

DENSITIES, REFRACTIVE INDICES AND EXCESS PROPERTIES OF N-METHYLMORPHOLINE AND BUTANOL MIXTURES AT DIFFERENT TEMPERATURES

الكثافات ومعاملات الانكسار والخواص الفائضة لمحاليل N- ميثيل مورفالين مع 1- بيوتانول بدرجات حرارة مختلفة

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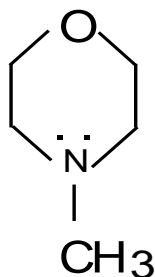
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ABSTRACT:

Densities and refractive indices have been measured at 303.15, 313.15 and 323.15 K for the binary mixtures of N-methylmorpholine and 1-butanol over the entire composition range. Those data have been used to compute the excess molar volumes, V^E and excess refractive indices, n^E . The results obtained are used to study the nature of molecular interactions in these mixtures. As far as we know, in the open literature, no study on mixtures containing N-methylmorpholine [I] has been reported.

الخلاصة:

تم قياس الكثافة ومعامل الانكسار لمخاليط ثنائية المكون من N- ميثيل مورفالين مع 1-بيوتانول عند درجات الحرارة 303.15 و 313.15 و 323.15 كلفن وعلى المدى التام من الكسور المولية. استخدمت القياسات العملية لكثافة ومعامل الانكسار لحساب الحجم المولارية الفائضة V^E ومعاملات الانكسار الفائضة n^E ومنها تم مناقشة التأثيرات المتبادلة لهذا النوع من المخاليط.



[I]

INTRODUCTION:

The physical and chemical properties of pure liquids and their mixtures is important both academically and industrially. Many industrial processes use mixtures of solvents and knowledge of the subject area is critical to the efficient utilization. Prepare development and economic design of appropriate equipment for these processes is only possible if the chemical and physical properties of the solvents or substances to be processed are known. The Thermodynamic properties of binary mixture are extensively studied. These studies include the excess molar volumes^(1,2), excess enthalpy of mixing⁽³⁾, excess free energy of mixing⁽⁴⁾, excess chemical potential⁽⁵⁾ and phenomena of lower critical miscible⁽⁶⁾.

(I) Ideal Mixture:

The ideal mixture is a hypothetical one whose properties are introduced into the thermodynamic description of real mixture as convenient standard of normal behavior. There is several definition of an ideal liquid mixture; one of the most convenient is that it is a mixture in which the chemical potentials of all components are given the equation

$$\mu_i(\rho, t, x) = \mu_i^\circ(\rho, t) + RT \ln x_i \dots \dots \dots (1)$$

i = 1 , 2 , 3,

Where $\mu_i^\circ(\rho, T)$ and x_i is the chemical potential and mole fraction of pure component, i, at the same pressure and temperature as the mixture being studied.

For an ideal mixture the molar function of mixing are given by the molar Gibbs function

$$\Delta_{mix} G_m^{id} = RT[x \ln X + (1-x) \ln(1-X)] \dots \dots \dots (2)$$

The molar entropy

$$\Delta_{mix} S_m^{id} = -R[x \ln X + (1-x) \ln(1-X)] \dots \dots \dots (3)$$

The molar enthalpy

$$\Delta_{mix} H_m^{id} = 0 \dots \dots \dots (4)$$

The molar volume

$$\Delta_{mix} V_m^{id} = 0 \dots \dots \dots (5)$$

For an ideal mixture the molar Gibbs energy of mixing is negative and the molar entropy of mixing is positive for any value of x mole fraction.

(II) Molar Mixing Functions

The molar function of mixing for a binary mixture $[xA+(1-x)B]$, where x denotes the molar function of A, are defined by :

$$\Delta_{mix} X_m = X_m - xX_A^* - (1-x)X_B^* \dots \dots \dots (6)$$

Where X_m is the molar quantity of a binary mixture $[XA+(1-x)B]$ at the temperature T and pressure P and where X_A^* and X_B^* are the molar quantities of the pure substances A and B at the same temperature and pressure. X denotes any extensive quantity such as G , H , S or V .

(III) Excess Function

Excess partial molar quantities can be written as the difference between the partial molar quantities for the non-ideal mixture and those of an ideal mixture.

