

Property Prediction for Binary and Ternary Systems with Water, 1,4-Dioxane, Ethyleneglycol and Diethyleneglycol

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The molar volume for pure compounds and binary and ternary liquid systems with water, 1,4-dioxane, ethyleneglycol and diethylene glycol was determined and predicted with the Hankinson-Brost-Thompson method and Rackett equation at various temperature between 298.15 and 313.15 K. The accuracy of methods applied for pure compounds and for binary and ternary systems was analyzed. The Rackett equation showed a better capability to predict the molar volume data for all the mixtures than the HBT method.

Keywords: molar volume, prediction, ethyleneglycol, diethylene glycol

Continuing our work on the thermodynamic of the non-electrolyte systems [1-4] this paper represents the first part of a series of investigations on physico-chemical properties: density, viscosity and refractive index of binary and ternary systems containing water, 1,4-dioxane, ethyleneglycol and diethyleneglycol.

Data referring to the properties of pure substances or mixtures are required for the optimal design of industrial chemical equipment. The studied systems have industrial utility; the water + organic type solvents are frequently used as reaction media; diethyleneglycol is a useful intermediate for polyester resins, polyurethane, and plastics production.

The study of physico-chemical properties of systems with glycols and water is important for understanding the influence of the intermolecular interactions between water and the compounds containing hydroxylic groups, the glycols having both hydrophilic and hydrophobic groups. Ethyleneglycol, the simplest glycol, and its mixtures are models for the study of more complex chemical and biochemical systems, from interactional point of view. The mixtures of unassociated and non-aprotic solvents such as 1,4-dioxane, or slightly associated solvents, present theoretical and practical interest. The study of solutions properties with non-polar or slight polar molecules represents the key of the understanding of the non-electrolyte solutions behaviour.

The physico-chemical and biochemical properties of pure substances and mixtures can be qualitatively or quantitatively expressed. These properties are dependent on the structure and nature of the compounds, and they can be correlated by mathematical models. Density / molar volume varies with the mixture composition, temperature and pressure. Density can be experimentally determined, or it can be predicted with various mathematical models [5 – 7].

In this paper the accuracy of Hankinson-Brost-Thompson (HBT) and Rackett equations for the prediction of the molar volume of 1,4-dioxane, ethyleneglycol, diethyleneglycol, water and their binary and ternary mixtures was analyzed and compared.

Experimental part

The analytical-reagent-grade 1,4-dioxane from Merck (Germany) was distilled at 374.15K to collect the middle fractions; the water was distilled twice and diethyleneglycol (DEG) from Merck, was distilled at 473.15K in vacuum (around 3.87 kPa). The analytical-reagent-grade ethyleneglycol (EG), from Merck (p.a.) was used without further purification. The purity of the materials was checked by the means of gas chromatographic analysis. It was better than 99.5 mass%.

Densities of pure liquids and mixtures were measured using a double-walled calibrated pycnometer having a bulb volume of 25 cm³ and a capillary with an internal diameter of 1 mm. The weightings were done with a HR-120 (A&D Japan) balance with a precision of 0.0001 g. An average of triplicate measurements was considered and this was accurate to $\pm 0.0002 \text{ g}\cdot\text{cm}^{-3}$.

Results and discussions

There are more models and techniques for estimating of molar volume (density) of saturated pure liquids and homogeneous mixtures. In this work the Hankinson-Brost-Thompson (HBT) and Rackett methods are used.

The Hankinson-Brost-Thompson method [8] is represented through the following equations:

$$\frac{V}{V^*} = V_R^{(0)} [1 - \omega_{SRK} V_R^{(\delta)}] \quad (1)$$

$$V_R^{(0)} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \quad 0.25 < T_r < 0.95 \quad (2)$$

$$V_R^{(\delta)} = (e + fT_r + gT_r^2 + hT_r^3) / (T_r - 1.00001) \quad 0.25 < T_r < 1.0 \quad (3)$$

$$T_r = T / T_c \quad (4)$$

The parameters of the equations (2) and (3) are:

$a = -1.52816$; $b = 1.43907$; $c = -0.81446$;

$d = 0.190454$; $e = -0.296123$; $f = 0.386914$;

$g = -0.0427258$; $h = -0.0480645$.

