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Received for review February 14, 1975. Accepted August 6, 1975. Project supported by Corporate Research and Development of General Electric.

Excess Gibbs Energies 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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Vapor-liquid equilibrium data were measured at 25°C for binary mixtures of *n*-pentanol with each of the five hexane isomers (*n*-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane) and also for isopentanol-*n*-hexane mixtures. Measurements were made with a total pressure static equilibrium still. The analytical group solution model of Ronc and Ratcliff gave good predictions of the excess free energy for all the systems studied. The presence of branched-chain molecules in these systems had only a small effect on excess free energies, and no modification of the group solution model to allow for molecular shape was necessary.

Group solution models have been successfully employed for representing the nonideality of liquid mixtures and for predicting thermodynamic and transport properties. The development of such models, starting from the early work of Langmuir (4) to date, has been extensively reviewed elsewhere (7, 8). 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 free energies, and the corresponding necessity to allow for molecular shape in the group solution models.

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Virtually no suitable excess free energy data on systems containing branched chain compounds are available in the literature. Experimental measurements were therefore made at 25°C on six binary systems, consisting of binary mixtures of *n*-pentanol with each of the five isomers of hexane and of isopentanol and *n*-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. The hydrocarbons and the *n*-pentanol were used as purchased, whereas the isopentanol was dried over molecular sieves as the main impurity in it (0.7%) was stated by the manufacturer to be water.

Vapor-liquid equilibrium data were measured in a total pressure static equilibrium still. Descriptions of the apparatus, experimental technique, and the computational procedure have been reported elsewhere (7, 8).

Analytical Group Solution Model

The analytical group solution model for excess Gibbs free energy developed by Ronc (7) may be summarized by the following equations:

$$\log \gamma_i = \log \gamma_i^S + \log \gamma_i^G \quad (1)$$

$$\log \gamma_i^G = \sum_k N_{ki} (\log \Gamma_k - \log \Gamma_k^*) \quad (2)$$

Table I. Materials Used as Pure Components

Material	Supplier	Grade	Purity, mol %	Refractive index @ 25°C	
				Lit (7)	This work
<i>n</i> -Hexane	PPC ^a	Pure	99.4	1.37226	1.3725
2-Methylpentane	PPC	Pure	99.2	1.36873	1.3687
3-Methylpentane	PPC	Pure	99.4 wt %	1.37386	1.3739
2,2-Dimethylbutane	PPC	Pure	99.4	1.36595	1.3662
2,3-Dimethylbutane	PPC	Pure	99.3	1.37231	1.3723
<i>n</i> -Pentanol	MCB ^b	Chromato-quality	99.79	1.4081	1.4079
<i>i</i> -Pentanol (3-methyl-1-butanol)	Fisher Scientific	Reagent	99.25 (0.7% H ₂ O)	1.4051	1.4046

^a Phillips Petroleum Co. ^b Matheson Coleman & Bell.

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

$$\log \Gamma_1 = C \left[-\log (X_1 + a_{12}X_2) + 0.4343 X_2 \left\{ \frac{a_{12}}{X_1 + a_{12}X_2} - \frac{a_{21}}{a_{21}X_1 + X_2} \right\} \right] \quad (3)$$

$$\log \Gamma_2 = C \left[-\log (X_2 + a_{21}X_1) - 0.4343 X_1 \left\{ \frac{a_{12}}{X_1 + a_{12}X_2} - \frac{a_{21}}{a_{21}X_1 + X_2} \right\} \right] \quad (4)$$

and the group fraction X_k is defined by:

$$X_k = \frac{\sum_i N_{ki}x_i}{\sum_i \sum_k N_{ki}x_i} \quad (5)$$

By use of experimental data for n -alkane- n -alcohol mixtures, the group Wilson parameters for mixtures of hydroxyl and methylene groups were (7)

$$a_{\text{OH}/\text{CH}_2} = \exp \left(-0.8895 - \frac{698.65}{T} \right) \quad (6)$$

$$a_{\text{CH}_2/\text{OH}} = 0.60 \quad (7)$$

and

$$C = 1.6 \quad (8)$$

For a binary molecular system

$$\log \gamma_i^S = (2.9239 - 5.4777 \rho + 12.8016 \rho^2) \left[\log \frac{N_i}{N_{\text{av}}} + 0.4343 \left(1 - \frac{N_i}{N_{\text{av}}} \right) \right] \quad (9)$$

where

$$\rho = \frac{N_1}{N_2} = \frac{\text{no. of groups in shorter molecule}}{\text{no. of groups in longer molecule}}$$

