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ANALYSIS OF VOLUMETRIC PROPERTIES OF LIQUID MIXTURES I. METHOD OF BINARY ADDITIVE QUASI-SOLVATES

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The method of binary additive quasi-solvates (BAQS) a new approach for analyzing the physicochemical properties of solutions is proposed. Quasi-solvate Q_{ij} is a hypothetical two-particle structure in which one particle *i* is the 'solute' and the other particle *j* is the 'solvent'. A set of similar quasi-solvates has the macroscopic property F_{ij}. The solution is an additive mixture of quasi-solvates with weight functions w_{ij}. Two models have been developed within the BAQS method: with symmetric weight functions (BAQS/S) and with asymmetric weight functions (BAQS/A). On the example of volumetric properties of non-electrolyte solutions the possibilities of the method are shown. Effective limiting partial molar volumes of components for mixtures of non-electrolytes are determined. The possibility of predicting the properties of multicomponent solutions from data for two-component systems is considered. Applications to other solution properties are shown. Each of the proposed models has its own advantages and limitations.

BAQS/S: describes molar volumes of mixtures, especially for aprotonic systems, can be used to predict properties of multicomponent systems, effective on small datasets. Limitations: applicability to other solution properties remains questionable, model parameters differ from those obtained by the independent method, approximation accuracy is inferior to empirical models.

BAQS/A: applicable for any solution properties, informative and illustrative. Limitations: very sensitive to the choice of approximating equation, difficult to interpret results, developed only for two-component systems.

Keywords: *physicochemical analysis, molar volume, limiting partial molar volume, Redlich-Kister equation, non-electrolyte solutions, multicomponent mixtures, binary additive quasi-solvates.*

Introduction

Solutions play a significant role in all areas of chemistry. One of the most important thermodynamic characteristics of solutions are volumetric properties: density, molar volume, excess molar volume[1]. A great number of data on volumetric properties of solutions have been collected[2] and they continue to be actively studied[3-6]. The properties of solutions are determined by the specifics of interparticle interactions. Therefore, analyzing the influence of the composition and nature of components on the physicochemical properties of solutions is an actual problem. In many cases, this requires special experiments. Which significantly limits the range of systems to be investigated.

Volumetric properties are usually considered in terms of molar volumes. For example, analysis of the dependence of molar volume on composition for two-component solutions. Excess molar volume is a measure of the deviation of molar volume from additivity:

$$V^E = V - V_1 x_1 - V_2 x_2 \quad (1)$$

Traditionally, the dependence of excess molar volume on composition is described by the empirical Redlich-Kister equation[7]:

$$V^E = x_1 x_2 \left(A_0 + \sum_{i=1}^{n} A_i (x_1 - x_2)^i \right) \quad (2)$$

Each system is characterized by a set of empirical parameters A_i.

Another approach is the partial molar volume method:

$$V = \overline{V}_1 x_1 + \overline{V}_2 x_2 \quad (3)$$

Of particular interest are the limiting partial molar volumes. Within the framework of the Redlich-Kister model, limiting partial molar volumes are determined:

$$\overline{V}_{12}^{\infty} = V_1 + \sum_{i=0}^{n} A_i \cdot (-1)^i \quad (4)$$

$$\overline{V}_{21}^{\infty} = V_2 + \sum_{i=0}^{n} A_i \tag{5}$$

A large amount of data in the dilute region of compositions is needed to correctly determine the limiting partial molar volumes. At the same time, most non-electrolyte solutions have been studied with a typical composition scale step of ~0.1 mole fraction units, which is only a dozen points for each system. Thus, using equation (2) with a large number of parameters seems incorrect. Despite the colossal number of systems studied (about a hundred thousand datasets, more than a million experimental points[2]), the vast majority of data more than to determine the excess molar volume is not used in any way.

This paper proposes a method to analyze the physicochemical properties of solutions within a single dataset. This will allow the extensive material collected in the scientific literature to be utilized.

Method

Binary Additive Quasi-Solvates (BAQS).

Let's introduce some definitions.

