Prediction of Excess Volumes and Excess Surface Tensions from Experimental Refractive Indices

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PREDICTION OF EXCESS VOLUMES AND EXCESS SURFACE TENSIONS FROM EXPERIMENTAL REFRACTIVE INDICES

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Refractive indices for the binary liquid mixtures: {hexane or heptane + ethanol}, {o-xylene + benzene} and {cyclohexane + benzene, toluene or hexane} were measured at 298.15 K. Excess refractive indices were calculated and fitted to a Redlich-Kister function. Using some mixture rules (Lorentz–Lorenz, Dale–Gladstone, Eykman, Oster, Arago-Biot and Newton), predictions for v^E have been made and compared with experimental data taken from the literature. Furthermore the Sugden equation has been used in two different ways for predicting excess surface tensions: the first one starting from densities and the other one from refractive indices. Results are plotted together with the literature data.

INTRODUCTION

The refractive index of liquids, n, can be easily measured with a high precision in a wide range of temperatures being only necessary a small volume of sample, so it is convenient to use n for calculating other liquid properties. Furthermore it has been found [1a] some relationships between refractive indices and densities ρ for liquid substances

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like the Lorentz–Lorenz (L–L) equation, reported in 1880:

$$\frac{n^2 - 1}{n^2 + 2}\frac{1}{\rho} = \text{cte} \tag{1}$$

or the empirical expression given by Dale–Gladstone (D–G) in 1858:

$$(n - 1)\frac{1}{\rho} = \text{cte}' \tag{2}$$

Both relations relate ρ with a function of n, $f(n)$, and they are independent on the temperature. The constants appearing in Eqs. (1) and (2) are characteristic of the substance and only depend on the wavelength of the light at which the refractive index is measured. Thus it can be thought about calculating excess molar volumes for liquid mixtures from n. This possibility was not considered until 1987, when M. Nakata and M. Sakurai [2] used the expressions given by L–L and D–G to predict this property. Their method is based on the mixture rules [3]: correlations between the refractive indices of solutions and those of the pure components.

$$f(n) = \phi_1 f(n_1) + \phi_2 f(n_2) \tag{3}$$

where $\phi_i = w_i \rho / \rho_i$ and w_i is the weight fraction of the component i. Until then Eq. (3) had been only used to estimate refractive indices of binary liquid mixtures [4, 5]. The combination of a mixture rule with the definition of excess molar volume leads to a relationship between n and v^E:

$$v^E = x_1 v_1 \frac{f(n_1)}{f(n)} + x_2 v_2 \frac{f(n_2)}{f(n)} - x_1 v_1 - x_2 v_2 \tag{4}$$

In the present work we have tested the predictive capability of this equation not only for both $f_{L-L}(n)$ and $f_{D-G}(n)$, but also for the following functions taken from the literature [6]:

Eykman:
$$\frac{n^2 - 1}{n + 0.4} \tag{5}$$

Arago-Biot:
$$n \tag{6}$$

Oster:
$$\frac{(n^2 - 1) \cdot (2n^2 + 1)}{n^2} \tag{7}$$

Newton:
$$n^2 - 1 \tag{8}$$

On the other hand, many efforts have been made to correlate surface tensions σ and densities, like the Macleod equation deduced empirically in 1923:

$$\frac{\sigma^{1/4}}{\rho_i - \rho_v} = \text{cte}'' \tag{9}$$

where cte'' only depends on the substance, and ρ_1, ρ_v are the densities for liquid and vapour phases respectively at the same temperature. This relationship can be also obtained theoretically [7] and at first it is strictly applicable only near the critical point, but it was observed in several experiments that the Macleod equation is also held at different temperatures [1b]. Multiplying the latter expression by the molecular weight and neglecting ρ_v in comparison with ρ_i we obtain the Sugden equation [8]:

