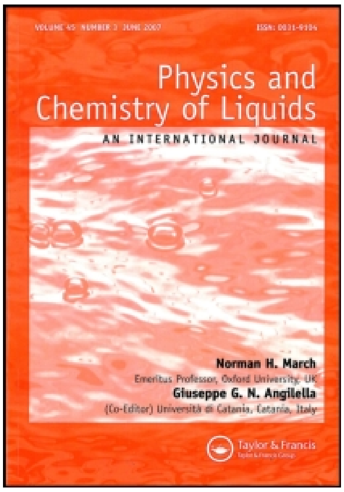

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EXCESS THERMODYNAMIC FUNCTIONS OF *n*-HEXANE + TOLUENE: APPLICATION OF FLORY'S THEORY

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Excess internal pressure, cohesive energy density, isothermal compressibility, heat capacity and volumes of the binary system *n*-hexane + toluene have been determined at 298.15 and 313.15 K. Using the excess volume data, other excess properties have been predicted on the basis of the statistical thermodynamical theory due to Flory. The theory provides a reasonable correlation of the results.

KEY WORDS: Excess thermodynamic functions, Flory's theory.

INTRODUCTION

A majority of liquid mixtures show deviations from ideal behaviour: a consequence of intercomponent interactions. It has become customary to represent quantitatively the departure of a real binary system from ideal behaviour by means of the excess thermodynamic functions. In continuation of our work on thermodynamic study of binary liquid mixtures[1–7], we report here the excess thermodynamic functions for the binary system *n*-hexane + toluene at 298.15 and 313.15 K and at three representative concentrations ($X_2 = 0.25$, 0.50 and 0.75). The results are discussed in the light of Flory's theory[8].

EXPERIMENTAL

Ultrasonic velocity (u) in liquids and binary solutions was determined using a single-crystal variable-path interferometer working at 3 MHz. For an accurate determination the errors due to diffraction[9] were taken into account. The diffraction free ultrasonic velocities are accurate to $\pm 0.01\%$. Densities of pure liquids (ρ) were determined using a bicapillary pycknometer with an accuracy of 2 in 10^5. Heat capacities (Cp) of pure liquids and solutions were measured by a Calorimetric method[10] with slight modifications and the reproducibility is within ±0.3%. Using the diffraction free velocity, heat capacities and densities, the isothermal compressibility (K_T) was evaluated through the relation:

$$K_T = 1/u^2\rho + TV\alpha^2/C_P \tag{1}$$

where V is the molar volume. The isothermal compressibilities are accurate to ±0.15%. Excess volumes were measured using a continuous dilution dilatometer similar in design to that of Stokes *et al.*[11] with slight modifications and these values are accurate to $\pm 0.001\ \text{cm}^3\text{mol}^{-1}$. The details of the technique were published elsewhere[12].

AR grade *n*-hexane and toluene were purified according to the standard procedures[13]. Densities of the final products are 0.65531 and 0.86220 gm cm^{-3} for *n*-hexane and toluene respectively at 298.15 K. These values are in good agreement with literature values[14].

Method of determining the excess functions

The excess isothermal compressibilities K_T^E were determined through the relation:

$$K_T^E = K_T - K_{T_0} = K_T - (y_1K_{T_1} + y_2K_{T_2}) \tag{2}$$

where y_1 and y_2 are the volume fractions of components 1 and 2 respectively.

The energy–volume coefficient (internal pressure) π of a system can be related to the thermal pressure coefficient by the following equation

$$\pi = T(\delta P/\delta T)_V - P$$

or

$$\pi = T\alpha/K_T - P \tag{3}$$

which is often called the thermodynamic equation of state. For most systems $T\alpha/K_T$ is very much greater than the external pressure P. The excess energy volume coefficient is derived from the expression

$$\pi^E = \pi - \pi_0 = T\frac{\alpha}{K_T} - T\left\{\frac{y_1\alpha_1 + y_2\alpha_2}{y_1K_{T_1} + y_2K_{T_2}}\right\} \tag{4}$$

The internal pressure is related to the cohesive energy density ($\Delta U_v/V$) by

$$\pi = n(\Delta U_v/V) \tag{5}$$

where ΔU_v is the energy of vaporization of the mixture to the perfect gas state, and n is an empirical parameter.