D1: Quasi-solvate Q_{ij} is a hypothetical two-particle structure in which one particle *i* is the 'solute' and the other particle *j* is the 'solvent'.

D2: A set of similar quasi-solvates has the macroscopic property F_{ij}.

D3: The solution is an additive mixture of quasi-solvates with weight functions w_{ij}.

From *D2* and *D3*, it follows that the property *F* of an *n*-component solution is composed of F_{ij} with weight functions w_{ij}:

$$F = \sum_{i=1}^{n}\sum_{j=1}^{n} F_{ij} w_{ij} \tag{6}$$

$$\sum_{i=1}^{n}\sum_{j=1}^{n} w_{ij} = 1 \tag{7}$$

Four types of quasi-solvates are possible for a two-component solution:

Q_{11} – component 1 particle is the 'solute', component 1 particle is the 'solvent';

Q_{22} – component 2 particle is the 'solute', component 2 particle is the 'solvent';

Q_{12} – component 1 particle is the 'solute', component 2 particle is the 'solvent';

Q_{21} – component 2 particle is the 'solute', component 1 particle is the 'solvent'.

Thus, the molar volume of the two-component solution is

$$V = V_{11}w_{11} + V_{12}w_{12} + V_{21}w_{21} + V_{22}w_{22} \tag{8}$$

Cases V_{11} and V_{22} – correspond to pure components. Based on *D1*, it can be assumed that

$$V_{12} = \frac{\overline{V}_{12}^{\infty} + V_{11}}{2} \text{ and } V_{21} = \frac{\overline{V}_{21}^{\infty} + V_{22}}{2} \tag{9}$$

It remains only to set the weight functions. Two approaches to solving this problem are proposed.

Binary Additive Quasi-Solvates with Symmetric weight functions (BAQS/S)

Let the quasi-solvates be randomly distributed in the solution. Then the weight function is equal to the probability of choosing two particles:

$$w_{11} = x_1^2 \text{ and } w_{22} = x_2^2 \tag{10}$$

$$w_{12} + w_{21} = 2x_1x_2 \tag{11}$$

On the other hand, by definition

$$\overline{V}_{12}^{\infty} = V_{22} - \frac{\partial V}{\partial x_1}\Big|_{x_1=0} \text{ and } \overline{V}_{21}^{\infty} = V_{11} - \frac{\partial V}{\partial x_2}\Big|_{x_2=0} \tag{12}$$

Conditions (8-12) satisfy the formulas:

$$w_{12} = 2x_1x_2^2 \text{ and } w_{21} = 2x_1^2x_2 \tag{13}$$

This suggests that the distribution of the quasi-solvates Q_{12} and Q_{21} cannot be completely random, but depends on the environment. Conditions (10, 13) satisfy the formula:

$$w_{ij} = \frac{2x_i x_j^2}{x_i + x_j} \tag{14}$$

Thus, the weight functions are symmetric with respect to substitution of indices.

From (8-10, 13) it follows that

$$V = V_{11}x_1^2(1+x_2) + \overline{V}_{12}^{\infty}x_1x_2^2 + \overline{V}_{21}^{\infty}x_1^2x_2 + V_{22}x_2^2(1+x_1) \tag{15}$$

The values of the molar volumes of pure components are assumed to be known. The limiting molar partial volumes are unknown and are calculated as fitting parameters. A special deviation function is used for approximation:

$$\Delta V = V - V_{11}x_1^2(1+x_2) - V_{22}x_2^2(1+x_1) = \overline{V}_{12}^{*}x_1x_2^2 + \overline{V}_{21}^{*}x_1^2x_2 \tag{16}$$

Normalized deviation function assumes linear dependence and allows visual assessment of model adequacy:

$$\Delta V_N = \frac{\Delta V}{x_1x_2} = \overline{V}_{12}^{*}x_2 + \overline{V}_{21}^{*}x_1 \tag{17}$$