$$\frac{M\sigma^{1/4}}{\rho_i} = P \tag{10}$$

Sugden named Parachor to the constant P, which has been widely studied in order to calculate its value for a substance by adding the contributions of the atomic groups that constitute the molecule. Thus, if we know the parachor and the density for a liquid at any temperature, we can obtain an estimation of its surface tension. The predictions achieved for σ in this way are not very good because the Sugden equation relates σ and P by a fourth power and the value of P depends largely on the reference chosen. In this work we have used this equation to predict excess surface tensions σ^E for six binary liquid systems, but in order to get more reliable values for P_i we have calculated them from experimental data of σ_i taken from the literature. We have assumed that the parachors of a mixture verify the additivity rule:

$$P = x_1 P_1 + x_2 P_2 \tag{11}$$

Since the molar refractivity R is a property defined from the $L-L$ equation as:

$$\frac{n^2-1}{n^2+2}\frac{M}{\rho} = R \tag{12}$$

by combining this expression and the Sugden equation we get [9]:

$$\left[\left(\frac{n^2-1}{n^2+2}\right)\frac{P}{R}\right]^4 = \sigma \tag{13}$$

Assuming again the additivity rule for R we can obtain surface tensions from only refractive indices. Thus we have two different ways for predicting σ (and σ^E): the first one from ρ and the second one from n. Here we have used both methods and compared the σ^E predicted with the literature values. We have measured the refractive index of the following binary liquid systems over the whole concentration range at 298.15 K: {hexane or heptane + ethanol}, {o-xylene + benzene} and {cyclohexane + benzene, toluene or hexane}. Data for ρ have been extensively reported, we have employed those supplied in Refs. [10 – 14].

EXPERIMENTAL SECTION

Sources and purities of the chemicals used were: hexane, Fluka, puriss. $\geq 99.5\%$; heptane, Fluka, puriss. $> 99.5\%$; ethanol, Panreac, 99.5% v/v; o-xylene, Fluka, puriss. $> 99.0\%$; benzene, Fluka, puriss. $> 99.5\%$; cyclohexane, Fluka, puriss. $> 99.5\%$; and toluene, Fluka, puriss. $> 99.5\%$. All liquids were used without further purification. When necessary, they were stored in the dark over molecular sieves (Union Carbide Type 4Å) before use. Mixtures were prepared by mass with a Mettler AT201 balance (precision $1\cdot10^{-5}$ g), and air-tight stoppered bottles. The possible error in the mole fraction is estimated to be less than 10^{-4}.

Refractive indices of the pure liquids and solutions were measured to an accuracy of $\pm 2\cdot10^{-5}$ with a refractometer RA-510M from Mettler Toledo. The measurement principle is the determination of the critical angle when the light (at the wavelength of the D line of sodium, 589.3 nm) passes through the boundary between two media. The

minimum amount of substance for measurement is 0.2 ml but we have prepared about 2 ml in order to avoid an air camera into the measuring cell. The temperature is controlled to within $\pm 1 \cdot 10^{-2}$ K by a built-in Peltier device. However, in order to achieve a quick thermal equilibrium that minimize possible changes in composition we have kept the solutions in an external thermostat at the temperature of 298.15 K before each measurement. The calibration of the refractometer was made by using bidistilled and deionized water and it was checked every few measurements. The source of light is composed of a LED (light emitting diode) and a system of filters and lens whose function is to polarize, filter and carry the beam to a sapphire prism over which is placed the sample. The critical angle is measured from the intensity of light reflected that is recorded by means of an optical sensor CCD (charge-coupled device).

Excess refractive indices have been calculated from our measurements as:

$$n^E = n - x_1 n_1 - x_2 n_2 \tag{14}$$

where n is the refractive index of the mixture and n_i is the value corresponding to the component i. The error estimated in n^E is less than $3 \cdot 10^{-5}$.

RESULTS AND DISCUSSION

The values of σ, ρ and n for the pure liquids at 298.15 K are reported in Table I and data of n and n^E for the mixtures at same temperature appear in Table II. Each set of results was fitted to a Redlich-Kister function using a weighted least-square fitting procedure:

$$n = x_1 n_1 + x_2 n_2 + x_1 x_2 \sum_{j=1}^{m} A_j (2x_1 - 1)^{j-1} \tag{15}$$

where coefficients A_j are also valid for the fitting of n^E. The values of these parameters together with the standard deviation are summarized in the Table III.