V^* which appears below is the characteristic volume for the pure substance (generally within 1 to 4% of critical

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Table 1
THERMODYNAMIC PROPERTIES OF WATER, 1,4-DIOXANE, ETHYLENEGLYCOL AND DIETHYLENEGLYCOL

	water	1,4-dioxane	ethylenglycol	diethylene glycol
T_c , K	647.37	587.00	647.15	680.15
P_c , bar	221.2	52.1	75.3	47
V_c , cm ³ mol ⁻¹	57.1	238	191	312
ω_{SRK}	0.3852	0.2779	1.2280	1.0713
V^* , cm ³ mol ⁻¹	43.6	252.3	212.0	352.2
Z_{RA}	0.2338	-	0.2488	0.2489
ω	0.344	0.281	0.507	0.622
M , g mol ⁻¹	18.02	88.11	62.07	106.12

volume) whereas ω_{SRK} is the acentric factor characterizing the fitting of vapor pressure data by the Soave equation [6]. The values of these constants and the pure components critical property data required to estimate the molar volume of the mixtures, as given in table 1, were obtained from the literature [6, 9].

The equation proposed by Rackett [6, 10] and modified by Spencer and Danner [11] to estimate the molar volume of saturated liquids, is:

$$V = \frac{RT_c}{P_c} Z_{RA}^{[1+(1-T)^{2/7}]} \quad (5)$$

where:

R is the universal constant of gas;

T_c and P_c are the critical temperature and pressure,

Z_{RA} , a constant characteristic for each pure substance which can be estimated from the acentric factor, ω :

$$Z_{RA} = 0.29056 - 0.08775\omega \quad (6)$$

To estimate the molar volume of the liquid mixture, the same equations for the prediction of the molar volume of the pure liquids are used with mixing rules. Therefore, the modified Rackett equation for mixture is:

$$V_m = R \left(\sum_i \frac{X_i T_{ci}}{P_{ci}} \right) Z_{RAm}^{[1+(1-T)^{2/7}]} \quad (7)$$

$$Z_{RAm} = \sum_i X_i Z_{RAi} \quad (8)$$

where V_m is the molar volume of the saturated liquid mixture, X_i represents the mole fraction of pure component i . The critical temperature of the mixture, T_{cm} , is recommended to be calculated using Chueh-Prausnitz rules [12]:

$$T_{cm} = \sum_i \sum_j \phi_i \phi_j T_{cij} \quad (9)$$

$$\phi_i = \frac{X_i V_{ci}}{\sum_i X_i V_{ci}} \quad (10)$$

$$T_{cij} = (1 - k_{ij}) (T_{ci} T_{cj})^{1/2} \quad (11)$$

$$1 - k_{ij} = \frac{8(V_{ci} V_{cj})^{1/2}}{(V_{ci}^{1/3} + V_{cj}^{1/3})^3} \quad (12)$$

where ϕ_i is the volume fraction of pure component i , V_{ci} and T_{ci} are the critical volumes and critical temperatures of pure substances, respectively, k_{ij} are calculated from the critical volume of the pure compounds. The mixing rules recommended for HBT equation are [8]:

$$T_{cm} = \frac{\sum_i \sum_j X_i X_j V_{ij}^* T_{cij}}{V_m^*} \quad (13)$$

$$V_m^* = \frac{1}{4} \left[\sum_i X_i V_i^* + 3 \left(\sum_i X_i V_i^{*2/3} \right) \left(\sum_i X_i V_i^{*1/3} \right) \right] \quad (14)$$

$$V_{ij}^* T_{cij} = (V_i^* T_{ci} V_j^* T_{cj})^{1/2} \quad (15)$$

$$P_{cm} = \frac{(0.291 - 0.080 \omega_{SRKm}) R T_{cm}}{V_m^*} \quad (16)$$

$$T_{rm} = T / T_{cm} \quad (17)$$

where P_{cm} is the critical pressure of the mixture, V_m^* the characteristic volume of the mixture, V_i^* characteristic volume of the pure components, ω_{SRKm} is the SRK acentric factor of the mixture.

In order to evaluate the accuracy of the methods, the average percentage deviation (ε) was calculated:

$$\varepsilon = \frac{100}{n} \sum_{i=1}^n \frac{|V_i^{exp} - V_i^{pred}|}{V_i^{exp}} \quad (18)$$

where V_i^{exp} and V_i^{pred} represent the experimental and n predicted molar volumes, respectively and n is the number of experimental data.

