Prediction of Heats of Mixing for Ternary Alcohols–Saturated Hydrocarbon Mixtures

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Ternary heat of mixing values for alcohol–alcohol–saturated hydrocarbon mixtures are successfully predicted by using an empirical equation based on the association model theory. Prediction is illustrated with 17 systems. Basic information necessary for prediction is the equilibrium constant of pure alcohol and one physical interaction parameter per binary pair. The enthalpy of a hydrogen bond formation is taken to be −6.0 kcal/mol, irrespective of alcohol species.

Heat of mixing values have been correlated by several analytical methods. Many methods represent the heat of mixing as the contribution of physical interaction terms. An alternate approach to correlate the heat of mixing is based on a chemical theory, which presumes that molecules in a liquid solution interact with each other to form new chemical species. Kretschmer and Wiebe (*4*) presented the theory of associated solutions with physical interactions. Renon and Prausnitz (*11*) gave a critical discussion of the Kretschmer-Wiebe equation in data reduction of 11 binary systems, showing that the theory gives a good representation of the properties of concentrated solutions of alcohols in saturated hydrocarbons. The present author extended the Kretschmer-Wiebe equation to ternary systems, including one alcohol and two saturated hydrocarbons (*5*) and, further, derived the pertinent expressions of excess properties for binary alcohol–unsaturated hydrocarbon and ternary alcohol–two unsaturated hydrocarbon mixtures (*6, 7*).

The objective of this work is to show that the method of Nagata (*5*), with minor modification, is applicable to predict the heat of mixing of ternary two alcohol–saturated hydrocarbon mixtures and to compare the accuracy of prediction obtained by this work with that of Chang and Lu's method (*2*), which uses an open-type equation derived from the local composition idea.

Working Equations

According to the Kretschmer-Wiebe equation, heat of mixing data for a binary alcohol–saturated hydrocarbon solution may be calculated by the following equation (*3*):

$$h^E = h_a K x_a(\phi_1 - \phi_1{}^\circ) + \beta(x_a v_a + x_h v_h)\phi_a\phi_h \qquad (1)$$

The first right-hand term of Equation 1 represents the total enthalpy of formation of hydrogen bonds present in alcohol i-mers. The enthalpy of formation of a hydrogen bond fixes the temperature dependence of chemical equilibrium constant K by the van't Hoff relation:

$$\frac{d \ln K}{d\,(1/T)} = -\frac{h_a}{R} \qquad (2)$$

The volume fraction of alcohol monomer in the solution ϕ_1 and that in pure alcohol solution $\phi_1{}^\circ$ are given by

$$\phi_1 = \frac{(2\,K\phi_a + 1) - \sqrt{1 + 4\,K\phi_a}}{2\,K^2\phi_a{}^2} \qquad (3)$$

$$\phi_1{}^\circ = \frac{2\,K + 1 - \sqrt{1 + 4\,K}}{2\,K^2} \qquad (4)$$

The second right-hand term of Equation 1 is the contribution of physical interaction expressed by the Hildebrand-Scatchard equation. β is a physical interaction parameter. For alcohol–alcohol mixtures we consider that heat effect is due to only the physical interaction between unlike molecules, probably because by mixing, breaking of hydrogen bonds in alcohol i-mers and production of alcohol copolymers might take place with equal probability; consequently, the chemical effect on the heat of mixing values may be negligible. Thus, heats of mixing for alcohol–alcohol systems are expressed by

$$h^E = \beta_{ab}(x_a v_a + x_b v_b)\phi_a\phi_b \qquad (5)$$

To evaluate heat of mixing values for ternary alcohol–alcohol–saturated hydrocarbon systems, we assume that mixing alcohols a and b yields a pseudo-single alcohol having the chemical equilibrium constant $\bar{K}$. The concentration of pseudo-single alcohol is x_{ab} $(=1 - x_h)$ or ϕ_{ab} $(=1 - \phi_h)$. When the pseudo-single alcohol is mixed with a saturated hydrocarbon, the total heat of mixing is expressed as follows:

$$h^E = h_a\bar{K}x_{ab}(\bar{\phi}_1 - \bar{\phi}_1{}^\circ) + (\beta_{ab}\phi_a\phi_b + \beta_{ah}\phi_a\phi_h + \beta_{bh}\phi_b\phi_h)(x_a v_a + x_b v_b + x_h v_h) \qquad (6)$$