The refractive index can be connected with dispersive interactions, which depend largely on the oscillation frequency of the electronic cloud in the molecule, ν. It can be showed [19] the following relation

between ν and n:

$$n - 1 = \frac{\vartheta}{\nu^2 - \nu_0^2} \tag{16}$$

where ν_0 is the frequency of the light at which the refractive index is measured and ϑ is inversely proportional to the molar volume.

TABLE I   Surface tensions, densities and refractive indices of the pure liquids

| | σ | ρ | n_D | |
	$mN \cdot m^{-1}$	$g \cdot cm^{-3}$	*this work*	*literature*
Hexane	17.95[a], 17.81[b]	0.65490[b]	1.37230	1.37226[c]
Heptane	19.60[b]	0.67942[b]	1.38522	1.38511[c]
Ethanol	21.76[b]	0.78519[b]	1.35936	1.35941[c]
Cyclohexane	24.38[d], 24.43[a]	0.77389[c]	1.42350	1.42354[c]
Benzene	28.20[d], 28.20[a]	0.87360[c]	1.49808	1.49792[c]
Toluene	27.94[d]	0.86219[c]	1.49426	1.49413[c]
o-xylene	29.44[d]	0.87594[c]	1.50288	1.50295[c]

[a] Ref. [15].
[b] Ref. [16].
[c] Ref. [17].
[d] Ref. [18].

TABLE II   Experimental refractive indices and excess refractive indices

	x_1	n	n^E	x_1	n	n^E
hexane + ethanol						
	0.0726	1.36055	0.00027	0.5543	1.36732	0.00080
	0.1523	1.36184	0.00053	0.6197	1.36801	0.00064
	0.2307	1.36305	0.00072	0.6992	1.36881	0.00041
	0.3094	1.36419	0.00084	0.7718	1.36956	0.00022
	0.3899	1.36530	0.00091	0.8480	1.37034	0.00001
	0.4522	1.36608	0.00088	0.9248	1.37120	−0.00013
heptane + ethanol						
	0.1011	1.36379	0.00179	0.5378	1.37685	0.00357
	0.1460	1.36561	0.00245	0.6145	1.37840	0.00314
	0.2337	1.36870	0.00327	0.6871	1.37973	0.00259
	0.3063	1.37105	0.00375	0.7826	1.38133	0.00173
	0.3756	1.37298	0.00389	0.8856	1.38313	0.00086
	0.4631	1.37523	0.00388	0.9432	1.38414	0.00039
o-xylene + benzene						
	0.0606	1.49815	−0.00022	0.5378	1.49997	−0.00069
	0.1520	1.49834	−0.00047	0.6132	1.50040	−0.00062
	0.2303	1.49858	−0.00061	0.7086	1.50097	−0.00051
	0.3052	1.49886	−0.00069	0.7475	1.50121	−0.00046
	0.3943	1.49924	−0.00073	0.8512	1.50188	−0.00029
	0.4525	1.49952	−0.00073	0.9067	1.50225	−0.00018

TABLE II (Continued)

cyclohexane + benzene						
	0.0731	1.49047	−0.00217	0.5457	1.45029	−0.00710
	0.1544	1.48246	−0.00411	0.6217	1.44507	−0.00665
	0.2346	1.47506	−0.00553	0.7102	1.43942	−0.00570
	0.3176	1.46785	−0.00655	0.7856	1.43490	−0.00459
	0.3915	1.46183	−0.00706	0.8619	1.43062	−0.00318
	0.4728	1.45559	−0.00724	0.9494	1.42603	−0.00124
cyclohexane + toluene						
	0.0712	1.48840	−0.00082	0.5401	1.45283	−0.00320
	0.1447	1.48248	−0.00154	0.6181	1.44740	−0.00311
	0.2294	1.47584	−0.00218	0.6797	1.44323	−0.00292
	0.3117	1.46954	−0.00266	0.7721	1.43719	−0.00242
	0.3155	1.46925	−0.00268	0.7856	1.43633	−0.00233
	0.3928	1.46347	−0.00299	0.8495	1.43233	−0.00180
	0.4514	1.45917	−0.00314	0.9393	1.42695	−0.00083
cyclohexane + hexane						
	0.0680	1.37511	−0.00067	0.5333	1.39646	−0.00315
	0.1477	1.37847	−0.00139	0.6246	1.40117	−0.00311
	0.2356	1.38233	−0.00203	0.6918	1.40479	−0.00293
	0.3073	1.38558	−0.00245	0.7628	1.40877	−0.00259
	0.3805	1.38899	−0.00279	0.8435	1.41350	−0.00199
	0.4755	1.39357	−0.00308	0.9315	1.41895	−0.00104

