

Magnetic Susceptibilities of Binary Non-electrolyte Mixtures

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Molar magnetic susceptibilities are determined by the *Gouy* method for the following four systems: dichloromethane + methyl acetate, *n*-pentane + dichloromethane, *n*-pentane + methyl acetate and 2-propanol + *n*-pentane, in which *n*-pentane is a non-polar molecule and the other three are polar while 2-propanol is associated in its 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.

(Keywords: Excess molar diamagnetic susceptibilities; Mixtures of non-electrolytes; Molecular polarizabilities)

Magnetische Suszeptibilitäten binärer Nicht-Elektrolyt-Mischungen

Für folgende vier Systeme wurden die molaren magnetischen Suszeptibilitäten mittels der *Gouy*-Methode bestimmt: Dichlormethan + Methylacetat, *n*-Pentan + Dichlormethan, *n*-Pentan + Methylacetat, und 2-Propanol + *n*-Pentan; dabei ist *n*-Pentan ein nicht-polares Molekül, die anderen sind polar, wobei 2-Propanol zusätzlich Assoziation zeigt. Es werden Exzess-diamagnetische Suszeptibilitäten berechnet, um Informationen bezüglich möglicher Wechselwirkungen zu erhalten. Die diamagnetischen Suszeptibilitäten wurden mit den molekularen Polarisierbarkeiten über die *Boyer-Donzelot-Beziehung* in Relation gesetzt und mit den experimentellen Resultaten verglichen.

Introduction

Excess magnetic susceptibility χ^E is defined as the difference between the experimental value and the linear law values, as shown in equation (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 behaviour can give us information about the possible interactions between the components of the mixture.

The following systems have been studied:

<i>DCM</i> (1) + <i>MA</i> (2)	dichloromethane + methyl acetate
<i>P</i> (1) + <i>DCM</i> (2)	<i>n</i> -pentane + dichloromethane
<i>P</i> (1) + <i>MA</i> (2)	<i>n</i> -pentane + methyl acetate
2- <i>PR</i> (1) + <i>P</i> (2)	2-propanol + <i>n</i> -pentane

In these systems, only *n*-pentane is a non-polar molecule, the other three are polar molecules and 2-propanol is associated by hydrogen bonds in its pure state.

An extension of *Kirkwood's* correlation, modified by *Boyer-Donzelot*¹, 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.

Experimental

n-Pentane Carlo Erba (puriss) was fractionally distilled over phosphorus pentoxide; dichloromethane Merck (puriss) was fractionally distilled over calcium chloride; methyl acetate Mallinckrodt (puriss) was heated by reflux with acetic anhydride and then distilled over potassium carbonate; finally, 2-propanol Merck (puriss) was distilled over sodium under reduce pressure; in all cases the middle fractions were collected.

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

Densities were determined with a *Robertson* specific gravity bottle. The total pycnometer volume was about $2 \cdot 10^{-5} \text{ m}^3$ and was calibrated with doubly distilled water. All weighings were made on a Mettler balance and corrected to vacuum. A thermostatically controlled bath, constant to $\pm 0.01 \text{ }^\circ\text{C}$, 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 H 20 T balance. Measurements were made in a 6.5 kG magnetic field. The *Gouy* force ranged from $(5 \text{ to } 15) \cdot 10^{-6} \text{ kg}$ and the accuracy of its determination was estimated to be $\pm 10^{-8} \text{ kg}$. Water twice distilled from alkaline permanganate ($\chi = -0.720 \cdot 10^{-9} \text{ m}^3 \text{ kg}^{-1}$) and mercuric tetrathiocyanate cobalt(II) ($\chi = 16.49 \cdot 10^{-9} \text{ m}^3 \text{ kg}^{-1}$)² were used as reference substances.

The magnetic susceptibility is defined as:

$$\chi = \chi' + \frac{g(\Delta m - \Delta m')}{C} \quad (2)$$

where the air susceptibility $\chi' = 0.029 \cdot 10^{-9} \text{ m}^3 \text{ kg}^{-1}$; gravity acceleration $g = 9.788 \text{ m s}^{-2}$; Δm is the weight difference of the empty tube with and without magnetic field; $\Delta m'$ is the weight difference of the filled tube with and without

magnetic field and C is a constant whose value is $9.5926 \cdot 10^4$. Molar susceptibilities are obtained from the following equation:

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

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

Results and Discussion

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

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 and refraction indices could be expressed by a polynomial function of the mole fraction of one of the components as the following equation:

$$P(x_1) = P_1 x_1 + P_2 x_2 + x_1 x_2 [a_1 + a_2(2x_1 - 1) + a_3(2x_1 - 1)^2 + \dots] \quad (5)$$

When $P(x_1) = \rho(x_1)$ the results were multiplied by 10^{-3} in order to maintain SI units.

The values adopted for the coefficients a_j (calculated with a Radio Shack TRS 80 microcomputer) and the standard error of the estimate are summarized in Table 2.

