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Prediction of Magnetic Susceptibilities in Diamagnetic Binary Fluid Mixtures

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Abstract A model is proposed to predict magnetic susceptibilities in diamagnetic binary fluid mixtures. The model predictions are compared to experimental information for nine binary systems including polar and non-polar compounds. The predictions are also compared to the results obtained from the traditional Boyer-Donzelot equation. For all systems analyzed, the model predicted magnetic susceptibilities closer to the experimental values than those predicted from the Boyer-Donzelot equation. The deviations from the experimental values decrease when the binary system exhibits a positive excess magnetic susceptibility.

Keywords Binary mixtures · Diamagnetic substances · Magnetic susceptibilities

1 Introduction

Recently, Cañas-Marín et al. [1] presented a simple model to predict the magnetic susceptibility in non-ferromagnetic multicomponent mixtures. However, the performance of such a model has not been compared to experimental data. In fact, experimental data on magnetic susceptibilities of multicomponent mixtures are very scarce. In the case of reservoir fluids, Ivakhnenko and Potter [2] measured magnetic susceptibilities of crude oils and formation waters of samples from various parts of the world. They suggested that these fluids might be classified in the future according to the magnetic susceptibilities exhibited.

The main goal of this work is to analyze the performance of the Cañas-Marín et al. model and compare its results to experimental data over conditions where the physical

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properties of the components and the composition of the mixtures are exactly known. Unfortunately, reservoir fluids are generally composed of thousands of components and it is difficult, if not impossible, to determine exactly all the components present in the mixture. In addition, the performance of the Cañas-Marín et al. model is compared to the predictions of the Boyer-Donzelot equation, which is based on the experimental variation of the optical dispersion in pure organic compounds due to valence electrons [3]. The Boyer-Donzelot equation is currently the most widely used model to predict magnetic susceptibilities, mainly in diamagnetic binary mixtures.

2 Models to Predict Mixture Magnetic Susceptibilities

2.1 Boyer-Donzelot Model (B-D)

For pure organic compounds, the molar magnetic susceptibility can be related to the molecular polarizability by the Boyer-Donzelot equation as

$$\delta_i = f(n'_i \alpha_i)^{1/2} \tag{1}$$

For mixtures, the additivity law for molar diamagnetic susceptibilities is assumed. Then,

$$\delta_{(\mathrm{m})} = f\left[\sum_{i=1}^{\mathrm{NC}} x_i (n'_i \alpha_i)\right]^{1/2} \tag{2}$$

where f is a constant equal to -3.46×10^{-6}, n'_i is the effective number of electrons, and α_i is the molecular polarizability of component i. The effective number of electrons can be calculated as

$$n'_i = n_i - n_{i0} \tag{3}$$

where n_i is the number of valence electrons of component i and n_{i0} is a characteristic constant for each family of substances (paraffins, alcohols, ketones, etc.).

2.2 Proposed Model (PM)

The present model was derived by Cañas-Marín et al. [1] (see Appendix in this reference for further details). Here, the molar susceptibility for a mixture is simply calculated as

$$\delta_{(\mathrm{m})} = \sum_{i=1}^{\mathrm{NC}} k_i x_i \bar{v}_i \tag{4}$$

Recall that

$$k_i = \frac{\delta_i}{v_i^0} \tag{5}$$

where k_i is the volumetric susceptibility (dimensionless) of component i, $\bar{v}_i$ is the partial molar volume of component i, and v_i^0 is the molar volume of component i.

3 Experimental Data

Molar binary susceptibilities have been experimentally determined for some diamagnetic fluid mixtures. Riggio et al. [3] reported molar susceptibilities for binary mixtures formed by methyl isobutyl ketone (MIK) with three butyl alcohols: *n*-butanol (B1), *sec*-butanol (B2), and isobutanol (B3), i.e., MIK + B1, MIK + B2, and MIK + B3. For these systems, the partial molar volumes (see Eq. 4) were calculated using the volumetric data also published by Riggio et al. [4]

de Soria et al. [5] determined molar magnetic susceptibilities for four binary mixtures: dichloromethane (DCM) + methyl acetate (MA), *n*-pentane (P) + dichloromethane (DCM), *n*-pentane (P) + methyl acetate (MA), and 2-propanol (2-PR) + *n*-pentane (P). They also reported volumetric data for all these systems. The pure-component properties pertaining to the above-mentioned binary systems are presented in Table 1.

