Heats of Mixing of Binary Systems of Isopentanol and *n*-Pentanol with Hexane Isomers at 25°C: Measurement and Prediction by Analytical Group Solution Model

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Heats of mixing are measured at 25°C for binary systems of normal or isopentanol with hexane isomers (2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, and *n*-hexane). Data are also presented for mixtures of isopentanol with *n*-heptane and *n*-octane. The analytical group solution model developed for *n*-alkane–*n*-alcohol systems gives satisfactory predictions of heats of mixing for the systems studied. Branching in these systems has only a second order effect on the heats of mixing, and no modification of the analytical group solution model is necessary.

Group solution models have been successfully employed for representing the nonideality of liquid mixtures and for predicting thermodynamic and transport properties. Such work has largely been based on experimental data for straight-chain hydrocarbons and their derivatives. This paper is concerned with the effect of branched hydrocarbon chains on solution excess properties, in this case, excess enthalpies or heats of mixing, and the corresponding necessity to allow for molecular shape in the group solution models.

Virtually no suitable heat of mixing data on branched chain compounds are available in the literature. Experimental measurements were therefore made at 25°C on the 12 binary systems listed in Table IV and consisting of *n*-pentanol or isopentanol with either *n*-heptane, *n*-octane, or one of the five isomers of hexane.

The specifications of the materials employed are listed in Table I. The refractive indices were measured for each of the substances and were in good agreement with values reported in the literature. Further purification was not considered necessary.

The isothermal semicontinuous dilution calorimeter of the Van Ness (*7*) type used to obtain the data has been described elsewhere (*4*). The accuracy of the calorimeter for alcohol–alkane systems is believed to be within 1%.

Analytical Group Solution Model

The analytical group solution model for heats of mixing developed recently by Nguyen and Ratcliff (*5*) may be summarized by the following equations:

$$\Delta H = \sum x_i \Delta \bar{H}_i \tag{1}$$

$$\Delta \bar{H}_i = \sum_k N_{ki}(H_k - H^*_{ki}) \tag{2}$$

where N_{ki} is the number of groups of type k in molecular species i, and H_k the excess enthalpy of group k. For a binary group system, the analytical expressions for H_k are:

$$\frac{H_1}{RT^2} = \frac{X_2{}^2 a_{12} b_{12}}{(X_1 + X_2 a_{12})^2} + \frac{X_2{}^2 b_{21}}{(X_2 + X_1 a_{21})^2} \tag{3}$$

$$\frac{H_2}{RT^2} = \frac{X_1{}^2 a_{21} b_{21}}{(X_2 + X_1 a_{21})^2} + \frac{X_1{}^2 b_{12}}{(X_1 + X_2 a_{12})^2} \tag{4}$$

where

$$b_{12} = \frac{\partial}{\partial T}(a_{12}) \tag{5}$$

$$b_{21} = \frac{\partial}{\partial T}(a_{21})$$

and the group fraction X_k is defined by:

$$X_k = \frac{\sum_k N_{ki} x_i}{\sum_i \sum_k N_{ki} x_i}$$

By use of experimental data for *n*-alkane–*n*-alcohol mixtures, the group Wilson parameters for mixtures of hydroxyl and methylene groups were (*5*):

$$a_{\mathrm{OH/CH_2}} = 34.95 \exp(-2908/T) \tag{7}$$

$$a_{\mathrm{CH_2/OH}} = 26.69 \exp(-1336/T) + 7.705 \tag{8}$$

where T is the absolute temperature.

The simple group solution model summarized above does not take into account molecular shape. It thus predicts identical heats of mixing for systems in which one or more compounds are replaced by their isomers. The necessity for taking account of molecular shape in the model is here judged by inspecting the experimental heats of mixing of binary systems of *n*-pentanol or isopentanol with hexane isomers.

Results and Discussion

The experimental data for the 12 systems were judged to be too extensive to reproduce here and consequently have been filed with the National Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ont., Canada. The data all lie on smooth curves, as can be seen from the typical results shown in Figures 1 and 2. The expanded spline-fit technique (*3*) was used to represent the experimental values of $\Delta H/x_1x_2$. Interpolated values of $\Delta H/x_1x_2$ from the spline-fits are presented in Table II.

