# Heats of Mixing of Normal Alcohols at 25° C.

H. D. PFLUG,[1] A. E. POPE,[2] and G. C. BENSON
Division of Pure Chemistry, National Research Council of Canada, Ottawa, Canada

**Heats of mixing of 10 binary normal alcohol systems were measured at 25° C. in an isothermal dilution calorimeter. The results are correlated with previously published data for 11 other similar systems.**

THE RESULTS of calorimetric measurements of the excess enthalpies at 25° C. for the 10 binary normal alcohol systems formed from methanol (MeOH), ethanol (EtOH), propanol (PrOH), hexanol (HxOH), and decanol (DeOH) are reported. The work is an extension of a previous investigation in which binary normal alcohol systems formed by mixing a component from the above set with either butanol (BuOH) or octanol (OcOH) were examined (*3*).

## EXPERIMENTAL

The heats of mixing were measured in an isothermally jacketed continuous dilution calorimeter similar in design to that of Savini, Winterhalter, Kovach, and Van Ness (*4*). Our version of the equipment is described by Pope *et al.* (*3*).

Basically, the calorimeter consists of a Dewar flask, initially containing one component liquid, which is connected by a tube to a reservoir containing the second component. The whole apparatus is immersed in a water thermostat controlled to within ±0.001° C. Mixing takes place in the Dewar, in the absence of any vapor space. The equilibrium (set) temperature of the contents of the Dewar (25.00° ± 0.03° C.) usually is 0.01° to 0.02° C. higher than that of the surrounding bath, because of the heating effect of the internal stirrer. During an endothermic mixing process, the set temperature is maintained within ±0.01° C. by simultaneously adding heat at a constant rate by means of an electric heater. When the dilution is temporarily discontinued, the temperature of the contents of the Dewar is restored to within ±0.0002° C. of the set value. The electric energy can be measured to ±0.05%. The concentration of the solution is obtained from the weight of the component initially placed in the Dewar, and the weight of the mercury used to displace the second component from the reservoir into the Dewar. The mole fractions are estimated to be accurate to ±0.0005.

In calculating the heat of mixing, the main correction which must be considered is the amount of electrical energy expended in warming the diluent liquid from the thermostat temperature to the set temperature within the Dewar. This may be as much as 4 joules, but usually is considerably smaller, and a satisfactory correction can be made from a knowledge of the temperature difference and the heat capacity of the liquid. Results obtained with our dilution calorimeter are in good agreement with other reliable data (*3*). In general, the over-all accuracy is estimated to be about ±1% for heat effects of the order of 100 joules per mole.

The component alcohols were checked in a Perkin-Elmer Vapor Fractometer and where necessary were purified by distillation and (or) chromatographic techniques. The purity of all the samples used for the calorimetric measurements exceeded 99.8%. Densities typical of these materials are: MeOH $0.7870_4$, EtOH $0.7850_8$, PrOH $0.7996_8$, HxOH $0.8157_2$, and DeOH $0.8268_7$ (grams per cubic centimeter at 25° C.

## RESULTS

The experimental results for the excess enthalpy ($H^E$, joules per mole) are listed in Table I. For each system, $x_1$ represents the mole fraction of the component of shorter chain length. Values of the coefficients in the equation

$$H^E = x_1 x_2 \sum_{p=0}^{n} C_p (x_2 - x_1)^p \qquad (1)$$

determined to fit the data by a least squares procedure, are given in Table II. The last column of the table lists the standard error of the estimate resulting from the use of Equation 1.

Heats of mixing of the systems MeOH-HxOH and MeOH-DeOH at 25° C. have also been measured by Díaz Peña and Fernández Martín (*1*). As in the cases of MeOH-BuOH and MeOH-OcOH compared previously (*3*), the results reported by these authors are somewhat lower than our data. For an equimolar solution the difference amounts to 12.2 joules per mole for MeOH-HxOH and 10.6 joules per mole for MeOH-DeOH.

The relative magnitudes of the heats of mixing of binary normal alcohol systems are illustrated in Figure 1, where values corresponding to the maximum of $H^E$ determined from Equation 1 are shown for 21 systems—i.e., the 10 considered in the present work along with the 11 studied previously (*3*). For convenience of presentation, points corresponding to systems with a common component of shorter chain length are joined by broken lines; in each case the abscissa is the number of carbons in the longer chain component. An analogous plot of $x_1$ values corresponding to the mole fraction at each maximum is given in Figure 2. The minor irregularities apparent in this plot are probably spurious, since location of the abscissa for the maximum of a fairly flat curve is inherently inaccurate.

