

DENSITY ESTIMATION OF TERNARY AQUEOUS SOLUTIONS

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Relations are presented for estimating the density of ternary aqueous solution on the basis of known densities of binary solutions of both components of the ternary solution. Accuracy of the estimation is tested using both the diluted and concentrated ternary solutions at temperatures of 15–100°C.

When calculating the processes taking place in aqueous solutions, the knowledge of density of the respective solution is mostly necessary. The densities of binary solutions are either measured and published or can be relatively reliably estimated¹. However, in practice we mostly meet with ternary and higher solutions in which the probability of finding their densities in literature is, as a rule, negligible. In such cases we are entirely dependent either on the direct experimental determination of densities of the given system or on their estimation on the basis of the knowledge of densities of simpler solutions.

A number of relations was suggested for the estimation of densities of ternary and higher solutions²⁻⁹. However, for practical applications, only such a relation is suitable which yields a sufficiently accurate estimate of the ternary solution density on the basis of the knowledge of densities of the respective binary solutions, if possible in an explicit form. In this work we present suitable relations for the density estimation and test their validity on a number of systems.

THEORETICAL

The apparent molar volume of a binary and ternary solution is defined by the relation

$$\phi_2 = \frac{V - n_1 V_1^0}{n_2} = \frac{1}{n_2} \left[\frac{n_1 M_1 + n_2 M_2}{\rho_2} - \frac{n_1 M_1}{\rho_1} \right] \quad (1)$$

and

$$\phi_t = \frac{V - n_1 V_1^0}{n_2 + n_3} = \frac{1}{n_2 + n_3} \left[\frac{n_1 M_1 + n_2 M_2 + n_3 M_3}{\varrho_t} - \frac{n_1 M_1}{\varrho_1} \right]. \quad (2)$$

If we express the molar concentration of solute, it means for a binary solution $n_2 = c_{2,b}$, $n_1 = (\varrho_2 - c_{2,b} M_2)/M_1$, and for a ternary solution $n_2 = c_2$, $n_3 = c_3$, $n_1 = (\varrho_t - c_2 M_2 - c_3 M_3)/M_1$, we get by rearranging Eqs (1) and (2)

$$\phi_2 = \frac{\varrho_1 - \varrho_2}{c_{2,b} \varrho_1} + \frac{M_2}{\varrho_1} \quad (3)$$

and

$$\phi_t = \frac{\varrho_1 - \varrho_t}{\varrho_1(c_2 + c_3)} + \frac{c_2 M_2 + c_3 M_3}{\varrho_1(c_2 + c_3)} \quad (4)$$

According to Young², the mixing rule

$$\phi_t = (c_2 \phi_2 + c_3 \phi_3)/(c_2 + c_3) \quad (5)$$

holds, where ϕ_2 and ϕ_3 are apparent molar volumes of binary solutions of the components 2 and 3 exhibiting a ionic strength equal to that of the ternary solution. By combining Eqs (3), (4) and (5) and after rearranging we get

$$\varrho_1 - \varrho_t = \frac{c_2}{c'_{2,b}} [\varrho_1 - \varrho_2(c'_{2,b})] + \frac{c_3}{c'_{3,b}} [\varrho_1 - \varrho_3(c'_{3,b})], \quad (6)$$

where $\varrho_2(c'_{2,b})$ and $\varrho_3(c'_{3,b})$ are the densities of binary solutions of components 2 and 3 of concentration $c'_{2,b}$ and $c'_{3,b}$, respectively. The concentrations $c'_{2,b}$ and $c'_{3,b}$ are such concentrations of components 2 and 3 in binary solutions that their ionic strength should be equal to that of the ternary solution. If component 2 is an electrolyte of the type $A_{\nu_A} B_{\nu_B}$ and component 3 an electrolyte $C_{\nu_C} D_{\nu_D}$, we get from the condition of equality of ionic strengths, *i.e.*

$$I(c'_{2,b}) = I(c'_{3,b}) = I(t) \quad (7)$$

the relation for component 2

$$c'_{2,b} = c_2 + c_3 (\nu_C z_C^2 + \nu_D z_D^2) / (\nu_A z_A^2 + \nu_B z_B^2), \quad (8)$$

and similarly for component 3

$$c'_{3,b} = c_3 + c_2(v_A z_A^2 + v_B z_B^2)/(v_C z_C^2 + v_D z_D^2). \quad (9)$$