The coefficients of the two-parameter Redlich-Kister equation are related to the effective limiting partial molar volumes:

$$A_0 = \frac{\left(\overline{V}_{21}^{*} - V_{22}\right) + \left(\overline{V}_{12}^{*} - V_{11}\right)}{2} = \frac{V_{21}^{E*} + V_{12}^{E*}}{2} \tag{18}$$

$$A_1 = \frac{\left(\overline{V}_{21}^{*} - V_{22}\right) - \left(\overline{V}_{12}^{*} - V_{11}\right)}{2} = \frac{V_{21}^{E*} - V_{12}^{E*}}{2} \tag{19}$$

The BAQS/S model can also describe multi-component systems:

$$V = \sum_{i=1}^{n}\sum_{j=1}^{n}\left(\overline{V}_{ij}^{\infty} + V_{jj}\right)\frac{x_i x_j^2}{x_i + x_j} \tag{20}$$

The applicability of this model is discussed below.

Binary Additive Quasi-Solvates with Asymmetric weight functions (BAQS/A).

Assume that the equilibrium between quasi-solvates is established:

$$Q_{11} + Q_{22} \leftrightarrow Q_{12} + Q_{21} \tag{21}$$

$$Q_{12} \leftrightarrow Q_{21} \tag{22}$$

Then

$$w_{11} = x_1 - \alpha \tag{23}$$

$$w_{22} = x_2 - \alpha \tag{24}$$

$$w_{12} = \alpha - \beta \tag{25}$$

$$w_{21} = \alpha + \beta \tag{26}$$

where α and β are the mole fractions of the particles involved in processes (21) and (22), respectively.

From (3, 8, 9, 23-27) it follows that

$$V = V_{11}\left(x_1 - \frac{\alpha}{2} + \frac{\beta}{2}\right) + \overline{V}_{12}^{\infty}\left(\frac{\alpha}{2} - \frac{\beta}{2}\right) + \overline{V}_{21}^{\infty}\left(\frac{\alpha}{2} + \frac{\beta}{2}\right) + V_{22}\left(x_2 - \frac{\alpha}{2} - \frac{\beta}{2}\right) = \overline{V}_1x_1 + \overline{V}_2x_2 \tag{27}$$

Suppose it can be divided into two component parts:

$$V_{11}\left(x_1 - \frac{\alpha}{2} + \frac{\beta}{2}\right) + \overline{V}_{12}^{\infty}\left(\frac{\alpha}{2} - \frac{\beta}{2}\right) = \overline{V}_1x_1 \tag{28}$$

$$V_{22}\left(x_2 - \frac{\alpha}{2} - \frac{\beta}{2}\right) + \overline{V}_{21}^{\infty}\left(\frac{\alpha}{2} + \frac{\beta}{2}\right) = \overline{V}_2x_2 \tag{29}$$

After simple transformations the system of equations has the form:

$$\alpha - \beta = 2x_1 \frac{\overline{V}_1 - V_{11}}{\overline{V}_{12}^{\infty} - V_{11}} \tag{30}$$

$$\alpha + \beta = 2x_2 \frac{\overline{V}_2 - V_{22}}{\overline{V}_{21}^{\infty} - V_{22}} \tag{31}$$

From (23-26, 30, 31) it follows that

$$w_{12} = 2x_1 \frac{\overline{V}_1^E}{\overline{V}_{12}^{E\infty}} \text{ and } w_{21} = 2x_2 \frac{\overline{V}_2^E}{\overline{V}_{21}^{E\infty}} \tag{32}$$

$$w_{11} = x_1 - \frac{w_{12} + w_{21}}{2} \text{ and } w_{22} = x_2 - \frac{w_{12} + w_{21}}{2} \tag{33}$$

Thus, a set of weight functions of quasi-solvates for any composition of the system is obtained. The weight functions in model BAQS/A are asymmetric with respect to index substitution.

