

EXCESS THERMODYNAMIC PROPERTIES OF THE n-PENTANE + METHYLACETATE SYSTEM AT 298.15 K *

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(Received 3 November 1987)

ABSTRACT

Densities, refraction indices, viscosities, enthalpies, vapor–liquid equilibria, surface tensions and magnetic susceptibilities, were determined for the n-pentane + methylacetate system at 298.15 K. From the experimental results, excess molar volumes, excess viscosities, excess molar enthalpies, excess molar Gibbs energies, excess surface tensions and excess diamagnetic susceptibilities were calculated. From these data, information could be obtained about the interactions between both chemical species. The method of UNIFAC was applied to obtain excess molar Gibbs energies and molar enthalpies and the values were compared with experimental data.

INTRODUCTION

Excess thermodynamic properties such as V^E (excess molar volume); η^E (excess viscosity); H^E (excess molar enthalpy); G^E (excess molar Gibbs free energy); σ^E (excess surface tension) and χ^E (excess molar magnetic susceptibility) have been determined in order to obtain information about the possible interactions between the molecules of n-pentane (1) + methylacetate (2) system at 298.15 K. This work is a continuation of our research on the thermodynamics properties of binary liquid mixtures of non-electrolytes [1,2].

Densities, refractive indices, viscosities, enthalpies, vapor–liquid equilibria, surface tensions and diamagnetic susceptibilities at different mole

* Presented at the 5° Congreso Argentino de Fisicoquímica, Mar del Plata, Argentina, 1987.

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fractions were measured for this system, in which compound (1) is non-polar and component (2) is highly polar with association in the pure state.

EXPERIMENTAL

The methods used in our laboratory have been described previously [1–4]. Densities were determined with a digital densimeter AP, DMA 45. A thermostatically controlled bath (constant to $\pm 0.01^\circ\text{C}$) was used. Calibration was carried out with doubly distilled water and air with an error of $\pm 0.1\text{ kg m}^{-3}$. All weighings were made on a Mettler H315 balance. Temperatures were read from calibrated thermometers. Refraction indices were measured with a Jena dipping refractometer with an estimated error of ± 0.00002 . Viscosities of the pure components and of the mixtures were determined with a Cannon–Fenske viscosimeter calibrated with doubly-distilled water and benzene. Kinetic energy corrections were applied to viscosity data. The estimated error was $\pm 0.005\text{ mPa s}$. The adiabatic calorimeter described by Loiseleur et al. [5] was used with some modifications to determine the enthalpy change. The estimated error was $\pm 5\text{ J mol}^{-1}$. Vapor–liquid equilibria data were determined using a modified version of the equilibrium still described by Boublik and Benson [6] with an estimated error of $\pm 0.05\text{ kPa}$ in pressures. Pressures were determined from boiling points of water in a ebullioscope adapted to the equipment. Temperatures were read with a Digitec thermometer to 0.01°C . Compositions of liquid phases and condensed vapor phases were determined by measuring refractive indices.

Surface tensions of the pure liquids and their binary mixtures were determined by the maximum bubble pressure method [4]. The bubbler was calibrated with benzene (Baker puriss.) assuming a surface tension of $28.10 \times 10^{-3}\text{ N m}^{-1}$ for that material at 298.15 K . Values of the surface tensions were generally reproducible to $\pm 0.05 \times 10^{-3}\text{ N m}^{-1}$. Finally, diamagnetic susceptibilities of the pure components and their mixtures were determined by the Gouy method using a Mettler H20T balance [7]. Water twice distilled ($\chi = -0.720 \times 10^{-9}\text{ m}^3\text{ kg}^{-1}$) and mercuric tetrathiocyanate cobalt(II) ($\chi = 16.49 \times 10^{-9}\text{ m}^3\text{ kg}^{-1}$) were used as reference substances. The Gouy force ranged from 5 to $15 \times 10^{-6}\text{ kg}$ and the accuracy of its determination was estimated to be $\pm 10^{-8}\text{ kg}$.

Materials and solutions

n-Pentane (Carlo Erba (puriss.)) was distilled over phosphorus pentoxide and the middle fraction was collected. Methylacetate (Mallinckrodt (puriss.)) was heated by reflux with acetic anhydride and then distilled over potassium carbonate. Mixtures were prepared by mixing weighed amounts of the pure liquids. Caution was taken to prevent evaporation.

RESULTS

The experimental results for the pure liquids are reported in Table 1, together with literature values for comparison.

