results obtained with the two above-mentioned methods concerning the systems summarized above is presented.

EXPERIMENTAL PART

All reagents have been of p.a. purity. The copper sulphate has been twice recrystallized from redistilled water acidulated with sulphuric acid (10^{-1} M) and brought into pentahydrated form by air-drying up to constant weight. The magnesium sulphate has been twice purified from redistilled water and dried at 140°C as heptahydrate. The lithium, sodium and potassium sulphates have been purified through the same procedure and brought to anhydrous state by drying at 320°C up to constant weight. Solutions' concentration has been verified by electrodeposition in the case of $CuSO_4$, by titration of Mg^{2+} with EDTA for $MgSO_4$ and by weighting in the case of alkaline sulphates. Experimental data at 20, 30, 40 and 50°C, constant total ionic strength ($I = 2.4$) and variable proportion between the two electrolytes were determined.

E.m.f. measurements were achieved in cells with thermostatic control, using a Weston bridge. Cells'types were:

$$\mathrm{Pt - Hg - HgSO_4/ZnSO_4}\,(m_1),\quad \mathrm{M^{I,II}SO_4}(m_2)/\mathrm{Zn}_x\mathrm{Hg - Pt}$$

$$\mathrm{Pt - Hg - HgSO_4/CuSO_4}(m_1),\quad \mathrm{M^{I,II}SO_4}(m_2)/\mathrm{Cu - Pt}$$

where $M^{I,II}$ = Li, Na, K, Mg.

Results' reproducibility was the main factor of the two electrodes choose [6]. Precision of e.m.f. measurements was 0.1 mV. For electrodes' stability, repeated determinations were done both for the binary and for the termary systems. Differences less than 2.5 mV were considered cell's satisfactory stability test. For measuring absorbencies in the 220–300 nm range, a VSU-2 (Karl Zeiss, Jena) Spectrophotometer equipped with thermostatic control cell compartment has been used. Stock solution concentrations prepared by weighting have been as it follows: $CuSO_4$ 0.13 M, Li_2SO_4 1.5M, Na_2SO_4 3 M, K_2SO_4 0.57 M, $MgSO_4$ 2.26 M, all of them having a content of 10^{-1}M perchloric acid as protection against hydrolysis. Ternary solutions have been obtained by mixing suitable volumes of binary stock solutions and completed with redistilled water $HClO_4$ 10^{-1} M acidulated.

Absorbency determinations for all the binary systems have been made against redistilled water acidulated with perchloric acid up to 10^{-1} M. In the range of interest of added sulphates' concentrations, the optic absorbencies of binary systems have been neglected as being much lower than the association effect. In binary system, each set of measurements for optical absorbencies of $CuSO_4$ solutions have been repeated. Determinations for ternary systems of optical absorbencies have been made differentially against the binary system having the same $CuSO_4$ concentration.

RESULTS AND DISCUSSIONS

For e.m.f. data, the calculation was directly done by the help of $\Delta\ln\gamma_1$ defined by:

$$\Delta\ln\gamma_1 = -\frac{E_t - E_b}{(RT/F)} - \ln\frac{m^t_{1\pm}}{m^b_{1\pm}} \tag{1}$$

where: $m^b_{1\pm}$ = mean activity coefficient of $CuSO_4$ and $ZnSO_4$ respectively, in the binary system;

$$m^t_{1\pm} = [m_1(m_1 + m_2)]^{1/2} \tag{2}$$

= mean activity coefficient of $CuSO_4$ and $ZnSO_4$ respectively, in the ternary system.

Then thermodynamic excess functions were calculated:

$$\mu^E_1 = RT\Delta\ln\gamma_1 \tag{3}$$

$$\bar{S}^E_1 = -R\Delta\ln\gamma_1 - RT\left(\frac{\partial\Delta\ln\gamma_1}{\partial T}\right)_P \tag{4}$$

$$\bar{H}^E_1 = -RT^2\left(\frac{\partial\Delta\ln\gamma_1}{\partial T}\right)_P \tag{5}$$

where $((\partial\Delta\ln\gamma_1/\partial T)_P)$ is the temperature coefficient of $\Delta\ln\gamma_1$.

The results obtained from e.m.f. measurements are presented in Table I and Figures 2–4 as dependencies of thermodynamic excess functions with ionic strength fractions given by the following relationships:

– for asymmetrical systems:

$$y_2 = \frac{I_2}{I} = \frac{3m_2}{4m_1 + 3m_2} = \frac{3m_2^t}{4m_1^b} \tag{6}$$

– for symmetrical systems:

$$y_2 = \frac{I_2}{I} = \frac{4m_1}{4m_1 + 4m_2} = \frac{m_2^t}{m_1^b} \tag{7}$$

A theoretical explanation of less classical behaviour of the ternary solutions studied is accounting for the obtained curves' shape. We assume that when mixing the two solutions, changes in common sulphate anion ionic sphere is expected. This produces an energy variation that might be decomposed in two terms:

$$w = w_1(\text{exotherm}) + w_2(\text{endotherm}) \tag{8}$$

Assuming the following equation:

$$\mu_1^{\text{ex}} = D_1 \cdot y_2 + D_2 \cdot y_2^n \tag{9}$$

where: D_1, D_2 – constants originally from w_1 energy and w_2 energy, respectively, we identified D_1 (exotherm component) with the value obtained for the curves in figures when $y_2 = 0$. As for D_2 (endotherm component), it has been calculated from "trace" excess chemical potential, when $y_2 = 1$:

$$D_2 = D_1 - \mu_1^{\text{ex,tr}} \tag{10}$$

Another possible explanation might be that D_1 is a kind of polarization energy of the common anion by two different cations, a concept introduced by Lumsden [7–10] for the evaluation of molten

