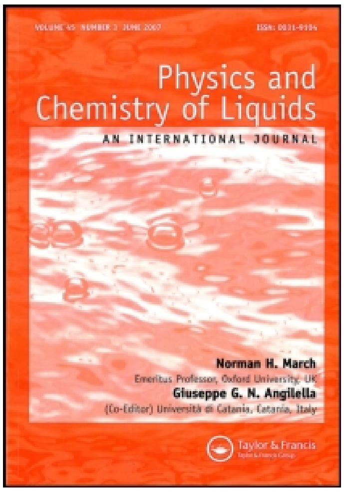

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RELATIONSHIP BETWEEN EXCESS MOLAR VOLUME AND REFRACTIVE INDEX IN BINARY NON-ELECTROLYTE MIXTURES

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It is possible to establish a relationship between the excess molar volume and refractive index in binary liquid mixtures. Correlations exist between the refractive index of a binary mixture and the refractive indices of the pure components. In this work, a comparison is made between the experimental values of excess molar volumes (for six binary mixtures) and the calculated values of refractive indices at one temperature. The analysis of the data shows that for the binary systems here studied, they cannot be described by a unique equation connecting both parameters, and that such an equation depends on the different kind of interactions between the components.

KEY WORDS: Excess molar volumes, refractive indices. Mixtures.

1 INTRODUCTION

The prediction of thermodynamic properties of binary liquid mixtures, like excess molar volumes from refractive indices, has been made by some authors[1], which considered a few isorefractive mixtures. There exist in the literature correlations between the refractive indices of mixtures and the refractive indices of their components[2], with different mixtures rules, like that of Lorentz-Lorenz, Dale and Gladstone, Eykman[3] and Oster[4].

The determination of the excess molar volume (V^E) of a mixture from refractive index data requires an examination of the additivity rule and equations for refractive indices.

In this paper, we have obtained V^E (determined from density measurements) and compared them with the ones calculated from the refractive indices, using different equations like those mentioned before. The comparison was made without knowing the equation of the refractive index explicitly. The results are discussed in terms of thermodynamic interactions with respect to the nature of mixing components and compared with data obtained by Nakata and Sakurai.

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2 EXPERIMENTAL SECTION

The method used in our laboratory have been described previously[5]. Densities were determined with a digital densimeter AP, model DMA 45. A thermostatically controlled bath (constant to ±0.01 K) was used. Calibration was carried out with air and doubly distilled water with an error of ±0.1 kg m^{-3}. Temperatures were read from calibrated thermometers. Refraction indices were measured with a Jena dipping refractometer with an estimated error of 2×10^{-5}. All the substances were purified following methods used in the original works. Mixtures were prepared by mixing weighed amounts of the pure liquids. Caution was taken to prevent evaporation.

3 RESULTS AND DISCUSSION

The experimental results for the pure liquids are reported in Table 1, together with literature values for comparison.

Densities and refractive indices of the binary mixtures can be calculated from known experimental data at any mole fraction with:

$$P = x_1P_1 + x_2P_2 + x_1x_2 \sum_{j=1}^{n} a_j(1 - 2x_1)^{j-1} \tag{1}$$

where P_1 and P_2 are the properties of the pure components and x_1 and x_2 are the mole fractions of the components.

The method of least squares was used to determine the coefficients. In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard error of estimate with n:

$$\sigma = [\sum (P_{obs} - P_{cal})^2/(n_{obs} - n)]^{1/2} \tag{2}$$

The values adopted for the coefficients and the standard error of estimate associated with the use of Eq. (2) are summarized in Table 2.

Table 1 Properties of the pure components at 298.15 K.

Substance	$\rho \times 10^{-3}/kg\ m^{-3}$		n	
	Exp.	*Lit.*	*Exp.*	*Lit.*
Cyclohexane (CH)	0.7739	0.77387^c	1.42372	1.4237^f
1,4-Dioxane (D)	1.0281	1.02797^a	1.42021	1.42025^a
n-Pentane (P)	0.6214	0.62139^a	1.35466	1.35472^a
Dichloromethane (DCM)	1.3163	1.3168^a	1.35870	1.3589^a
Methylacetate (MA)	0.9272	0.9274^a	1.39933	1.3992^e
n-Butylamine (BA)	0.7330	0.73308^b	1.41990	1.42058^a
3,3-Dimethyl-2-oxipentane (T)	0.76577^g	—	1.3858^g	—

[a] Ref. (6), [b] Ref. (7), [c] Ref. (8), [d] Ref. (9), [e] Ref. (10), [f] Ref. (11), [g] Ref. (12).

