DENSITY ESTIMATES OF BINARY AQUEOUS SOLUTIONS

Otakar Söhnel[a], Petr Novotný[a] and Zdeněk Šolc[b]

[a] *Chemopetrol, Research Institute of Inorganic Chemistry, 400 60 Ústi n.L. and*
[b] *Department of Inorganic Technology,*
Institute of Chemical Technology, 532 10 Pardubice

Two methods are given for assessment of density of binary aqueous solutions of electrolytes; one is based on partial molar volume of the dissolved electrolyte at infinite dilution, and the other is based on additivity of apparent molar volumes at a given concentration. The density estimates of aqueous solutions by means of the two methods are compared with experimental values for some electrolytes of the type 1—1 to 4 and 2—2. In all the cases the estimates agree with experimental densities up to concentrations of the saturated solutions.

In technical, technological, and physico-chemical calculations of processes taking place in aqueous solutions it is often necessary to know density of the aqueous solution in question. Experimental data on densities of binary aqueous solutions in broad temperature and concentration range are available for about 200 systems only. For about 200 other systems values are published concerning one or two temperatures. All other compounds belong either to systems not measured at all, or information on densities is only very limited.

From practical point of view it is desirable to asses densities of binary systems not yet measured. The present paper gives two methods of the assessment based on physico-chemical characteristics of the solutions.

THEORETICAL

The previous reports[1-3] showed that concentration-temperature dependence of densities of binary aqueous solutions is expressed well by Eq. (1) within the range from 0 to 100°C up to the saturation concentration.

$$\varrho = \varrho_0 + Ac + Bct + Cct^2 + Dc^{3/2} + Ec^{3/2}t + Fc^{3/2}t^2 \qquad (1)$$

The parameters α and β of the Masson's equation[4] (2) can be obtained from the constant A through F of Eq. (1) with the use of Eqs (3) and (4), and physical meaning is given by Eqs (5) and (6).

$$\varrho = \varrho_0 + \alpha c - \beta c^{3/2} \qquad (2)$$

$$\alpha = A + Bt + Ct^2 \qquad (3)$$

$$\beta = -(D + Et + Ft^2) \tag{4}$$

$$\alpha = M - \varrho_0 \phi_v^0 \tag{5}$$

$$\beta = s_{exp} \varrho_0 \tag{6}$$

From the constants A, B, and C of Eq. (1) is is possible to obtain, using Eqs (3) and (5), the quantity ϕ_v^0 which will be denoted further as $\phi_{v,exp}^0$. Although this quantity has (according to Eq. (5)) the meaning of partial molar volume of the dissolved component at infinite dilution, it must be viewed as an empirical parameter[5], as the constants of Eq. (1) are adjusted in such way that the density-concentration dependence might be expressed best in the range of medium and high concentrations and not for very diluted solutions. Real ϕ_v^0, on the contrary, is determined by extrapolation, of the ϕ_v values obtained in diluted solutions to infinite dilution. If slope of the dependence $\phi_v = f(\sqrt{c})$ is not changed in the range of high dilution, then it will be $\phi_{v,exp}^0 = \phi_v^0$.

At infinite dilution, partial molar volumes of the dissolved compound obey the additivity principle[7], *i.e.*

$$\phi_v^0(M_a X_b) = a\, \phi_v^0(M^{b+}) + b\, \phi_v^0(X^{a-}), \tag{7}$$

the values ϕ_v^0 for ions being given in published tables, *e.g.*[7].

From the constants D, E, and F of Eq. (1), using Eqs (4) and (6), it is possible to termine the quantity s_{exp} which is the slope of the dependence $\phi_v \doteq f(\sqrt{c})$. This quantity must be additive at least with simple compounds[6]. If the system obeys the Debye–Hückel limit law, then s_{exp} assumes the precisely determined values s_{theor}. Numerical of s_{theor} is only a function of temperature and type of electrolyte and not a function of properties of the substance dissolved. Its value at 25°C are given in Table I for various electrolyte types.

The additive principle in the form

$$\phi_v(MA) = \phi_v(MX) + \phi_v(NA) - \phi_v(NX) \tag{8}$$

TABLE I

The s_{theor} values for 25°C

Electrolyte type	1—1	1—2	2—2	1—3	1—4
$s_{theor} \cdot 10^3$	1·87	9·71	14·94	27·45	59·07

is not restricted to infinitely diluted solutions only, but it applies to any concentration[6]. Combination of Eq. (8) with the definition (9) of apparent molar volume gives Eq. (10)

$$\phi_v = (\varrho_0 - \varrho)/c\varrho_0 + M/\varrho_0 \qquad (9)$$

$$\varrho(MA) = \varrho(MX) + \varrho(NA) - \varrho(NX), \qquad (10)$$

where densities of solutions of the compounds MX, NA, and NX are taken at the same molar concentration of the solution as the density of the solution of compound MA.