TABLE I Thermodynamic excess functions from e.m.f. measurements for the studied systems

Nr.	*Temp*	$CuSO_4 + Na_2SO_4 + H_2O$				$CuSO_4 + Li_2SO_4 + H_2O$				$ZnSO_4 + Na_2SO_4 + H_2O$			
crt.	(°*C*)	y_2	μ_1^E (*cal/kg* H_2O *echivg*)	$\bar{H}_1^E$ (*cal/kg* H_2O *echivg*)	$\bar{S}_1^E$ (*cal/kg* H_2O *echivg K*)	y_2	μ_1^E (*cal/kg* H_2O *echivg*)	$\bar{H}_1^E$ (*cal/kg* H_2O *echivg*)	$\bar{S}_1^E$ (*cal/kg* H_2O *echivg K*)	y_2	μ_1^E (*cal/kg* H_2O *echivg*)	$\bar{H}_1^E$ (*cal/kg* H_2O *echivg*)	$\bar{S}_1^E$ (*cal/kg* H_2O *echivg K*)
1	20	0.25	−81.5	1080.4	3.9	0.2	−39.5	400	1.5	0.125	29.11	221.76	0.66
		0.5	−186.3	2046.9	7.6	0.3	−43.9	630	2.3	0.25	81.51	511.74	1.47
		0.6875	−308.6	1705.8	6.9	0.4	−111.8	650	2.6	0.375	157.19	904.08	2.55
		0.8120	−360.9	1705.8	7.1	0.5	−111.1	680	2.7	0.5	238.69	1245.25	3.43
		0.9375	−401.7	5117.5	18.8	0.6	−137.6	800	3.2	0.625	343.49	1125.84	2.67
						0.7	−142.7	1000	3.9	0.6875	454.11	1535.24	3.69
						0.8	−203.6	1320	5.2	0.75	535.61	1364.65	2.83
										0.8125	663.39	1637.59	3.32
										0.875	873.29	2729.31	6.33
										0.9375	1211.98	4145.14	10.35
2	30	0.25	−126.4	1149.3	4.2	0.2	−74.8	410	1.6				
		0.5	−270.9	2189.1	8.1	0.3	−97.5	660	2.5				
		0.6875	−373.3	1824.2	7.3	0.4	−102.95	700	2.65				
		0.8125	−439.5	1824.2	7.5	0.5	−148.7	730	2.9				
		0.9375	−499.7	5472.7	19.7	0.6	−139.9	860	3.3				
						0.7	−182.6	1090	4.2				
						0.8	−236.2	1400	5.4				
3	40	0.25	−167.9	1226.4	4.5	0.2	−82.1	450	1.7				
		0.5	−342.1	2336	8.5	0.3	−93.8	720	2.6				
		0.6875	−460.2	1946.6	7.7	0.4	−157.7	750	2.9				
		0.8125	−509.8	1946.6	7.8	0.5	−190.3	780	3.1				
		0.9375	−586.6	5839.9	20.5	0.6	−206.8	920	3.6				
						0.7	−207.2	1170	4.4				
						0.8	−224.1	1560	5.7				

4	50	0.25	−211.8	1306	4.7	0.2	−95.25	470	1.75	0.125	6.42	269.49	0.81
		0.5	−436.4	2487.6	9	0.3	−122.1	750	2.7	0.25	32.09	621.91	1.83
		0.6875	−539.1	2073	8.1	0.4	−199	770	3	0.375	70.59	1098.69	3.18
		0.8125	−596.7	2073	8.2	0.5	−253.6	780	3.2	0.5	121.94	1513.3	4.31
		0.9375	−1026.8	6219.1	19.2	0.6	−291.25	920	3.75	0.625	250.3	1368.19	3.86
						0.7	−315.8	1170	4.6	0.6875	327.32	1865.71	4.76
						0.8	−410.3	1560	6.1	0.75	436.42	1658.41	3.78
										0.8125	545.53	1865.71	4.09
										0.875	654.64	3316.82	8.24
										0.9375	757.33	5037.43	13.25

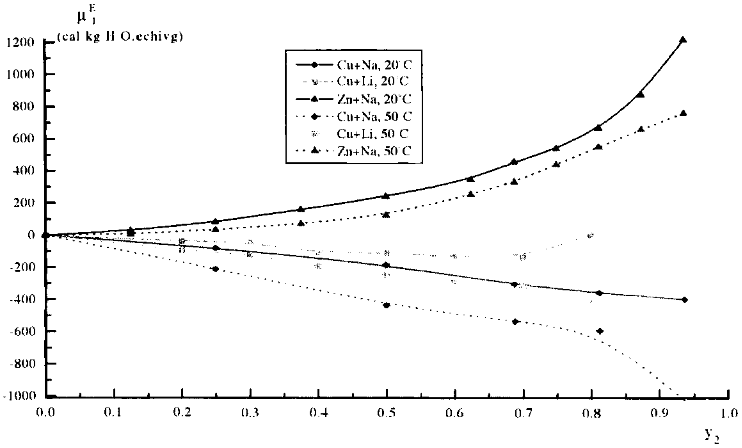

FIGURE 2 Excess chemical potential variation with ionic strength fraction for all studied systems ($I = 2.4$).