Let us determine the excess partial molar volumes using the tangent to the excess volume function (1). If we use (2), the weight functions are determined using the coefficients of the Redlich-Kister equation and special polynomials ($x \equiv x_2$):

$$w_{12} = 2(1-x) \frac{\sum_{i=0}^{n} A_i P_{1i}}{\sum_{i=1}^{n} A_i \cdot (-1)^i} \tag{34}$$

$$w_{21} = 2x \frac{\sum_{i=0}^{n} A_i P_{2i}}{\sum_{i=1}^{n} A_i} \tag{35}$$

The following are special polynomials:

$$P_{10} = x^2 \tag{36}$$

$$P_{11} = 3x^2 - 4x^3 \tag{37}$$

$$P_{12} = 5x^2 - 16x^3 + 12x^4 \tag{38}$$

$$P_{13} = 7x^2 - 36x^3 + 60x^4 - 32x^5 \tag{39}$$

$$P_{14} = 9x^2 - 64x^3 + 168x^4 - 192x^5 + 80x^6 \tag{40}$$

$$P_{15} = 11x^2 - 100x^3 + 360x^4 - 640x^5 + 560x^6 - 192x^7 \tag{41}$$

$$P_{16} = 13x^2 - 144x^3 + 660x^4 - 1600x^5 + 2160x^6 - 1536x^7 + 448x^8 \tag{42}$$

$$P_{20} = 1 - 2x + x^2 \tag{43}$$

$$P_{21} = 1 - 6x + 9x^2 - 4x^3 \tag{44}$$

$$P_{22} = 1 - 10x + 29x^2 - 32x^3 + 12x^4 \tag{45}$$

$$P_{23} = 1 - 14x + 61x^2 - 116x^3 + 100x^4 - 32x^5 \tag{46}$$

$$P_{24} = 1 - 18x + 105x^2 - 288x^3 + 408x^4 - 288x^5 + 80x^6 \tag{47}$$

$$P_{25} = 1 - 22x + 161x^2 - 580x^3 + 1160x^4 - 1312x^5 + 784x^6 - 192x^7 \tag{48}$$

$$P_{26} = 1 - 26x + 229x^2 - 1024x^3 + 2660x^4 - 4192x^5 + 3952x^6 - 2048x^7 + 448x^8 \tag{49}$$

For the two-parameter Redlich-Kister equation considering (18, 19), where ς is the ratio of the effective excess limiting partial molar volumes:

$$w_{11} = x_1^2 + 4x_1^2 x_2^2 \cdot \left(1 - \frac{\varsigma_{12} + \varsigma_{21}}{2}\right) \tag{50}$$

$$w_{22} = x_2^2 + 4x_1^2x_2^2 \cdot \left(1 - \frac{\varsigma_{12} + \varsigma_{21}}{2}\right) \quad (51)$$

$$w_{12} = 2x_1x_2^2 + 4x_1^2x_2^2 \cdot (\varsigma_{21} - 1) \quad (52)$$

$$w_{21} = 2x_1^2x_2 + 4x_1^2x_2^2 \cdot (\varsigma_{12} - 1) \quad (53)$$

Restriction on the ratio of excess limiting partial molar volumes:

$$\frac{1}{2} \le \varsigma_{ij} \le 2 \quad (54)$$

When the excess limiting partial molar volumes are equal, the weight functions correspond to equations (10) and (13).

Model testing

BAQS/S:Two-component systems.

Let us consider the applicability of the model for the well-studied Ethanol-Water system. Data on the density of water-alcohol mixtures at 298.15 K and atmospheric pressure are taken from [8]. Based on these data, the ΔV functions were calculated and approximated by equation (16). (Fig. 1). As fitting parameters, the limiting partial molar volumes of Ethanol in Water and Water in Ethanol were determined (Table 2, 2 parameters). The values obtained are slightly different from the traditional values 55.195 and 13.904 cm^3/mol, respectively [9]. Thus, the calculated limiting partial molar volumes should be considered as effective within the model.

The data are presented more clearly in the form of linearized equation (17). Figure 2 also shows the values for binary mixtures of Water, Acetonitrile and DMSO at 293.15 K and pressure of 81.5 kPa calculated from [10].