The equation (8) and, hence, also (10) do not take into account changes of volume of the solution due to formation of ion pairs, so the result can appreciably differ from reality, especially so at higher concentrations.

RESULTS AND DISCUSSION

In the following calculations the numerical values of the constants $A - F$ of Eq. (1) and densities of aqueous solutions of the individual compounds were from ref.[1].

Comparison of the values $\phi_{v,exp}^0$ and ϕ_v^0 (in Table II denoted as exp and ad, respectively) at 25°C for alkali metal salts is given in Table II. Difference between the value calculated from the parameters of the correlation Eq. (1) and the partial molar volume at infinite dilution defined by the relation:

$$\Delta = 100(\phi_v^0 - \phi_{v,exp}^0)/\phi_v^0 \qquad (11)$$

does not exceed 5% for 1–1 electrolytes (except for fluorides) and 20% for 1–2 electrolytes. The same differences (i.e. below 20%) were also found for the electrolytes of the types 1–2 and 1–3 (ref.[3]). The given differences are caused, first of all, by the

TABLE II
Comparison of calculated and experimentally found $\phi_v^0 . 10^3$ values for some alkali metal salts at 25°C

Metal	F		Cl		Br		I		NO$_3$		SO$_4$	
	ad	exp	ad	exp	ad	exp	ad	exp	ad	exp	ad	exp
Li	—		16·95	18·82	—		35·34	36·93	28·12	28·56	12·22	10·98
Na	−2·37	−1·0	16·62	15·66	23·5	23·18	35·01	34·82	27·79	27·10	11·56	9·85
K	7·86	6·28	26·85	26·23	33·73	32·24	45·24	44·78	38·02	38·68	32·02	26·57
Rb	12·91	7·07	31·9	30·94	38·78	38·48	—		43·07	45·42	42·12	45·79
Cs	20·18	19·92	39·17	38·77	46·05	45·84	57·56	57·9	50·34	50·09	56·66	61·23

TABLE III
The $s_{exp} \cdot 10^3$ values for some alkali metal salts at 25°C

	F	Cl	Br	I	NO$_3$
Na	0·809 (1·658) (2·529)	2·467 (−0·599) (−0·090)	1·868 (−0·426) (0·911)	1·442 (0·286) (0·341)	2·753 (−0·927)
K	3·338 (−0·961) (1·368)	2·377 (0·402) (0·258)	2·779 (−0·996) (−0·589)	1·783 (−0·551)	1·826 (−0·862)
Rb	4·706 (−2·071) (−1·441)	2·635 (−0·445) (−0·353)	2·190 (−0·118)	—	0·964 (1·627)
Cs	3·265 (−0·983)	2·282 (−0·210)	2·072 (−0·762)	1·310 (1·281)	2·591

fact that Eq. (2) presumes validity of the relation

$$\phi_v = \phi_v^0 + s_{exp} \sqrt{c} \tag{12}$$

in the whole concentration range. In the cases when formation of ion pairs in the solutions becomes significant, marked positive deviations of real concentration dependence of ϕ_v from Eq. (9) (ref.[6]) are encountered, thus Eq. (9) does not fit equally well the experimental data in the whole concentration range. Another possible reason of the differences between $\phi_{v,exp}^0$ and ϕ_v^0 is the fact that the ionic values ϕ_v^0 given by individual authors are often markedly different. So e.g. for Zn^{2+} the values given in refs[6,8,9] are $-21\cdot6 \cdot 10^{-3}$, $-26\cdot6 \cdot 10^{-3}$, and $-24\cdot4 \cdot 10^3$, respectively, for WO_4^{2-} refs[6,10] give $25\cdot7 \cdot 10^{-3}$ and $32\cdot4 \cdot 10^{-3} \, m^3 \, kmol^{-1}$, respectively, etc. In such situation it is a quenstion which of the ϕ_v^0 values given in literature should be considered correct and taken as a basis for the comparison. With respect to the fact that even great differences between $\phi_{v,exp}^0$ and ϕ_v^0 affect relatively little the numerical value of the α parameter (a consequence of Eq. (5)), and, moreover, agreement between the two quantities is generally satisfactory, the values ϕ_v^0 given in tables
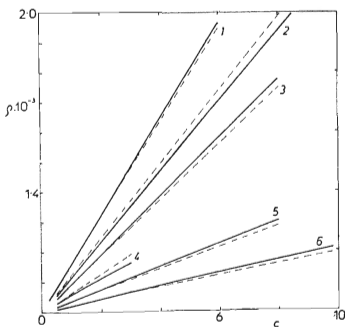

