

Magnetic Susceptibilities of Binary Non-Electrolyte Mixtures

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Abstract Molar magnetic susceptibilities are determined by the Gouy method for the following two systems: 1-propanol + methyl acetate and 2-propanol + methyl acetate at 298 K where the three molecules are polar and the alcohol molecules are associated in their pure state. Excess diamagnetic susceptibilities are calculated to obtain information about possible interactions. Diamagnetic susceptibilities were related with molecular polarizabilities by Boyer-Donzelot's equation and compared with experimental results.

1. INTRODUCTION

The excess magnetic susceptibility χ_M^E is defined as the difference between the experimental value and the linear law value, as shown in eq. (1)

$$\chi_M^E = \chi_M - (x_1\chi_1 + x_2\chi_2) \quad (1)$$

where χ_M is the molar susceptibility of the solution, χ_1 and χ_2 are the molar susceptibilities of the pure components and x_1 and x_2 are the mole fractions.

This magnetic behavior can give us information about the possible interactions between the components of the mixture.

The following systems have been studied

1-PR(1) + MA(2)	1-propanol + methyl acetate
2-PR(1) + MA(2)	2-propanol + methyl acetate

In these systems the three molecules are polar and the molecules of both alcohols are associated by hydrogen bonds in their pure state.

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An extension of Kirkwood's correlation modified by Boyer-Donzelot¹ has been used to calculate χ_M in a wide range of concentrations, knowing the polarizabilities of the components and these values have been compared with experimental ones.

2. EXPERIMENTAL

1-propanol Merck (puriss) and 2-propanol Merck (puriss) were used without further purification; methyl acetate Mallinckrodt (puriss) was heated by reflux with acetic anhydride and then distilled over potassium carbonate.

The binary systems were prepared by mixing weighed amounts of the pure liquids. Caution was taken to prevent evaporation.

Densities were determined with a digital densimeter A.P., DMA 45. A thermostatically controlled bath, constant to ± 0.01 °C was used. Temperatures were read from calibrated thermometers. The refractive indices for the sodium D line of the pure components and the mixtures were measured with a Jena dipping refractometer in the same thermostat.

Magnetic susceptibilities were determined by the Gouy method using a Mettler H20T balance. Measurements were made in a 6.5 kG magnetic field. The Gouy force ranged from 5 to 15×10^{-6} kg. Water, twice distilled from alkaline permanganate² ($\chi = -0.720 \times 10^{-9}$ m³ kg⁻¹) and mercuric tetrathiocyanate cobalt (III)³ ($\chi = 16.49 \times 10^{-9}$ m³ kg⁻¹) were used as reference substances.

The magnetic susceptibility is defined as

$$\chi = \frac{\chi_w - \chi_a}{\Delta m_w - \Delta m_a} \Delta m = \frac{\chi_a \cdot \Delta m - \chi_w \cdot \Delta m_a}{\Delta m_w - \Delta m_a} \quad (2)$$

where:

χ_w = water magnetic susceptibility.

χ_a = air magnetic susceptibility = 0.029×10^{-9} m³ kg⁻¹.

Δm_w = weight difference of the tube filled with water, with and without magnetic field.

Δm_a = weight difference of the tube filled with air, with and without magnetic field.

Δm = weight difference of the tube filled with solution, with and without magnetic field.

Molar susceptibilities are obtained from the following equation

$$\chi_M = \chi \frac{M}{\rho} \quad (3)$$

where M is the molecular weight and ρ the density of the solution.

3. RESULTS AND DISCUSSION

Table 1 shows the experimental values of densities, refraction indices, molar susceptibilities and polarizabilities at 298.15K for the pure components, together with literature values for comparison.

Table 1 - Densities, refraction indices, molar susceptibilities and polarizabilities for the pure components at 298.15K.

COMPOUND	$\rho \times 10^{-3}$ (kg m ⁻³)		n _D		$-\chi_M \times 10^{12}$ (m ³ mol ⁻¹)		$a \times 10^{30}$ (m ³ molec ⁻¹)
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	
1-PR	0.7996	0.7989 ⁵	1.38316	1.38325 ⁶	45.65	45.45 ⁷	6.951
2-PR	0.7800	0.7807 ⁸	1.37492	1.3747 ⁹	46.20	46.11 ⁷	6.989
MA	0.9270	0.9273 ⁹	1.35876	1.3587 ¹⁰	42.95	42.89 ⁷	6.969

Polarizabilities of the pure components were calculated with the Lorentz-Lorenz formula

$$\left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{M}{\rho} = \frac{4}{3} \pi N \alpha \quad (4)$$

where n is the refractive index, N is Avogadro's number and α the polarizability.