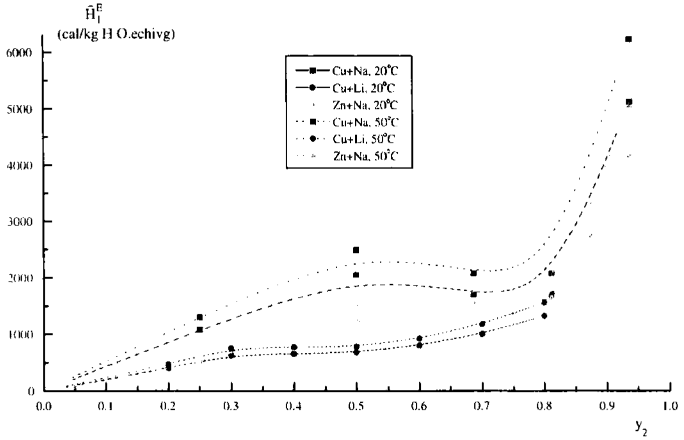

FIGURE 3 Excess partially molar enthalpy variation with ionic strength fraction for all studied systems.

salts' mixing enthalpy. He proposed for polarization energy the following relationship:

$$E_{\text{pol}} = -z \cdot \Psi \cdot 0.32 \cdot N_A \cdot \alpha \cdot e^2 \left(\frac{q_1}{R^2_{AB}} - \frac{q_2}{R^2_{AC}} \right)^2 \tag{11}$$

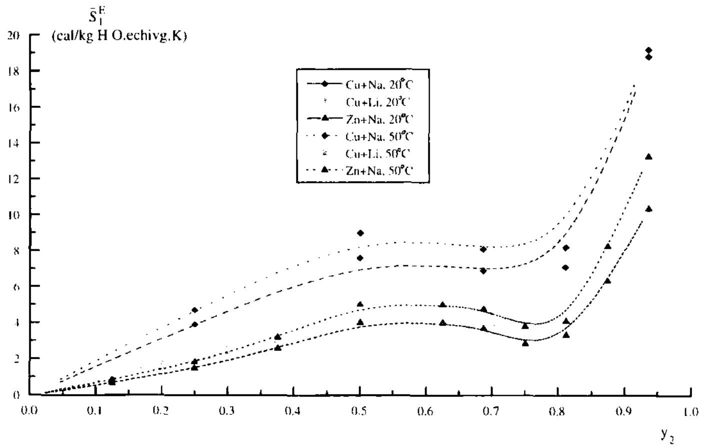

FIGURE 4 Excess partially molar enthropy variation with ionic strength fraction for all studied systems ($I = 2.4$).

where: α – polarizability of common sulphate anion;
N_A – Avogadro's number;
z – coordination number;
$\Psi < 1$ – coefficient introduced by us expressing polarization energy diminution due to dielectric solvent;
R_{AB}, R_{AC} – interionic distances equal to ion rays sum;
q_1, q_2 – cations electric charges.

In Figure 5 a linear variation between D_1 (approx. equal to E_{pol}) and distance-charge parameter from Eq. (11) is observed. This has justified the quasi-ideal comportment of symmetric systems, the high negative deviations of asymmetric systems (with $q_{Cu^{2+}} = 2$ and $q_{alk^+} = 1$) and also the increasing sequence: Li, Na, K for D_1.

Endotherm constant D_2 results from variation of energy appeared when the destroying of binary structures and the forming of ternary structure's ion sphere take place. It has small values for $CuSO_4$ + Li_2SO_4 + H_2O system (approx. 100 cal) and practically the same value for $CuSO_4$ + Na_2SO_4 + H_2O and $CuSO_4$ + K_2SO_4 + H_2O systems (500 cal).

As one can see from Figures 2–4, high positive values both for the partial molar excess enthalpy and for the partial molar excess entropy,

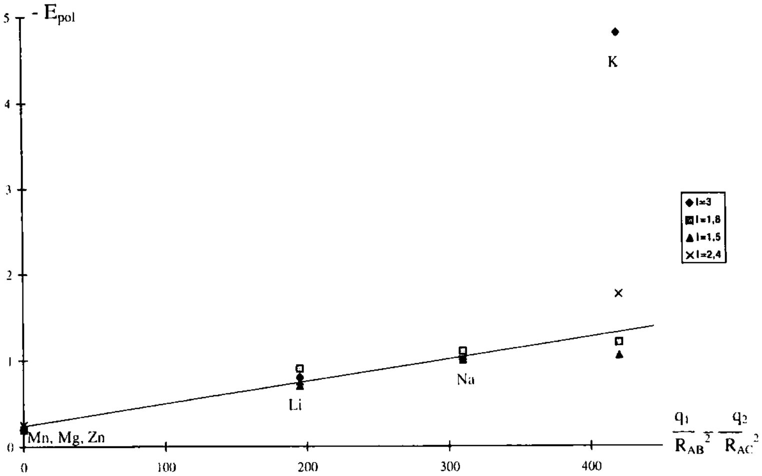

FIGURE 5 Variation of polarisation energy with distance-charge parameter for all studied systems.