TABLE III Redlich-Kister coefficients and standard deviations for the $n - x_1$ and $n^E - x_1$ curves

	A_1	A_2	A_3	A_4	s
hexane + ethanol	0.00345	−0.00213	−0.00292	−0.00170	0.000016
heptane + ethanol	0.01497	−0.00731	−0.00160		0.000023
o-xylene + benzene	−0.00287	0.00098			0.000008
cyclohexane + benzene	−0.02901	0.00326			0.000020
cyclohexane + toluene	−0.01279	−0.00130	−0.00092		0.000007
cyclohexane + hexane	−0.01246	−0.00294	−0.00126		0.000010

Therefore, n^E can be related to the formation and/or rupture of dispersive interactions during the mixing process.

Figure 1 compares experimental curves with the predictions for v^E from the different mixture rules. It can be seen that the estimations obtained employing the functions of Lorentz–Lorenz, Dale–Gladstone and Eykman are better than the other ones. For the systems analized in this work Arago-Biot relation proved unsatisfactory.

Aminabhavi *et al.* [6] analized the validity of some mixture rules for predicting the refractive index of solutions and reported exactly the
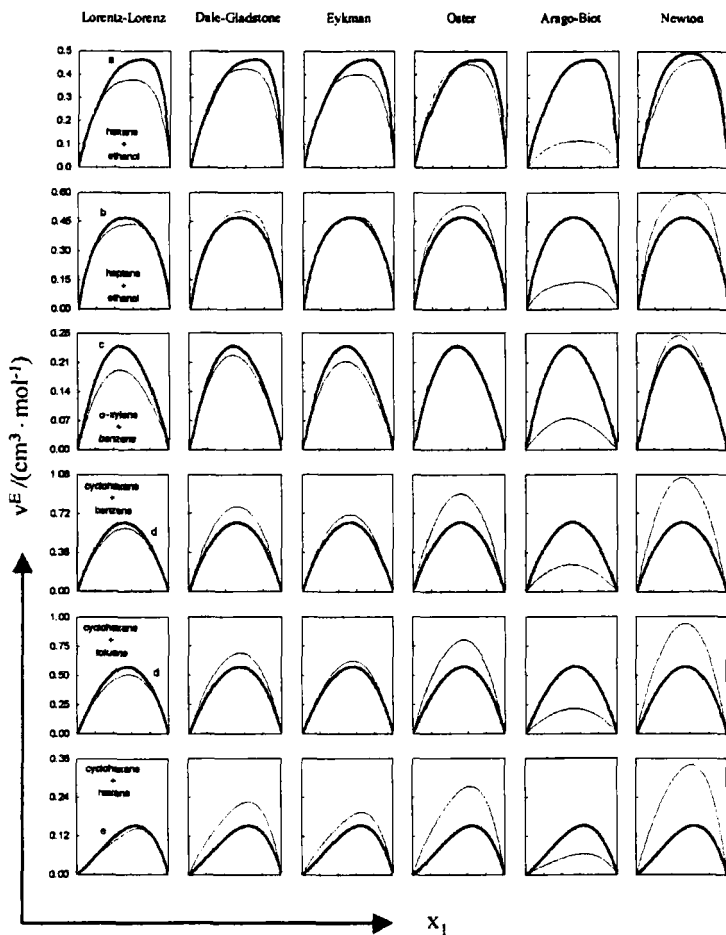
FIGURE 1   Plot of experimental and calculated excess molar volumes, for the 6 mixture rules analysed in this work. — Experimental: (a) Ref. [10]; (b) Ref. [11]; (c) Ref. [12]; (d) Ref. [13]; (e) Ref. [14] — Prediction based on the correlation with refractive index.

same estimations for two of them: Dale-Gladstone and Arago-Biot. They justified this match on the basis of similarities in the functional form of both mixture rules, but it has to be also due to the assumption of volume additivity, *i.e.*, $\Sigma \phi_i = 1$. In fact, Heller [3] showed that assuming volume additivity both cases lead to identical results.