The excess thermodynamic functions were calculated with the equations

$$V^E = x_1 M_1 (\rho^{-1} - \rho_1^{-1}) + x_2 M_2 (\rho^{-1} - \rho_2^{-1}) \quad (1)$$

$$\eta^E = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2) \quad (2)$$

$$H^E = H - (x_1 H_1 + x_2 H_2) \quad (3)$$

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (4)$$

$$\sigma^E = \sigma - (x_1 \sigma_1 + x_2 \sigma_2) \quad (5)$$

$$\chi^E = \chi - (x_1 \chi_1 + x_2 \chi_2) \quad (6)$$

where M_1 and M_2 are the molecular weights of the components; ρ , ρ_1 and ρ_2 are the densities of the solutions and of the pure components; η , η_1 and η_2 are the viscosities of the solutions and of the pure components; H , H_1 and H_2 are the enthalpies of the mixtures and of the pure components; γ_1 and γ_2 are the activity coefficients of the components; σ , σ_1 and σ_2 are the surface tensions of the mixtures and of the pure components and χ , χ_1 and χ_2 are the magnetic susceptibilities of the solutions and of the pure components.

Table 2 shows the experimental values of densities, refractive indices, viscosities and vapor pressures, and Table 3 the enthalpies, surface tensions and magnetic susceptibilities for this binary system at various mole fractions in a wide range of concentration.

The activity coefficients of the components in the liquid phase were calculated from the experimental data, by employing the equation

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i} + \frac{(B_{ii} - V_i)(P - P_i)}{RT} + (1 - y_i)^2 \frac{P \delta}{RT} \quad (7)$$

TABLE 1

Properties of the pure components at 298.15 K

	n-Pentane		Methylacetate	
	Exp.	Lit.	Exp.	Lit.
Density $\rho \times 10^{-3}$ (kg m ⁻³)	0.6214	0.62139 ^a	0.9252	0.9274 ^a
Refractive index n_D	1.35466	1.35472 ^a	1.35925	1.3589 ^a
Viscosity η (mPa s)	0.214	0.225 ^a	0.363	0.364 ^a
Vapor pressure P (kPa)	68.25	68.37 ^b	28.87	28.26 ^b
Surface tension $\sigma \times 10^3$ (N m ⁻¹)	15.51	15.48 ^a	24.70	24.1 ^a
Magnetic susceptibility - $\chi \times 10^{12}$ (m ³ mol ⁻¹)	63.14	63.05 ^c	42.69	42.10 ^c

^a Ref. 8. ^b Ref. 9. ^c Ref. 10.

TABLE 2

Experimental densities, refractive indices, viscosities and vapor pressures for the n-pentane (1) + methylacetate (2) system at 298.15 K

x_1	$\rho \times 10^3$ (kg m^{-3})	η (mPa s)	x_1	n_D	x_1	P (kPa)
0.1087	0.8782	0.322	0.1036	1.35712	0.0166	35.18
0.2088	0.8379	0.295	0.1928	1.35593	0.0351	42.15
0.3035	0.8028	0.273	0.2976	1.35470	0.0711	53.83
0.4010	0.7700	0.258	0.3882	1.35342	0.1094	58.48
0.5022	0.7389	0.243	0.5074	1.35271	0.1498	61.68
0.5972	0.7123	0.232	0.6041	1.35235	0.2639	67.62
0.7028	0.6857	0.223	0.6848	1.35247	0.3091	69.26
0.8002	0.6634	0.219	0.8108	1.35298	0.3845	71.54
0.9009	0.6419	0.218	0.9009	1.35355	0.5051	73.39
					0.5827	74.06
					0.6751	74.62
					0.8269	74.65
					0.9033	72.57

where x_i and y_i are the mole fractions in the liquid and vapor phase respectively; P and P_i are the vapor pressure of the mixtures and of the components. The value of δ is given by

$$\delta = 2B_{12} - B_{11} - B_{22} \quad (8)$$

where B_{11} , B_{22} are the virial coefficients of the pure components and B_{12} the cross virial coefficient. For n-pentane $B_{11} = -1.184 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$;