The energy of vaporization of a real mixture to the perfect gas state can be calculated using the relation

$$\Delta U_v = X_1H_{v_1} + X_2H_{v_2} - H^E - RT \tag{6}$$

where H_{v_1} and H_{v_2} are the enthalpies of vaporization of components 1 and 2 respectively. The values for H_{v_1}, H_{v_2} and H^E are taken from the literature[15,16].

By definition, ideal mixing occurs with no change in the enthalpy of the system. Thus, the energy of vaporization for the ideal mixture is given by the following equation

$$\Delta U_v^{id} = X_1 H_{V_1} + X_2 H_{V_2} - RT \tag{7}$$

Division of ΔU_v^{id} by the molar volume of the ideal mixture yields the cohesive energy density of the system.

It has been suggested by Macdonald and his co-workers[17–19] that the ratio of internal pressure to the cohesive energy density is a useful indication of the extent of strength of intermolecular interactions in a liquid mixture. Accordingly, the ratio for a real mixture can be obtained from Eq. 5.

Flory's theory

The statistical thermodynamical theory of binary liquid mixtures, developed by Flory and co-workers[8], has been extensively used to predict the excess thermodynamic functions of mixing for several binary systems with non-polar or slightly polar molecule.

The reduced volume $\tilde{v}_i$ of a liquid is defined by the relation[8]

$$(\tilde{v}_i^{1/3} - 1) = \frac{\alpha T}{3}(1 + \alpha T)^{-1} \tag{8}$$

The reduced volume $\tilde{v}$ of the mixture can be determined from any one of the excess functions. When determined on the basis of V^E, the reduced volume $\tilde{v}$ is given by

$$\tilde{v} = \phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2 + \tilde{v}^E \tag{9}$$

where ϕ_1 and ϕ_2 are segment fractions of the components and $\tilde{v}^E$ is the excess reduced volume of the mixture obtained from the relation:

$$\tilde{v}^E = V^E/(X_1 V_1^* + X_2 V_2^*) \tag{10}$$

V_1^* and V_2^* are the characteristic volumes of the component liquids. The value of $\tilde{v}$ thus obtained is used to evaluate other excess functions. Excess enthalpy and isothermal compressibilities of the mixture are evaluated through the following relations[7,8].

$$H^E = X_1 V_1^* P_1^*(1/\tilde{v}_1 - 1/\tilde{v}) + X_2 V_2^* P_2^*(1/\tilde{v}_2 - 1/\tilde{v}) + (X_1 V_1^* \theta_2 X_{12})\tilde{v} \tag{11}$$

$$K_T^E = \frac{3\tilde{v}^2(\tilde{v}^{1/3} - 1)}{P^*[1 - 3(\tilde{v}^{1/3} - 1)]} - \{\tfrac{1}{3}(\phi_1 \tilde{v}_1 K_{T_1} + \phi_2 \tilde{v}_2 K_{T_2})\} \tag{12}$$

Excess internal pressure

The equation for internal pressure of the binary mixture[20] in terms of $\tilde{v}$ and P^* can be derived as

$$\pi = P^*/\tilde{v}^2 \tag{13}$$

Hence, the internal pressure can be obtained from P^* and $\tilde{v}$ of the solution directly. The excess internal pressures are evaluated from the following equation

$$\pi^E = \pi - \pi_0 = (P^*/\tilde{v}^2) - \left[\frac{y_1\alpha_1 + y_2\alpha_2}{y_1K_{T_1} + y_2K_{T_2}}\right] \tag{14}$$

Excess cohesive energy density

The excess cohesive energy densities are derived from the expression

$$(\Delta U_v/V)^E = (\Delta U_v/V) - (\Delta U_v^{id}/V_{id}) \tag{15}$$

The excess enthalpies derived from Eq. (11) are used to evaluate the enthalpy of vaporization of the system.