The magnitude of the excess enthalpy increases as the difference in chain length of the components increases. In such cases the curves also tend to become more asymmetric and are difficult to fit with the function given in Equation 1 unless a substantial number of constants (5 or 6) is used. In this respect Equation 1 appears to be ill suited to fitting the data; use of the analogous form with volume fractions replacing mole fractions does not significantly improve the capability to fit the results. We have adopted Equation 1, since it is convenient for interpolation and is the form most frequently employed to represent excess enthalpies (*2*).

Further characterization of the excess enthalpies of binary normal alcohol systems is provided in Figure 3, where values of $(\bar{H}_i^E)^{\infty}/n_i$ are plotted against $n_j$. $(\bar{H}_i^E)^{\infty}$ is the value of the partial molal excess enthalpy in the limit as $x_i \rightarrow 0$; $n_i$ and $n_j$ are the numbers of carbon atoms in the hydrocarbon chains of the two alcohol molecules. The points in Figure 3 were obtained from plots of $H^E/x_1 x_2$ (*5*). In general, the uncertainty associated with the extrapolation

---

[1] Present address: Universität des Saarlandes, Institut für Physikalische Chemie, 66 Saarbrücken 15, Germany.

[2] Present address: British American Research and Development Co., Sheridan Park, Ontario, Canada.

## Table I. Excess Enthalpies at 25° C.

($x_1$ mole fraction of component with shorter chain length, $H^E$ joules per mole)

| MeOH-EtOH | | MeOH-PrOH | | MeOH-HxOH | | MeOH-DeOH | | EtOH-PrOH | |
|---|---|---|---|---|---|---|---|---|---|
| $x_1$ | $H^E$ | $x_1$ | $H^E$ | $x_1$ | $H^E$ | $x_1$ | $H^E$ | $x_1$ | $H^E$ |
| 0.0734 | 0.9 | 0.0319 | 7.5 | 0.0647 | 34.6 | 0.0777 | 71.3 | 0.0342 | 2.5 |
| 0.1460 | 1.7 | 0.0916 | 21.4 | 0.1467 | 78.3 | 0.2137 | 188.8 | 0.0926 | 6.1 |
| 0.2348 | 2.5 | 0.1794 | 39.8 | 0.2550 | 133.7 | 0.3654 | 309.3 | 0.1777 | 10.8 |
| 0.3167 | 3.2 | 0.2693 | 56.2 | 0.3772 | 191.2 | 0.4886 | 389.1 | 0.2653 | 14.5 |
| 0.3974 | 3.9 | 0.3577 | 69.8 | 0.4797 | 230.1 | 0.5900 | 437.2 | 0.3548 | 17.0 |
| 0.4712 | 4.4 | 0.4427 | 78.3 | 0.5747 | 253.2 | 0.6716 | 455.4 | 0.4358 | 18.6 |
| 0.5394 | 4.6 | 0.5226 | 83.1 | 0.6503 | 260.0 | 0.7340 | 451.4 | 0.5100 | 19.1 |
| 0.6002 | 4.7 | 0.5816 | 83.8 | 0.6827 | 260.6 | 0.7822 | 434.1 | 0.5914 | 19.1 |
| 0.6519 | 4.6 | 0.5894 | 84.1 | 0.7126 | 255.5 | 0.7883 | 425.6 | 0.6552 | 18.4 |
| 0.6965 | 4.4 | 0.6347 | 82.7 | 0.7299 | 254.3 | 0.8239 | 406.0 | 0.7223 | 16.8 |
| 0.7998 | 3.5 | 0.6488 | 82.2 | 0.7742 | 241.6 | 0.8244 | 401.3 | 0.7858 | 14.5 |
| 0.8535 | 2.7 | 0.6916 | 78.9 | 0.8198 | 220.1 | 0.8551 | 371.2 | 0.8494 | 11.3 |
| 0.9049 | 1.9 | 0.6981 | 78.5 | 0.8606 | 191.9 | 0.8559 | 374.0 | 0.9051 | 7.7 |
| 0.9465 | 1.2 | 0.7403 | 73.6 | 0.8985 | 157.1 | 0.8845 | 332.7 | 0.9490 | 4.5 |
| 0.9756 | 0.6 | 0.7475 | 72.5 | 0.9221 | 129.1 | 0.9109 | 287.2 | 0.9806 | 1.8 |
| | | 0.8030 | 63.0 | 0.9297 | 119.9 | 0.9339 | 237.3 | | |
| | | 0.8525 | 51.8 | 0.9522 | 87.7 | 0.9534 | 184.9 | | |
| | | 0.8970 | 39.2 | 0.9574 | 79.3 | 0.9714 | 125.6 | | |
| | | 0.9319 | 27.4 | 0.9738 | 52.9 | 0.9845 | 73.7 | | |
| | | 0.9646 | 15.0 | 0.9789 | 42.0 | 0.9942 | 28.9 | | |
| | | 0.9875 | 5.5 | 0.9884 | 24.9 | | | | |
| | | | | 0.9927 | 15.2 | | | | |