Equation 6 is analogous to the one proposed by the present author for a ternary alcohol–two saturated hydrocarbon mixture. $\bar{K}$ may be given by a function of the chemical equilibrium constants and compositions of component alcohols. Four methods are proposed to estimate $\bar{K}$.

$$\text{I} \quad \bar{K} = K_a\bar{x}_a{}^2 + 2\sqrt{K_a K_b}\,\bar{x}_a\bar{x}_b + \bar{K}_b\bar{x}_b{}^2 \qquad (7)$$

$$\text{II} \quad \bar{K} = K_a\bar{x}_a + K_b\bar{x}_b \qquad (8)$$

$$\text{III} \quad \bar{K} = K_a\bar{x}_a{}^2 + 2\,\bar{x}_a\bar{x}_b/(\bar{x}_a/K_a + \bar{x}_b/K_b) + K_b\bar{x}_b{}^2 \qquad (9)$$

$$\text{IV} \quad \bar{K} = 1/(\bar{x}_a/K_a + \bar{x}_b/K_b) \qquad (10)$$

where

$$\bar{x}_a = \frac{x_a}{x_a + x_b} \qquad (11)$$

$$\bar{x}_b = \frac{x_b}{x_a + x_b} \qquad (12)$$

The monomer volume fractions of pseudo-single alcohol, $\bar{\phi}_1$ and $\bar{\phi}_1{}^\circ$, are obtainable by substituting $\bar{K}$ and ϕ_{ab} into Equations 3 and 4, respectively.

Table I. Association Constants of Alcohols at 50°C

Compound	K	Ref
Methanol	450	(*11*)
Ethanol	190	(*11*)
n-Propanol	90	(*11*)
Isopropanol	60	(*11*)
n-Butanol	80	(*6*)
n-Pentanol	72	This work
n-Hexanol	66	This work
n-Octanol	58	This work
n-Decanol	54	This work

Table II. Calculated Results for Binary Alcohol–Saturated Hydrocarbon Mixtures with Kretschmer-Wiebe Equation

System	Temp, °C	No. of data points	β, cal/cc	Deviation Δ,[a] cal/mol	Data source
Ethanol–*n*-hexane	25	14	1.239	3.39	(*1*)
	35	9	1.621	3.76	
	45	8	2.231	6.68	
Ethanol–*n*-heptane	20	13	1.415	5.21	(*9*)
	25	12	1.442	5.00	
	30	18	1.568	4.88	
Ethanol–*n*-octane	20	12	1.355	7.58	(*9*)
	25	12	1.444	6.01	
	30	15	1.585	5.66	
n-Propanol–*n*-hexane	25	8	0.306	3.03	(*1*)
	35	8	0.672	0.59	
	45	9	1.267	4.98	
n-Propanol–*n*-heptane	20	12	0.122	4.28	(*9*)
	25	13	0.223	3.63	
	30	13	0.329	2.79	
n-Propanol–*n*-octane	20	12	0.259	5.04	(*9*)
	25	13	0.285	4.83	
	30	14	0.321	5.18	
n-Propanol–*n*-tetradecane	20	14	0.374	14.79	(*9*)
	25	14	0.436	12.22	
	30	15	0.459	10.17	
n-Butanol–*n*-hexane	25	8	0.189	1.96	(*1*)
	35	9	0.608	2.61	
	45	8	1.139	5.28	
n-Pentanol–*n*-heptane	20	13	0.278	3.90	(*9*)
	25	14	0.435	3.74	
	30	14	0.478	3.11	
n-Pentanol–*n*-octane	20	12	0.532	5.34	(*9*)
	25	13	0.515	3.81	
	30	14	0.496	3.60	
n-Pentanol–*n*-tetradecane	20	14	0.973	6.44	(*9*)
	25	13	0.907	5.01	
	30	13	0.854	5.92	
n-Hexanol–*n*-hexane	25	9	0.335	3.85	(*1*)
	35	9	0.568	2.58	
	45	8	0.895	2.99	
n-Octanol–*n*-hexane	25	8	0.302	3.17	(*1*)
	35	7	0.519	3.67	
	45	8	0.848	5.91	
n-Octanol–*n*-heptane	20	12	0.210	3.95	(*9*)
	25	13	0.330	3.51	
	30	13	0.446	3.89	
n-Octanol–*n*-octane	20	14	0.314	4.04	(*9*)
	25	14	0.354	3.43	
	30	13	0.392	4.79	
n-Octanol–*n*-tetradecane	20	13	0.534	6.71	(*9*)
	25	14	0.605	6.08	
	30	14	0.659	5.99	
n-Decanol–*n*-heptane	20	13	0.494	3.81	(*9*)
	25	14	0.440	3.55	
	30	14	0.383	4.65	
n-Decanol–*n*-octane	20	13	0.337	3.00	(*9*)
	25	14	0.314	3.00	
	30	14	0.294	4.37	
n-Decanol–*n*-tetradecane	20	14	0.529	5.49	(*9*)
	25	14	0.542	5.55	
	30	14	0.548	6.02	