TABLE 3

Experimental enthalpies, surface tensions and magnetic susceptibilities for the n-pentane (1) + methylacetate (2) system at 298.15 K

x_1	H (J mol^{-1})	x_1	$\sigma \times 10^3$ (N m^{-1})	x_1	$-\chi \times 10^{12}$ ($\text{m}^3 \text{ mol}^{-1}$)
0.1096	430	0.1086	23.09	0.1036	43.64
0.2052	750	0.1974	21.88	0.2021	45.05
0.3014	1025	0.2927	20.56	0.3129	46.57
0.3961	1300	0.4275	18.95	0.4032	48.20
0.4483	1400	0.4931	18.35	0.4108	48.30
0.4840	1424	0.5909	17.57	0.5001	49.90
0.5557	1320	0.6936	16.78	0.6078	52.48
0.5987	1240	0.7854	16.40	0.6958	54.69
0.7070	1020	0.8795	16.01	0.8007	57.41
0.7955	776			0.9009	60.38
0.9124	406				

TABLE 4

Coefficients a_j , b_k and standard deviations ϵ determined by the method of least squares for the n-pentane (1) + methylacetate (2) system at 298.15 K

Function	a_1	a_2	a_3	a_4	a_5	b_1	b_2	b_3	ϵ
$V^E \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	3.1264	-1.0026	-1.5846	0.10705	-1.4443	-	-	-	0.009
η^E (mPa s)	-0.14288	-0.05909	-0.02774	-	-	-	-	-	0.001
H^E (J mol^{-1})	5635.0	-117.00	53288	94207	-9147.8	-0.3699	11.534	21.597	5
G^E (J mol^{-1})	4148.0	-2703.1	817.00	-790.50	-1141.7	-0.90262	-	-	10
$\sigma^E \times 10^3$ (N m^{-1})	-7.75991	0.59962	1.43756	-	-	-	-	-	0.04
$\chi^E \times 10^{12}$ ($\text{m}^3 \text{mol}^{-1}$)	11.5252	1.2910	-2.2162	-	-	-	-	-	0.09

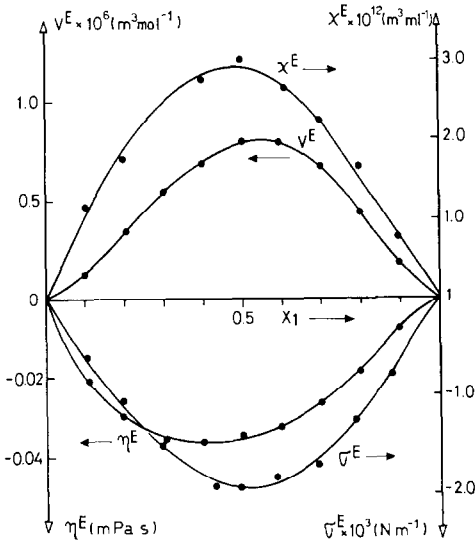


Fig. 1. Excess thermodynamic properties for the n-pentane (1) + methylacetate (2) systems at 298.15 K. Experimental results (· · ·); continuous curves are calculated from eqn. (9).

for methylacetate $B_{22} = -1.626 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ and $B_{12} = -1.367 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$. These values were estimated from the Hayden and O'Connell method [11].

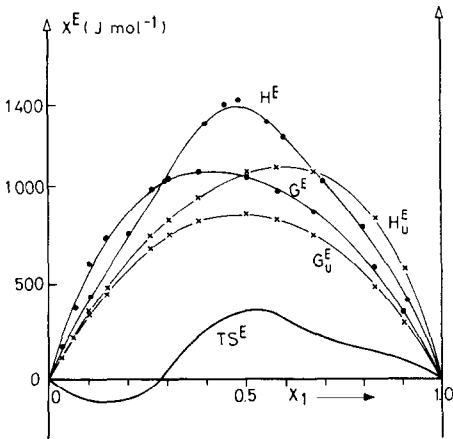


Fig. 2. Excess molar enthalpies, Gibbs free energies and molar entropies for the n-pentane (1) + methylacetate (2) system at 298.15 K. Experimental results (· · ·); continuous curves were calculated from eqn. (9); curves from UNIFAC × × × ×

Each set of results was fitted with a Padé equation of the type

$$X^E = x_1(1 - x_1) \frac{\sum_{j=1}^n a_j (1 - 2x_1)^{j-1}}{1 + \sum_{k=1}^m b_k (1 - 2x_1)^k} \quad (9)$$

where a_j and b_k are parameters obtained by a linear least squares fitting procedure. In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard error of estimate with $n + m$

$$\varepsilon = \left[\sum (X_{\text{obs}}^E - X_{\text{cal}}^E)^2 / (n_{\text{obs}} - n - m) \right]^{1/2} \quad (10)$$

The values adopted for the coefficients a_j , b_k and the standard error of estimate associated with the use of eqn. (10) are summarized in Table 4.