for all studied systems, were obtained ($\bar{H}_1^E$ and $\bar{S}_1^E$ take values of maximum 6000 cal/kg H_2O echivg, and 21 cal/kg H_2O echivg K respectively, the system $CuSO_4 + Na_2SO_4 + H_2O$ having the greatest values). These values are compared with the order of magnitude for some reaction quantities and also much higher than those corresponding to ternary alkaline halides systems [11].

Generally, taking into account formation of ternary system from the corresponding binaries, we can write for $\bar{H}_1^E$ and $\bar{S}_1^E$ excess functions that:

$$\bar{H}_1^E = (\Delta^f H_1)^t_{\text{complex}} - (\Delta^f H_1)^b_{\text{complex}} \tag{12}$$

$$\bar{S}_1^E = (\Delta^f S_1)^t_{\text{complex}} - (\Delta^f S_1)^b_{\text{complex}} \tag{13}$$

Because these functions of ionic associations' formation have very high values in binary system and because measured differences between ternary and binary systems (the excess functions) are also important, complexes' formation in ternary systems takes place with even greater mixing effects than those quoted for the native binaries.

Considering:

$$\mu_1^E = H_1^E - TS_1^E \tag{14}$$

at systems with $CuSO_4$(I) dominantly is the enthropic term (TS_1^E), thus resulting positive values for μ_1^E.

Structural explanation of this behaviour might be that complexes' formation from single ions is an endothermic process (both for the binary and for the ternary system) and it is encouraged from the enthropic point of view ($\Delta S > 0$ both for the binaries and for the ternaries). Davies [12] explained that this phenomenon is correlated with increased number of liberty degrees due to partial destruction of single ions' hydration sphere during complexes' formation.

Regarding the studied excess functions, we can say that the alternation of the hydration sphere is stronger for $CuSO_4$(I) systems that for $ZnSO_4$(I) ones; for the latter the enthropic term (TS_1^E) and the mixing enthalpy (H_1^E) is smaller comparatively with those from the systems with copper, the result being a negative value for μ_1^E.

Taking into account the uncommonly large values of the studied ternary systems' excess functions comparative to real systems, structural investigation of these solutions was needed. Hypotheses concerning some ion–ion interaction modification appeared when mixing component binary solutions and also damages of the pre-existing hydration structure were assumed. For lower concentrations in $CuSO_4 + H_2O$ binary system (no more than 10^{-2} M) sufficient proof of ion association existence (including determination of ion association constant and its dependence of temperature) was found [13–15].

For a quantitative characterization of the association phenomenon in the ternary systems studied, determination of concentrations for the present species (associates and free ions) from the spectral data obtained has been tried.

The formalism used for the binary system was:

- considered association equilibria:

$$Cu^{2+} + SO_4^{2-} \rightarrow CuSO_4 \tag{15}$$

$$H^+ + SO_4^{2-} \rightarrow HSO_4^- \tag{16}$$

For simplicity of calculations one consider also the HSO_4^- ion pair formation (for which the association constant is well-determined [13]) and only $CuSO_4$ ion pair formation (ignoring the formation of: $Cu^{2+}HSO_4^-$; $(Cu^{2+}SO_4^{2-})$; $(Cu^{2+})_2SO_4^{2-}$ and $Cu^{2+}(SO_4^{2-})_2$).

– association constants for these equilibria:

$$K_{CuSO_4} = \frac{[CuSO_4]}{[Cu^{2+}]\cdot[SO_4^{2-}]\cdot\gamma_{Cu^{2+}}\gamma_{SO_4^{2-}}} \tag{17}$$

$$K_{HSO_4^-} = \frac{[HSO_4^-]}{[H^+]\cdot[SO_4{}^{2-}]\cdot\gamma_{H^+}\gamma_{SO_4^{2-}}} \tag{18}$$

– mass balances for the present species:

$$\begin{aligned} c_{Cu^{2+}} &= [Cu^{2+}] + [CuSO_4] \\ c_{SO_4{}^{2-}} &= [SO_4^{2-}] + [HSO_4^-] + [CuSO_4] \\ c_{H^+} &= [H^+] + [HSO_4^-], \end{aligned} \tag{19}$$

where $c_{Cu^{2+}}, c_{SO_4{}^{2-}}, c_{HSO_4{}^-}$ are the total molar concentrations of system's species and the amounts in the brackets represent free or associated existing species concentrations.