Each set of results of excess diamagnetic susceptibilities was fitted with a *Redlich-Kister*⁷ form of the type:

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

where a_j is the polynomial coefficient and n the polynomial degree. The results were multiplied by 10^{-6} in order to maintain SI units.

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 estimate with n :

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

where n_{obs} is the number of measurements.

Table 3 shows the values adopted for the coefficients a_j for the four systems.

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

Compound	$\rho \cdot 10^{-3} \text{ kg m}^{-3}$	n_D	$-\chi_M \cdot 10^{30} \text{ m}^3 \text{ mol}^{-1}$	$\alpha \cdot 10^{30} \text{ m}^3 \text{ molec}^{-1}$
	Exp.	Lit.	Exp.	Lit.
DCM	1.3152	1.3148 ³	1.42119	1.4211 ⁴
MA	0.9252	0.9273 ⁴	1.35817	1.360 ⁵
P	0.6219	0.62139 ⁴	1.35466	1.35472 ⁴
2-PR	0.7800	0.7807 ⁶	1.37492	1.3747 ⁴
			45.76	45.76 ⁵
			47.94	—
			42.69	42.10 ⁵
			63.14	63.05 ⁵
			45.76	45.76 ⁵
				6.495
				6.992
				10.014
				6.990

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

	DCM(1) + MA(2)		P(1) + DCM(2)		P(1) + MA(2)		2-PR(1) + P(2)	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
a_1	ρ	-0.0882759	-0.4109500	-0.4109500	-0.1351470	-0.1351470	-0.0742860	-0.0742860
	n_D	-0.0220173	-0.0484944	-0.0484944	-0.0174605	-0.0174605	-0.0516411	-0.0516411
a_2	ρ	-0.0114225	0.1237700	0.1237700	0.0222837	0.0222837	0.0088478	0.0088478
	n_D	-0.0028549	0.0121661	0.0121661	-0.0019508	-0.0019508	-0.0018866	-0.0018866
a_3	ρ	$4.56 \cdot 10^{-4}$	0.0280753	0.0280753	0.0773980	0.0773980	0.0146371	0.0146371
	n_D	0.0126175	-0.0096753	-0.0096753	0.0084407	0.0084407	0.0042051	0.0042051
a_4	ρ	$7.32 \cdot 10^{-4}$	0.0047632	0.0047632	0.0012760	0.0012760	$-2.694 \cdot 10^{-4}$	$-2.694 \cdot 10^{-4}$
	n_D	-0.0131938	-0.0142016	-0.0142016	0.0020838	0.0020838	0.0122163	0.0122163
a_5	ρ	$-3.15 \cdot 10^{-4}$	-0.0050614	-0.0050614	0.0108191	0.0108191	-0.008301	-0.008301
	n_D	-0.0372745	-0.0148441	-0.0148441	-0.0156006	-0.0156006	—	—
σ		$4.4 \cdot 10^{-5}$	$7 \cdot 10^{-5}$	$7 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$
		$3.1 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$	$7.9 \cdot 10^{-5}$	$7.9 \cdot 10^{-5}$	$9 \cdot 10^{-5}$	$9 \cdot 10^{-5}$

Table 3. Polynomial coefficients a_j from equation (6) and standard deviations

	$DCM(1) + MA(2)$	$P(1) + DCM(2)$	$P(1) + MA(2)$	$2 \cdot PR(1) + P(2)$
a_1	$8.815141 \cdot 10^{-6}$	$-1.81021 \cdot 10^{-5}$	$1.7835 \cdot 10^{-5}$	$-1.66829 \cdot 10^{-5}$
a_2	$-8.59734 \cdot 10^{-6}$	$2.24828 \cdot 10^{-6}$	$2.594998 \cdot 10^{-6}$	$1.89468 \cdot 10^{-6}$
a_3	$2.10578 \cdot 10^{-7}$	$-6.83315 \cdot 10^{-6}$	$-5.09699 \cdot 10^{-6}$	$4.55463 \cdot 10^{-5}$
a_4	$1.81420 \cdot 10^{-5}$	$-1.08766 \cdot 10^{-5}$	$-1.26598 \cdot 10^{-5}$	$2.55643 \cdot 10^{-5}$
a_5	$-2.43680 \cdot 10^{-6}$	$-1.22321 \cdot 10^{-5}$	$4.92726 \cdot 10^{-6}$	$-2.22786 \cdot 10^{-6}$
a_6	$-1.91619 \cdot 10^{-5}$	$-1.30784 \cdot 10^{-5}$	$2.03439 \cdot 10^{-5}$	$-3.45072 \cdot 10^{-5}$
σ	$8 \cdot 10^{-8}$	$7 \cdot 10^{-8}$	$8 \cdot 10^{-8}$	$8 \cdot 10^{-8}$

