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THERMODYNAMIC PROPERTIES OF BINARY AND TERNARY SYSTEMS. VAPOUR–LIQUID EQUILIBRIUM DATA IN THE TRIETHYLAMINE + TOLUENE SYSTEM

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ABSTRACT

The vapour pressures of the triethylamine – toluene system have been measured by a static method at several temperatures between 293 and 333 K. The isothermal results at 293.15, 303.15, 313.15, 323.15 and 333.15 K were used to obtain the parameters for the van Laar activity coefficient equation. The parameters for the van Laar equation were determined by taking into account the correlation between the mean excess enthalpies, calculated from the temperature dependence of the excess Gibbs energies, and the experimental excess enthalpies at 303.15 K. The excess energies and excess enthalpies are positive over the whole composition range. The thermodynamic excess functions are compared with those for the triethylamine + benzene and triethylamine + mesitylene systems.

INTRODUCTION

The isothermal total vapour pressures for triethylamine + benzene within the temperature range 293–333 K have been determined earlier by Siedler et al. [1]. This work continues the study on the thermodynamic excess functions of binary and ternary mixtures with triethylamine as one component [2–5]. The results on the volume and heat of mixing behaviour for triethylamine(2) + toluene(3) mixtures have been reported elsewhere [4]. The present communication reports the isothermal vapour pressure data for the triethylamine(2) + toluene(3) system calculated by the van Laar equation, which was found to be more suitable than NRTL or Wilson equations according to earlier studies [2].

EXPERIMENTAL

Materials

Triethylamine (Fluka AG, puriss., p.a.) was shaken for about 12 h with a mixture of calcium oxide and potassium hydroxide [6]. The liquid was then distilled in the presence of freshly activated molecular sieves (British Drug Houses Ltd., type 4A). Distilled triethylamine was stored in the dark. Toluene (Fluka AG, puriss., p.a.) was distilled at atmospheric pressure through a Vigreux column and then passed through an aluminium oxide column (Fluka AG, chromatography, basic, activity I). The purified solvent was stored over molecular sieves (British Drug Houses Ltd., type 4A). The values of the physical properties of the purified chemicals were the same as before [4].

Instrumental

The total vapour pressures were measured between 293 and 333 K at about 5 K intervals by a static method described in detail elsewhere [2,7–8]. The difference between the vapour pressure of water used as a reference liquid and that of the pure component or mixture was measured with a large-diameter mercury manometer [9]. Before each experimental run the mixing cell was evacuated to below 1×10^{-2} mmHg and the dissolved gases were removed from the mixture and reference liquid as described earlier [2]. The mercury levels in both arms of the U-shaped manometer were read by a cathetometer (KM-9, Leningrad United Optical Mechanical Enterprises) to the nearest 0.001 mm. All manometer readings were corrected for gravity and temperature [10]. A correction for the difference in composition of the liquid and vapour phases was applied to the concentrations of the liquid phase [2]. The accuracy of the final liquid phase mole fractions was estimated to be $\pm 1 \times 10^{-4}$.

The temperature of the water bath, where the vapour pressure apparatus was immersed, was measured with a digital thermometer (Lauda R 42/2, Messgeräteverk Lauda) with an accuracy of ± 0.01 K. Temperature variations of this magnitude result in an uncertainty of vapour pressures of approximately 0.02 kPa, for the system studied. The experimental vapour pressures observed for the mixture were smoothed as a function of temperature by fitting Antoine's equation to them.

All the regression analyses were carried out on a Univac 1100/22 computer.