The simple group solution model summarized above does not take into account molecular shape. It thus predicts identical activity coefficients 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 vapor-liquid equilibria for binary pentanol-hexane systems.

Results

The raw experimental data for the six systems were judged to be too extensive to reproduce here and have been filed with the National Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ont., Canada. These are also found in refs. 7 and 8, together with details of the computational procedures and a discussion of experimental errors. The data all lie on smooth curves, as can be seen from the typical results shown in Figure 1. The triangles represent experimental points obtained when starting from pure alcohol, and the inverted triangles when starting from pure alkane. The excellent agreement in the overlapping region is evident.

The expanded spline-fit technique (3) was used to represent the experimental pressure-composition data. Interpolated values of the vapor pressures from the spline fits are presented in Tables II-VII. These tables also show the calculated vapor-phase compositions, activity coefficients, and excess free energies at regular composition intervals. The vapor-phase compositions were obtained by integrating Van Ness's

coexistence equation (5, 9). The activity coefficients and excess free energies were calculated from the P - x - y data by:

$$\ln \gamma_1 = \ln \frac{y_1 P}{x_1 P_1^S} + \frac{(B_{11} - V_1^L)(P - P_1^S)}{RT} + \frac{P \delta_{12} y_2^2}{RT} \quad (10)$$

$$\ln \gamma_2 = \ln \frac{y_2 P}{x_2 P_2^S} + \frac{(B_{22} - V_2^L)(P - P_2^S)}{RT} + \frac{P \delta_{12} y_1^2}{RT} \quad (11)$$

where $\delta_{12} = 2 B_{12} - B_{11} - B_{22}$ and

$$\frac{g^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (12)$$

Figures 2 and 3 show typical results; all the other systems studied exhibited similar behavior.

Discussion and Conclusions

Table VIII compares the excess free energies of the branched-chain systems with those of the n -pentanol- n -hexane system. The differences are a measure of the effect of chain branching on the excess free energy and are small. Replacement of n -hexane with branched-chain hexanes in mixtures with n -pentanol usually lowers the excess free energy, but the differences do not systematically increase with increased branching of the alkane. Thus, replacement of n -hexane by the highly branched 2,2-dimethylbutane has virtually no effect on the excess free energy. On the other hand, there is a small but significant difference between mixtures