[a] $\Delta = \frac{1}{n} \sum_{n} |h_{\mathrm{exptl}}^E - h_{\mathrm{calc}}^E|$, where n = no. of experimental points.

Table III. Calculated Results for Binary Alcohol–Alcohol Solutions with Hildebrand-Scatchard Equation

System	Temp, °C	No. of data points	β, cal/cc	Deviation Δ,[a] cal/mol	Data source
Methanol–*n*-butanol	25	20	2.452	0.24	(*8*)
Methanol–*n*-octanol	25	18	5.104	1.01	(*8*)
Ethanol–*n*-propanol	20	10	0.331	0.11	(*9*)
	25	10	0.286	0.10	
	30	10	0.255	0.08	
Ethanol–*n*-butanol	25	16	0.647	0.14	(*8*)
Ethanol–*n*-pentanol	20	12	1.198	0.10	(*9*)
	25	16	1.118	0.12	
	30	19	1.037	0.21	
Ethanol–*n*-octanol	20	13	2.421	0.50	(*9*)
	25	14	2.274	0.73	
	30	13	2.103	0.67	
Ethanol–*n*-octanol	25	18	2.411	0.56	(*8*)
Ethanol–*n*-decanol	20	14	3.355	1.87	(*9*)
	25	15	3.109	1.39	
	30	14	2.877	1.41	
n-Propanol–*n*-butanol	25	21	0.064	0.01	(*8*)
n-Propanol–*n*-pentanol	20	9	0.390	0.24	(*9*)
	25	18	0.347	0.18	
	30	16	0.302	0.11	
n-Propanol–*n*-octanol	20	13	1.438	1.00	(*9*)
	25	13	1.361	1.14	
	30	19	1.438	1.37	
n-Propanol–*n*-octanol	25	20	1.388	1.11	(*8*)
n-Propanol–*n*-decanol	20	11	2.321	2.52	(*9*)
	25	13	2.150	2.51	
	30	13	2.005	2.83	
n-Butanol–*n*-octanol	25	17	0.787	2.92	(*8*)
n-Pentanol–*n*-octanol	20	11	0.535	0.29	(*9*)
	25	11	0.473	0.27	
	30	11	0.418	0.31	
n-Pentanol–*n*-decanol	20	13	1.082	0.97	(*9*)
	25	13	1.009	0.96	
	30	12	0.944	1.25	

[a] $\Delta = \frac{1}{n} \sum_{n} |h_{\mathrm{exptl}}^E - h_{\mathrm{calc}}^E|$, where n = no. of experimental points.