Also, Cáceres et al. [6] presented magnetic susceptibilities and volumetric data for two binary systems: 2-propanol (2-PR) + methyl acetate (MA) and 1-propanol (1-PR) + methyl acetate (MA). The pure-component properties used by them are shown in Table 2.

Unfortunately, no experimental data on binary systems involving only hydrocarbons were found in the literature.

Table 1 Pure-component properties at 25°C used by de Soria et al. [5][a]

	ρ, $g \cdot cm^{-3}$	MW, $g \cdot mol^{-1}$	$-\delta \times 10^6$, $cm^3 \cdot mol^{-1}$	$\alpha \times 10^{24}$	n_0
MIK	0.7963	100.160	70.71	11.914	4.3
B1	0.8060	74.123	56.52	8.785	2.6
B2	0.8025	74.123	57.67	8.782	2.6
B3	0.7980	74.123	57.70	8.804	2.6
DCM	1.3152	84.933	47.94	6.495	Unknown
MA	0.9252	74.080	42.69	6.992	7.6
P	0.6219	72.151	63.14	10.014	0.0
2-PR	0.7800	60.096	45.76	6.990	2.6

[a] MW—molar mass; MIK—methyl isobutyl ketone; B1—*n*-butanol; B2—*sec*-butanol; B3—isobutanol; DCM— dichloromethane; MA—methyl acetate; P—*n*-pentane; 2-PR—2-propanol

Table 2 Pure-component properties at 25°C used by Cáceres et al. [6][a]

	ρ, g $\cdot$ cm^{-3}	MW, g $\cdot$ mol^{-1}	$-\delta \times 10^6$, cm$^3 \cdot$ mol^{-1}	$\alpha \times 10^{24}$	n_0
MA	0.9270	74.080	42.95	6.969	8.2
1-PR	0.7996	60.096	45.65	6.951	2.6
2-PR	0.7800	60.096	46.20	6.989	2.6

[a] MW—molar mass; MA—methyl acetate; 1-PR—1-propanol; 2-PR—2-propanol

4 Results and Discussion

Results for the MIK-butyl alcohol systems are summarized in Tables 3–5. These systems give positive excess magnetic susceptibilities, ($\delta^{\mathrm{E}}_{(\mathrm{m})} = \delta_{(\mathrm{m})} - (x_1\delta_1 + x_2\delta_2)$), over the complete range of composition. This is a consequence of the breaking of hydrogen bonds when MIK is added, since the alcohols are associated in the pure state. In these systems, dispersion forces are dominant [3]. For all three systems, PM predicts better the molar magnetic susceptibilities than does B-D (average absolute deviations, AAD(%) $= \frac{1}{N}\sum^{N}\left|\frac{\text{calc.}-\text{exp.}}{\text{exp.}}\right| \times 100$).

Tables 6–9 show the results for the systems reported by de Soria et al. [5]. As explained by them, two systems, P + DCM and 2-PR + P, exhibit negative excess magnetic susceptibilities; P is nonpolar and DCM is polar, thus generating a dipole-induced interaction and subsequently a negative $\delta^{\mathrm{E}}_{(\mathrm{m})}$. According to de Soria et al., in the 2-PR + P mixture, the breaking of the hydrogen bonds in the alcohol molecules causes a positive $\delta^{\mathrm{E}}_{(\mathrm{m})}$. Afterward, a possible association with P (n-pentane) would cause a negative $\delta^{\mathrm{E}}_{(\mathrm{m})}$. This deviation would overcome the first contribution, thus producing the negative $\delta^{\mathrm{E}}_{(\mathrm{m})}$. On the other hand, both systems, P + MA and DCM + MA, produce

Table 3 Molar magnetic susceptibilities ($-\delta_{(\mathrm{m})} \times 10^6$ cm$^3 \cdot$ mol^{-1}) calculated using the Boyer-Donzelot equation (B-D) and the proposed model (PM)

