

## The Applicability of the Density Rule of Pathwardhan and Kumer and the Rule Based on Linear Isopestic Relation\*

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**Abstract** The applicability of the density rule of Pathwardhan and Kumer and the rule based on the linear isopiestic relation is studied by comparison with experimental density data in the literature. Predicted and measured values for 18 electrolyte mixtures are compared. The two rules are good for mixtures with and without common ions, including those containing associating ions. The deviations of the rule based on the linear isopiestic relation are slightly higher for the mixtures involving very strong ion complexes, but the predictions are still quite satisfactory. The density rule of Pathwardhan and Kumer is more accurate for these mixtures. However, it is not applicable for mixtures containing non-electrolytes. The rule based on the linear isopiestic relation is extended to mixtures involving non-electrolytes. The predictions for the mixtures containing both electrolytes and non-electrolytes and the non-electrolyte mixtures are accurate. All these results indicate that this rule is a widely applicable approach.

**Keywords** binary density rules, density, apparent molar volume, multicomponent system, binary sub-system

### 1 INTRODUCTION

The densities of multicomponent solutions are very important for areas such as chemistry and chemical engineering, steam power and so on. Extensive data of binary aqueous solutions have been reported in the literature. However, few experimental measurements have been made on multicomponent solutions. Therefore, it is interesting and practically important to develop a corresponding approach that can make use of the available information of binary solutions and provide reasonable predictions for multicomponent solutions.

Pathwardhan and Kumer<sup>[1]</sup> have recently presented a density rule for the density of multicomponent solution with the densities of the constituent binary solutions evaluated at the molar ionic strength of the mixture. This method has been shown to yield very satisfactory predictions for strong electrolyte solutions without very strong ion-ion complexes even at high concentrations. However, since ionic strength is undefined for non-electrolytes, this rule is strictly not applicable to mixtures containing non-electrolytes.

More recently Hu presented a new density rule for multicomponent solutions<sup>[2]</sup>. This rule provides the densities of multicomponent systems obeying the linear isopiestic relation by using only the data of the binary sub-systems of equal water activity. The accuracy of the new rule has been tested by comparison with the experimental data for ternary electrolyte solutions with or without common ions and the agreement is excellent. Since the linear isopiestic relation is applicable to mixtures involving non-electrolytes, it might be expected that this rule could be used for these mixtures.

A very important question is the extent to which

the simple density rule can be applied. Therefore, the present paper aims at the breadth of the applicability of the above rules and includes the following two parts: (1) Since the densities of mixtures containing both electrolytes and non-electrolytes play a very important role in the field of food engineering and fragile biological material processing, it is interesting and practically important to extend the new rule to such mixtures and mixtures of non-electrolytes; (2) An extensive comparison is given to examine the accuracy of the above two rules for strong electrolyte solutions, electrolyte solutions with moderate ion associations and those having very strong ion complexes.

### 2 THE RULE BASED ON THE LINEAR ISOPIESTIC RELATION AND THE DENSITY RULE OF PATHWARDHAN AND KUMER

The linear isopiestic relation<sup>[2]</sup> for multicomponent solutions can be expressed as

$$\sum_j (m_j/m_j^o) = 1$$
$$(a_w = \text{constant and } 0 \leq (m_j/m_j^o) \leq 1) \quad (1)$$

where the subscript w denotes water, *j* denotes the quantity of solute *j* in the mixed solutions, and the superscript o together with subscript *j* represents the quantity of solute *j* in binary solutions (*j*-H<sub>2</sub>O). Recently Hu<sup>[2]</sup> have used Eq. (1) together with the well-known thermodynamic equations to obtain the density rule for density of a multicomponent system from the properties of its binary sub-systems of equal water

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activity

$$d = \frac{\sum_j Y_j}{\sum_j (Y_j/d_j^0)} \quad (2)$$

with  $Y_j = m_j/m_j^0 + m_j M_j$ , where  $M_j$  is the molar mass ( $\text{kg}\cdot\text{mol}^{-1}$ ) of solute  $j$ .

Patwardhan and Kumer<sup>[1]</sup> derived a density rule for density of the mixed solution from the values of  $d_{o,j}$

$$d = \frac{\sum_j \Psi_j}{\sum_j (\Psi_j/d_{o,j})} \quad (3)$$

with  $\Psi_j = y_j + m_j M_j$ . Here  $y_j$  is the ionic strength fraction of electrolyte  $j$ . The values of  $d_{o,j}$  are evaluated at the same ionic strength as that of the mixture.