| EtOH-HxOH | | EtOH-DeOH | | PrOH-HxOH | | PrOH-DeOH | | HxOH-DeOH | |
|---|---|---|---|---|---|---|---|---|---|
| $x_1$ | $H^E$ | $x_1$ | $H^E$ | $x_1$ | $H^E$ | $x_1$ | $H^E$ | $x_1$ | $H^E$ |
| 0.0841 | 30.3 | 0.0676 | 60.0 | 0.0410 | 8.5 | 0.0677 | 57.0 | 0.0386 | 14.2 |
| 0.1476 | 51.1 | 0.0748 | 65.2 | 0.1016 | 20.1 | 0.1664 | 126.5 | 0.0587 | 20.8 |
| 0.2451 | 77.7 | 0.1000 | 84.1 | 0.1787 | 32.9 | 0.2814 | 189.2 | 0.0931 | 32.1 |
| 0.3381 | 101.5 | 0.1728 | 140.2 | 0.2659 | 45.0 | 0.3825 | 227.6 | 0.1395 | 44.9 |
| 0.4270 | 117.5 | 0.2044 | 161.2 | 0.3536 | 54.1 | 0.4763 | 248.5 | 0.1639 | 51.9 |
| 0.5132 | 127.4 | 0.2841 | 209.7 | 0.4380 | 59.3 | 0.5586 | 255.1 | 0.2212 | 64.5 |
| 0.5849 | 130.7 | 0.3130 | 224.3 | 0.5152 | 61.4 | 0.6280 | 250.9 | 0.2511 | 70.6 |
| 0.6481 | 129.2 | 0.3993 | 268.7 | 0.5705 | 61.5 | 0.6886 | 238.9 | 0.3117 | 80.2 |
| 0.7026 | 124.1 | 0.5011 | 301.6 | 0.6260 | 60.6 | 0.6971 | 234.5 | 0.3383 | 84.2 |
| 0.7130 | 121.4 | 0.5892 | 315.0 | 0.6824 | 57.9 | 0.7371 | 222.5 | 0.4234 | 92.1 |
| 0.7482 | 116.6 | 0.6618 | 313.2 | 0.7377 | 53.3 | 0.7484 | 217.4 | 0.5125 | 95.9 |
| 0.7656 | 112.3 | 0.7242 | 305.0 | 0.7922 | 46.8 | 0.7788 | 202.7 | 0.5674 | 95.0 |
| 0.8173 | 98.8 | 0.7609 | 293.6 | 0.8447 | 38.5 | 0.7978 | 194.3 | 0.6231 | 91.8 |
| 0.8641 | 81.8 | 0.7675 | 288.3 | 0.8892 | 29.7 | 0.8123 | 182.3 | 0.6807 | 85.3 |
| 0.9064 | 62.0 | 0.8009 | 272.7 | 0.9292 | 20.3 | 0.8430 | 166.4 | 0.7381 | 77.1 |
| 0.9438 | 40.6 | 0.8089 | 265.7 | 0.9594 | 12.3 | 0.8852 | 133.4 | 0.7955 | 65.3 |
| 0.9688 | 23.9 | 0.8405 | 244.5 | 0.9784 | 6.8 | 0.9226 | 98.0 | 0.8517 | 51.2 |
| 0.9862 | 11.0 | 0.8471 | 237.1 | | | 0.9541 | 62.7 | 0.9026 | 36.0 |
| | | 0.8755 | 211.9 | | | 0.9810 | 27.9 | 0.9491 | 19.9 |
| | | 0.8802 | 205.3 | | | | | 0.9792 | 8.6 |
| | | 0.9101 | 170.4 | | | | | | |
| | | 0.9384 | 127.3 | | | | | | |
| | | 0.9386 | 128.1 | | | | | | |
| | | 0.9610 | 87.4 | | | | | | |
| | | 0.9615 | 87.6 | | | | | | |
| | | 0.9779 | 52.9 | | | | | | |
| | | 0.9795 | 50.1 | | | | | | |
| | | 0.9911 | 22.5 | | | | | | |
| | | 0.9922 | 20.2 | | | | | | |