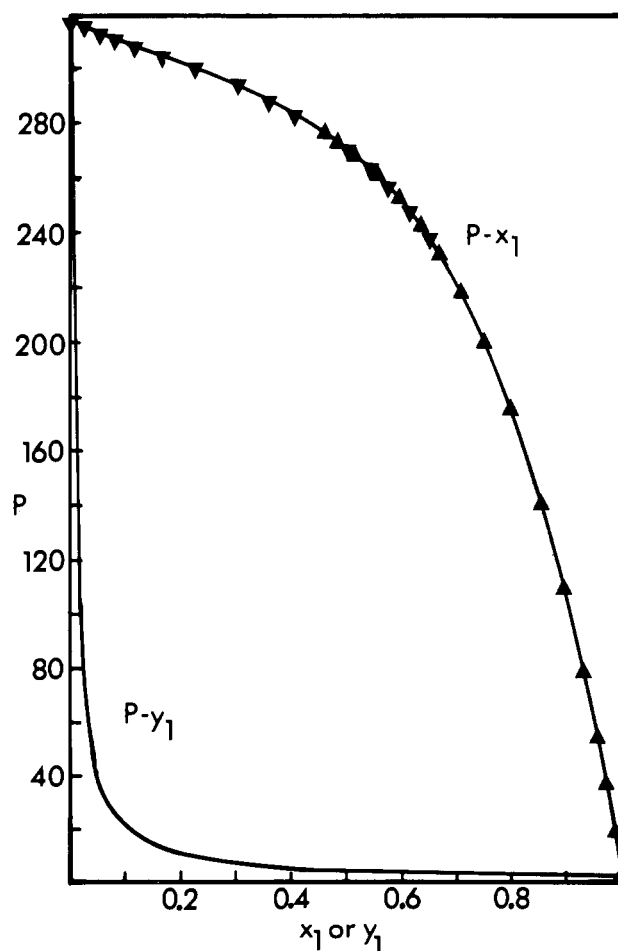


Figure 1. P - x - y diagram for n -pentanol(1)-2,2-dimethylbutane(2) mixtures at 25°C

P = total vapor pressure, mm Hg; x_1 = mole fraction of n -pentanol in liquid mixture; y_1 = mole fraction of n -pentanol in vapor mixture; P - x_1 curve: ▲ = points obtained when starting experimental run with pure alcohol; ▼ = points obtained when starting experimental run with pure alkane; — = smoothed curve; P - y_1 curve: — = y_1 values calculated from smoothed P - x_1 values

containing 2-methylpentane and those containing 3-methylpentane.

Replacement of *n*-pentanol with isopentanol increases the excess free energy significantly at the higher alcohol concentrations. A comparison of the *n*-pentanol–2-methylpentane system with the isopentanol–*n*-hexane system at equimolar composition (where the two systems are homomorphic) shows that the latter has the higher excess free energy. We may conclude that the branching in isopentanol has had some

Table II. Vapor-Liquid Equilibrium Data at 25°C for *n*-Pentanol(1)–*n*-Hexane(2) Mixtures

x_1	y_1	P	$\ln \gamma_1$	$\ln \gamma_2$	g^E/RT
0.0	0.0	151.20	3.8402	0.0	0.0
0.100	0.00826	148.06	1.5714	0.0764	0.2259
0.200	0.00970	144.76	1.0168	0.1706	0.3398
0.300	0.01089	140.72	0.6993	0.2750	0.4023
0.400	0.01202	135.98	0.4767	0.3948	0.4273
0.500	0.01329	129.97	0.3093	0.5307	0.4200
0.600	0.01515	120.85	0.1865	0.6803	0.3840
0.700	0.01836	106.49	0.1003	0.8397	0.3221
0.800	0.02485	84.67	0.0429	1.0117	0.2367
0.900	0.04367	52.15	0.0089	1.2041	0.1284
1.000	1.00000	2.49	0.0	1.3370	0.0

Table III. Vapor-Liquid Equilibrium Data at 25°C for *n*-Pentanol(1)–2-Methylpentane(2) Mixtures

x_1	y_1	P	$\ln \gamma_1$	$\ln \gamma_2$	g^E/RT
0.0	0.0	211.87	4.0780	0.0	0.0
0.100	0.00534	205.95	1.5907	0.0723	0.2241
0.200	0.00619	201.68	1.0239	0.1686	0.3397
0.300	0.00689	196.33	0.7002	0.2751	0.4026
0.400	0.00760	189.64	0.4771	0.3946	0.4276
0.500	0.00840	181.15	0.3096	0.5311	0.4204
0.600	0.00955	168.63	0.1852	0.6827	0.3842
0.700	0.01150	149.12	0.0962	0.8474	0.3216
0.800	0.01554	118.48	0.0379	1.0218	0.2347
0.900	0.02784	71.57	0.0056	1.2030	0.1253
1.000	1.00000	2.18	0.0	1.2533	0.0