Providing that the concentration dependence of density of the binary solution is described by the relation

$$\varrho_i = \varrho_1 + \alpha_i c_{i,b} - \beta_i c_{i,b}^{3/2}, \quad (10)$$

we obtain, by combining Eqs (6) and (8)–(10) and by subsequent rearranging, the relation

$$\varrho_t = \varrho_1 + \sum_{i=1}^3 \alpha_i c_i - (c_2 + X c_3)^{1/2} (\beta_2 c_2 + \beta_3 c_3 / \sqrt{X}), \quad (11)$$

where

$$X = (v_C z_C^2 + v_D z_D^2)/(v_A z_A^2 + v_B z_B^2). \quad (12)$$

Provided that the condition expressed by Eq. (7) is not inserted into the mixing rule (Eq. (5)) but we take ϕ_2 and ϕ_3 at the concentration of binary solution equal to the concentration of the ternary solution³, then $c_2 = c'_{2,b}$ and $c_3 = c'_{3,b}$ hold, and consequently Eq. (6) combined with Eq. (10) gives

$$\varrho_t = \varrho_1 + \sum_{i=2}^3 \alpha_i c_i - \sum_{i=2}^3 \beta_i c_i^{3/2}. \quad (13)$$

By using the mixing rule⁴

$$\varrho_t = \varrho_2 \xi_2 + \varrho_3 \xi_3, \quad (14)$$

where the volume fractions are defined by

$$\xi_2 = V_2/(V_2 + V_3) \quad \text{and} \quad \xi_3 = V_3/(V_2 + V_3), \quad (15)$$

we get, on combining with Eq. (10), the relation

$$\varrho_t = \varrho_1 + \sum_{i=2}^3 \alpha_i c_{i,b} \xi_i - \sum_{i=2}^3 \beta_i c_{i,b}^{3/2} \xi_i. \quad (16)$$

Eq. (15) comprises the assumption that, by mixing the binary solutions of components 2 and 3, a ternary solution is formed of the volume

$$V = V_2 + V_3. \quad (17)$$

According to ref.⁵ Eq. (17) is fulfilled on condition that

$$\bar{V}_{1,2} = \bar{V}_{1,3} . \quad (18)$$

Since the partial molar volume of water in binary solution is expressed⁶ as

$$\bar{V}_{1,2} = 2V_1^0/[2 + c_{2,b}^{3/2}(\partial\phi_w/\partial\sqrt{c_{2,b}})] , \quad (19)$$

Eq. (18) is fulfilled when

$$c_{2,b}^{3/2}\beta_2 = c_{3,b}^{3/2}\beta_3 , \quad (20)$$

taking into account that⁶

$$\partial\phi_w/\partial\sqrt{c_{i,b}} = \beta_i/\varrho_1 . \quad (21)$$

On inserting the relation

$$c_i = c_{i,b}\xi_i \quad (22)$$

and Eq. (20) into Eq. (16) we get after arrangement

$$\varrho_t = \varrho_1 + \sum_{i=2}^3 \alpha_i c_i - \left(\sum_{i=2}^3 \beta_i^{2/3} c_i \right)^{3/2} . \quad (23)$$

Eq. (23) is identical with a relation derived in a different way by Mikulin⁷.

In both the mixing rules used – Eqs (5) and (14) – the terms representing the possible interaction between components 2 and 3 in the ternary solution have not been considered. This interaction causes deviations in properties of real solution from those predicted on the basis of additivity.

The interaction term^{2,3} was proposed for Eq. (5) in the form $K_1 c_2 c_3 / (c_2 + c_3)^2$ or $K_2 c_2 c_3$ which in Eq. (11) take the form $K_1 c_2 c_3 / (c_2 + c_3)$ and $K_2 c_2 c_3$. Eq. (14) is extended by an interaction term in the form⁴ $K_3 \xi_2 \xi_3$ which can be rearranged to $K_3 \prod_{i=2}^3 c_i \beta_i^{2/3} / (\sum \beta_i^{2/3} c_i)^2$, where $i = 1, 2$. The constants K_1, K_2 and K_3 are empirical parameters which are functions of temperature and should not be a function of concentration.