Table 4. Values of mole fraction, experimental and

System $P(1) + MA(2)$		
x_1	$-\chi_M^{exp} \cdot 10^{12} \text{ m}^3 \text{ mol}^{-1}$	$-\chi_M^{cal} \cdot 10^{12} \text{ m}^3 \text{ mol}^{-1}$
0.0000	42.69	43.30
0.1036	43.64	45.23
0.2021	45.05	47.07
0.3129	46.57	49.13
0.4032	48.20	50.82
0.4108	48.30	50.96
0.5001	49.90	52.62
0.6078	52.48	54.63
0.6958	54.69	56.27
0.8007	57.41	58.22
0.9009	60.38	60.09
1.0000	63.14	61.94

The diamagnetic susceptibility can be related with 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:

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

where f is a constant equal to $-3.46 \cdot 10^{-3}$, n_i' 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 our systems, n_0 is unknown for dichloromethane. For 2-propanol, $n_0 = 2.6$; for *n*-pentane, $n_0 = 0$ and for methyl acetate $n_0 = 7.6$ (obtained by interpolation).

Table 4 shows calculated diamagnetic susceptibilities which can be compared with experimental values for both systems. The agreement is better for the system $P + MA$ than for the system $2-PR + P$. This fact may be explained taking into account the association of 2-propanol in its pure state which produces more interaction effects than in the first system.

Fig. 1 shows the experimental values obtained for the magnetic susceptibilities as a function of the mole fraction of one of the compo-

calculated [eq. (9)] diamagnetic susceptibility

System 2-PR(1) + P(2)		
x_1	$-\chi_M^{exp} \cdot 10^{12} \text{ m}^3 \text{ mol}^{-1}$	$-\chi_M^{cal} \cdot 10^{12} \text{ m}^3 \text{ mol}^{-1}$
0.0000	63.14	61.94
0.1033	62.39	60.11
0.2005	61.56	58.39
0.2120	61.39	58.19
0.3024	60.81	56.59
0.3942	60.04	54.97
0.5004	58.68	53.09
0.5898	57.05	51.51
0.6978	54.70	49.60
0.8052	52.28	47.70
0.8872	49.56	46.25
1.0000	45.76	44.25

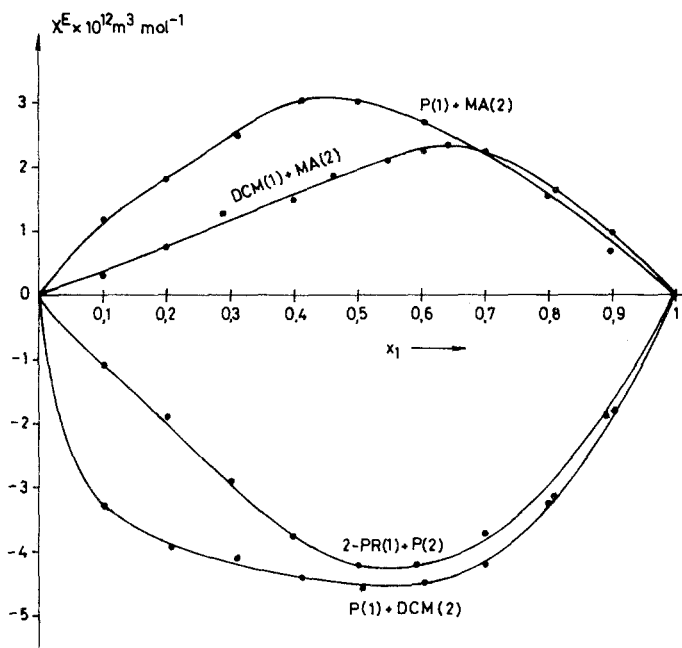


Fig. 1. Excess molar susceptibilities vs. mole fractions x_1 for the studied systems at 298.15 K

nents. Two systems: $P + DCM$ and $2-PR + P$ show a negative χ_M^E and the other two: $P + DCM$ and $DCM + MA$ a positive χ_M^E over the whole concentration range.

In the system where χ_M^E is positive, dispersion forces are dominant between polar molecules, like DCM and MA , and between a polar molecule (MA) and a dipole-induced (P) molecule.

Considering that neither of the components exhibits hydrogen bonding in the pure state, it is not possible to explain positive excess susceptibilities by hydrogen bond rupture. In the cases of mixtures where χ_M^E is negative and one component (DCM) is a polar molecule and the other one is non-polar (P) there is an induced dipole interaction. As expected, this interaction gives rise to negative deviation in χ_M which in turn produce negative χ_M^E .

In the mixture $2-PR + P$, the breaking of hydrogen bond in the alcohol molecule causes a positive χ_M^E . A possible association with *n*-pentane would originate negative χ_M^E , and this deviation surpasses the former positive values. *Gopalakrishnan*⁸ reported positive χ_M^E in mixtures of alcohols with triethylamine and negative χ_M^E in mixtures of chlorobenzene or nitrobenzene with ethylamine.

Other excess thermodynamic properties, like molar excess volumes, excess viscosities and excess molar enthalpies, seem to confirm the above mentioned results^{9,10}.

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