The measurements of excess surface tensions taken from the literature [15, 16, 18] together with the predictions made from densities
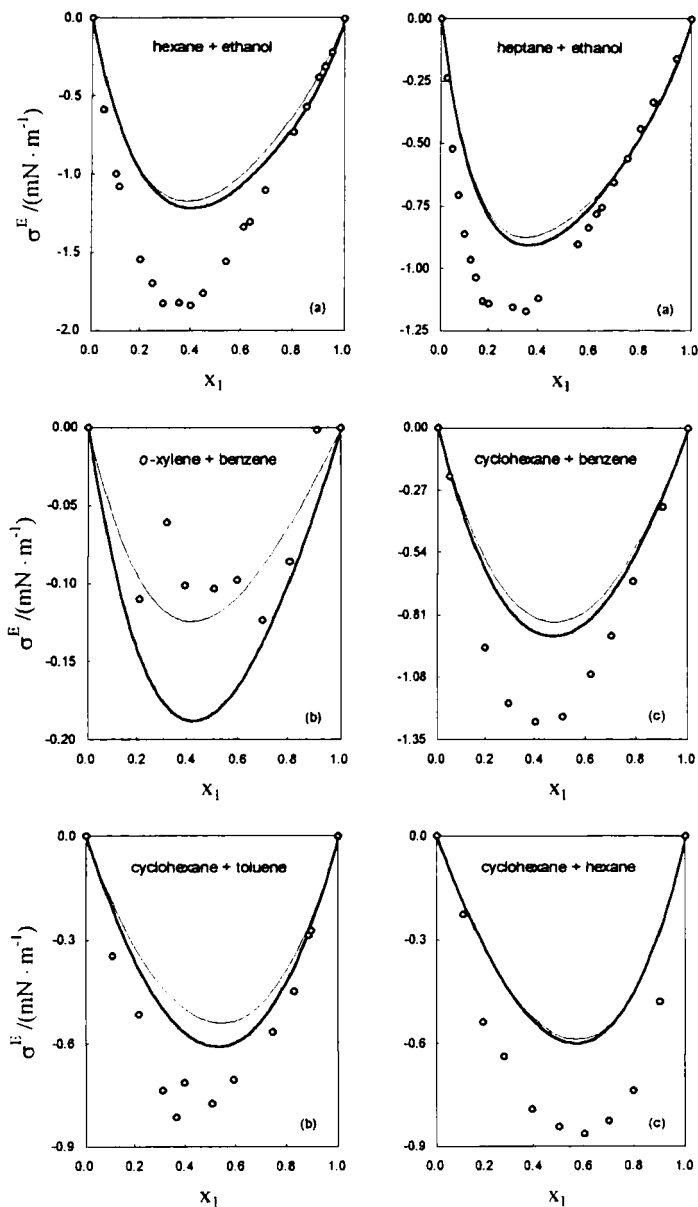
FIGURE 2   Comparison between experimental and predicted excess surface tensions. o Experimental: (a) Ref. [16]; (b) Ref. [18]; (c) Ref. [15] — Prediction based on the correlation with refractive index — Prediction based on the correlation with density.

and refractive indices appear in Figure 2. Generally, the correlation between σ and ρ provides better results than the correlation between σ and n. It can be deduced an equivalence that provides a link between both methods:

$$R = x_1 R_1 + x_2 R_2 \Longleftrightarrow v^E = v^E_{L-L} \qquad (17)$$

This means that predicting σ from n is equivalent to replace ρ by the predicted ρ_{L-L} in the Sugden equation. Then we expect that the estimation made for σ from n was worse than the one made from ρ. On the other hand, both of them would be similar when $f_{L-L}(n)$ makes a good prediction for v^E.

In view of these results we can confirm that the methods analysed in this work have shown its applicability for predicting σ^E and v^E.

Acknowledgements

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