RESULTS AND DISCUSSION

At first we will investigate to what extent differ the estimates of densities of ternary solutions derived on the basis of different mixing rules – Eqs (5) and (14).

The difference between the density estimates of ternary solution on the basis of Eqs (11) and (13), i.e. $\Delta_t = \varrho_t$ (Eq. (23)) – ϱ_t (Eq. (11)) for a solution whose one component is always 1–1 electrolyte, is given in Fig. 1 as a function of the para-

meter β of component 3 ($c_2 = c_3 = 1$, $\beta_2 = 1.87 \cdot 10^{-6}$). The parameter β of component 3 is here taken as an independent variable acquiring here continuously the values from 0 to $80 \cdot 10^{-6}$. Since the constant β for most binary solutions of electrolytes of the type 1-1 lies within the range of 1 to $4 \cdot 10^{-6}$, of the type 1-2 5 to $14 \cdot 10^{-6}$, of the type 2-2 7 to $22 \cdot 10^{-6}$, of the type 1-3 13 to $37 \cdot 10^{-6}$ and of the type 1-4 17 to $70 \cdot 10^{-6}$ (ref.¹), we can see from Fig. 1 that negligible differences can be expected with the exception of mixtures of electrolytes 1-1 and 1-4. The maximum possible differences in densities of ternary solutions, resulting from mixing electrolytes of different types at concentrations $c_2 = c_3 = 1$, owing to different constants β_2 and β_3 are given in Table I. When evaluating Table I, the maximum differences of densities were always sought owing to the combination of numerical

TABLE I

The maximum difference in the density estimation Δ (kg m^{-3}) in a ternary solution for $c_2 = c_3 = 1 \text{ kmol m}^{-3}$

Type of electrolyte	1-1	1-2	2-2	1-3	1-4
1-1	0.5	1.1	1.4	1.8	3.4
1-2	1.1	1.1	1.5	2.0	4.5
2-2	1.4	1.5	2.0	10.8	45.4
1-3	1.8	2.0	10.8	12.9	23.9
1-4	3.4	4.5	45.4	23.9	7.9

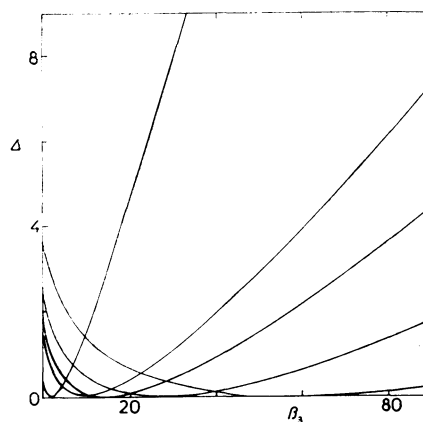


FIG. 1

The difference $\Delta = \rho_t$ (Eq. (23)) - ρ_t (Eq. (11)) (kg. m^{-3}) as a function of β_3 for $c_2 = 1$, $c_3 = 1$, $\beta_2 = 1.87 \cdot 10^{-6} = 1.87 \cdot 10^{-6}$ and 25°C . Component 2 is 1-1 electrolyte, component 3 is with curve 1 1-1 electrolyte, 2 1-2 electrolyte, 3 2-2 electrolyte, 4 1-3 electrolyte and 5 1-4 electrolyte

values of constants β_2 and β_3 within the range in which they may occur (see above). Providing that the concentrations c_2 and c_3 increased above 1, the difference Δ would increase, too. However, it follows from Table I that with the exception of the region below the dashed line, *i.e.* when one component of the ternary solution is an electrolyte of the 1–4 type and for the combinations of an electrolyte 1–3 with 1–3 or 2–2, the differences between the estimates on the basis of Eqs (11) and (23) are negligible. It means that with the exception of the given systems, it is possible to use both the equations to estimate the densities of ternary solutions with practically identical results. Because of a more suitable form of Eq. (23) for numerical evaluation, we will use it further.

The constants α and β in Eq. (10) are taken from ref.¹⁶ for binary solutions of the compounds.