It has become customary to use instead of the molar function of mixing $\Delta_{mix} X_m$, the excess molar function:

$$X_m^E = \Delta_{mix} X_m - \Delta_{mix} X_m^{id} \dots\dots\dots(7)$$

so that “excess” means excess over ideal.

Thermodynamic function like Gibbs energy, molar polarization, entropy and enthalpy and excess molar volume are used by workers⁽⁷⁻⁹⁾ in investigating the orientation of molecular dipoles and molecular interaction in binary and ternary mixture in polar- polar, polar-non polar liquids . Payne and Theodorou⁽¹⁰⁾ have suggested that the excess function are more useful than the thermodynamic functions in interpreting the molecular interactions in such binary mixtures . The miscibility between the two liquids in a mixture is maximum when the molecular interaction between them is more.

Refractive Index of Mixtures:

The refractive index, n_D , is the ratio of the velocity of light in a particular substance to the velocity of light in vacuum. Values usually reported refer to the ratio of the velocity in air to that in the substance. The refractive index is useful for characterizing compounds and also for calculating other physical properties. Bauer and Fajans⁽¹¹⁾ have discussed the refractive index, including some of its uses and methods of determination. The principles and uses of the several refractometers have been treated by Reilly and Roa⁽¹²⁾ . The refractive index is a function of both temperature and the wavelength of the incident light usually sodium lines are used.

The present paper studies the binary mixtures containing a common solvent one of morpholine derivatives⁽¹³⁻¹⁵⁾. We present here new experimental data on density, ρ , and refractive indices, n_D , of N-methylmorpholine and 1-butanol as co-solvent in the temperature range from 303.15 to 323.15 K. This system is particularly chosen in view of its importance in chemical engineering design processes and polymer processing industries⁽¹⁶⁾.

EXPERIMENTAL:

Materials:

1-Butanol and N-methylmorpholine (pure grade) were obtained from Aldrich. N-methylmorpholine was purified as previously described⁽¹⁵⁾. Both solvents were checked by gas liquid chromatographic analysis, density and refractive index. All binary mixtures were prepared over the whole mole fraction range $0 < x_2 < 1$ using Sartorius balance (precision 1×10^{-4}) and air tight stoppered bottles. The more volatile component liquid was directly poured into the bottle. The second component liquid was injected into the bottle through the stopper by means of a syringe.

This procedure hindered any vapour loss and contamination. The mole fraction x_i of component liquid i in the binary mixture was calculated from the following relation:

$$x_i = \frac{W_i/M_i}{W_i/M_i + W_j/M_j} \dots\dots\dots(8)$$

where W_i , M_i are the weight and the molecular weight of the component liquid i . The possible error in the mole fraction is estimated to be lower than 2×10^{-4} . The uncertainty in the mole fraction was $\pm 2 \times 10^{-4}$.

Measurements:

Densities were measured with a digital precision system DMA 60/602 (Anton Paar). Details of the system and the calibration procedure were adequately covered in previous work⁽¹³⁾. The reproducibility of density measurements was $\pm 3 \times 10^{-4} \text{ g. cm}^{-3}$.

Refractive indices for the sodium D-line were measured with an Abbe refractometer. A minimum of three independent readings was taken for each mixtures. The refractive index values were accurate to 2×10^{-4} .

For all measurements, a Schott-Gerate CT 1150 thermostat was used at a constant digital temperature control of $\pm 0.01 \text{ K}$ at the desired temperature.

RESULTS AND DISCUSSION:

The experimental results of density, ρ , and refractive indices, n_D , of pure liquids and binary mixtures of N-methylmorpholine and 1-butanol at the three temperatures are presented in Table 1. Excess molar volumes, V^E and excess refractive indices, n^E for binary mixture have been calculated from the following equations⁽¹⁷⁻¹⁹⁾.

$$V^E / \text{cm}^3 \cdot \text{mol}^{-1} = [(x_1 M_1 + x_2 M_2) / \rho - (x_1 M_1 / \rho_1) + (x_2 M_2 / \rho_2)] \dots\dots\dots(9)$$

$$n^E = n - (x_1 n_1 + x_2 n_2) \dots\dots\dots(10)$$

Where:

- x_1, x_2 : mole fractions of liquids 1 and 2 .
- M_1, M_2 : molar masses of liquids 1 and 2 .
- ρ_1, ρ_2 : density of liquids 1 and 2 .
- n_1, n_2 : refractive index of liquids 1 and 2 .
- ρ : density of mixture .
- n : refractive index of mixture .