### 3 COMPARISON WITH LITERATURE DENSITY DATA

The experimental densities in the literature for 23 mixtures at 298.15 K are used to test the accuracy of the density rule of Patwardhan and Kumer<sup>[1]</sup> and the rule proposed by Hu<sup>[2]</sup>. The test procedure required by the former method has been described elsewhere<sup>[1]</sup> and the procedure for the test of the latter is as follows:

(1) Represent the experimental densities of the binary solutions [ $d_{j,\text{Exp}} (j=\text{B, C or D})$ ] and multicomponent solutions ( $d_{\text{Exp}}$ ) by the following polynomials

$$d_{j,\text{Exp}} = d_w + \sum_{j=1}^n A_k (m_j)^{k/2} \quad (4)$$

$$\begin{aligned} d_{\text{Exp}} = & d_w + \sum_k A_k (m_j)^{k/2} + \sum_k B_k (m_B m_C)^{k/2} + \\ & \sum_k C_k (m_B m_D)^{k/2} + \sum_k D_k (m_C m_D)^{k/2} + \\ & \sum_k E_k (m_B m_C m_D)^{k/2} \end{aligned} \quad (5)$$

where  $d_w = 0.997047 \text{ g}\cdot\text{cm}^{-3}$  is the density of water at 298.15 K. The optimum fit is obtained by increasing  $k$  until the resulting polynomial is accurate to a few parts in  $10^5$ .

(2) Determine the compositions of the ternary or quaternary systems ( $m_j$ ) and their binary sub-systems ( $m_j^0$ ) of equal water activity by the following procedure. (a) The values of  $m_j^0 (j=\text{B, C and D})$  are calculated from the osmotic data ( $\varphi_i$ ) in binary solutions<sup>[3]</sup> and the relation  $\nu_B m_B^0 \varphi_B^0 = \nu_C m_C^0 \varphi_C^0 = \nu_D m_D^0 \varphi_D^0$ , where  $\nu_j$  is the salt stoichiometric coefficient, which is formally taken as unity if  $j$  is a non-electrolyte solute. Parameter  $\varphi_j$  is the osmotic coefficient. (b) The compositions of the ternary solutions of equal water activity are determined by choosing the values of  $m_B$  and then calculating the values of  $m_C$  from Eq. (1).

(c) Determine the compositions of the quaternary systems by choosing the values of  $m_B$  and  $m_C$ , and then calculating the values of  $m_D$  from Eq. (1).

(3) Calculate the values of  $d_{j,\text{Exp}}^0 (j=\text{B, C or D})$  from Eq. (4) and then insert them into Eq. (2) to yield the values of  $d_{\text{Cal}}$ .

(4) Compare the predictions with the values of  $d_{\text{Exp}}$  obtained from the polynomial fits, Eq. (5).

The binary systems used in this paper are listed in Table 1<sup>[4-13]</sup>. Densities predicted by the two rules are compared in Table 2, where the average absolute deviation,  $\Delta_d$ , between predicted and measured densities is defined by

$$\Delta_d \stackrel{\text{def.}}{=} \frac{\sum_{j=1}^N |(d_{\text{Cal}} - d_{\text{Exp}})_j|}{N} \quad (6)$$

where  $N$  is the number of experimental data. The following systems are used: (1) nine strong electrolyte mixtures having common ions (CISE mixtures, including those involving associating ions)<sup>[4,5,8,11,14]</sup>; (2) five strong electrolyte mixtures without common ions (NCISE mixtures, including those containing associating ions)<sup>[7,12,14]</sup>; (3) four electrolyte mixtures which contain the transition metal chlorides (TMCE mixtures, including three mixtures with very strong cation-anion complexes)<sup>[6]</sup>; (4) two ternary mixtures containing both electrolyte and non-electrolyte<sup>[9]</sup>; (5) three ternary non-electrolyte mixtures<sup>[13]</sup>. Both rules are good for the CISE and NCISE mixtures, but neither of them gives universal better predictions. The predictions by the two methods are very close for the first two TMCE mixtures, but the density rule of Patwardhan and Kumer shows an advantage for HCl-ZnCl<sub>2</sub>-H<sub>2</sub>O and HCl-CdCl<sub>2</sub>-H<sub>2</sub>O systems. However, the density rule of Patwardhan and Kumer is not applicable to mixtures containing non-electrolytes, so the densities of these mixtures are predicted by Eq. (2) and the results are in general very accurate.