The comparison of the density estimates of several ternary solutions on the basis of Eqs (13) and (23) with experimental values is given in Table II. The systems saturated by both components at a given temperature are chosen on purpose for the estimated and experimental values will differ most under these conditions. It is evident from Table II that Eq. (23) yields very accurate estimates which do not differ from experimental value by more than approximately 1% and exceptionally by at most 5%. Eq. (13) yields usually higher values than corresponds to experiment even though in some cases in such a way determined values agree with the reality better than the estimate in terms of Eq. (23). The said agreement between the density estimate on the basis of Eq. (23) and the experimental value is satisfied not only for 25°C but also for temperatures up to 100°C as it is shown in Table II and III. For diluted solutions or solutions with low density, the difference between the estimate and reality is as a rule negligible (Table III).

Providing that the experimental values of constants α and β are not known for respective binary solutions, α can be replaced by the value determined from an apparent molar volume of solute at infinite dilution and the empirical constant β by its theoretical value¹. The densities of ternary solutions calculated on the basis of estimated values of α and β are given in Table II. It is evident that even the densities of ternary solutions determined like this are relatively close to experimental values.

In this way, over 50 systems were checked, and in all cases the estimated densities agreed well with the actual ones.

It follows from the above-said that in a great many cases Eq. (23) without the interaction term suffices. However, there are systems where the estimate in terms of Eq. (23) is so far from reality that it is necessary to give precision to it by inserting the interaction term. To be able, however, to use this procedure, we must know at least one experimental value of density of the ternary solution.

Since the interaction constant has purely empirical character, we investigated its behaviour for a number of ternary systems. The interaction term in the form

TABLE II
The density estimates ρ (kg m^{-3}) of concentrated ternary solutions

Mass % (2)	Mass % (3)	$t, ^\circ\text{C}$	ρ (exp)	ρ (Eq. (23))	$\delta^a, \%$	ρ (Eq. (13))	$\delta^a, \%$	Z^b	$\delta^a, \%$
KCl(2)–KClO ₃ (3), ref. ¹⁰									
25.56	2.40	25	1 189	1 190	0.08	1 187	–0.17	1 193	0.33
17.27	2.70	25	1 135	1 132	0.62	1 132	–0.26	1 133	–0.18
5.17	4.90	25	1 064	1 063	–0.09	1 059	–0.47	1 063	–0.09
29.67	1.05	50	1 196	1 198	0.17	1 205	0.75	—	—
19.84	7.42	50	1 166	1 172	0.51	1 175	0.76	—	—
7.20	12.04	50	1 107	1 115	0.72	1 122	1.34	—	—
CaCl ₂ (2)–ZnCl ₂ (3), ref. ¹¹									
10.00	28.97	15	1 400	1 413	0.92	1 431	2.17	—	—
20.00	19.05	15	1 400	1 406	0.43	1 428	1.96	—	—
30.00	9.52	15	1 400	1 401	0.07	1 418	1.27	—	—
10.00	36.90	15	1 500	1 523	1.51	1 547	3.04	—	—
20.00	27.78	15	1 500	1 522	1.44	1 555	3.54	—	—
30.00	18.65	15	1 500	1 520	1.31	1 552	3.35	—	—
10.00	46.82	15	1 800	1 834	1.85	1 899	5.21	—	—
20.00	55.16	15	1 800	1 833	1.80	1 873	3.90	—	—
CsNO ₃ (2)–Al(NO ₃) ₃ (3), ref. ¹²									
11.39	23.07	25	1 328	1 302	–2.00	1 309	–1.45	1 298	–2.31
13.02	28.84	25	1 426	1 380	–3.33	1 379	–0.07	1 377	–0.22
12.63	35.33	25	1 489	1 435	–3.76	1 447	0.83	1 436	–3.69
Ca(NO ₃) ₂ (2)–AgNO ₃ (3), ref. ¹³									
48.35	17.77	25	1 796	1 801	0.28	1 817	0.88	1 780	–0.90
35.41	23.50	25	1 763	1 730	–1.91	1 748	1.03	1 718	–2.62
23.15	35.72	25	1 800	1 780	–1.12	1 799	1.06	1 776	–1.35
12.02	49.76	25	1 944	1 918	–1.36	1 934	–0.52	1 921	–1.20
CuSO ₄ (2)–MgSO ₄ (3), ref. ¹⁴									
25.07	2.32	25	1 325	1 319	–0.45	1 327	0.15	1 337	0.90
16.36	11.26	25	1 319	1 318	–0.07	1 340	1.64	1 327	0.60
9.36	14.86	25	1 273	1 272	–0.08	1 289	1.32	1 274	0.08
3.46	17.30	25	1 232	1 228	–0.32	1 236	0.65	1 226	–0.49
NaNO ₃ (2)–Co(NO ₃) ₂ (3), ref. ¹⁵									
39.51	7.73	25	1 409	1 408	–0.07	1 418	0.63	1 415	0.42
34.15	11.45	25	1 417	1 405	–0.85	1 418	0.07	1 410	–1.14
21.94	26.24	25	1 464	1 472	0.54	1 491	2.01	1 466	0.14
5.63	45.57	25	1 586	1 581	–0.32	1 591	0.31	1 559	–1.73