The effect of molecular shape on the heat of mixing may be judged from Table III, which shows the heats of mixing of the 10 pentanol–hexane systems at equimolar composition at 25°C. The small differences in heats of mixing of these systems suggest that there is only a small contact energy difference between methyl and methylene groups. Clearly defined trends can be seen: ΔH decreases slightly as the chain branching of the hexane increases but increases if *n*-pentanol is replaced by the branched isopentanol. Hexane isomers with similar degrees of branching (e.g., 2,2-dimethylbutane and 2,3-dimethylbutane) have almost identical heats of mixing, the differences (<1%) being comparable to the experimental errors. Very recently, Patterson (*6*) has studied the effect of molecular shape on heats of mixing for mixtures of alkane isomers of formula C_6H_{14} or $C_{16}H_{34}$.

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Table I. Specification of Materials

Material	Supplier	Specification	Refractive index Measd, 25°C	Refractive index Lit (1)
n-Pentanol	Aldrich Chemical Co.	99 mol %	1.4079	1.4081
Isopentanol	Matheson Coleman & Bell	Chromatoquality, 99+ mol %	1.4046	1.4051
n-Hexane	Phillips Petroleum Co.	Pure grade, 99+ mol %	1.3725	1.37226
n-Heptane			1.3850	1.38511
n-Octane			1.3954	1.39505
2,2-Dimethylbutane			1.3662	1.36595
2,3-Dimethylbutane			1.3723	1.37231
2-Methylpentane			1.3687	1.36873
3-Methylpentane			1.3739	1.37386

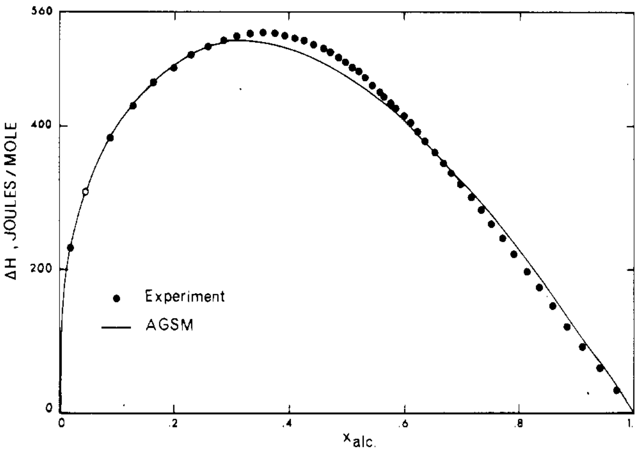

Figure 1. Heats of mixing at 25°C for system isopentanol–2,2-dimethylbutane

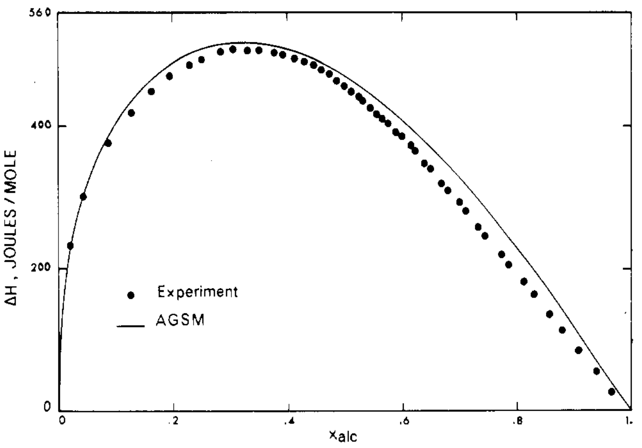

Figure 2. Heats of mixing for system *n*-pentanol–2,2-dimethylbutane

Table II. Heats of Mixing at 25°C for Binary Alcohol–Alkane Systems, J/Mol[a]

$$\frac{\Delta H}{x_1 x_2}$$

x_{alc}	*n*-C_5OH–*n*-C_6	*n*-C_5OH–I	*n*-C_5OH–II	*n*-C_5OH–III	*n*-C_5OH–IV	*i*-C_5OH–*n*-C_6
0.05	6699.	6557.	6593.	6389.	6583.	6859.
0.15	3546	3434.	3456.	3415.	3475.	3689.
0.25	2734.	2636.	2651.	2640.	2675.	2890.
0.35	2321.	2227.	2235.	2243.	2266.	2501.
0.45	2043.	1942.	1954.	1969.	1985.	2248.
0.55	1800.	1707.	1703.	1747.	1745.	2013.
0.65	1582.	1492.	1478.	1538.	1515.	1797.
0.75	1393.	1301.	1284.	1345.	1320.	1607.
0.85	1227.	1144.	1116.	1186.	1153.	1439.
0.95	1097.	1008.	973.	1064.	1012.	1284.
x_{alc}	*i*-C_5OH–I	*i*-C_5OH–II	*i*-C_5OH–III	*i*-C_5OH–IV	*i*-C_5OH–*n*-C_7	*i*-C_5OH–*n*-C_8
0.05	6655.	6444.	6855.	6892.	7416.	7873.
0.15	3514.	3467.	3634.	3562.	3998.	4302.
0.25	2719.	2707.	2821.	2776.	3132.	3385.
0.35	2328.	2330.	2422.	2394.	2740.	2993.
0.45	2074.	2077.	2164.	2144.	2495.	2756.
0.55	1837.	1855.	1929.	1907.	2295.	2573.
0.65	1610.	1638.	1712.	1684.	2115.	2384.
0.75	1416.	1438.	1522.	1488.	1940.	2230.
0.85	1242.	1259.	1351.	1322.	1781.	2092.
0.95	1085.	1092.	1202.	1164.	1631.	1968.