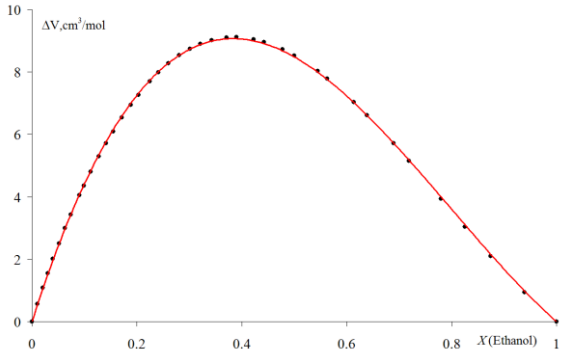

Fig. 1 Dependence of the function ΔV on the composition of the mixture of Water and Ethanol. The dots show experimental data, the line – calculation by equation (16).

It can be seen that the model describes the experimental data quite satisfactorily. Small deviations are observed for water-organic systems in the region of low water content.

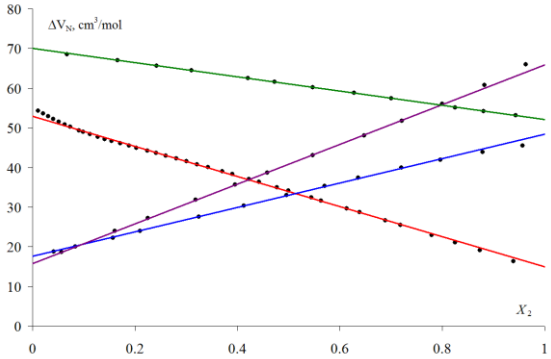

Fig. 2 Dependence of the function ΔV_N on the content of the second component of the mixture. Dots – experimental data. Lines – calculations according to equation (17): Ethanol-Water (red), Water-Acetonitrile (blue), Water-DMSO (purple), DMSO-Acetonitrile (green). See text for explanations.

However, it should be noted that BAQS/S is equivalent to the two-parameter Redlich-Kister equation and is inferior in accuracy to higher order equations. Nevertheless, it is reasonable to use it for small datasets and data visualization.

BAQS/S: Three-component systems.

The BAQS/S model can be used for multicomponent systems. The molar volumes of the three-component Water-Acetonitrile-DMSO system were calculated from the above data of the two-component systems and compared with experimental data [10]. Table 2 summarizes the parameters obtained for the two-component systems. Similar parameters determined only for three-component systems are also given.

Table 1. Effective limiting partial molar volumes V_{ij} (cm^3/mol) for two- and three-component systems.

i	*j*	2 components	3 components
Water	Acetonitrile	17.60±0.17	17.40±0.12
Acetonitrile	Water	48.43±0.17	48.82±0.11
Water	DMSO	15.77±0.16	15.63±0.11
DMSO	Water	65.90±0.16	65.91±0.11
Acetonitrile	DMSO	52.07±0.04	52.08±0.11
DMSO	Acetonitrile	70.08±0.04	68.97±0.12

The differences between the parameters obtained from different data are insignificant. The standard deviation for a three-component system is of the same order of magnitude as for two-component systems. Thus, the BAQS/S model can be applied to predict the properties of multicomponent systems.

BAQS/A: Molar volume.

The data of molar volumes of Water-Ethanol mixtures [8] were approximated by Redlich-Kister equations of different orders. The calculated parameters are summarized in Table 2.

Table 2. Parameters of equation (2), limiting partial molar volumes and sum of squares of deviations.

	2 parameters	3 parameters	4 parameters	5 parameters	6 parameters	7 parameters
A_0	-4.44±0.04	-4.29±0.03	-4.27±0.03	-4.20±0.02	-4.23±0.01	-4.26±0.01
A_1	1.29±0.09	1.10±0.06	1.34±0.10	1.16±0.08	0.77±0.06	0.88±0.03
A_2		-1.08±0.13	-1.23±0.13	-2.51±0.22	-2.01±0.13	-0.95±0.10
A_3			-0.74±0.26	-0.21±0.20	2.82±0.35	1.97±0.17
A_4				2.42±0.39	1.46±0.23	-3.23±0.40
A_5					-4.06±0.44	-2.91±0.22
A_6						4.81±0.40
$\overline{V}_{12}^{\infty}$	52.94±0.09	52.20	52.58	53.42	54.37	55.10
$\overline{V}_{21}^{\infty}$	14.92±0.11	13.80	13.17	14.72	12.82	14.38
σ	0.0574	0.0203	0.0166	0.0079	0.0023	0.0004