^a $\delta = 100[(\rho(\text{exp}) - \rho(\text{calc}))/\rho(\text{calc})]$; ^b Z estimates of constants α and β used instead of experimental values.

$K_2c_2c_3$ proved to be quite unsuitable for the constant K_2 changes too much with varying concentration. The interaction terms $K_1c_2c_3/(c_2 + c_3)$ and $K_3 \prod(\beta_i^{2/3}c_i)/(\sum\beta_i^{2/3}c_i)^2$ are approximately equivalent from this point of view. The constants K_1 and K_3 can exhibit for a system considerable variations on changing composition of the system, and may acquire even positive and negative values. It means that the constants K_1 and K_3 are functions not only of temperature but also of composition of system, and consequently, that the concentration term does not bring out, nor in one case, exactly the ensuing interactions.

From the reasons said it is to proceed circumspectly when applying the interaction term. If we know several experimental values of densities, then we use in all cases the constant of lowest absolute value from the calculated interaction constants. Providing that constants with positive and negative sign occur for the given system, it is better not to use the interaction term.

Unlike the binary solutions where we can estimate the density with a considerable certainty, in case of ternary solutions we must proceed circumspectly. In most cases, however, the density of ternary solution is estimated with an accuracy better than 5%, which is sufficient for the purposes of chemical-engineering calculations.

TABLE III
The density estimates of diluted binary solutions

Mass % (2)	Mass % (3)	$t, ^\circ\text{C}$	ρ (exp)	ρ (Eq. (23))
NaCl(2)-MgSO ₄ (3)				
5.40	3.32	25	1 069.0	1 069.4
12.38	3.28	25	1 119.5	1 122.1
5.32	3.26	65	1 050.6	1 050.0
12.18	3.23	65	1 099.5	1 101.1
5.21	3.20	100	1 029.3	1 028.5
11.97	3.16	100	1 077.8	1 079.8
NaCl(2)-Na ₂ SO ₄ (3)				
5.39	2.03	25	1 053.2	1 053.9
12.15	1.97	25	1 104.6	1 105.5
5.30	2.00	65	1 034.7	1 035.0
11.95	1.94	65	1 084.3	1 084.6
5.20	1.96	100	1 013.4	1 012.7
11.74	1.90	100	1 062.7	1 062.5

LIST OF SYMBOLS

c_2, c_3	molar concentration of component 2 and 3, respectively, in ternary solution kmol m^{-3}
$c_{2,b}, c_{3,b}$	molar concentration of component 2 and 3, respectively, in binary solution kmol m^{-3}
I	ionic strength
K_1, K_2, K_3	interaction constant
M	molar mass kg kmol^{-1}
n	amount of substance kmol
V	volume of solution m^3
$V_{j,2}$	partial molar volume of water in binary solution of i -th component $\text{m}^3 \text{kmol}^{-1}$
V_1^0	molar volume of water $\text{m}^3 \text{kmol}^{-1}$
X	defined by Eq. (12)
z_i	charge of i -th ion
α_i, β_i	constants in Eq. (10)
Δ	difference of the density estimates of Eq. (23) and (11) kg m^{-3}
ϕ_i	apparent molar volume of binary solution of i -th component $\text{m}^3 \text{kmol}^{-1}$
ξ	volume fraction
v_i	stoichiometric coefficient of i -th ion
ρ_t, ρ_s	density of ternary solution and mixture, respectively kg m^{-3}
ρ_2, ρ_3	density of binary solution of component 2 and 3, respectively kg m^{-3}
ρ_1	density of water kg m^{-3}

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