RESULTS AND DISCUSSION

The vapour pressures of triethylamine and toluene were measured at nine temperatures ranging from 273 to 333 K. To interpolate between the points the Antoine equation was used

$$\ln(P/\text{kPa}) = 14.7795 - 3356.5717/(T/\text{K} - 31.3964) \qquad (1)$$

which was derived from the equilibrium data for triethylamine by the

TABLE 1

Isothermal vapour pressures at different temperatures for the triethylamine(2) + toluene(3) system

293.15 K		303.15 K		313.15 K		323.15 K		333.15 K	
x_2	P(kPa)	x_2	P(kPa)	x_2	P(kPa)	x_2	P(kPa)	x_2	P(kPa)
0	2.978	0	4.933	0	7.913	0	12.326	0	18.524
0.0779	3.30	0.0778	5.55	0.0777	9.03	0.0776	14.25	0.0774	21.89
0.1585	4.58	0.1584	6.99	0.1583	10.57	0.1582	15.83	0.1580	23.49
0.2514	4.39	0.2514	7.07	0.2513	11.06	0.2511	16.86	0.2509	25.09
0.3431	4.76	0.3430	7.64	0.3429	11.93	0.3427	18.14	0.3425	26.95
0.4004	5.12	0.4003	8.16	0.4002	12.68	0.4000	19.23	0.3998	28.53
0.4837	5.11	0.4836	8.30	0.4835	13.03	0.4833	19.84	0.4831	29.36
0.5475	5.75	0.5474	9.09	0.5473	14.01	0.5471	21.08	0.5468	31.05
0.6338	6.07	0.6337	9.58	0.6336	14.73	0.6334	22.13	0.6332	32.55
0.7410	6.14	0.7409	9.94	0.7408	15.52	0.7406	23.47	0.7404	34.48
0.8700	6.68	0.8700	10.66	0.8699	16.49	0.8698	24.82	0.8697	36.41
1	7.072	1	11.336	1	17.573	1	26.435	1	38.705

TABLE 2

Molar volumes V_i^* of pure liquids and the second virial coefficients B_{ii} and B_{ij}

T(K)	$C_6H_{15}N$			C_7H_8	
	V_2^* (cm^3 mol^{-1})	$-B_{22}$ (cm^3 mol^{-1})	$-B_{23}$ (cm^3 mol^{-1})	V_3^* (cm^3 mol^{-1})	$-B_{33}$ (cm^3 mol^{-1})
293.15	139.15	2477	2546	106.31	2610
303.15	140.94	2235	2286	107.45	2330
313.15	142.80	2031	2070	108.63	2100
323.15	144.73	1859	1888	109.86	1909
333.15	146.70 [a]	1710	1733	111.12 [a]	1747

[a] Extrapolated value.

method of least squares. For the vapour pressures of toluene the following equation was obtained for the temperature interval studied

$$\ln(P/\text{kPa}) = 16.3920 - 4485.3998(T/\text{K})^{-1} \tag{2}$$

The values calculated using eqns. (1) and (2) are in good agreement with those reported in the literature [11–14]. The vapour pressures of pure components and those of the binary mixture are listed in Table 1 along with the liquid mole fractions. The binary mixture vapour pressure data were fitted to the van Laar equation of fourth order [15]. The technique used for the data fitting was basically that described by Prausnitz et al. [16] in which vapour-phase nonidealities were determined from the virial equation, truncated after the second term. The liquid molar volumes of the pure components reported earlier, as well as the second virial coefficients calculated according to the method of Hayden and O'Connell are listed in Table 2 [4,17]. The critical properties and the acentric factors needed for the calculation of the virial coefficients were obtained from the literature [16]. The nonlinear regression routine was used to determine the parameters of the van Laar equation by minimizing the objective function

$$S = \sum_{i=1}^{N} \left(\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{calc}}} \right)^2 \tag{3}$$

where P_{exp} and P_{calc} are the experimental and calculated values of the total vapour pressure for mixture i, respectively, and N is the number of experimental points in the range $0 < x_2 < 1$.

Since even a small error in the vapour–liquid data will lead to erroneous excess Gibbs energies (G^E) and, further, to an erroneous dependence of the G^E values on temperature, the calculated excess enthalpies by using the Gibbs–Helmholtz equation will often deviate considerably from the experimental ones. In the present work the dependence of G^E values on temperature was corrected by the following equation

$$G^E = H^E - TS^E \tag{4}$$

TABLE 3

Parameters of the van Laar equation and standard deviations at different temperatures for the triethylamine(2)+toluene(3) system