As the number of parameters increases, the approximation accuracy improves. However, the uncertainty of the limit values increases. Figures 3, 4, 5 show the dependences of weight functions for the two-, three-, and four-parameter Redlich-Kister equation calculated from equations (34, 35) and parameters of Table 3. Index 1 refers to Ethanol, index 2 to Water. The calculated weight functions depend significantly on the number of parameters of the approximating equation. Moreover, negative values of weight functions are observed for five and more parameters. However, qualitatively, the dependencies in Figs. 3-5 are similar. Thus, the question of choosing an approximating equation for the dependence of molar volume on composition remains open. Other approximating functions are also found in the literature[11]. For example, the Padé approximation or orthogonal Legendre polynomials are used.

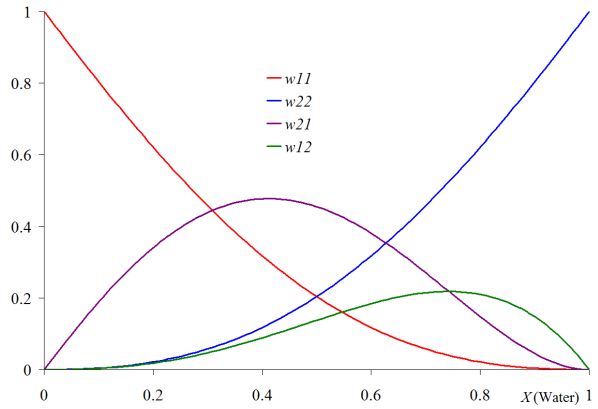

Figure 3. Dependence of weight functions on mixture composition for the two-parameter Redlich-Kister equation (see text for notations).

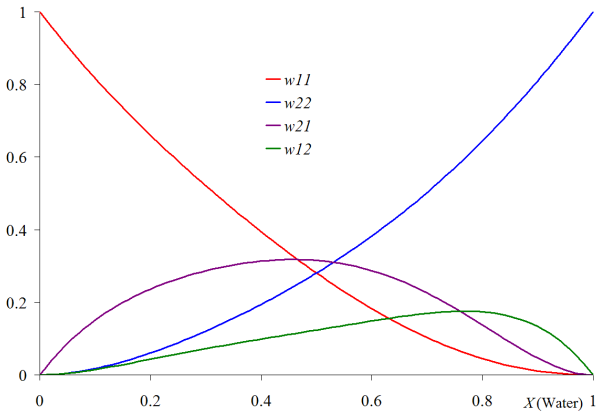

Figure 4. Dependence of weight functions on mixture composition for the three-parameter Redlich-Kister equation (see text for notations).

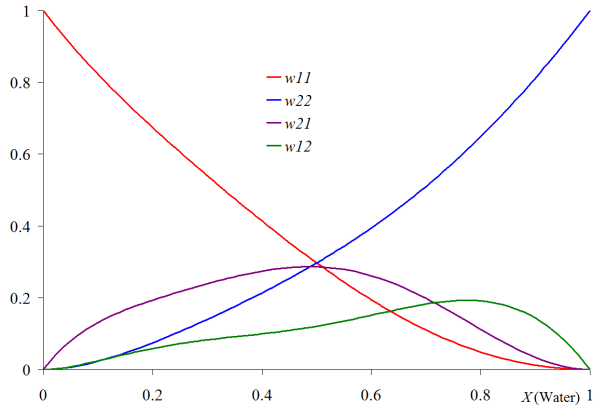

Figure 5. Dependence of weight functions on mixture composition for the four-parameter Redlich-Kister equation (see text for notations).