Binary Data Reduction

In this work we used the enthalpy of formation of a hydrogen bond of −6.0 kcal/mol as proposed by Renon and Prausnitz. This value was assumed to be temperature independent. The values of chemical equilibrium constants for pure alcohols are listed in Table I. Table II presents the calculated results of 19 completely miscible hydrocarbon systems. The values of β were obtained by minimizing the sum of squares of deviation of calculated from experimental h^E data. Figure 1 illustrates a graphical representation of experimental and calculated results for *n*-pentanol–hydrocarbon systems. Figure 2 compares calculated values derived by using the Hildebrand-Scatchard equation with experimental data for alcohol–alcohol systems. Solid lines represent the calculated values fitted to the data of Ramalho and Ruel (*9*). The broken line was fitted to the data of Pope et al. (*8*). This figure and Table III show that the Hildebrand-Scatchard equation reproduces accurately the h^E data of alcohol–alcohol systems.

Prediction of Heats of Mixing for Ternary Alcohol-Alcohol-Saturated Hydrocarbon Mixtures

Ternary heat of mixing data reported by Ramalho and Ruel (*10*) for 17 alcohol-alcohol-hydrocarbon systems at 25°C were used for this work. All binary heat of mixing data used for prediction were those obtained by the same authors. Table IV presents the absolute deviations and percent relative deviations of predicted values from experimental results. The table also includes the results of Chang and Lu (*2*) who used a total of 18 binary parameters (six parameters per each binary system). Combination of Equations 6 and 10 gives the best predicted results.

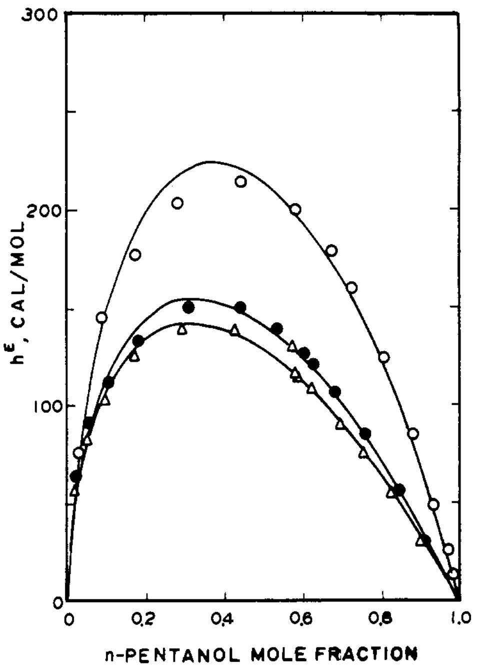

Figure 1. Heats of mixing for *n*-pentanol-normal alkane systems at 25°C

Experimental: *n*-pentanol–*n*-heptane, △ (*9*); *n*-pentanol–*n*-octane, ● (*9*); *n*-pentanol–*n*-tetradecane, ○ (*9*). Calculated: ———

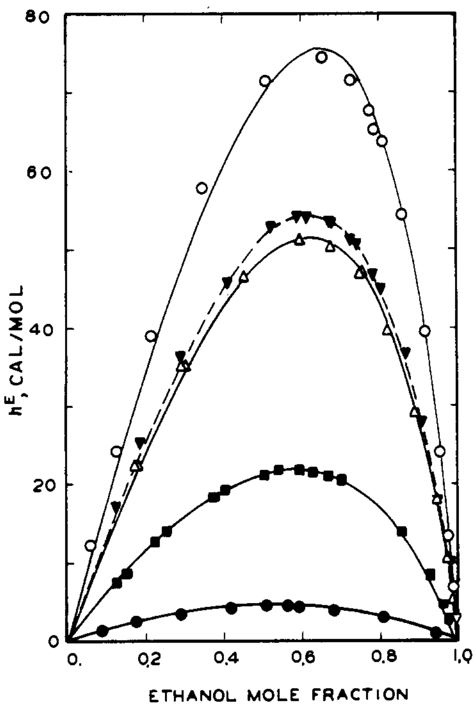

Figure 2. Heats of mixing for ethanol-normal alcohol systems at 25°C

Experimental: ethanol–*n*-propanol, ● (*9*); ethanol–*n*-pentanol, ■ (*9*); ethanol–*n*-octanol, △ (*9*); ethanol–*n*-octanol, ▼ (*8*); ethanol–*n*-decanol, ○ (*9*). Calculated: ———, ----