Table 1 References for aqueous binary systems

Solute	$m_{\text{Max}}$	Refs.
HCl	16.000	[4,5]
NaCl	6.0216	[4,6,8,9]
KCl	4.6030	[4,6,9]
MgCl <sub>2</sub>	1.4749	[10]
CaCl <sub>2</sub>	7.8783	[11]
SrCl <sub>2</sub>	3.0900	[8]
MnCl <sub>2</sub>	6.0292	[5]
CuCl <sub>2</sub>	3.5741	[5]
ZnCl <sub>2</sub>	7.3213	[5]
CdCl <sub>2</sub>	6.3608	[5]
KBr	4.4793	[7]
Na <sub>2</sub> SO <sub>4</sub>	1.5000	[10]
K <sub>2</sub> SO <sub>4</sub>	0.3976	[12]
MgSO <sub>4</sub>	1.4825	[10]
glycerol	10.104	[13]
glucose	20.999	[13]
sucrose	2.0745	[13]

**Table 2** Comparison of densities predicted by the two rules

System	$I_{Max}^{\text{①}}$	$\Delta_d^H \times 10^5$ ②	$\Delta_d^{PK} \times 10^5$	Ref.
NaCl-KCl	4.3719	32	32	[6]
NaCl-MgCl <sub>2</sub>	1.8266	7	7	[14]
NaCl-CaCl <sub>2</sub>	4.6091	34	31	[11]
NaCl-SrCl <sub>2</sub>	6.9396	43	48	[8]
KCl-CaCl <sub>2</sub>	3.5699	22	22	[11]
Na <sub>2</sub> SO <sub>4</sub> -NaCl	1.9180	36	59	[14]
MgSO <sub>4</sub> -MgCl <sub>2</sub>	3.1192	28	23	[14]
MgSO <sub>4</sub> -Na <sub>2</sub> SO <sub>4</sub>	1.9916	36	31	[14]
HCl-KCl-NaCl	2.1230	36	38	[4]
NaCl-KBr	3.9619	89	89	[7]
KCl-Na <sub>2</sub> SO <sub>4</sub>	2.1156	34	32	[12]
NaCl-K <sub>2</sub> SO <sub>4</sub>	1.9500	50	69	[12]
NaCl-MgSO <sub>4</sub>	1.3324	56	69	[12]
Na <sub>2</sub> SO <sub>4</sub> -MgCl <sub>2</sub>	2.9160	37	58	[14]
HCl-MnCl <sub>2</sub>	3.3884	66	59	[5]
HCl-CuCl <sub>2</sub>	3.5831	94	66	[5]
HCl-ZnCl <sub>2</sub>	3.0246	136	59	[5]
HCl-CdCl <sub>2</sub>	3.0452	196	48	[5]
NaCl-sucrose	1.9896 ③	92		[9]
KCl-sucrose	1.8070 ③	72		[9]
glucose-sucrose	2.3256 ③	172		[13]
glucose-glycerol	3.8986 ③	20		[13]
glycerol-sucrose	2.1340 ③	42		[13]

①  $I = \sum_j m_j Z_j^2 / 2$  is the ionic strength (mol·kg<sup>-1</sup>).

② The superscripts H and PK refer to the rule proposed by Hu<sup>[2]</sup> and the density rule of Patwardhan and Kumer<sup>[1]</sup>, respectively.

③ Total molality (mol·kg<sup>-1</sup>).

## NOMENCLATURE

$A_k$	coefficient in Eqs. (4) and (5)
$a$	activity coefficient
$B_k, C_k, D_k, E_k$	coefficients in Eq. (5)
CISE	strong electrolyte mixture containing common ions
$d$	density, g·cm <sup>-3</sup>
$I$	ionic strength, mol·kg <sup>-1</sup>
$M$	molar mass, kg·mol <sup>-1</sup>
$m$	molality, mol·kg <sup>-1</sup>
$N$	number of experimental data
NCISE	strong electrolyte mixture without common ions
TMCE	salt mixture containing the transition metal chlorides
$Y$	function defined by $Y_j = m_j / m_j^0 + m_j M_j$
$y$	ionic strength fraction of electrolyte
$Z$	charge number of ionic species
$\Delta$	average absolute deviation defined by Eq. (6)
$v$	salt stoichiometric coefficient
$\varphi$	osmotic coefficient
$\psi$	function defined by $\psi_j = y_j + m_j M_j$

## Superscripts

H	density rule based on the linear isopiestic relation
o	quantity in binary systems at the same water

PK	activity as that of a mixture density rule of Patwardhan and Kumer
Subscripts	
B, C, D, $j$	component
Cal	calculated quantity
Exp	experimental quantity
Max	maximum quantity
o	quantity in binary salt solutions at the same ionic strength as that of a mixture
w	water

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