– the observed absorbency at working wavelength is owning to free Cu^{2+} ions and $CuSO_4$ ion pair:

$$D = \varepsilon_{Cu^{2+}}\cdot[Cu^{2+}]\cdot l + \varepsilon_{CuSO_4}\cdot[CuSO_4]\cdot l$$

As: $1 = 0.5\,cm$,

$$2D = \varepsilon_{Cu^{2+}}\cdot c_{Cu^{2+}} + (\varepsilon_{CuSO_4} - \varepsilon_{Cu^{2+}})\cdot[CuSO_4] \tag{20}$$

where: $\varepsilon_{Cu^{2+}} = 12.14$ mole/l (experimentally measured by Yokoyama and Yamatera [13]).

Using the above mentioned formalism one can obtain the following relationship:

$$P = \frac{1}{\varepsilon_{CuSO_4} - \varepsilon_{Cu^{2+}}}\cdot Q + \frac{1}{\varepsilon_{CuSO_4} - \varepsilon_{Cu^{2+}}} \tag{21}$$

where:

$$P = \frac{(c_{SO_4^{2-}} - [HSO_4^-]) \cdot \gamma_{Cu^{2+}} \gamma_{SO_4^{2-}}}{(D/c_{Cu^{2+}}) - \varepsilon_{Cu^{2+}}}$$

$$Q = (c_{Cu^{2+}} + c_{SO_4^{2-}} - [CuSO_4] - [HSO_4^-]) \cdot \gamma_{Cu^{2+}} \gamma_{SO_4^{2-}}$$

For determining activity coefficients the Debye–Hückel relationship was used:

$$\log \gamma_{Cu^{2+}} = \log \gamma_{SO_4^{2-}} = -\frac{4 \cdot A \cdot \sqrt{I}}{1 + B \cdot a \cdot \sqrt{I}} \tag{22}$$

where: $A = 0.5115$;
$B = 0.3291$;
I – is the ionic strength and
a – Bjerrum's theory critical distance (from 3 to 14.3 A°).

Unknown $K_{CuSO_4}, \gamma_{Cu^{2+}}$ values were calculated with the *optimization method using evolutionary computation* (which includes genetic algorithms, evolution strategies and evolutionary programming) [16]. It presumes concentration values' optimization by random initialization while changing them till the best solution is determined with an error of 10^{-5}. This calculus consists of calculating the concentrations on the basis of theirs initialisation and then, unknown parameters' determination whilst between P and Q exists a linear dependence. All this is repeated until the approximation line converges.

The results thereby obtained are presented as dependence of association constant's logarithm ($\log K_{CuSO_4}$) with the closest approach distance parameter ("a") as seen in Figure 6. The association constant value at 240 nm for $a = 10$ A° is $K_{CuSO_4} = 237$ l/mole, which is closer to that obtained by Yokoyama and Yamatera [13, 14] (241 l/mole) or Davies [12] (250 l/mole).

Considering now the ternary system, one had to take into account the third ion association equilibrium:

$$Me^{2+} + SO_4^{2-} \rightarrow MeSO_4$$

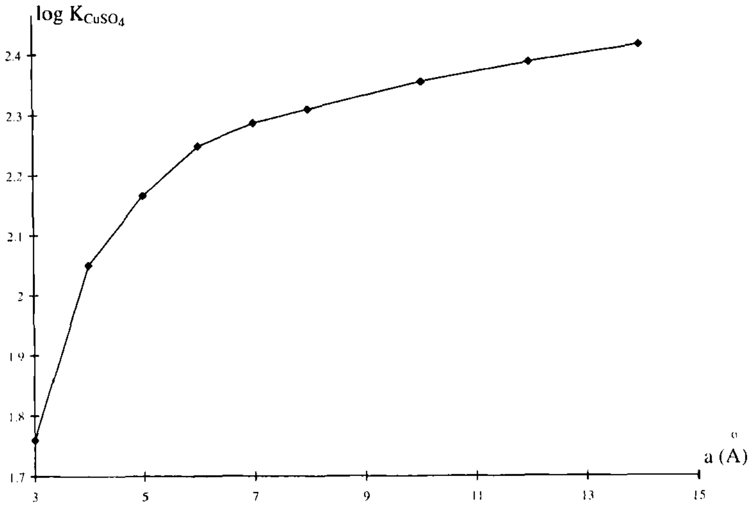

FIGURE 6 Variation of association constant logarithm with parameter "a" for $CuSO_4 + H_2O$ system.

where: $Me = Li_2$, Na_2, K_2, Mg. For this equilibrium the association constant is:

$$K_{MeSO_4} = \frac{[MeSO_4]}{[M^{2+}] \cdot [SO_4^{2-}] \cdot \gamma_{Me^{2+}} \gamma_{SO_4^{2-}}} \tag{23}$$

In this case mass balance of the existing species is:

$$\begin{aligned} c_{Cu^{2+}} &= [Cu^{2+}] + [CuSO_4] \\ c_{SO_4^{2-}} &= [SO_4^{2-}] + [HSO_4^-] + [CuSO_4] + [MeSO_4] \\ c_{H^+} &= [H^+] + [HSO_4^-] \\ c_{Me^{2+}} &= [Me^{2+}] + [MeSO_4] \end{aligned} \tag{24}$$

Ion pair concentration would be given by:

$$[CuSO_4] = \frac{D - \varepsilon_{Cu^{2+}}}{\varepsilon_{CuSO_4} - \varepsilon_{Cu^{2+}}} \tag{25}$$