Fig. 1

Comparison of densities (———)(kg m^{-3}) of binary aqueous solutions of some 1—1 electrolytes at 25°C determined experimentally with those assessed from the ϕ_v^0 values given in tables. 1 AgClO$_4$, 2 AgF, 3 LiI, 4 NH$_4$H$_2$PO$_4$, 5 LiNO$_3$, 6 LiCl (c in kmol m^{-3})
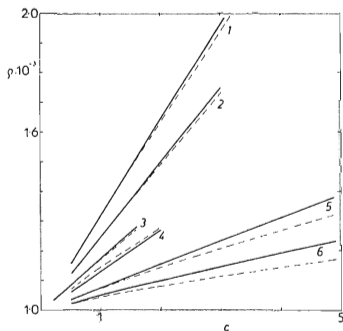
Fig. 2

Comparison of experimentally (———) determined densities (kg m^{-3}) of binary aqueous solutions of some 1—2 electrolytes at 25°C with those assessed from the ϕ_v^0 values given in tables. 1 BaI$_2$, 2 BaBr$_2$, 3 BaCl$_2$, 4 FeSO$_4$, 5 Be(NO$_3$)$_2$, 7 BeCl$_2$ (c in kmol . m^{-3})

can be used in calculation of α for the purpose of the assessment of densities of binary solutions.

Table III gives s_{exp} values calculated from D, E, F constants of Eq. (1) for salts of alkali metals. The figures in brackets representing the differences between adjacent in a line or column show that the s_{exp} calculated from Eq. (1) is not additive in any case. The values s_{exp} calculated from Eq. (1) vary within the following ranges: 1—1 electrolytes from $1 \cdot 10^{-3}$ to $4 \cdot 10^{-3}$ (except for salts of Li^+, Tl^+, $NH_4H_2PO_4$, and $KMnO_4$); 1—2 electrolytes about $(5 \text{ to } 14) \cdot 10^{-3}$ (except for salts of Ba^{2+}, Be^{2+}, and $Na_2B_4O_7$); 2—2 electrolytes about $(7 \text{ to } 22) \cdot 10^{-3}$ (except for $FeSO_4$ and $CoSO_4$); 1—3 electrolytes about $(13 \text{ to } 37) \cdot 10^{-6}$; $K_4Fe(CN)_6Fe(CN)_6$ $20.07 \cdot 10^{-3}$; $ThCl_4$ $17.7 \cdot 10^{-3}$; $Na_4P_2O_7$ $70.3 \cdot 10^{-3}$. In spite of considerable discrepances among electrolytes of the same type, comparison with Table I shows that the s_{theor} values line always approximately in the middle of the found s_{exp} interval except for 1—4 electrolytes. If it is taken into account that $\beta \sim (0.1 \text{ to } 0.01) \cdot \alpha$, then it is obvious that possible differences between the s_{theor} and s_{exp} values will not make themselves felt until at higher concentrations.
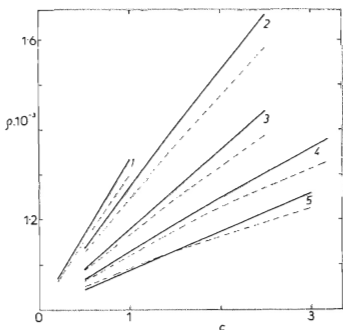

FIG. 3

Comparison of the experimentally (———) determined (25°C) densities (kg m^{-3}) of binary aqueous solutions of some 1—3 and 1—4 electrolytes with those assessed from the ϕ_v^0 values given in tables. 1 $ThCl_4$, 2 $La(NO_3)_3$, 3 $Fe(NO_3)_3$, 4 $FeCl_3$, 5 $AlCl_3$ (c in kmol . m^{-3})
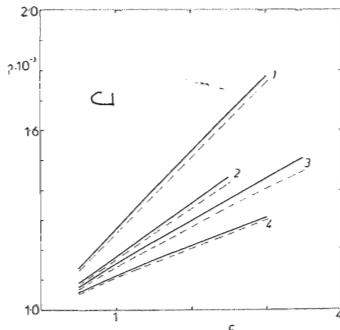
FIG. 4