Table 2 Polynomial coefficients and standard deviations at 298.15 K

System	a_1	a_2	a_3	a_4	a_5	a_6	σ
CH(1) + D(2)[13]							
$\rho \times 10^{-3}/\mathrm{kg\ m^{-3}}$	−0.09147	−0.01356	0.00929	0.04148	−0.02817	−0.03617	1×10^{-4}
n	−0.01459	-0.28×10^{-4}	0.00591	0.34×10^{-3}	0.00716	0.00407	3×10^{-4}
P(1) + DCM(2)[14]							
$\rho \times 10^{-3}/\mathrm{kg\ m^{-3}}$	−0.41319	−0.12523	−0.02887	−0.01146	−0.01281	—	6×10^{-5}
n	−0.04832	−0.01516	0.00257	−0.00115	−0.00961	—	4×10^{-5}
DCM(1) + MA(2)[15]							
$\rho \times 10^{-3}/\mathrm{kg\ m^{-3}}$	−0.10761	0.01240	-0.5×10^{-2}	0.89×10^{-3}	−0.01614	—	6×10^{-5}
n	−0.02319	0.00432	0.00465	−0.00345	−0.01281	—	5×10^{-5}
BA(1) + D(2)[16]							
$\rho \times 10^{-3}/\mathrm{kg\ m^{-3}}$	−0.05077	−0.004378	-0.7×10^{-3}	0.66×10^{-3}	0.002714	—	3×10^{-5}
n	−0.00875	−0.003365	0.001645	0.01969	−0.00298	−0.02157	4×10^{-5}
P(1) + MA(2)[17]							
$\rho \times 10^{-3}/\mathrm{kg\ m^{-3}}$	−0.13522	−0.02233	0.00902	−0.00136	0.008493	—	3×10^{-5}
n	−0.01719	0.001772	0.008485	−0.00285	−0.014585	—	8×10^{-5}
CH(1) + T(2)[12]							
$\rho \times 10^{-3}/\mathrm{kg\ m^{-3}}$	—	—	—	—	—	—	—
n	0.007058	−0.019503	0.033435	−0.030238	—	—	1×10^{-4}

Excess molar volume were calculated from:

$$V^E = x_1 M_1(\rho^{-1} - \rho_1^{-1}) + x_2 M_2(\rho^{-1} - \rho_2^{-1}) \tag{3}$$

where M_1 and M_2 are the molecular weights and ρ, ρ_1 and ρ_2 are the densities of the solution and of the pure components.

Following Heller[2]:

$$\frac{f(n)}{\rho} = \frac{w_1 f(n_1)}{\rho_1} + \frac{w_2 f(n_2)}{\rho_2} \tag{4}$$

where w is the weight fraction of the components 1 and 2. Substituting $1/\rho$ and w_1 and w_2 for his mole fractions x_1 and x_2, we obtain from Eq. (3), for a binary mixture the following expression:

$$V^E = x_1 V_1 f(n_1) + x_2 V_2 f(n_2)/f(n) - \sum x_i V_i \tag{5}$$

Typical equations of $f(n)$ are the Lorentz-Lorenz formula:

$$f(n) = (n^2 - 1)/(n^2 + 2) \tag{6}$$

The Dale-Gla stone:

$$f(n) = n - 1 \tag{7}$$

Eykman equation[3]:

$$f(n) = (n^2 - 1)/(n + 0.4) \tag{8}$$

Oster equation[4]:

$$f(n) = [(n^2 - 1)(2n^2 + 1)]/n^2 \tag{9}$$

Nagata y Sakurai[1] find a correlation between V^E, the refractive indices and the volume fraction, with the following form:

$$V^E = -\frac{f'(n_1)}{f(n_1)}\left\{\frac{M_1 x_1}{\rho_1} + \frac{M_2 x_2}{\rho_2}[n - (n_1\phi_1 + n_2\phi_2)]\right\} \tag{10}$$

where $f'(n_1)$ denotes the value of the derivative of $f(n_1)$ and ϕ_i is the volume fraction based on the molar volume of the pure components.

Excess molar volumes are calculated with the applications of Eqs. (6), (7), (8) and (9) in Eqs. (5) and (10) and compared with experimental data obtained with Eq. (3).

Table 3 Percentual error in excess volumes at 298.15 K

System	*with Eq. (5)*				*with Eq. (10)*			
	Eq. (6)	*Eq. (7)*	*Eq. (8)*	*Eq. (9)*	*Eq. (6)*	*Eq. (7)*	*Eq. (8)*	*Eq. (9)*
CH(1) + D(2)	14	15	12	19	14	9	10	15
P(1) + DCM(2)	9	42	28	60	36	11	11	57
DCM(1) + MA(2)	19	8	8	60	16	51	43	90
BA(1) + D(2)	66	94	82	103	76	195	179	209
P(1) + MA(2)	75	101	85	102	75	122	110	131
CH(1) + T(2)	4	11	19	40	10	22	13	26

The percentual error determined with the following equation:

$$\text{P.E.} = \frac{100}{n} \frac{|\sum (V^E_{\text{exp}} - V^E_{\text{cal}})|}{V^E_{\text{exp}}} \tag{11}$$

are summarized in Table 3.

Table 3 shows generally that the Lorentz-Lorenz equation gives values more in according with experimental data.

The V^E for all these systems are positive and this means that dispersion forces are dominant, and in some systems a complex formation by hydrogen bonds is obtained, corroborated by other thermodynamic properties. Eq. (10) of Nakata and Sakurai is no better than Eq. (5).

For the systems DCM(1) + MA(2) (this last one associated in its pure state) Eykman's and Dale-Gladstone's equations gives small errors, which means that there is not an equation which correlate refractive indices with excess molar volumes for all binary systems.

Generally, great V^E produces minor deviation and Eq. (5) with Lorentz-Lorenz application gives small deviations. Eq. (10) of Nagata and Sakurai is not better than Eq. (5) which is more simple.

The condition of isorefractive substances said by these authors is not important, like CH(1) + MCH(2) system.

We conclude, that the binary systems here studied, could not be described by a unique equation for the refractive index which permits the calculus of excess molar volume.

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