With the same optimization method using evolutionary computation there are obtained the results from Figure 7, where the

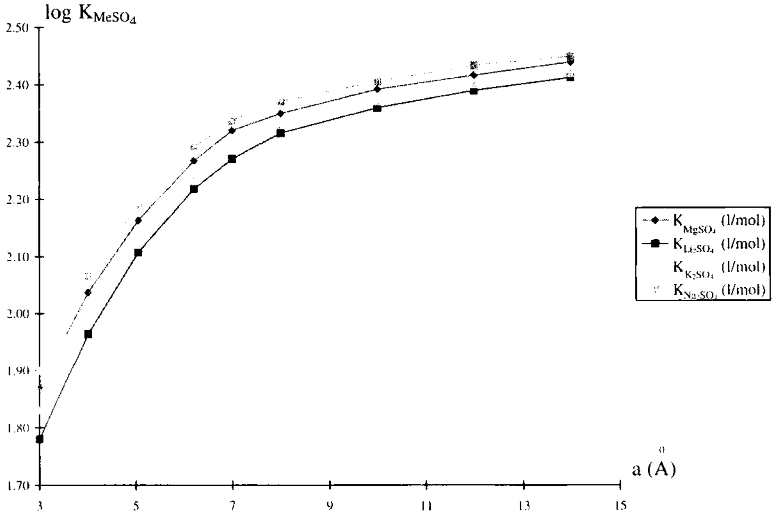

FIGURE 7 Variation of association constant logarithm with parameter "a" for $CuSO_4$ + added sulphate + H_2O systems.

dependencies of ion association constants' logarithm of the parameter "a" (distance of the closest approach) for the studied systems are presented. At the same "a" value, for ternary symmetric sulphates systems, higher association constants are obtained. In the case of asymmetric systems, an increasing in the sequence Li, Na, K is observed. Also, K_{MeSO_4} vary in the same way with K_{CuSO_4}, but their values are smaller than those obtained by other authors [17]. As the main existing ionic species in the ternary mixture are Cu^{2+}, Me^{2+} and SO_4^{2-}, sulphate ion being predominantly, the Cu^{2+} ion distance of the closest approach in the electrolytes' mixture might be approximated with "a" parameter value for binary solution.

Spectrophotometric experimental data from absorbencies' variation with temperature were calculated with the above mentioned optimization method.

The results obtained for all four studied ternary systems are presented in Figures 8–11 as association constants' logarithm dependencies of parameter "a" (the distance of the closest approach). Association constants increase in all cases while increasing parameter "a", the greatest values being obtained for symmetric systems (adding

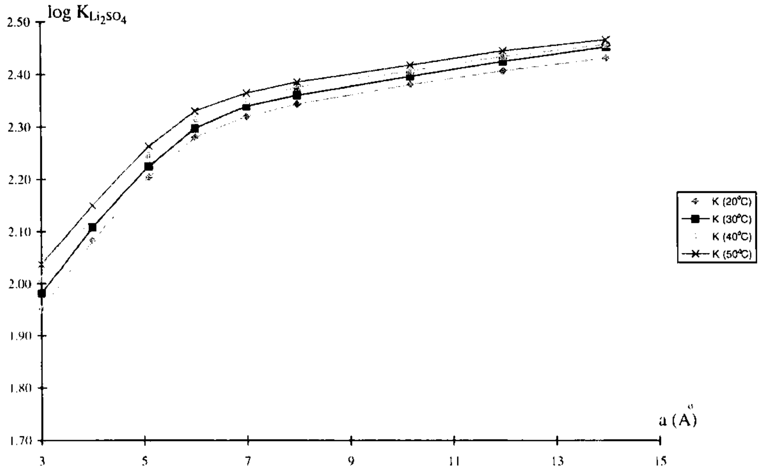

FIGURE 8 Dependencies of association constants' logarithm with parameter "a" for $CuSO_4 + Li_2SO_4 + H_2O$ system.

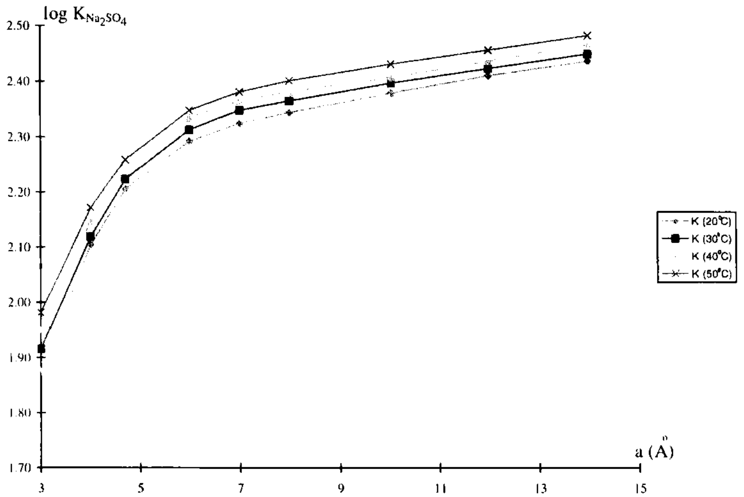

FIGURE 9 Dependencies of association constants' logarithm with parameter "a" for $CuSO_4 + Na_2SO_4 + H_2O$ system.

of divalent sulphate). A variation in the sequence Li, Na, K for asymmetric systems (adding of monovalent sulphate) is observed.

