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## Thermodynamic Properties of Alcohol–Amine Mixtures: Excess Enthalpies of Methanol–Triethylamine and Ethanol–Triethylamine

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**Molar excess enthalpies have been measured for methanol–triethylamine and ethanol–triethylamine at 298.15 K using a Larkin–McGlashan calorimeter. The results are compared with earlier calorimetric measurements and with molar excess enthalpies obtained from isothermal liquid–gas equilibrium studies. For these systems at 298 K, the molar excess Gibbs functions are positive and the molar excess enthalpies and molar excess entropies negative.**

There have been several thermodynamic studies of alcohol–amine, liquid and liquid–gas systems: isothermal and isobaric liquid–gas equilibrium (2–4, 8, 14), calorimetric (6, 15, 17), volumetric (4, 16, 17). The alcohol–amine complex formation has been investigated in "inert" solvents (9, 17) and in the gas phase (12). References to a few spectroscopic studies can be found in the literature cited. While most of this work has been associated with azeotrope formation, some has been concerned primarily with the analysis of the experimental results in terms of intermolecular interactions. In the belief that alcohol systems "... may be more immediately amenable to detailed theoretical analysis," Copp and Everett (3) included alcohol–amine mixtures in their thermodynamic study of critical phenomena in H<sub>2</sub>O–amine mixtures.

Chun and Davison (2) measured the vapor pressures of methanol–triethylamine and ethanol–triethylamine at a number of temperatures in the range 283–313 K. From their results they obtained molar excess Gibbs functions  $G_m^E$  at each of the temperatures studied, and the molar excess enthalpies  $H_m^E$  [ $= -\partial(G_m^E/T)/\partial(1/T)$ ] and molar excess entropies  $S_m^E$  [ $= (H_m^E - G_m^E)/T$ ] at 298 K. The  $H_m^E$  results obtained by differentiation are in considerable disagreement with earlier calorimetric work (6). Given this discrepancy and the appreciable uncertainties in published  $H_m^E$  results for methanol–triethylamine and ethanol–triethylamine, we have measured  $H_m^E$  for these systems using a calorimeter and carefully purified materials.

### Experimental Section

**Purification of Materials.** In our studies of triethylamine mixtures we have attempted to ensure the removal of CO<sub>2</sub> from the pure liquids by careful degassing.

Triethylamine (B.D.H., Laboratory Reagent) was refluxed over KOH pellets, distilled from KOH, and then fractionally distilled in a column of 15 theoretical plates at a reflux ratio of 20. During

these steps, dry, oxygen-free nitrogen was passed through the apparatus and light was excluded. The middle fraction was dried over freshly activated molecular sieve and degassed using the vacuum sublimation apparatus described by Bell et al. (1) and then by successive freezing (using dry ice–acetone), pumping, distillation cycles. The degassed liquid was finally distilled under vacuum into ampoules which were stored in the dark. During use, the material was stored over mercury out of contact with air and in the dark. It has been found (7) that the vapor pressure of a sample of triethylamine prepared in this way did not change when successive amounts of material were distilled from it. Methanol (Mallinckrodt, Spectrar) and ethanol (B.D.H., Aristar) were dried, degassed, and stored as in the case of triethylamine. Normal hexane (Phillips Petroleum, research grade) and cyclohexane (Phillips Petroleum, research grade), for use in testing the calorimeter, were dried over freshly activated molecular sieve, degassed by vacuum sublimation (1), and stored as in the case of triethylamine.

High amplification NMR studies of all materials indicated no proton-containing impurities.

**Calorimeter.** This was based on the design used by Larkin and McGlashan (10) and has been discussed elsewhere (5). Recent modifications include the use of a crystal oscillator timer (Forth Instruments Ltd., Model 112) and, following Morcom and Travers (13), instead of evacuating the vacuum jacket, the mixing vessel was placed in a polystyrene enclosure which was fitted into the "vacuum" jacket. The experimental procedure has been discussed previously (5).

Following the recommendation of the IUPAC Commission on

**Table I. Molar Excess Enthalpies  $H_m^E$  of Methanol–Triethylamine and Ethanol–Triethylamine at 298.15 K**

Methanol–triethylamine		Ethanol–triethylamine	
<i>x</i>	$H_m^E$ , J mol <sup>-1</sup>	<i>x</i>	$H_m^E$ , J mol <sup>-1</sup>
0.0633	-711	0.0401	-341
0.1449	-1399	0.1252	-861
0.2065	-1676	0.2232	-1219
0.3783	-2000	0.3099	-1381
0.4062	-1965	0.4035	-1415
0.4837	-1932	0.5167	-1322
0.6073	-1604	0.6645	-1012
0.7051	-1278	0.7318	-849
0.8327	-761	0.9145	-289

**Table II. Least-Squares Parameters  $h_n$ , Their Standard Deviations, and the Standard Deviations  $\sigma$  in the Molar Excess Enthalpies**