Table IV. Vapor-Liquid Equilibrium Data at 25°C for *n*-Pentanol(1)–3-Methylpentane(2) Mixtures

x_1	y_1	P	$\ln \gamma_1$	$\ln \gamma_2$	g^E/RT
0.0	0.0	190.14	3.9781	0.0	0.0
0.100	0.00583	184.74	1.5722	0.0712	0.2213
0.200	0.00677	180.87	1.0080	0.1673	0.3354
0.300	0.00756	176.00	0.6857	0.2732	0.3970
0.400	0.00837	169.76	0.4655	0.3911	0.4209
0.500	0.00929	161.89	0.3003	0.5258	0.4130
0.600	0.01062	150.27	0.1784	0.6743	0.3767
0.700	0.01291	132.05	0.0930	0.8322	0.3148
0.800	0.01764	104.10	0.0376	0.9978	0.2296
0.900	0.03205	62.21	0.0077	1.1656	0.1234
1.000	1.00000	2.18	0.0	1.3012	0.0

Table V. Vapor-Liquid Equilibrium Data at 25°C for *n*-Pentanol(1)–2,2-Dimethylbutane(2) Mixtures

x_1	y_1	P	$\ln \gamma_1$	$\ln \gamma_2$	g^E/RT
0.0	0.0	319.40	4.4785	0.0	0.0
0.100	0.00350	310.20	1.5794	0.0734	0.2240
0.200	0.00408	303.40	1.0168	0.1690	0.3386
0.300	0.00456	294.92	0.6961	0.2745	0.4010
0.400	0.00505	284.41	0.4752	0.3928	0.4257
0.500	0.00560	271.22	0.3091	0.5282	0.4186
0.600	0.00638	251.89	0.1858	0.6783	0.3828
0.700	0.00773	221.33	0.0996	0.8380	0.3211
0.800	0.01056	174.13	0.0437	1.0048	0.2359
0.900	0.01902	104.39	0.0121	1.1838	0.1293
1.000	1.00000	2.15	0.0	1.4488	0.0

effect on the properties of the hydroxyl group. A similar effect was found for excess enthalpies (6).

However, the effect of branching is small, and the deviations (except for $x_{\text{alc}} = 0.9$ for the isopentanol–*n*-hexane system) are within the accuracy of the predictions of the analytical group solution model. Table IX shows the deviations between the experimental data and the predictions of Ronc's model. The average root-mean-square deviation of 3.2% compares favorably with that found by Ronc (7) for 30 meth-

Table VI. Vapor-Liquid Equilibrium Data at 25°C for *n*-Pentanol(1)–2,3-Dimethylbutane(2) Mixtures

x_1	y_1	P	$\ln \gamma_1$	$\ln \gamma_2$	g^E/RT
0.0	0.0	234.65	4.0852	0.0	0.0
0.100	0.00475	227.46	1.5749	0.0701	0.2206
0.200	0.00550	222.70	1.0082	0.1665	0.3349
0.300	0.00617	216.44	0.6890	0.2714	0.3967
0.400	0.00685	208.55	0.4703	0.3885	0.4212
0.500	0.00762	198.64	0.3062	0.5223	0.4143
0.600	0.00872	184.18	0.1849	0.6701	0.3790
0.700	0.01060	161.72	0.0996	0.8279	0.3181
0.800	0.01445	127.67	0.0433	0.9963	0.2339
0.900	0.02587	77.14	0.0110	1.1787	0.1278
1.000	1.00000	2.17	0.0	1.3953	0.0

Table VII. Vapor-Liquid Equilibrium Data at 25°C for Isopentanol(1)–*n*-Hexane(2) Mixtures

x_1	y_1	P	$\ln \gamma_1$	$\ln \gamma_2$	g^E/RT
0.0	0.0	151.29	3.6331	0.0	0.0
0.100	0.01055	148.28	1.5801	0.0750	0.2255
0.200	0.01245	144.95	1.0298	0.1685	0.3407
0.300	0.01395	140.99	0.7115	0.2732	0.4047
0.400	0.01543	136.18	0.4902	0.3917	0.4311
0.500	0.01710	130.05	0.3244	0.5269	0.4257
0.600	0.01944	121.15	0.2006	0.6777	0.3915
0.700	0.02340	107.27	0.1123	0.8412	0.3310
0.800	0.03138	85.93	0.0530	1.0190	0.2462
0.900	0.05332	54.54	0.0149	1.2380	0.1372
1.000	1.00000	3.16	0.0	1.5241	0.0