Comparison of the experimentally (—·—) determined (25°C) densities (kg m^{-3}) of binary aqueous solutions of some 2—2 and 1—3 electrolytes with those assessed according to Eq. (10). 1 $La(NO_3)_3$, 2 $Fe(NO_3)_3$, 3 $ZnSO_4$, 4 $MgSO_4$ (c in kmol m^{-3})

From above discussion it follows that density of a binary aqueous solution can be assessed with the use of Eq. (2), if the parameters α and β are determined according to Eqs (5) and (6). The quantity ϕ_v^0 is determined by the additivity principle (Eq. (7)) with the use of ionic volumes given in literature and s_{theor} from Table I (for 25°C) instead of s_{exp}.

Figs 1 to 3 present comparison of the real and assessed density of solutions of electrolytes type $1-1$ to 3 at 25°C for the compounds for which great differences between $\phi_{v,exp}^0$ and ϕ_v^0 and between s_{exp} and s_{theor} were found. Agreement between the experimental (full line) and assessed densities (dashed line) is very good for $1-1$ and $1-2$ electrolytes, whereas with $1-3$ electrolytes significant differences are observed at concentrations. The density estimates of solutions of fluorides, for which there is the greatest difference between $\phi_{v,exp}^0$ and ϕ_v^0 (Table II), differ from the experimental value by at most 5 kg m^{-3}. For $2-2$ electrolytes the maximum difference between the assessed and the experimental values is 10 kg m^{-3}.

Summarily it can be stated that for $1-1$, $1-2$, and $2-2$ electrolytes the solution densities assessed on the basis of partial molar volume at infinite dilution agree very well with the experimental values. The agreement is worse with $1-3$ and $1-4$ electrolytes. This method of density assessment has its drawback in its being limited mostly to temperature 25°C, because the necessary ϕ_v^0 values at other temperatures are known for few ions only.

The density estimate of aqueous binary solution according to Eq. (8) necessitates knowledge of experimental data on densities within sufficiently broad concentration interval for three other suitable compounds. In Fig. 4 the assessed and experimental densities are compared for the compounds for which the above method gave the worst results. The densities of the given nitrate and sulphate solutions were assessed by means of the equations:

$$\varrho(M(NO_3)_3) = \varrho(MCl_3) + 3\varrho(RbNO_3) - 3\varrho(RbCl) \qquad (13)$$

$$\varrho(MSO_4) = \varrho(MCl_2) + \varrho(Cs_2SO_4) - 2\varrho(CsCl) + \varrho_0 \qquad (14)$$

From Fig. 4 it follows that the agreement between the experimental and the assessed values is markedly better than that in the previous method (*cf.* Figs 3 and 4). For the compounds for which the previous method enabled satisfactory assessments the method using Eq. (8) gives assessments either more accurate than or at least as accurate as the using Eq. (2). So *e.g.* for Be(NO$_3$)$_2$ solution the difference between the experimental value and the assessment according to Eq. (8) is below 10 kg m^{-3} within the whole concentration interval up to the saturated solution which contrasts with Eq. (2), where the differences reach as high as 70 kg m^{-3} (Fig. 2).

The results described show that Eq. (8) gives always better density estimates of binary aqueous solutions of electrolyte than Eq. (2), and also Eq. (8) should be preferred because it is not restricted to 25°C. However, Eq. (2) is used for the assessment, if experimental values of densities of solutions of three suitable compounds are unavailable. In such cases the density estimates are sufficiently close to reality except for solutions of $1 - 3$ and 4 electrolytes where the obtained data only approach to real values at higher concentrations. However, for technical calculations such solution density estimates are usually acceptable.

LIST OF SYMBOLS

A, B, C, D, E, F	constants of Eq. (1)
c	molar concentration, $kmol\ m^{-3}$
M	molar mass $kg\ kmol^{-1}$
s_{exp}, s_{theor}	experimental and theoretical slope of the dependence $\phi = f(\sqrt{c})$, $m^{9/2}\ kmol^{-3/2}$
t	temperature, °C
α, β	parameters of Eq. (2)
ϕ_v	apparent molar volume of the dissolved compound, $m^3\ kmol^{-1}$
ϕ_v^0	partial molar volume of the dissolved compound at infinite dilution, $m^3\ kmol^{-1}$
$\phi_{v,exp}^0$	empirical parameter, $m^3\ kmol^{-1}$
ϱ	density of the solution, $kg\ m^{-3}$
ϱ_0	density of water, $kg\ m^{-3}$
Δ	difference, %

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