MIK(1) + B1(2)					
$X(1)$	Exp	B-D	Dev. (%)[a]	PM	Dev. (%)[a]
0	56.52	55.61	−1.61	56.52	0.00
0.1016	57.39	57.41	0.03	57.94	0.96
0.1952	58.41	59.06	1.11	59.26	1.46
0.2965	59.73	60.86	1.89	60.68	1.59
0.3834	60.83	62.40	2.58	61.91	1.78
0.5062	62.64	64.57	3.08	63.64	1.60
0.6055	64.09	66.34	3.51	65.06	1.51
0.6965	65.39	67.95	3.91	66.36	1.48
0.7962	67.11	69.72	3.89	67.78	1.00
0.8984	68.76	71.53	4.03	69.25	0.71
1	70.71	73.33	3.71	70.71	0.00
		AAD (%)	2.67		1.10

Results are compared to experimental data [3] for MIK (1) + B1 (2) (methyl isobutyl ketone + n-butanol) at 25°C

[a] (Calc − Exp)/Exp

Table 4 Molar magnetic susceptibilities ($-\delta_{(m)} \times 10^6\,\text{cm}^3\cdot\text{mol}^{-1}$) calculated using the Boyer-Donzelot equation (B-D) and the proposed model (PM)

MIK(1) + B2(2)					
$X(1)$	Exp	B-D	Dev. (%)[a]	PM	Dev. (%)[a]
0	57.67	55.60	−3.59	57.67	0.00
0.1028	57.99	57.42	−0.98	59.10	1.91
0.2131	59.26	59.37	0.19	60.59	2.24
0.2934	60.10	60.80	1.16	61.66	2.60
0.4034	61.36	62.75	2.27	63.12	2.87
0.5008	62.75	64.47	2.74	64.40	2.63
0.6013	64.30	66.26	3.05	65.70	2.18
0.6991	65.46	67.99	3.86	66.96	2.29
0.7979	67.04	69.74	4.03	68.20	1.73
0.8998	68.82	71.55	3.97	69.48	0.96
1	70.71	73.33	3.71	70.71	0.00
		AAD (%)	2.69		1.76

Results are compared to experimental data [3] for MIK (1) + B2 (2) (methyl isobutyl ketone + *sec*-butanol) at 25°C

[a] (Calc − Exp)/Exp

Table 5 Molar magnetic susceptibilities ($-\delta_{(m)} \times 10^6\,\text{cm}^3\cdot\text{mol}^{-1}$) calculated using the Boyer-Donzelot equation (B-D) and the proposed model (PM)

MIK(1) + B3(2)					
$X(1)$	Exp	B-D	Dev. (%)[a]	PM	Dev. (%)[a]
0	57.70	55.66	−3.54	57.70	0.00
0.0923	58.73	57.29	−2.45	58.90	0.29
0.1970	59.88	59.14	−1.24	60.26	0.63
0.2936	61.03	60.85	−0.29	61.51	0.79
0.4025	62.41	62.77	0.58	62.93	0.83
0.4990	63.66	64.48	1.29	64.18	0.82
0.6023	65.07	66.31	1.91	65.53	0.71
0.6973	66.45	67.98	2.30	66.76	0.47
0.7984	67.87	69.77	2.80	68.08	0.31
0.8906	69.08	71.39	3.34	69.28	0.29
1	70.71	73.33	3.71	70.71	0.00
		AAD (%)	2.13		0.47

Results are compared to experimental data [3] for MIK (1) + B3 (2) (methyl isobutyl ketone + isobutanol) at 25°C

[a] (Calc − Exp)/Exp

a positive $\delta^{E}_{(m)}$. Here, dispersion forces are dominant between two polar molecules (DCM and MA), or between a polar molecule (MA) and a dipole-induced molecule (P) [5].

For DCM, the characteristic constant, n_0, is unknown, making it impossible to apply the Boyer-Donzelot equation. For the DCM + MA and P + DCM systems, only the predictions obtained with PM are presented in Tables 7 and 8, respectively. Where it was possible to use B-D (P + MA and 2-PR + P), PM predicted again, on average, better results than does the B-D model.