T (K)	A_{23}	A_{32}	D_{23}	Standard deviation ($\times 10^2$) [a]
293.15	0.2091	0.0721	−0.2141	5.64
303.15	0.2051	0.0694	−0.2189	3.13
313.15	0.2012	0.0670	−0.2243	1.75
323.15	0.1973	0.0646	−0.2305	1.35
333.15	0.1941	0.0624	−0.2357	1.27

[a] The standard deviation of the fit $\{1/N \sum_{i=1}^{N} [(P_{exp} - P_{calc})/P_{calc}]^2\}^{1/2}$, where N is the number of experimental points in the range $0 < x_2 < 1$.

and the experimental excess enthalpies at 303.15 K by the method described elsewhere [2]. This procedure is justified by the very weak dependence of H^E on temperature in the triethylamine(2) + toluene(3) system [4]. The parameter values and the respective values of standard deviations are presented in Table 3.

The total vapour pressure isotherms given at 293.15, 303.15, 313.15, 323.15 and 333.15 K in Fig. 1 show that the triethylamine(2) + toluene(3) mixture behaves like an ideal system. Only a small positive departure from ideality is shown.

Figure 2 shows the values of G^E, H^E and TS^E at 303.15 K. The excess enthalpies for the triethylamine(2) + toluene(3) system have been determined before at 293.15, 303.15 and 313.15 K [4]. A comparison of the G^E values of

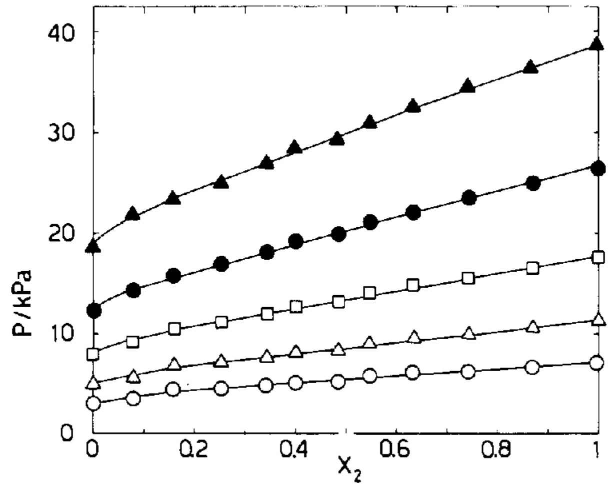

Fig. 1. Experimental vapour pressures of triethylamine(2)+toluene(3) at 293.15 (○), 303.15 (△), 313.15 (□), 323.15 (●) and 333.15 K (▲). The solid lines are vapour pressures calculated in accordance with the van Laar equation.

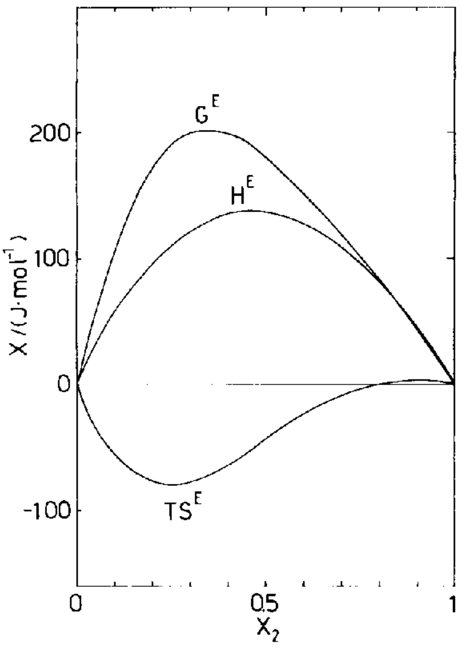

Fig. 2. Thermodynamic excess functions of triethylamine(2) + toluene(3) at 303.15 K calculated according to the van Laar equation.

this work with those for triethylamine(2) + benzene(3) and triethylamine(2) + mesitylene(3) systems shows that the G^E values increase with the increasing basicity of the aromatic components [1,18]. The excess entropies shown as a TS^E curve are small and in practice negative and the TS^E curve at 303.15 K nearly coincides with that of the triethylamine(2) + mesitylene(3) system.

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