Densities, refraction indices and molar susceptibilities can be expressed by a polynomial function of the mole fraction of one of the components, as the following equation

$$P(x_1) = x_1 P_1 + x_2 P_2 + x_1 x_2 \sum_{i=0}^n a_i (x_1 - x_2)^i \quad (5)$$

where $P(x_1)$ represents the property under consideration.

The values adopted for the coefficients a_i (calculated with a Vax 11/780) and the standard error of the estimate are summarized in Table 2.

Table 2 - Polynomial coefficients of eq. (5) and standard deviations

System	a_0	a_1	a_2	a_3	a_4	σ	
1-PR(1)+MA(2)	$\rho \times 10^{-3}$ (kg m ⁻³)	-0.0079	0.0014	-0.0022	-	-	4×10^{-5}
	n_D	-0.00754	-0.00763	-0.0043	-0.0025	-0.0055	4×10^{-5}
	$-\chi_M \times 10^{12}$ (m ³ mol ⁻¹)	-1.20	-0.34	-	-	-	8×10^{-5}
2-PR(1)+MA(2)	$\rho \times 10^{-3}$ (kg m ⁻³)	-0.0157	-0.0073	0.016	-	-	7×10^{-4}
	n_D	-0.00922	-0.00822	-	-	-	6×10^{-4}
	$-\chi_M \times 10^{12}$ (m ³ mol ⁻¹)	-1.51	-0.505	-0.69	-	-	8×10^{-3}

Each set of results of excess diamagnetic susceptibilities was fitted with a Redlich-Kister⁴ form of the type

$$\chi_M^E = x_1 (1-x_1) \sum_j^n a_j (2x_1-1)^{j-1} \quad (6)$$

where a_j is the polynomial coefficient and n the polynomial degree. The method of least squares was used to determine the values of the coefficients a_j . In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard error of the estimate with n :

$$\sigma = [\sum (\chi_{obs}^E - \chi_{cal}^E)^2 / (n_{obs} - n)]^{1/2} \quad (7)$$

where $n_{obs,i}$ is the number of measurements.

Table 3 shows the values adopted for the coefficients a_j for the two systems and the respective standard deviations.

Table 3 - Polynomial coefficients a_j from eq. (6) and standard deviations, from eq. (7).

	1-PR(1) + MA(2)			2-PR(1) + MA(2)			
	a_1	a_2	σ	a_1	a_2	a_3	σ
$\chi_M^E \times 10^{12}$ ($m^3 \text{ mol}^{-1}$)	1.21	0.32	8×10^{-3}	1.50	0.5	0.7	9×10^{-3}

The diamagnetic susceptibility can be related to the molecular polarizability by Boyer-Donzelot's equation¹ for organic compounds

$$\chi_i = f(n_i^! \alpha_i)^{1/2} \quad (8)$$

For mixtures, we can assume to a first approximation that the additivity law for molar diamagnetic susceptibilities is correct, then**

$$\chi_M = f[\sum_i x_i (n_i^! \alpha_i)]^{1/2} \quad (9)$$

where $n_i^!$ is the effective number of electrons and α_i the molecular polarizability of component i . The effective number of electrons can be calculated by the difference

$$n_i^! = n_i - n_0 \quad (10)$$

where n_i is the number of valence electrons of component i and n_0 a characteristic constant for every family of substances. For alcohols $n_0 = 2.6$ and for methyl acetate $n_0 = 8.3$. Eq. (9) for our systems was not in agreement with experimental results. Making an adjustment for Boyer-Donzelot's values, a better agreement is obtained with this expression

$$\chi_M = f \left[\sum x_i (n_i^2 \alpha_i) \right]^{1/2} + b \tag{11}$$

where $f = -3.4509 \times 10^3$ and $b = -0.496 \times 10^{-12} \text{ m}^3 \text{ mol}^{-1}$.

Table 4 shows calculated diamagnetic susceptibilities which can be compared with experimental values for both systems. The agreement is good.