Figures 1 and 2 shows the experimental values determined for the excess properties as a function of the mole fraction of n-pentane. The continuous curves were calculated from eqn. (9) using the adopted values for the coefficients.

The excess molar entropy is given by

$$S^E = (H^E - G^E) / T \quad (11)$$

and the curve TS^E at 298.15 K is shown in Fig. 2.

DISCUSSION

Figure 1 shows the excess volumes for this system over the whole concentration range. Several effects may contribute to the values of V^E , such as breaking the liquid order on mixing, unfavorable interaction between groups, differences in molecular volumes and differences in free volumes between liquid components [12]. The two first effects produce a positive excess volume and considering that the methylacetate is an associated molecule, the addition of n-pentane which is non-polar, produces the rupture of hydrogen bonds with a value of $V^E > 0$. Then, dispersion forces must be dominant [13].

Generally, a positive excess volume corresponds to a negative excess viscosity as in this system. More qualitative evidence of this interaction is a large excess endothermic enthalpy for this system (about 1400 J mol⁻¹ at $x_1 \cong 0.5$). Methylacetate is a polar molecule which induces a dipole moment on a non-polar molecule like n-pentane. The endothermic effect of rupture of molecular order is corroborated by the excess free energy and molar entropy both of which are positive, but smaller than H^E . This system with little values of excess entropy, means that the enthalpic effect is greater than

the entropic, and following Prigogine [14] this mixture has the properties of a regular solution.

Normally, due to Gibbsian enrichment of the component of lower surface tension in the surface phase, σ^E is negative for most binary mixtures of non-polar, small sized or non-associated compounds. In this case, since n-pentane is non-polar, then enrichment of the surface phase with n-pentane produce a negative σ^E value.

Figure 1 also shows excess diamagnetic susceptibilities over the whole concentration range. The breaking of hydrogen bonds in the methylacetate molecule causes a positive χ^E value. The methylacetate has a high polarizability and when mixed with n-pentane there arises an induced dipole interaction which as expected, gives rise to positive deviations in χ , which produce a positive χ^E value.

A possible association with n-pentane would give negative values of χ^E and this deviation is not observed in this case. Gopalakrishnan [15] reported positive χ^E values in mixtures of alcohols with triethylamine, as did Riggio et al. [16] in mixtures of methylisobutylketone with alcohols.

We conclude that in this system, dispersion forces are dominant between both molecules.

We now applied the method of UNIFAC to calculate G^E and H^E [17–19] to compare with experimental data.

According to the UNIFAC model

$$G^E/RT = \sum x_i (\ln \gamma_i^C + \ln \gamma_i^R) \quad (12)$$

where γ_i^C is the combinatorial activity coefficient and γ_i^R is the residual coefficient, in this case the most important. Using R_k , Q_k and a_{mn} parameters [18] in Tables 5 and 6, it is possible to obtain G^E from eqn. (12).

Since the combinatorial activity coefficients do not depend upon temperature, only a residual part enters into the calculation of the excess enthalpy. The resulting expression for H^E [19] is given by the equation

$$H^E = -RT \sum_i \sum_k x_i \nu_k^{(i)} \left[T \left(\frac{\partial \ln \Gamma_k}{\partial T} \right)_{P,x} - T \left(\frac{\partial \ln \Gamma_k^{(i)}}{\partial T} \right)_{P,x} \right] \quad (13)$$

The group interaction parameters to calculate H^E are listed in Table 7 and are taken from ref. [19].

TABLE 5

Group volume and surface parameters

Sub-group	R_k	Q_k
CH ₃	0.9011	0.848
CH ₂	0.6744	0.540
CH ₃ COO	1.9031	1.728

TABLE 6

Group interaction parameters

<i>n</i>	<i>m</i>		
	CH ₃	CH ₂	CH ₃ COO
CH ₃	0	0	232.1
CH ₂	0	0	232.1
CH ₃ COO	114.8	114.8	0

TABLE 7

Group interaction parameters for excess enthalpy

<i>n</i>	<i>m</i>		
	CH ₃	CH ₂	CH ₃ COO
CH ₃	0	0	521.3
CH ₂	0	0	521.3
CH ₃ COO	234.0	234.0	0

The values obtained (calculated with a VAX 11/780 computer) for G_U^E and H_U^E at the same experimental mole fractions are plotted in Fig. 2 showing a good agreement with experimental work.

ACKNOWLEDGMENTS

We are grateful to Ing. M.R. Cesca for aid in computer programming. This work was financed by a CONICET (PID) and CIUNT grant.

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