Table IV. Predicted Results for Ternary Alcohol-Alcohol-Saturated Hydrocarbon Systems at 25°C

		Deviation								
	No. of data	Δ_1,[a] cal/mol				Δ_2[b], %				
System	points	I[c]	II[d]	III[e]	IV[f]	I	II	III	IV	Chang-Lu[g]
Ethanol–*n*-propanol–*n*-heptane	32	4.09	4.54	4.80	3.81	4.89	5.44	5.38	4.08	3.02
Ethanol–*n*-pentanol–*n*-heptane	35	2.45	3.27	3.56	4.29	3.65	4.30	4.93	4.98	6.94
Ethanol–*n*-octanol–*n*-heptane	30	4.58	5.75	3.97	2.21	5.31	6.43	4.86	3.00	6.84
Ethanol–*n*-decanol–*n*-heptane	30	4.70	5.83	3.99	2.06	4.82	5.84	4.26	2.45	2.31
n-Propanol–*n*-pentanol–*n*-heptane	30	1.31	1.32	1.56	1.30	1.83	1.84	2.19	1.81	4.60
n-Propanol–*n*-octanol–*n*-heptane	35	3.01	3.18	2.81	2.53	3.50	3.66	3.26	3.06	3.30
n-Propanol–*n*-decanol–*n*-heptane	30	4.43	4.60	4.11	3.96	4.87	4.99	4.49	4.53	6.36
Ethanol–*n*-propanol–*n*-octane	30	6.07	6.27	6.90	6.05	8.50	8.83	9.18	7.85	1.60
Ethanol–*n*-pentanol–*n*-octane	30	3.87	4.45	4.83	4.67	5.78	6.40	6.86	5.94	10.10
Ethanol–*n*-octanol–*n*-octane	30	6.29	7.58	5.61	2.98	7.16	8.30	6.69	4.03	6.53
Ethanol–*n*-decanol–*n*-octane	30	6.28	7.48	5.53	2.58	6.46	7.50	5.86	3.22	4.62
n-Propanol–*n*-pentanol–*n*-octane	37	2.25	2.25	2.52	2.27	2.99	3.00	3.34	2.95	8.99
n-Propanol–*n*-octanol–*n*-octane	30	3.92	4.14	3.93	3.30	4.16	4.35	4.22	3.60	7.84
n-Propanol–*n*-decanol–*n*-octane	30	4.89	5.12	4.70	4.24	4.87	5.04	4.65	4.38	3.58
n-Propanol–*n*-pentanol–*n*-tetradecane	30	10.03	10.06	10.27	9.96	11.37	11.40	11.60	11.28	12.69
n-Propanol–*n*-octanol–*n*-tetradecane	35	10.38	10.72	10.42	9.45	9.11	9.33	9.28	8.46	7.20
n-Propanol–*n*-decanol–*n*-tetradecane	30	11.61	11.96	11.85	10.58	9.86	10.09	10.10	9.16	2.41
Total average		5.06	5.80	5.37	4.48	4.89	6.28	5.95	4.35	5.81