[a] I = 2,2-dimethylbutane, II = 2,3-dimethylbutane, III = 2-methylpentane, IV = 3-methylpentane.

Table III. Heat of Mixing at Equimolar Composition for Pentanol-Hexane Systems at 25°C[a]

System	ΔH, J/mol
n-Pentanol–*n*-hexane	480.
n-Pentanol–2,2-dimethylbutane	455.
n-Pentanol–2,3-dimethylbutane	457.
n-Pentanol–2-methylpentane	462.
n-Pentanol–3-methylpentane	465.
Isopentanol–*n*-hexane	533.
Isopentanol–2,2-dimethylbutane	490.
Isopentanol–2,3-dimethylbutane	491.
Isopentanol–2-methylpentane	512.
Isopentanol–3-methylpentane	507.
Mean	485

[a] Rms deviation from mean is 5.1% (25 J/mol).

Table IV. Comparison of Experiment and Prediction for Alcohol-Alkane Systems at 25°C

System	Rms dev % of prediction from expt
n-Pentanol–*n*-hexane	5.8
n-Pentanol–2,2-dimethylbutane	10.3
n-Pentanol–2,3-dimethylbutane	11.8
n-Pentanol–2-methylpentane	7.7
n-Pentanol–3-methylpentane	9.2
Isopentanol–*n*-hexane	9.1
Isopentanol–2,2-dimethylbutane	5.9
Isopentanol–2,3-dimethylbutane	5.7
Isopentanol–2-methylpentane	6.0
Isopentanol–3-methylpentane	5.5
Isopentanol–*n*-heptane	10.6
Isopentanol–*n*-octane	12.1

He found a very small contact energy difference between methyl and methylene groups in the *n*-hexane–2,2-dimethylbutane system. The heats of mixing of *n*-hexane and of 2,2-dimethylbutane with heptamethylnonane were comparable, indicating a similar conclusion.

However, the effect of branching is significant in systems containing *n*-alkanes and branched alcohols (2). The heats of mixing of branched butanols with *n*-hexane decrease appreciably in the order tertiary > secondary > isopentanol > *n*-pentanol.

A comparison of our results for *n*-pentanol and for isopentanol is interesting. While the differences are small, isopentanol gives equimolar heats of mixing that are consistently a little (an average of 49 J/mol) above those for *n*-pentanol. A comparison of *n*-hexane with 2-methylpentane (a homomorph of isopentanol) shows that results for the latter are some 20 J/mol below those for *n*-hexane. Clearly, the branching in isopentanol has had some effect on the properties of the hydroxyl group. However, we may conclude that moderate branching in an alkyl group will have only a small effect on heats of mixing as long as it is located so as not to interfere directly with a polar group.

Table IV compares experimental results with heats of mixing predicted by the simple model. The average root-mean-square deviation of all the predictions is about 8%. The average root-mean-square deviation of the predictions for the *n*-pentanol–hexane systems is about 9%, and for the isopentanol–hexane systems is about 6%. These figures compare with a figure of about 5% for comparable straight-chain systems (5). Modification of the model to take chain branching into account thus seems unjustified.

Acknowledgment

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Nomenclature

a = group Wilson parameter in Equations 4 and 5
b = group Wilson parameter in Equations 4–6
H_k = excess enthalpy of group k
N_{ki} = number of groups k in molecular species i
T = absolute temperature
x = mole fraction
X = group fraction
ΔH = molar heat of mixing
$\Delta \bar{H}_i$ = partial molar heat of mixing

Subscripts

i, j = molecular species
k = group species

Superscript

$*$ = standard state

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