The difference in weight functions for BAQS/S and BAQS/A models characterizes the specificity of interparticle interactions:

$$\delta_{11} = w_{11} - x_1^2 \tag{55}$$

$$\delta_{22} = w_{22} - x_2^2 \tag{56}$$

$$\delta_{12} = w_{12} - 2x_1x_2^2 \tag{57}$$

$$\delta_{21} = w_{21} - 2x_1^2x_2 \tag{58}$$

what accounts for the deviations from linear dependence in equation 17.

Fig. 6 shows the differences of the weight functions for the four-parameter model.

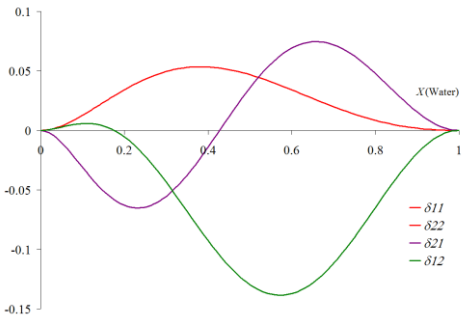

Figure 6. Dependence of the weight function difference on the mixture composition (see text for explanations).

Weight function differences for a two-parameter model:

$$\delta_{11} = \delta_{22} = 4x_1^2 x_2^2 \cdot \left(1 - \frac{\varsigma_{12} + \varsigma_{21}}{2}\right) \tag{59}$$

$$\delta_{12} = 4x_1^2 x_2^2 \cdot \left(\varsigma_{21} - 1\right) \tag{60}$$

$$\delta_{21} = 4x_1^2 x_2^2 \cdot \left(\varsigma_{12} - 1\right) \tag{61}$$

Parameters δ_{ij} show which interactions between components predominate. However, the interpretation of the results obtained requires special caution. It should be remembered that we are not talking about real particles, but about hypothetical quasi-solvates, and the results obtained are only a method for describing the effects of interparticle interactions. The relationship of the BAQS method with other approaches remains to be studied.

BAQS/A. Molar heat capacity.

The BAQS/A model can also be used to analyze other properties of solutions. From the data [12] of molar heat capacity of Water-Ethanol solutions at 298.15K and atmospheric pressure, the parameters of the Redlich-Kister equation were calculated. Based on these parameters, weighting functions (32-35) and deviation parameters (55-58) are determined. Figure 7 shows the deviation functions calculated from the three-parameter Redlich-Kister model.

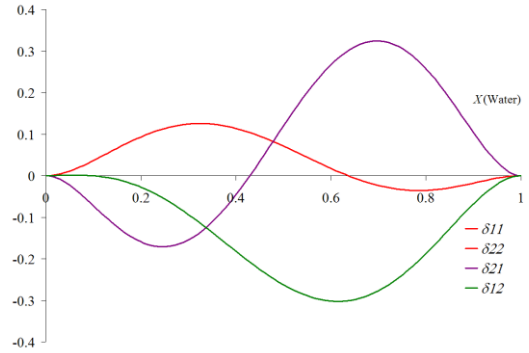

Figure 7. Dependence of the weight function difference on the mixture composition (see text for explanations).

Comparison with similar data for molar volumes (Fig. 6) shows that, despite the difference in the amplitude of deviations, general regularities in the distribution of weight functions of quasi-solvates are observed.

Conclusions

The method of binary additive quasisolvates is proposed. Two models considering in different aspects interparticle interactions in solutions are developed. Each of the proposed models has advantages and limitations.

BAQS/S: describes molar volumes of mixtures, especially for aprotonic systems, can be used to predict properties of multicomponent systems, effective on small datasets. Limitations: applicability to other solution properties remains questionable, model parameters differ from those obtained by the independent method, approximation accuracy is inferior to empirical models.

BAQS/A: applicable for any solution properties, informative and illustrative. Limitations: very sensitive to the choice of approximating equation, difficult to interpret results, developed only for two-component systems.