Table 6 Molar magnetic susceptibilities ($-\delta_{(m)} \times 10^6 \text{cm}^3 \cdot \text{mol}^{-1}$) calculated using the Boyer-Donzelot equation (B-D) and the proposed model (PM)

P(1) + MA(2)

$X(1)$	Exp	B-D	Dev. (%)[a]	PM	Dev. (%)[a]
0	42.69	43.30	1.43	42.69	0.00
0.1036	43.64	45.23	3.64	44.19	1.26
0.2021	45.05	47.07	4.48	45.72	1.49
0.3129	46.57	49.13	5.50	47.56	2.13
0.4032	48.20	50.82	5.44	49.17	2.01
0.4108	48.30	50.96	5.51	49.31	2.09
0.5001	49.90	52.62	5.45	51.02	2.24
0.6078	52.48	54.63	4.10	53.23	1.43
0.6958	54.69	56.27	2.89	55.18	0.90
0.8007	57.41	58.22	1.41	57.70	0.51
0.9009	60.38	60.09	−0.48	60.32	−0.10
1	63.14	61.94	−1.90	63.14	0.00
		AAD (%)	3.52		1.18

Results are compared to experimental data [5] for P (1) + MA (2) (*n*-pentane + methyl acetate) at 25°C
[a] (Calc − Exp)/Exp

Table 7 Molar magnetic susceptibilities ($-\delta_{(m)} \times 10^6 \text{cm}^3 \cdot \text{mol}^{-1}$) calculated using the Boyer-Donzelot equation (B-D) and the proposed model (PM)

2-PR(1) + P(2)

$X(1)$	Exp	B-D	Dev. (%)[a]	PM	Dev. (%)[a]
0	63.14	61.94	−1.90	63.14	0.00
0.1033	62.39	60.11	−3.65	60.82	−2.52
0.2005	61.56	58.39	−5.15	58.78	−4.52
0.2120	61.39	58.19	−5.21	58.54	−4.64
0.3024	60.81	56.59	−6.94	56.77	−6.64
0.3942	60.04	54.97	−8.44	55.06	−8.29
0.5004	58.68	53.09	−9.53	53.20	−9.34
0.5898	57.05	51.51	−9.71	51.72	−9.34
0.6978	54.70	49.60	−9.32	50.02	−8.56
0.8052	52.28	47.70	−8.76	48.44	−7.35
0.8872	49.56	46.25	−6.68	47.28	−4.60
1	45.76	44.25	−3.30	45.76	0.00
		AAD (%)	6.55		5.48

Results are compared to experimental data [5] for 2-PR (1) + P (2) (2-propanol + *n*-pentane) at 25°C
[a] (Calc − Exp)/Exp

It is interesting to note that the highest deviations were observed for the 2-PR + P and P + DCM systems, both systems with negative $\delta^{E}_{(m)}$. In other words, in both cases the dispersion forces are not dominant, but polar. Even in these cases, PM shows smaller deviations than does the B-D model.

Tables 10 and 11 show the results for the binary 1-PR + MA and 2-PR + MA systems, respectively. $\delta^{E}_{(m)}$s are positive for both systems over the whole concentration range. For mixtures of alcohols with methyl acetate, the breaking of the hydrogen bonds in the alcohol molecule causes a positive $\delta^{E}_{(m)}$. A possible association with

Table 8 Molar magnetic susceptibilities ($-\delta_{(\mathrm{m})} \times 10^6\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$) calculated using the proposed model (PM)

DCM(1) + MA(2)			
$X(1)$	Exp	PM	Dev. (%)[a]
0	42.69	42.69	0.00
0.1036	42.84	43.25	0.96
0.2021	42.81	43.78	2.27
0.3129	42.96	44.37	3.28
0.4032	43.05	44.86	4.20
0.4108	43.06	44.90	4.27
0.5001	43.11	45.37	5.24
0.6078	43.38	45.93	5.88
0.6958	43.96	46.38	5.51
0.8007	45.09	46.92	4.06
0.9009	46.36	47.43	2.31
1	47.94	47.94	0.00
		AAD (%)	3.16

Results are compared to experimental data [5] for DCM (1) + MA (2) (dichloromethane + methyl acetate) at 25°C

[a] (Calc − Exp)/Exp

Table 9 Molar magnetic susceptibilities ($-\delta_{(\mathrm{m})} \times 10^6\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$) calculated using the proposed model (PM)