System	298.15 K		303.15 K		313.15 K	
	ε_R , %	ε_{HBT} , %	ε_R , %	ε_{HBT} , %	ε_R , %	ε_{HBT} , %
water	3.21	22.62	2.92	22.40	2.33	21.97
1,4-dioxane	9.31	11.34	9.29	11.35	9.19	11.45
ethylenglycol (EG)	2.90	5.81	2.62	5.42	1.99	4.54
diethylene glycol (DEG)	3.38	4.99	3.26	4.78	3.01	4.34
water + EG	4.52	8.98	4.18	8.57	3.50	7.75
water + DEG	4.40	10.85	4.21	10.62	3.86	10.19
water+1,4-dioxane	8.88	8.38	8.82	8.34	8.62	8.24
1,4-dioxane + EG	5.18	4.31	4.97	4.30	4.57	4.30
1,4-dioxane + DEG	3.94	4.92	3.87	4.94	3.65	5.06
water+1,4-dioxane+EG	26.45	28.31	26.58	28.44	26.64	28.72
water+1,4-dioxane+DEG	26.12	27.83	26.26	27.97	26.55	28.26

Table 2
AVERAGE PERCENTAGE DEVIATION IN THE CALCULATION OF MOLAR VOLUME WITH THE RACKETT AND HBT METHODS FOR SYSTEMS WITH WATER, 1,4-DIOXANE, EG AND DEG

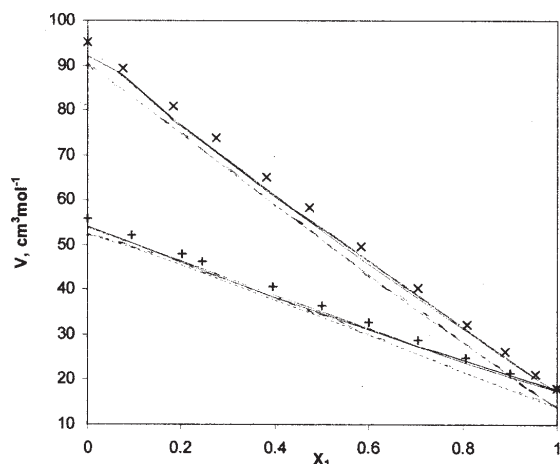


Fig. 1 Experimental and calculated molar volume with Rackett (—) and HBT (---) methods for binary systems: (+) water (1)+EG (2) and (x) water (1) +DEG (2) at 298.15 K

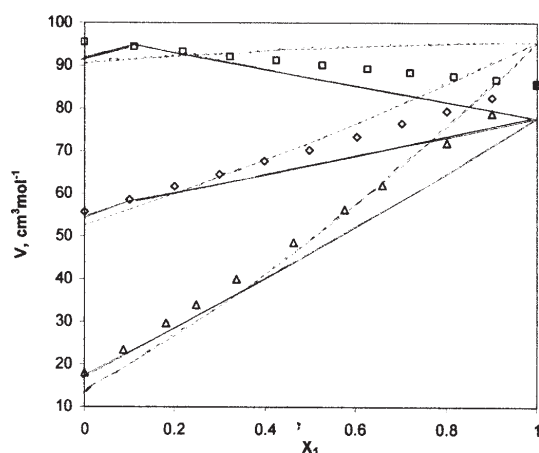


Fig. 2 Experimental and calculated molar volume with Rackett (—) and HBT (---) methods for binary systems: (◇) 1,4-dioxane (1)+EG (2), (□) 1,4-dioxane (1) +DEG (2) and (Δ) water (1) + 1,4-dioxane (2) at 298.15 K

The Rackett and HBT methods for pure liquids and mixing rules were used to predict the molar volume for binary and ternary systems with water, 1,4-dioxane, ethyleneglycol and diethyleneglycol at temperatures 298.15, 303.15 and 313.15 K. The results of experimental measurements for binary and ternary systems compared with those predicted by Rackett and HBT methods are listed in table 2 as average percentage deviation (ϵ).