RESULTS AND DISCUSSION

The results of our measurements on pure liquids and solutions are presented in Tables 1 and 2 respectively. The excess thermodynamic functions H^E, K_T^E, π^E and $(\Delta U_v/V)^E$ determined from the experimental results and the predictions of Flory's theory are presented in Table 3.

The excess volumes of the present system were studied previously by Ghai and Dullien[21], Mathieson and Thynne[22], Thacker and Rowlinson[23] and Letcher[24] at 298.15 K. In view of their discrepancies in their measurements, the excess volumes were redetermined throughout the concentration range using a continuous dilution dilatometer. The results of our measurements on excess volumes, summarized by the following equations:

$$\begin{aligned} V^E &= X_1X_2[-0.1326 - 0.0409(X_2 - X_1) + 0.0083(X_2 - X_1)^2] \\ &= X_1X_2[-0.1801 - 0.0555(X_2 - X_1) + 0.0113(X_2 - X_1)^2] \end{aligned} \tag{16}$$

at 298.15 and 313.15 K respectively, are plotted in Figure 1. The results of Letcher[24] are in good agreement with the results of the present study. The results also indicate that the temperature dependence of excess volumes is not significant.

The excess functions π^E, $(\Delta U_v/V)^E$, K_T^E, H^E, V^E for this system reflected truly their dependence on concentration and temperature (please see Table 3). The excess functions derived from Flory's theory also have similar dependence on concentration and temperature. The excess functions for this system are moderate thereby indicating correspondingly the strength of intermolecular interactions. The interaction energy term X_{12} of Flory's theory, which is moderate for this system, also indicates that the strength of the intermolecular interactions is moderate. The experimental excess functions are reasonably in good agreement with those of the values derived from Flory's theory.

Flory's theory is quite successful in predicting the excess functions for the system n-hexane + toluene. Prediction of excess internal pressures and cohesive energy densities apart from other constant pressure excess functions is an extension of the previous tests of Flory's theory.

Table 1 Properties of pure liquids.

Property *Liquid*	T (K)	u $(m\ s^{-1})$	V $(cm^3\ mol^{-1})$	C_p $(J\ mol^{-1}\ K^{-1})$	$\alpha \times 10^3$ (K^{-1})	$K_T \times 10^6$ (bar^{-1})	π (bar)	$(\Delta U_v/V)$ (bar)	n
n-hexane	298.15	1078.9	131.510	198.0	1.387	169.19	2444	2423	1.009
	313.15	1010.9	134.218	200.6	1.428	195.13	2292	—	—
toluene	298.15	1303.7	106.866	156.5	1.067	91.42	3480	3592	0.968
	313.15	1240.2	108.651	161.9	1.094	101.82	3365	—	—

Table 2 Properties of the systems: *n*-hexane + toluene.

T (K)	X_2	u $(m\ s^{-1})$	V $(cm^3\ mol^{-1})$	C_p $(J\ mol^{-1}\ K^{-1})$	$\alpha \times 10^3$ (K^{-1})	$K_T \times 10^6$ (bar^{-1})	π (bar)	$(\Delta U_v/V)$ (bar)	n	X_{12} $(J\ cm^{-3})$
298.15	0.2502	1120.4	125.328	186.8	1.310	152.57	2635	2444	1.078	18.90
	0.5001	1170.8	119.155	175.3	1.236	128.45	2869	2699	1.063	19.79
	0.7498	1228.2	112.999	166.2	1.154	109.63	3139	3000	1.046	20.88
313.15	0.2502	1054.2	127.803	212.1	1.352	165.66	2555	—	—	18.69
	0.5001	1095.7	121.387	194.4	1.270	144.93	2745	—		19.16
	0.7498	1154.8	115.011	178.4	1.184	123.48	3003	—		20.71

Table 3 Excess properties of the system: *n*-hexane + toluene.