## Table II. Coefficients for Least Squares Fit of Data by Equation 1

(Units joules per mole)

| System | $C_0$ | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $\sigma^H$ |
|---|---|---|---|---|---|---|---|
| MeOH-EtOH | 17.94 | −8.01 | −0.76 | 3.17 | | | 0.05 |
| MeOH-PrOH | 328.57 | −99.02 | 23.94 | −9.03 | −7.68 | | 0.17 |
| MeOH-HxOH | 944.45 | −574.83 | 231.75 | −209.98 | 170.43 | | 0.69 |
| MeOH-DeOH | 1589.70 | −1163.61 | 539.66 | 122.17 | 719.70 | −1046.86 | 2.62 |
| EtOH-PrOH | 76.84 | −10.62 | 8.81 | | | | 0.10 |
| EtOH-HxOH | 505.76 | −183.33 | 49.62 | −35.41 | 57.68 | | 0.45 |
| EtOH-DeOH | 1203.94 | −503.41 | 301.62 | −215.06 | 238.89 | −101.80 | 1.17 |
| PrOH-HxOH | 245.89 | −43.34 | 26.86 | −14.60 | | | 0.24 |
| PrOH-DeOH | 1008.21 | −221.65 | 108.21 | 11.98 | 99.50 | −128.23 | 1.00 |
| HxOH-DeOH | 382.34 | −27.72 | 17.38 | 14.04 | | | 0.21 |

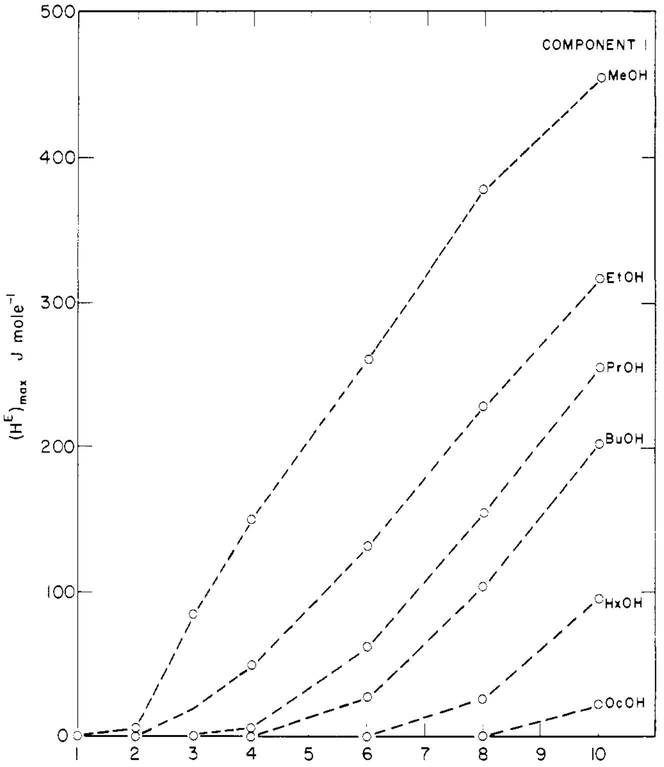

Figure 1. Maximum values of excess enthalpy for binary normal alcohol systems at 25° C.

Labels on lines indicate common (shorter chain) component; abscissa is number of carbons in longer chain component.