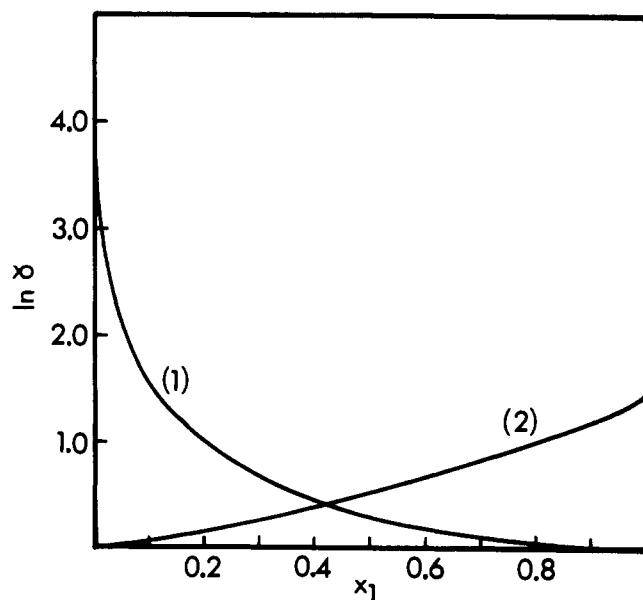


Figure 2. Activity coefficients for *n*-pentanol(1)–2,2-dimethylbutane(2) mixtures at 25°C
 $\ln \gamma$ = natural logarithm of activity coefficients; x_1 = mole fraction of *n*-pentanol in liquid mixture; curve (1) = activity coefficients of *n*-pentanol; curve (2) = activity coefficients of 2,2-dimethylbutane

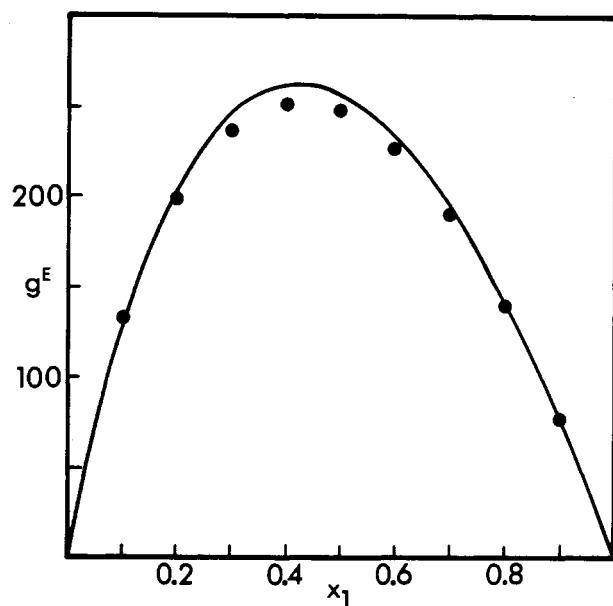


Figure 3. Excess free energies of *n*-pentanol(1)-2,2-dimethylbutane (2) mixtures at 25°C
 g^E = excess free energy, cal/g-mol; x_1 = mole fraction of *n*-pentanol in liquid mixture; ● = points calculated from experimental $x - P$ data; — = predictions of analytical group solution model

ylene-hydroxyl systems, even though no allowance has been made for molecular shape. Figure 3 compares predicted and experimental excess free energies for a typical system (*n*-pentanol-2,2-dimethylbutane). No experimental data on the mixtures are used in making the predictions.

We conclude that for highly nonideal mixtures such as those studied here, no modification of the group solution model is necessary to enable it to handle systems containing branched-chain molecules. In such mixtures all alkyl groups (CH₃, CH₂, CH, or C) may be considered equivalent. This conclusion is consistent with the very small excess free energies found by Chen and Zwolinski (2) for binary mixtures of hexane isomers.