So, finally, drawing a conclusion from these results, one might say that association constants' values depend on the added cation.

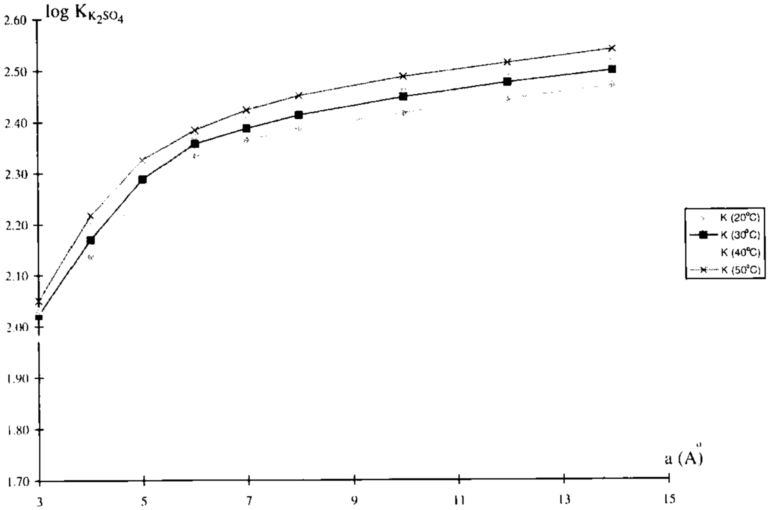

FIGURE 10 Dependencies of association constants' logarithm with parameter "a" for $CuSO_4 + K_2SO_4 + H_2O$ system.

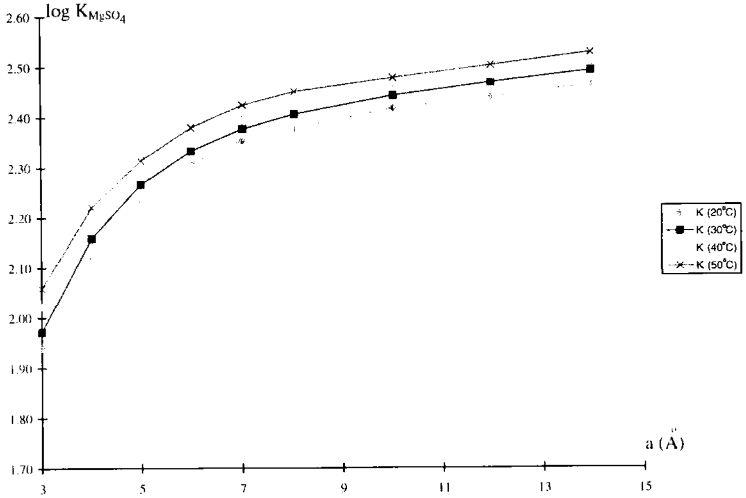

FIGURE 11 Variation of association constants' logarithm with parameter "a" for $CuSO_4 + MgSO_4 + H_2O$ system.

Moreover, this is responsible of solvent (water) structure destruction and of ion associates' formation in solution. For larger cations (K^+, Mg^{2+}) this phenomenon is more intense than for the others. These are due to a Li^+ and Mg^{2+} ions higher hydration in solution which, in this form (almost screened), affects in a smaller manner Cu(II) hydration sphere.

As regards the method of calculating association constants, results are satisfactory and in agreement with data obtained by other authors [14, 17, 18]. Compared to association constants' values obtained from conductivity measurements or from osmometric data [14], for the same value of parameter "a" our values are smaller. Also, for the last two types of mentioned measurements, owning to same electrostatic arrangements, association constants increase with the decreasing of "a".

In Table II results obtained for thermodynamic excess functions from variation of absorbencies with temperature are presented. While excess chemical potential have some important values ($-20 \div -100$ cal/kg H_2O echivg), for partial molar excess enthalpy and partial molar excess enthropy results are smaller, and comparable for all studied systems (symmetric and asymmetric). (On calculating these thermodynamic functions the same model as for e.m.f. measurements was used. It is valid only for solutions in the range of dilute concentrations). In contrast to other authors' results for thermodynamic excess functions [14, 17, 18], our values are higher and explicable because of our greater sulphate concentrations.