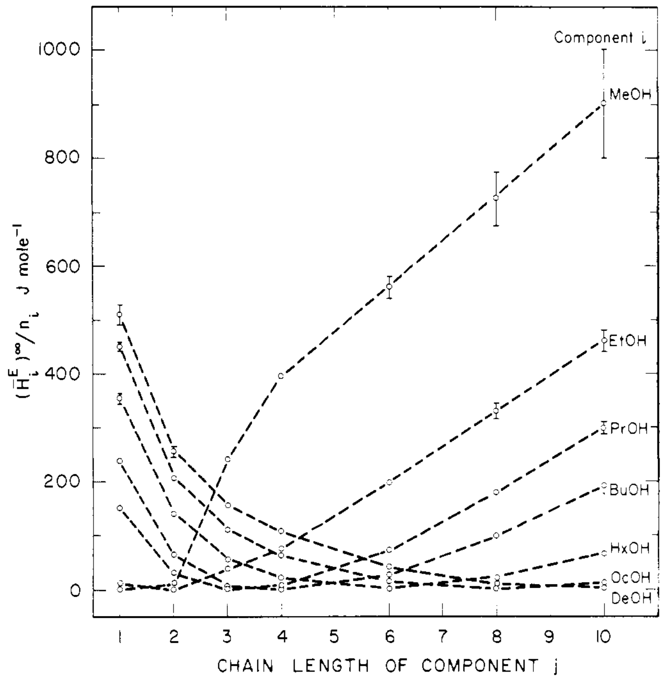

Figure 3. Partial molal excess enthalpy of an alcohol with chain length $n_i$ at infinite dilution in an alcohol with chain length $n_j$

Labels on lines indicate component $i$; abscissa is number of carbons in chain of component $j$.

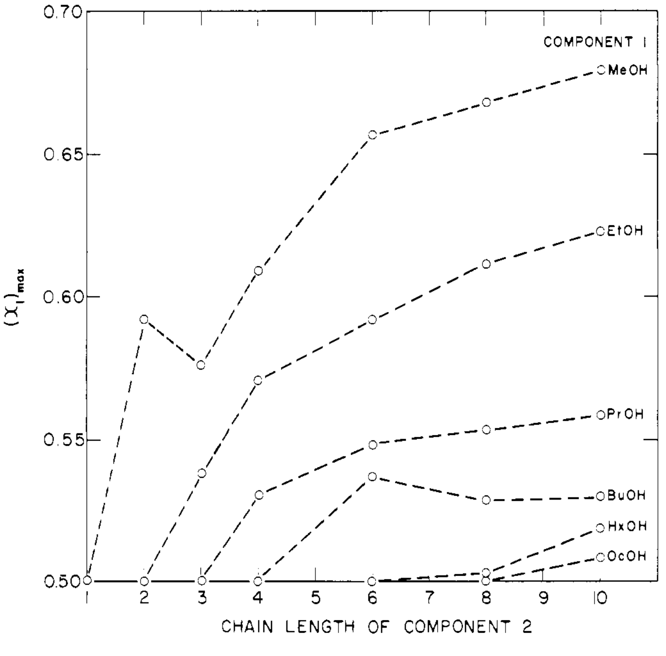

Figure 2. Mole fractions of shorter chain component corresponding to maxima of $H^E$ for binary normal alcohol systems at 25° C.

Labels on lines indicate common (shorter chain) component; abscissa is number of carbons in longer chain component.

to infinite dilution is estimated to be equal to or less than the radius of the circles used in plotting the points, except where indicated explicitly by a vertical line. Since solutions with mole fractions close to 0.0 and 1.0 were not studied experimentally, the results in Figure 3 may be somewhat inaccurate. Nevertheless the dashed lines should indicate the magnitudes of the enthalpy changes which occur when a molecule of a particular alcohol is transferred between infinitely dilute solutions in two different solvent alcohols.

## ACKNOWLEDGMENT

We are indebted to P. J. D'Arcy for assisting with the calorimetric measurements and to C. J. Halpin for carrying out the chromatographic purifications and analyses of the alcohols.

## LITERATURE CITED

(1) Díaz Peña, M., Fernández Martín, F., *Anal. Real Soc. Espãn. Fís. Quím. (Madrid)* **59B**, 331 (1963).
(2) McGlashan M.L., "Experimental Thermochemistry," Vol. **II**, H.A. Skinner, ed., p. 339, Interscience, New York, 1962.
(3) Pope, A.E., Pflug, H.D., Dacre, B., Benson, G.C., *Can. J. Chem.* **45**, 2665 (1967).
(4) Savini, C.G., Winterhalter, D.R., Kovach, L.H., Van Ness, H.C., J. CHEM. ENG. DATA **11**, 40 (1966).
(5) Van Ness, H.C., Mrazek, R.V., *A.I. Ch. E. J.* **5**, 209 (1959).

RECEIVED for review November 29, 1967. Accepted April 23, 1968. Issued as NRCC No. 10272.