The experimental molar volumes for pure liquids were compared with those predicted by the Rackett equations and HBT method. The Rackett equation showed a deviation of about 3%, except 1,4-dioxane, with higher deviations, of about 9%. HBT method gives satisfactory results for ethyleneglycol and diethyleneglycol with deviations in the range of 4-5% and poor results for 1,4-dioxane (11%) and water (22%). Therefore, the Rackett equation presents better accuracy in the prediction of the molar volume than HBT method.

For all the binary and ternary investigated systems smaller average deviations are obtained with Rackett predictive equation than those obtained with HBT method. The deviations remain in the same range for each method at all investigated temperatures.

For aqueous binary mixtures, the Rackett equation showed an average deviation of about 3-4% for water-glycols binary systems, and of about 8% for water-1,4-

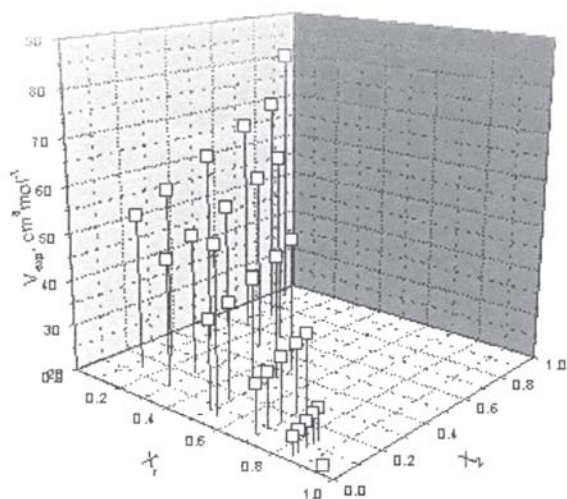


Fig. 3 Molar volume for the ternary system water (1) + 1,4-dioxane (2) +EG (3) at 298.15 K

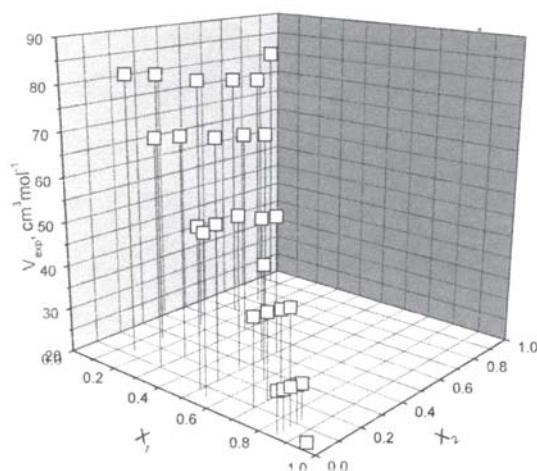


Fig.4 Molar volume for the ternary system water (1) + 1,4-dioxane (2) +DEG (3) at 298.15 K

dioxane system, as is reflected in table 2. For 1,4-dioxane - glycols binary systems, the Rackett equation showed an average absolute deviation of about 4-5%. For all tested binary systems the HBT method gives poor results, with average deviations of about 8-11% for aqueous systems and about 5% for the systems with 1,4-dioxane and glycols. Therefore, the Rackett equation is suitable to predict the molar volume of binary water-glycols and 1,4-dioxane-glycols systems and HBT method is recommended only for 1,4-dioxane-glycols systems.

The figures 1-2 present the experimental and calculated molar volume with Rackett and HBT methods for the binary systems at 298.15 K.

For ternary systems, both predictive methods are comparable. However, the deviations obtained for the ternary systems are higher than for the binary systems (20-25%), as is reflected in tables 2. According to Reinhard and Drefahl [13] the Rackett and HBT methods could be used only for rough estimation. The figures 3-4 present the molar volume for the ternary systems at 298.15K.

Conclusions

Molar volumes of pure substances: 1,4-dioxane, ethyleneglycol, diethyleneglycol, water and their binary and ternary mixtures were experimentally determined and

predicted with HBT and Rackett methods at temperatures between 298.15 and 313.15 K.

For all investigated pure liquids and their mixtures, the Rackett equation gives better accuracy in the prediction of the molar volume. Rackett method presents better results for water – glycols and 1,4-dioxane- glycols binary systems. For ternary systems, Rackett and HBT methods could be used only for rough estimation.

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