T (K)	X_2	V^E ($cm^3\ mol^{-1}$)	H^E ($J\ mol^{-1}$)		$K_T^E \times 10^6$ (bar^{-1})		π^E (bar)		$(\Delta U_v/V)^E$ (bar)		C_P^E ($J\ mol^{-1}\ K^{-1}$)
		exp.	*exp.*	*Flory*	*exp.*	*Flory*	*exp.*	*Flory*	*exp.*	*Flory*	*exp.*
298.15	0.2502	−0.0206	360	332	−4.4	−4.4	57	62	−29	−26	−1.0
	0.5001	−0.0332	460	474	−5.9	−6.2	109	110	−38	−39	−1.6
	0.7498	−0.0283	340	385	−4.9	−4.4	106	113	−29	−33	−0.9
313.15	0.2502	−0.0280	—	331	−5.3	−4.7	70	63	—	—	−0.7
	0.5001	−0.0450	—	463	−5.8	−6.5	82	94	—	—	−1.4
	0.7498	−0.0384	—	386	−4.5	−5.0	76	84	—	—	−0.5

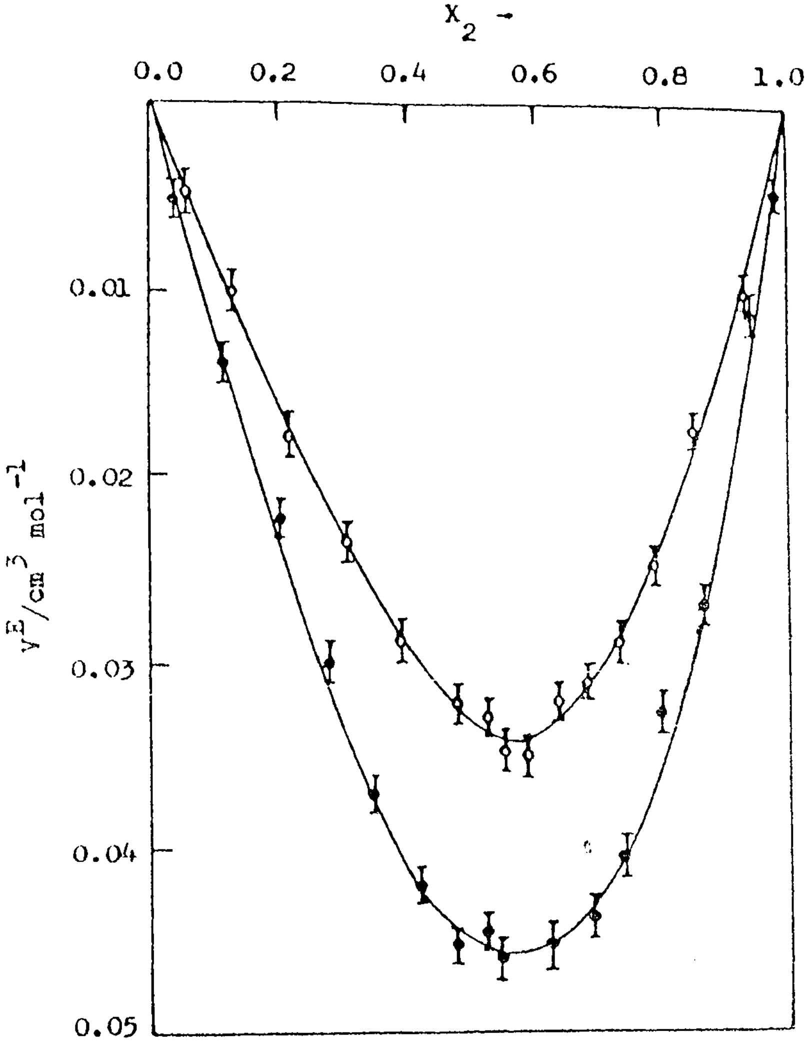

Figure 1 Excess volumes of the system: *n*-hexane + toluene, solid line—least square fit, ○—25°C, ●—40°C.

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