The obtained results of V^E and n^E for the mixture of N-methylmorpholine and 1-butanol at the three temperatures are presented in Table 1 N-methylmorpholine and 1-butanol at the three temperatures are listed in Table 1 .

The excess molar volumes V^E for the binary mixtures of N-methylmorpholine and 1-butanol are all positive over the whole mole fraction range at all temperatures studied, as shown in Fig. 1. This behavior may be explained qualitatively:

- (i) Strong self – association in 1- butanol through hydrogen bonding .
- (ii) Steric effect of methyl group connected to nitrogen atom with lone pairs of electrons in N-methylmorpholine prevent any molecular interactions between the hydroxyl group of 1-butanol and the lone pair of electrons on the nitrogen atom .
- (iii) Added 1-butanol to N-methylmorpholine enhances the N-methylmorpholine structure.

Figure 2 shows the variation of n^E with mole fraction X_2 which is negative at 303.15 K but it is positive at higher temperatures (313.15 and 323.15 K). The results of n^E suggest higher electron perturbations of the molecular orbital of the mixing liquids due to dipolar association interactions at higher temperatures but inverse to that at low temperature (303.15 K). This trend is quite different from those observed for V^E values.

Table (1). Experimental Values of the density (ρ), Refractive index (n_D), Excess molar volume (V^E) and Excess refractive index (n^E) for x_1 N-methylmorpholine and x_2 1-butanol at (303.15 , 313.15 and 323.15 K) .

x_2	$\rho / \text{g.cm}^{-3}$	$V^E / \text{Cm}^3 \text{mol}^{-1}$	n_D	$n^E \times 10^{-3}$
303.15 K				
0.0000	0.9123	0.0000	1.4312	0.00
0.0986	0.9021	0.1282	1.4276	-0.03
0.1988	0.8910	0.2986	1.4239	-0.04
0.2997	0.8800	0.4062	1.4202	-0.06
0.3979	0.8690	0.5036	1.4167	-0.09
0.4989	0.8585	0.4611	1.4130	-0.14
0.5999	0.8484	0.3243	1.4093	-0.18
0.6986	0.8376	0.2531	1.4057	-0.20
0.7888	0.8272	0.2068	1.4024	-0.21
0.8998	0.8146	0.0682	1.3984	-0.22
1.0000	0.8022	0.0000	1.3950	0.00
313.15 K				
0.0000	0.9054	0.0000	1.4260	0.00
0.0986	0.8940	0.2333	1.4228	0.01
0.1988	0.8835	0.3791	1.4196	0.06
0.2997	0.8724	0.4263	1.4164	0.15
0.3979	0.8615	0.5098	1.4132	0.21
0.4989	0.8500	0.5933	1.4100	0.26
0.5999	0.8393	0.5241	1.4068	0.29
0.6986	0.8285	0.4550	1.4036	0.30
0.7888	0.8180	0.3472	1.4006	0.27
0.8998	0.8053	0.2618	1.3969	0.24
1.0000	0.7942	0.0000	1.3935	0.00

Table (1) cont.

x_2	$\rho / \text{g.cm}^{-3}$	$V^E / \text{cm}^3 \text{mol}^{-1}$	n_D	$n^E \times 10^{-3}$
323.15 K				
0.0000	0.8965	0.0000	1.4208	0.00
0.0986	0.8855	0.3333	1.4178	0.01
0.1988	0.8747	0.4595	1.4148	0.01
0.2997	0.8632	0.5940	1.4119	0.17
0.3979	0.8515	0.6833	1.4090	0.21
0.4989	0.8402	0.7056	1.4059	0.21
0.5999	0.8290	0.6660	1.4029	0.22
0.6986	0.8182	0.4928	1.3999	0.17
0.7888	0.8084	0.3346	1.3972	0.14
0.8998	0.7955	0.2118	1.3938	0.11
1.0000	0.7852	0.0000	1.3907	0.00