[a] $\Delta_1 = \frac{1}{n}\sum_n \left|h_{\text{exptl}}^E - h_{\text{calc}}^E\right|$, where n = no. of experimental points. [b] $\Delta_2 = \frac{100}{n}\sum_n \left\{\left|h_{\text{exptl}}^E - h_{\text{calc}}^E\right|/h_{\text{exptl}}^E\right\}$. [c] I. $\bar{K} = K_a\bar{x}_a^2 + 2\sqrt{K_aK_b}\,\bar{x}_a\bar{x}_b + K_b\bar{x}_b^2$, where $\bar{x}_a = x_a/(x_a + x_b)$ and $\bar{x}_b = x_b/(x_a + x_b)$. [d] II. $\bar{K} = K_a\bar{x}_a + K_b\bar{x}_b$. [e] III. $\bar{K} = K_a\bar{x}_a^2 + 2K_{ab}\bar{x}_a\bar{x}_b + K_b\bar{x}_b^2$, where $K_{ab} = 1/(\bar{x}_a/K_a + \bar{x}_b/K_b)$. [f] IV. $\bar{K} = 1/(\bar{x}_aK_a + \bar{x}_b/K_b)$. [g] Equation 15 without ternary constant in Ref. 2.

In conclusion, the present method, though empirical, gives the results comparable to the method of Chang and Lu in predicting heat of mixing data for ternary alcohol-alcohol-saturated hydrocarbon mixtures from binary parameters.

Acknowledgment

The author thanks the Computer Center, Osaka University, and the Data Processing Center, Kyoto University, for the use of their facilities.

Nomenclature

h_a = enthalpy of formation of a hydrogen bond, −6.0 kcal/mol
h^E = heat of mixing, cal/mol
K = chemical equilibrium constant of pure alcohol
$\bar{K}$ = chemical equilibrium constant of pseudo-single alcohol
R = gas constant
T = absolute temperature, K
v = molar volume, ml/mol
x = liquid mole fraction
$\bar{x}_a = x_a/(x_a + x_b)$

Greek Letters

β = physical interaction parameter, cal/cc
ϕ = volume fraction
$\bar{\phi}$ = volume fraction of pseudo-single alcohol

Subscripts

a, b = alcohols
h = hydrocarbon
i = alcohol monomer

Superscript

° = property of a pure substance in its particular reference state

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Received for review May 14, 1974. Accepted August 20, 1974.

NEW COMPOUND SECTION

Synthesis of 1-Fluoro-1,1,3,3-tetranitro-5-oxahexane, 3-Trifluoromethoxy-2,2-dinitropropanol, and 3-Fluoro-2,2-dinitropropanol

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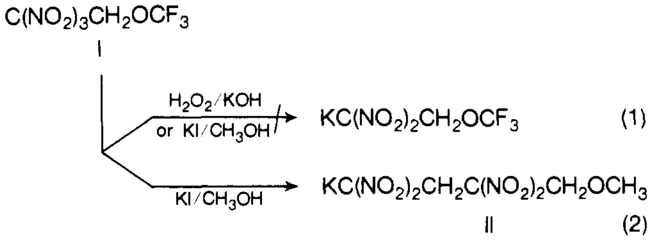
The synthesis of 1-fluoro-1,1,3,3-tetranitro-5-oxahexane by an aqueous fluorination procedure is described. The intermediate, potassium, 1,1,3,3-tetranitro-5-oxahexane, was obtained unexpectedly by basic reduction of 2,2,2-trinitroethyl trifluoromethyl ether. A limited amount of sulfur tetrafluoride produced two novel alcohols, 3-trifluoromethoxy-2,2-dinitropropanol and 3-fluoro-2,2-dinitropropanol. The acetate, acrylate, and formal derivatives of the alcohols were also prepared. The physical properties of the compounds are given.

A report in the Russian literature by Eremenko et al. (*3*) on the preparation of 1-fluoro-1,1,3,3-tetranitro-5-oxahexane, III, prompts us to report our recent synthesis and characterization of this compound.

In our research on the synthesis and reactions of fluorinated nitroaliphatic compounds (*10–12*), it was desirable to prepare potassium 2,2-dinitroethyl trifluoromethyl ether, $KC(NO_2)_2CH_2OCF_3$, as an intermediate. The reduction of a terminal trinitromethyl group to a potassium dinitromethyl group is well established (*7, 8*). Therefore, we anticipated that I would undergo this reaction to give the desired intermediate, $KC(NO_2)_2CH_2OCF_3$, as shown in Reaction 1.



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