Enthalpies of Mixing of Ethanol and Water at 25° C.

J. A. BOYNE and A. G. WILLIAMSON

Department of Chemistry, Otago University, Dunedin, N.Z.

New measurements of the enthalpies of mixing of ethanol and water at 25° C. are reported. The data are in excellent agreement with the results of Lama and Lu and confirm the unusual shape of the enthalpy of mixing vs. composition curve for this system.

IN A RECENT paper, Lama and Lu (2) reported enthalpies of mixing of a series of alcohols with water. The rather unusual shape of the curve of $\Delta_m H vs$. mole fraction given by these workers for ethanol and water at 25° C. is confirmed by the present data shown in Figure 1 and Table I. These data, which the authors believe to be accurate to better than $\pm 2\%$, agree very well with those of Lama and Lu except in the region of the minimum where the present work appears to define the curve more accurately. Table II gives the parameters in the equation

$$-H^{E}/J \text{ mole}^{-1} = x(1-x) \sum_{n=0}^{5} B(n)(1-2x)^{n}$$
 (1)

fitted by the method of least squares to our data and to those of Lama and Lu. Also shown are the 95% confidence limits for each parameter and the standard deviations for each set of data. These figures show that the authors' data appear to be slightly more precise than those of Lama and Lu although there is very little difference between the final least squares curves through the two sets of data. The solid line in Figure 1 is the curve for Equation 1 fitted to the authors' data.

Table I. Enthalpies	of Mixing o	f Ethanol	and Water	at 25° C
---------------------	-------------	-----------	-----------	----------

X (Ethanol)	-H/J Mole ⁻¹ , Exptl.	-H/J Mole ⁻¹ , Equation 1
0.077	594	605
0.130	761	756
0.157	789	782
0.176	782	785
0.198	782	777
0.226	752	753
0.268	703	700
0.267	704	702
0.287	668	672
0.373	532	542
0.409	488	494
0.457	448	437
0.609	322	316
0.746	232	243
0.818	205	202
0.840	191	188
0.894	145	145

Table II. Parameters in Equation 1

	This Work	Lama and Lu
B(0) B(1) B(2) B(3) B(4) Std. dev.	$egin{array}{rlr} 1580\ \pm\ 46 \ 1785\ \pm\ 144 \ 3487\ \pm\ 424 \ 3187\ \pm\ 359 \ 1957\ \pm\ 772 \ \pm\ 7.9\ J\ \mathrm{mole}^{-1} \end{array}$	1594 ± 86 1787 ± 174 3174 ± 699 2933 ± 410 1906 ± 999 $\pm 12.3 J \text{ mole}^{-1}$



Figure 1. Heats of mixing of ethanol and water at 25°C. ▲ Lama and Lu ● This work O Bertrand et al. — Equation 1

Also shown on Figure 1 are the values of $\Delta_m H$ calculated from the partial molar heats of solution measured by Bertrand *et al.* (1) and which agree moderately well with the other data.

The calorimeter used in this work has been described in detail elsewhere (5). The two components of the mixture are contained separately under mercury in concentric bellshaped vessels and are mixed by breakage of a thin glass membrane at the top of the inner bell. Temperature changes are measured with a single thermistor in a wheatstone bridge, the off balance voltage of which is amplified using a Hewlett-Packard Model 425a amplifier and recorded on a Honeywell-Brown 0 to 1 mv. recorder. The apparatus is calibrated for each measurement by passing a measured current for a measured time through a heater of known resistance wound on the outer bell.

The ethanol was purified by a method described previously (3) and the water by the method described by Weisberger (4).

LITERATURE CITED

- Bertrand, G.L., Millero, F.J., Wu, C-h., Hepler, L.G., J. Phys. Chem. 70, 699 (1966).
- (2) Lama, R.F., Lu., B.C-Y., J. CHEM. ENG. DATA 10, 216 (1965).
- (3) McKinnon, I.R., Williamson, A.G., Australian J. Chem. 17, 1374 (1964).
- (4) Weisberger, A., "Physical Methods of Organic Chemistry," Vol. 1, p. 72, Interscience, N.Y., 1945.

(5) Williamson, A.G., Scott, R.L., J. Phys. Chem. 64, 440 (1960). RECEIVED for review December 18, 1966. Accepted February 6, 1967.