TABLE II Thermodynamic excess functions from spectrophotometric measurements for the studied systems

T(°C)	*Symmetric sulphates*			*Asymmetric sulphates*		
	μ_1^{ex}	$\bar{H}_1^E$	$\bar{S}_1^E$	μ_1^{ex}	$\bar{H}_1^E$	$\bar{S}_1^E$
	(cal/kg H_2O echivg)	*(cal/kg H_2O echivg)*	*(cal/kg H_2O echivg K)*	*(cal/kg H_2O echivg)*	*(cal/kg H_2O echivg)*	*(cal/kg H_2O echivg K)*
	−52,38		2,3	−57,23		2,7
20	−23,17	2,54	2,43	−32,31	2,96	2,81
	−22,26		2,44	−31,65		2,82
	−78,8		3,58	−86,14		4,2
30	−35,98	3,82	3,71	−48,61	4,46	4,31
	−33,5		3,72	−47,62		4,32
	−81,21		3,7	−88,76		4,33
40	−37,1	3,94	3,83	−50,1	4,59	4,41
	−34,52		3,84	−49,1		4,42
	−83,64		3,82	−91,43		4,47
50	−38,2	4,06	3,95	−51,6	4,73	4,58
	−35,55		3,96	−50,54		4,59

Comparing the results obtained using the two above mentioned methods (e.m.f. and spectrophotometric – see Tabs. I and II) very disparate values are observed. If for partial molar excess enthropy values are comparable for both methods (2–5 cal/kg H_2O echivg K), for the other two thermodynamic excess functions disparity is more or less important. For partial molar excess enthropy decreasing variation with little quantity differences is noted, whilst for partial molar excess enthalpy a few orders of magnitude are observed (especially in the case of Na_2SO_4 adding).

All these might be explained by the limited validity of our proposed model at concentrations range of very dilute solutions (no more than 10^{-2} mole/l). For higher values, of 10^{-2}–10^{-1} mole/l, when inter-ionic attractions and ion-association phenomena are dominant, hypotheses appropriate to very dilute solutions are no longer useful.

Above, the solvent was considered as a continuous medium, results being interpreted accounting of ion's hydration till a certain distance. The possibility might exist for hydrated anions and cations to contact each other sometimes or to form ion pairs by replacing a water molecule from the outside ions' coordination sphere. As water molecules from the first metallic ion shell are strongly coordinated to the respective cation, solvent dielectric constant in that area might be different from the remaining part of it. In such situations, the solvent would not have to be treated as a continuous medium and the ions as rigid spheres. Moreover, interactions between ions in the first coordination sphere might not be of electrostatic nature, this meaning a limitation on both Debye–Hückel theory and of our ion association model. In this situation a changing of parameter's "a" (distance of the closest approach) physical meaning is needed.

CONCLUSIONS

Thermodynamic excess functions values determined from e.m.f. measurements for ternary mixtures of sulphates confirm previous results regarding non-ideal behaviour of these systems. These are owning to an endothermic, entropical driven process of ion associations' formation from single ions with a grown number of degrees of freedom caused by the partial destruction of the hydration sphere.

Moreover, existence of ion association process in ternary aqueous sulphates solutions is also confirmed by the high values obtained for association constants. Influence of added cation over association constants demonstrates their involvement in solvent (water) structure's destruction.

Association constants calculated with the proposed model (which considers only binary associates' formation and uses as working algorithm the optimisation method using evolutionary computation) are close to data presented by other authors (50–300 l/mole).

Association constants increase at the same time with "a" parameter (distance of the closest approach between two ions), having higher values for symmetric systems (2:2 sulphates) and a variation in the sequence Li, Na, K for asymmetric systems.

Using the proposed method for the evaluation of association constants similar results with other authors were obtained. Unexpectedly different results concerning thermodynamic excess functions determined by the two mentioned methods, e.m.f. and spectrophotometric, limit the validity of the proposed association model to the concentration range of dilute solutions.

References

[1] Sternberg, S. and Draganoiu, M. (1984). *Rev. Roumaine Chim.*, **29**(1), 859.
[2] Sternberg, S. and Draganoiu, M. (1985). *Rev. Roumaine Chim.*, **30**(3), 209.
[3] Draganoiu, M. (1986, Bucharest). Doctoral Dissertation.
[4] Sternberg, S., Draganoiu, M. and Grigore, L. (1987). *Rev. Chim.*, **38**(3), 250.
[5] Grigore, L. (1997, Bucharest). Doctoral Dissertation.
[6] Ives, D. J. D. and Janz, E. J. (1961). Reference Electrodes (Academic Press, New York).
[7] Sternberg, S. and Herdlika, C. (1968). *Rev. Roumaine Chim.*, **13**(1), 13.
[8] Sternberg, S. (1969). *Rev. Roumaine Chim.*, **17**(12), 859.
[9] Lumsden, I. (1960). *Discuss. Faraday Soc.*, **32**, 138.
[10] Lumsden, I. (1996). Thermodynamics of Molten Salt Mixtures (Academic Press, London).
[11] Davies, C. W. (1962). Ion Association (Butterworths, London).
[12] Bale, W. D., Davies, E. W. and Monk, G. B. (1956). *Trans. Faraday Soc.*, **52**, 816.
[13] Yokoyama, H. and Yamatera, H. (1975). *Bull. of the Chem. Soc. of Japan*, **48**, 2719.
[14] *Ibidem*, **48**, 2708.
[15] Yokoyama, H. and Yamatera, H. (1981). *Bull. of the Chem. Soc. of Japan*, **54**, 2286.
[16] Fogel, J. (1997). Computational intelligence. Theory and Applications (Eds., Reusch, B. and Dortmund).
[17] Yokoyama, H. and Yamatera, H. (1975). *Bull. of the Chem. Soc. of Japan*, **48**, 1770.
[18] Hemmes, H. and Petrucci, S. (1968). *J. Phys. Chem.*, **72**, 3296.