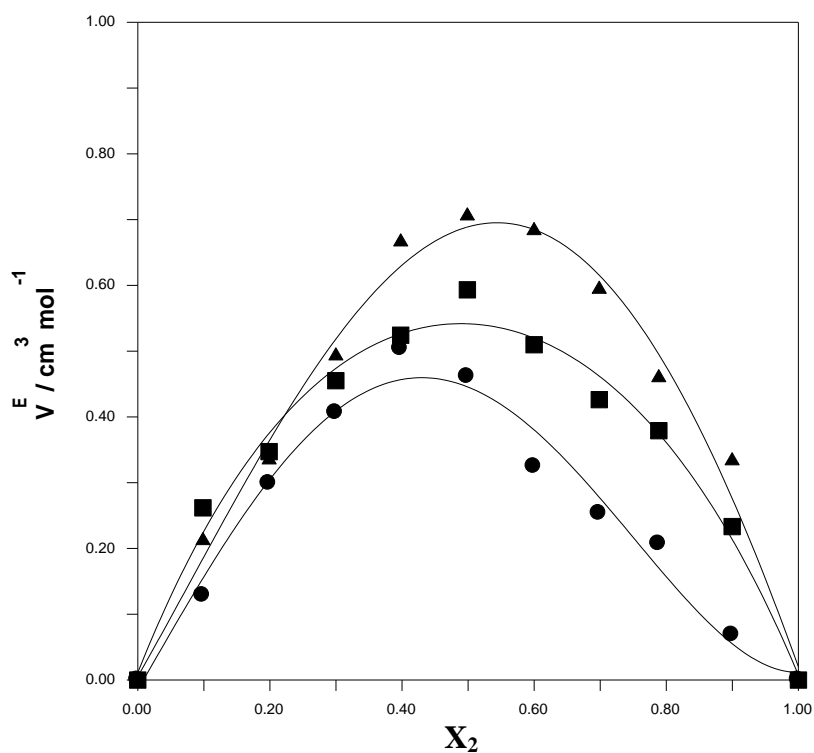


Fig. 1-Excess molar volumes V^E versus x_2 , the mole fraction of 1- butanol at ●, 303.15; ■, 313.15; ▲, 323.15 K.

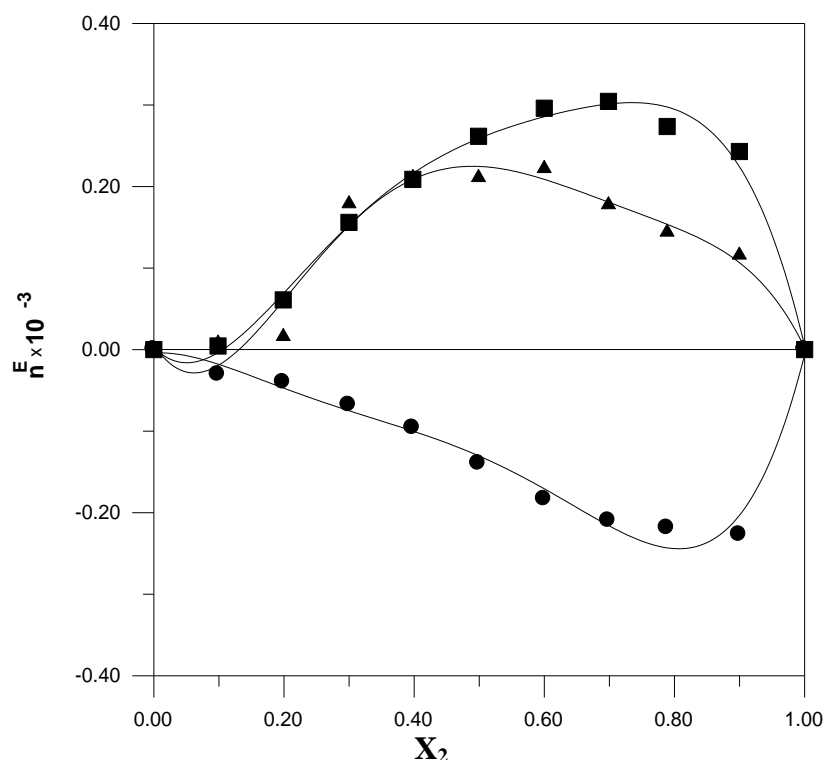


Fig. 2-Excess refractive indices, n^E versus x_2 , the mole fraction of 1- butanol at
 ●, 303.15; ■, 313.15; ▲, 323.15K..

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