Nomenclature

ρ – solution density (g/cm^3);
ρ_i – density of i-th component (g/cm^3);
M_i – molar mass of i-th component (g/mol);
x_i – mole fraction of i-th component in solution;
x – mole fraction of the second component in the two-component solution ($x \equiv x_2$);
V_i – molar volume of pure i-th component (cm^3/mol)

$$V_i = \frac{M_i}{\rho_i};$$

V – molar volume of the n-component solution (cm^3/mol)

$$V = \frac{\sum_{i=1}^{n} M_i x_i}{\rho};$$

$\overline{V}_i$ – partial molar volume of i-th component in solution (cm^3/mol);
$\overline{V}_{ij}^{\infty}$ – limiting partial molar volume of solute i in solvent j (cm^3/mol);
$\overline{V}_{ij}^{*}$ – effective limiting partial molar volume of solute i in solvent j (cm^3/mol);
$\overline{V}_i^E$ – excess partial molar volume of i-th component in solution (cm^3/mol)

$$\overline{V}_i^E = \overline{V}_i - V_i;$$

$\overline{V}_{ij}^{E\infty}$ – excess limiting partial molar volume of solute i in solvent j (cm^3/mol)

$$\overline{V}_{ij}^{E\infty} = \overline{V}_{ij}^{\infty} - V_i;$$

$\overline{V}_{ij}^{E*}$ – effective excess limiting partial molar volume of solute i in solvent j (cm^3/mol)

$$\overline{V}_{ij}^{E*} = \overline{V}_{ij}^{*} - V_i;$$

ς_{ij} – ratio of the effective excess limiting partial molar volumes

$$\varsigma_{ij} = \frac{\overline{V}_{ij}^{E*}}{\overline{V}_{ji}^{E*}};$$

V_{ij} – molar volume of quasi-solvate Q_{ij} (cm^3/mol);
A_i – parameter of the Redlich-Kister equation (cm^3/mol);
ΔV – special deviation function (cm^3/mol);
ΔV_N – normalized special deviation function (cm^3/mol);
w_{ij} – weight function of the quasi-solvate Q_{ij};
δ_{ij} – difference of weight functions of the quasi-solvate Q_{ij};

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П.В. Єфімов. Аналіз волюмометричних властивостей рідких сумішей. І. Метод бінарних адитивних квазісольватів

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Запропоновано новий підхід до аналізу фізико-хімічних властивостей розчинів – метод бінарних адитивних квазісольватів (BAQS). Квазісольват Q_{ij} —гіпотетична двочастинкова структура, в якій одна частинка *i* є «розчиненою речовиною», а інша частинка *j* — «розчинником». Набір подібних квазісольватів має макроскопічну властивість F_{ij}. Розчин є адитивною сумішшю квазісольватів з ваговими функціями w_{ij}. У рамках методу BAQS розроблено дві моделі: із симетричними ваговими функціями (BAQS/S) та з асиметричними ваговими функціями (BAQS/A). На прикладі об'ємних властивостей розчинів неелектролітів показано можливості методу. Визначено ефективні граничні парціальні молярні об'єми компонентів для сумішей неелектролітів. Розглянуто можливість прогнозування властивостей багатокомпонентних розчинів за даними для двокомпонентних систем. Показано застосування до інших властивостей розчину. Кожна із запропонованих моделей має свої переваги та недоліки.

BAQS/S: описує молярні об’єми сумішей, особливо для апротонних систем, може бути використана для прогнозування властивостей багатокомпонентних систем, ефективна на невеликих наборах даних. Обмеження: застосовність до інших властивостей розчинів залишається під питанням, параметри моделі відрізняються від отриманих незалежним методом, точність апроксимації поступається емпіричним моделям.

BAQS/A: застосовна для будь-яких властивостей розчину, інформативна та ілюстративна. Обмеження: дуже чутлива до вибору апроксимуючого рівняння, важко інтерпретувати результати, розроблено лише для двокомпонентних систем.

***Ключові слова**: фізико-хімічний аналіз, молярний об’єм, граничний парціальний молярний об’єм, рівняння Редліха-Кістера, розчини неелектролітів, багатокомпонентні суміші, бінарні адитивні квазісольвати.*

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