Nomenclature

a = group Wilson parameter
 B_{11}, B_{12}, B_{22} = second virial coefficients
 C = constant for the Wilson equation
 g = Gibbs free energy per mole
 N_i = number of groups in molecule i
 N_{av} = average number of groups per molecule in a mixture
 N_{ki} = number of groups of type k in molecular species i
 P = pressure
 P_1^S, P_2^S = vapor pressure of pure component
 R = gas constant
 T = absolute temperature
 V_1^L, V_2^L = molar volumes of pure component
 x = mole fraction in liquid
 X = group fraction in liquid
 y = mole fraction in vapor

Greek Letters

γ = activity coefficient
 Γ = group activity coefficient
 ρ = molecular size ratio N_1/N_2

Superscripts

E = excess property
 G = group contribution
 S = size contribution

Table VIII. Comparison of Excess Free Energies at 25°C of Systems with Branched-Chain Components with Those of *n*-Pentanol-*n*-Hexane System^a

x_1	Deviation % = $\frac{g^E(\text{system}) - g^E(\text{system 1})}{g^E(\text{system 1})} \times 100$					
	System 1	System 2	System 3	System 4	System 5	System 6
0.1	133.82	132.77	131.12	132.71	130.70	133.59
		-0.79	-2.02	-0.83	-2.33	-0.17
0.2	201.31	201.25	198.72	200.59	198.37	201.86
		-0.03	-1.29	-0.36	-1.46	0.27
0.3	238.34	238.53	235.17	237.55	235.01	239.76
		-0.08	-1.33	-0.33	-1.40	0.60
0.4	253.11	253.30	249.33	252.21	249.54	255.40
		0.07	-1.50	-0.36	-1.41	0.90
0.5	248.82	249.03	244.69	248.02	245.41	252.16
		0.08	-1.66	-0.32	-1.37	1.34
0.6	227.49	227.61	223.19	226.80	224.50	231.92
		0.05	-1.89	-0.30	-1.31	1.94
0.7	190.85	190.52	186.48	190.21	188.44	196.09
		-0.17	-2.29	-0.34	-1.26	2.75
0.8	140.22	139.03	136.04	139.78	138.57	145.86
		-0.85	-2.98	-0.32	-1.17	4.02
0.9	76.06	74.26	73.13	76.58	75.72	81.29
		-2.37	-3.85	0.68	-0.45	6.88

^a System 1 = *n*-pentanol-*n*-hexane; system 2 = *n*-pentanol-2-methylpentane; system 3 = *n*-pentanol-3-methylpentane; system 4 = *n*-pentanol-2,2-dimethylbutane; system 5 = *n*-pentanol-2,3-dimethylbutane; system 6 = *i*-pentanol-*n*-hexane; g^E = excess free energy at 25°C; x_1 = mole fraction of the alcohol.

Table IX. Root-Mean-Square Deviation (Rmsd) Between Predicted and Experimental Excess Free Energies at 25°C

System	Rmsd	
	Cal/mol	%
<i>n</i> -Pentanol- <i>n</i> -hexane	5.9	3.1
<i>n</i> -Pentanol-2-methylpentane	5.3	2.8
<i>n</i> -Pentanol-3-methylpentane	7.7	4.1
<i>n</i> -Pentanol-2,2-dimethylbutane	5.9	3.1
<i>n</i> -Pentanol-2,3-dimethylbutane	7.1	3.8
<i>i</i> -Pentanol- <i>n</i> -hexane	4.7	2.5
Average	6.1	3.2

Subscripts

1, 2, i = molecular species (1 normally refers to alcohol, and 2 to alkane)
 k = group species k
 CH₂ = methylene group
 OH = hydroxyl group

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Received for review March 13, 1975. Accepted August 25, 1975. McGill University awarded a McConnell Memorial Fellowship to S.S.