Table 4 - Values of mole fraction, experimental and calculated (eq.(12)) diamagnetic susceptibility at 298.15 K.

System 1-PR(1) + MA(2)			System 2-PR(1) + MA(2)		
x_1	$-\chi_M^{\text{exp}} \times 10^{12}$ ($\text{m}^3 \text{ mol}^{-1}$)	$-\chi_M^{\text{cal}} \times 10^{12}$ ($\text{m}^3 \text{ mol}^{-1}$)	x_1	$-\chi_M^{\text{exp}} \times 10^{12}$ ($\text{m}^3 \text{ mol}^{-1}$)	$-\chi_M^{\text{cal}} \times 10^{12}$ ($\text{m}^3 \text{ mol}^{-1}$)
0.1054	43.14	43.10	0.1179	43.17	43.14
0.1279	43.19	43.14	0.2174	43.42	43.33
0.1985	43.33	43.25	0.3043	43.64	43.46
0.3111	43.55	43.59	0.3976	43.89	43.62
0.4107	43.79	43.77	0.5086	44.22	43.80
0.4984	44.01	43.89	0.6107	44.54	43.98
0.6058	44.28	44.05	0.6965	44.84	44.12
0.7039	44.56	44.19	0.7986	45.22	44.30
0.7934	44.86	44.35	0.8982	45.64	44.46
0.8961	45.24				

Figure 1 shows the experimental values for the excess magnetic susceptibilities as a function of the mole fraction of one of the components, in this case the alcohols. The values of χ_M^E for both systems are positive over the whole concentration range. In the mixture of alcohols with methyl acetate, the breaking of hydrogen bond in the alcohol molecule causes a positive χ_M^E . A possible association with methyl acetate would originate a negative χ_M^E , and this deviation is not observed in this case.

Gopalakrishnan¹² reported positive χ_M^E in mixtures of alcohols

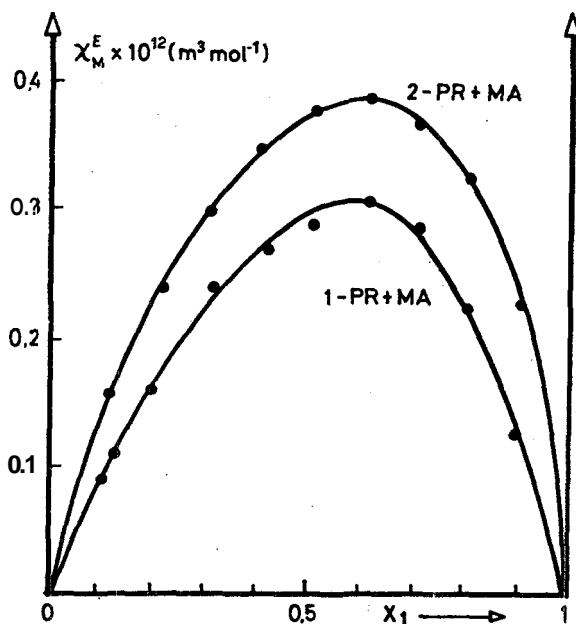


Fig.1 - Excess molar susceptibilities vs. mole fractions x_1 for the studied systems at 298.15K. Experimental results: ...; continuous curves were calculated from eq. (6).

with triethylamine or nitrobenzene with ethylamine; also Riggio et al.¹³ reported positive χ_M^E in mixtures of methylisobutylketone with alcohols.

In both systems, consequently, dispersion forces are dominant between polar molecules and in the 1-PR + MA system, the hydrogen bond $\text{O-H} \cdots \text{O}$ in the alcohol is stronger than in the 2-PR in the other system. Other excess thermodynamic properties like molar excess volumes, excess viscosities and excess molar enthalpies seem to confirm the above mentioned results¹⁴.

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Resumo

Neste trabalho foi determinado a susceptibilidade magnética molar dos sistemas: 1-propanol e 2-propanol + acetato de metila pelo método de Gouy a 298,15 K onde as três moléculas são polares e as do álcool estão associadas no estado puro. As possíveis interações entre as moléculas são interpretadas através da susceptibilidade diamagnética de excesso. A susceptibilidade diamagnética molar foi correlacionada com a polarizabilidade molecular por meio da equação de Boyer-Donzelot e a comparação com os dados experimentais é fornecida.