	$h_0$ , kJ mol <sup>-1</sup>	$h_1$ , kJ mol <sup>-1</sup>	$h_2$ , kJ mol <sup>-1</sup>	$h_3$ , kJ mol <sup>-1</sup>	$\sigma$ , J mol <sup>-1</sup>
	<i>n</i> -C <sub>6</sub> H <sub>14</sub> -C-C <sub>6</sub> H <sub>12</sub>				
This work	$(864 \pm 3) \times 10^{-3}$	$-(264 \pm 6) \times 10^{-3}$	$(92 \pm 16) \times 10^{-3}$		1.5
McGlashan-Stoeckli (17)	$866.10 \times 10^{-3}$	$-249.4 \times 10^{-3}$	$97.0 \times 10^{-3}$	$-31.8 \times 10^{-3}$	1.1
	Methanol-Triethylamine				
This work	$-7.48 \pm 0.05$	$-3.93 \pm 0.11$	$-1.52 \pm 0.25$		23
Nakanishi et al. (15)	$-7.55 \pm 0.12$	$-4.03 \pm 0.37$			78
	Ethanol-Triethylamine				
This work	$-5.34 \pm 0.02$	$-2.65 \pm 0.04$	$-0.87 \pm 0.10$		9
Findlay (6)	$-6.08 \pm 0.09$	$-2.82 \pm 0.25$			69

**Table III. Molar Excess Properties of Methanol-Triethylamine and Ethanol-Triethylamine at 298.15 K**

<i>x</i>	Methanol-Triethylamine			Ethanol-Triethylamine		
	$G_m^E$ , J mol <sup>-1</sup>	$H_m^E$ , J mol <sup>-1</sup>	$TS_m^E$ , J mol <sup>-1</sup>	$G_m^E$ , J mol <sup>-1</sup>	$H_m^E$ , J mol <sup>-1</sup>	$TS_m^E$ , J mol <sup>-1</sup>
0.1	14	-1044	-1058	47	-722	-769
0.2	63	-1663	-1726	110	-1159	-1269
0.3	129	-1953	-2082	176	-1374	-1550
0.4	193	-1999	-2192	197	-1418	-1615
0.5	241	-1871	-2112	277	-1336	-1613
0.6	262	-1622	-1884	298	-1164	-1462
0.7	253	-1292	-1545	291	-929	-1220
0.8	211	-908	-1119	250	-651	-901
0.9	131	-478	-609	162	-341	-503

Thermodynamics and Thermochemistry, *n*-C<sub>6</sub>H<sub>14</sub>-C-C<sub>6</sub>H<sub>12</sub> was used to test the calorimeter. The least-squares parameters from our results at 298.15 K are compared with those of McGlashan and Stoeckli (17) in Table II.

### Results

The molar excess enthalpies  $H_m^E$  of methanol-triethylamine and ethanol-triethylamine at 298.15 K are given in Table I, in which *x* is the mole fraction of triethylamine. The results were fitted to the equation:

$$H_m^E = x(1-x) \sum_{n=0}^m h_n(1-2x)^n \quad (1)$$

In Table II are given the parameters  $h_n$ , their standard deviations, and the standard deviations,  $\sigma$ , of the molar excess enthalpies defined by,

$$\sigma^2 = \sum \delta^2 / (p - m) \quad (2)$$

where  $\delta$  is the deviation of the calculated  $H_m^E$  from the experimental  $H_m^E$ , *p* is the number of measurements, and *m* the number of parameters.

Our  $H_m^E$  results are compared with some earlier calorimetric studies in Table II; the number of parameters  $h_n$  is that corresponding to the minimum  $\sigma$ . While our results for methanol-triethylamine are within experimental error of those of Nakanishi et al. (15), the uncertainties in the latter are considerable. The three measurements reported by Findlay (6) for this system at 298.15 K scatter by up to 10% from our results. As can be seen in Table II, for ethanol-triethylamine at 298.15 K the molar excess enthalpies obtained by Findlay (6) are considerably more negative (exothermic) than ours over the entire mole fraction range.

For  $x \geq 0.5$  the agreement between our molar excess enthalpies and those obtained by differentiation of the  $G_m^E$  results of Chun et al. (2) is excellent for both methanol-triethylamine

and ethanol-triethylamine. Over the rest of the mole fraction range, however, our results for both systems are more negative, with the maximum differences being about 200 J mol<sup>-1</sup> at  $x \approx 0.3$  for methanol-triethylamine and 300 J mol<sup>-1</sup> at  $x \approx 0.2$  for ethanol-triethylamine.

### Discussion

The  $H_m^E$  values for various mole fractions, obtained from our results using the  $h_n$  parameters given in Table II, together with  $G_m^E$  from Chun and Davison (2) and  $TS_m^E$  ( $= H_m^E - G_m^E$ ) are given in Table III. (Again, *x* represents the mole fraction of triethylamine.) For both systems at 298.15 K,  $G_m^E > 0$  and  $TS_m^E < H_m^E < 0$ . At lower temperatures  $G_m^E$  for methanol-triethylamine becomes negative over part of the mole fraction range (2). Negative values of  $G_m^E$  have been reported for other alcohol-amine systems (3, 15) but in all cases studied  $H_m^E$ ,  $TS_m^E$ , and the molar excess volumes  $V_m^E$  (4, 16, 17) are negative.

Qualitatively our  $H_m^E$  results can be interpreted as the sum of two contributions: an asymmetric, positive (endothermic) contribution, with a maximum in the alcohol-rich mole fraction range, arising from the breaking of the alcohol self-association upon the addition of triethylamine, and an approximately symmetric, negative (exothermic) contribution arising from 1:1 complex formation between the alcohol and triethylamine. The latter has been studied in dilute solution (9, 17) and in the gas phase (12). The complexity of the intermolecular interactions in alcohol-amine mixtures precludes a more quantitative discussion.

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