P(1) + DCM(2)			
$X(1)$	Exp	PM	Dev. (%)[a]
0	47.94	47.94	0.00
0.104	52.76	49.46	−6.25
0.202	54.88	50.97	−7.12
0.313	56.81	52.75	−7.15
0.403	58.41	54.24	−7.14
0.411	58.54	54.36	−7.14
0.5	60.07	55.81	−7.09
0.608	61.66	57.46	−6.81
0.696	62.65	58.70	−6.30
0.801	63.32	60.05	−5.16
0.901	63.37	61.38	−3.14
1	63.14	63.14	0.00
		AAD (%)	5.28

Results are compared to experimental data [5] for P (1) + DCM (2) (*n*-pentane + dichloromethane) at 25°C

[a] (Calc − Exp)/Exp

methyl acetate would originate a negative $\delta^{\mathrm{E}}_{(\mathrm{m})}$, but this deviation is not observed in this case [6]. Therefore, dispersion forces are dominant. PM is again superior to B-D.

After all these comparisons, the model proposed here seems to be more appropriate for application in hydrocarbon reservoir fluids than the Boyer-Donzelot equation. There are basically two reasons. First, for these type of fluids, it is very difficult to calculate the effective number of electrons required in the B-D model, since the number of valence electrons cannot be well calculated due to the practical impossibility to know exactly all the constituents of the mixtures (thousands of components). And second, dispersion forces are dominant in this case (positive $\delta^{\mathrm{E}}_{(\mathrm{m})}$); and, in fact, PM generally predicts better results under such a condition.

5 Conclusions

A model is proposed to predict magnetic susceptibilities in diamagnetic binary fluid mixtures. This model was compared to experimental data of nine diamagnetic binary

Table 10 Molar magnetic susceptibilities ($-\delta_{(m)} \times 10^6\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$) calculated using the Boyer-Donzelot equation (B-D) and the proposed model (PM)

1-PR(1) + MA(2)

$X(1)$	Exp	B-D	Dev. (%)[a]	PM	Dev. (%)[a]
0	42.95	42.55	−0.93	42.95	0.00
0.1054	43.14	42.72	−0.97	43.32	0.42
0.1279	43.19	42.75	−1.02	43.40	0.49
0.1985	43.33	42.86	−1.08	43.63	0.69
0.3111	43.55	43.04	−1.17	43.97	0.96
0.4107	43.79	43.20	−1.35	44.26	1.07
0.4984	44.01	43.34	−1.52	44.50	1.11
0.6058	44.28	43.50	−1.76	44.78	1.13
0.7039	44.56	43.66	−2.02	45.02	1.03
0.7934	44.86	43.80	−2.36	45.23	0.82
0.8461	45.24	43.88	−3.01	45.34	0.22
1	45.65	44.13	−3.33	45.65	0.00
		AAD (%)	1.71		0.66

Results are compared to experimental data [6] for 1-PR (1) + MA (2) (1-propanol + methyl acetate) at 25°C

[a] (Calc − Exp)/Exp

Table 11 Molar magnetic susceptibilities ($-\delta_{(m)} \times 10^6\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$) calculated using the Boyer-Donzelot equation (B-D) and the proposed model (PM)

2-PR(1) + MA(2)

$X(1)$	Exp	B-D	Dev. (%)[a]	PM	Dev. (%)[a]
0	42.95	42.55	−0.93	42.95	0.00
0.1179	43.17	42.75	−0.97	43.37	0.46
0.2174	43.42	42.92	−1.15	43.77	0.81
0.3043	43.64	43.07	−1.31	44.12	1.10
0.3976	43.89	43.22	−1.53	44.49	1.37
0.5086	44.22	43.41	−1.83	44.89	1.52
0.6107	44.54	43.59	−2.13	45.21	1.50
0.6965	44.84	43.73	−2.48	45.45	1.36
0.7986	45.22	43.91	−2.90	45.71	1.08
0.8982	45.64	44.07	−3.44	45.95	0.68
1	46.20	44.25	−4.22	46.20	0.00
		AAD (%)	2.08		0.90

Results are compared to experimental data [6] for 2-PR (1) + MA (2) (2-propanol + methyl acetate) at 25°C

[a] (Calc − Exp)/Exp

fluid mixtures and to the predictions of the traditional Boyer-Donzelot model. For all systems analyzed, the magnetic susceptibilities predicted using PM showed a lower average deviation from experimental results than those from the Boyer-Donzelot equation. The deviations decrease when the binary systems exhibit positive excess magnetic susceptibilities.

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