Prediction of Excess Heat Capacities of Alcohol–Hydrocarbon Mixtures

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The Wilson, Heil, and NRTL equations were used to represent the temperature dependence of excess thermodynamic functions of highly nonideal alcohol–hydrocarbon mixtures. Under the assumption that the parameters of these equations are temperature-dependent, the simultaneous correlation of excess free energy and enthalpy of mixing over a considerable temperature range was made for the three alcohol–hydrocarbon systems, ethanol–*n*-heptane, 2-propanol–*n*-heptane, and ethanol–toluene, and subsequent prediction of excess heat capacity was attempted for the same systems. The Wilson equation, whose energy parameters are expressed by a quadratic function of temperature, was found to be more accurate for the mixtures studied than other equations and the method of Van Ness et al. (1967a,b).

The excess Gibbs free energy functions, the Wilson (*13*), Heil (*5*), and nonrandom two-liquid (NRTL) equations (*10*), which are derived from the local composition concept, have received considerable attention in recent years. A great deal of study concerning these semitheoretical equations has been performed on vapor-liquid equilibria of nonideal solutions and some on excess enthalpy of mixing, but little work has been done for prediction of excess heat capacity.

The excess enthalpies, h^E, are calculated from the excess free energy data, g^E, by differentiation of the semitheoretical equations using the well-known Gibbs-Helmholtz relation:

$$h^E = \{[\partial(g^E/T)]/[\partial(1/T)]\}_{P,x} \tag{1}$$

Various authors have proposed that the temperature dependence of the parameters of the semitheoretical equations should be taken into consideration in curve-fitting of h^E data for a number of nonideal binary mixtures. Asselineau and Renon (*1*) extended the NRTL equation so that the parameters varied linearly with temperature. Duran and Kaliaguine (*3*) discussed the temperature dependence of the Wilson parameters in a manner different from the treatment of Asselineau and Renon. Under the assumption that the parameters of the Wilson, Heil, and NRTL equations vary linearly with temperature, the present authors (*8*) have made a comparative study on the workability of these equations in the following cases: estimation of heats of mixing from vapor-liquid equilibrium data, estimation of excess free energies from heat of mixing data, a simultaneous fit of both data, and prediction of ternary heats of mixing from binary data.

Semitheoretical Equations

Wilson (*13*) proposed to replace overall volume fractions with local volume fractions in the theoretical equation of Flory and Huggins by intuitive reasoning. Wilson's equation, having two parameters, is suitable for representing experimental vapor-liquid equilibrium data for a variety of completely miscible mixtures and is especially useful for solutions of polar or associating components in nonpolar solvents. Heil and Prausnitz (*5*) extended Wilson's equation for describing thermodynamic properties of strongly nonideal polymer solutions. Renon and Prausnitz (*10*) have derived their NRTL equation by applying Wilson's idea of local composition to the two-liquid concept.

The general expressions of the Wilson, Heil, and NRTL equations for the excess Gibbs free energy and excess enthalpy of a binary mixture are given as follows:

$$\begin{aligned} g^E/RT = {} & -q[x_1 \ln(x_1 + x_2G_{21}) + x_2 \ln(x_2 + x_1G_{12})] + \\ & px_1x_2[\tau_{21}G_{21}/(x_1 + x_2G_{21}) + \tau_{12}G_{12}/(x_2 + x_1G_{12})] \end{aligned} \tag{2}$$

where $\tau_{12} = (g_{12} - g_{22})/RT$; $\tau_{21} = (g_{21} - g_{11})/RT$; $G_{12} = \rho_{12} \exp(-\alpha_{12}\tau_{12})$; $G_{21} = \rho_{21} \exp(-\alpha_{21}\tau_{21})$; and $(g_{21} - g_{11})$, $(g_{12} - g_{22})$, and α_{12} are three adjustable parameters. The definitions of p, q, ρ_{12}, and α_{12} are given below according to the type of the equation to be used.

Equation	p	q	$\rho_{12}{}^a$	$\alpha_{12}{}^b$
Wilson	0	1	V_1/V_2	1
Heil	1	1	V_1/V_2	1
NRTL	1	0	1	α_{12}

$^a\rho_{12} = 1/\rho_{21}$. $^b\alpha_{12} = \alpha_{21}$.

The excess enthalpy, h^E, may be calculated from Equations 1 and 2.

$$\begin{aligned} h^E/R = {} & -q[x_1x_2G_{21}'/(x_1 + x_2G_{21}) + x_1x_2G_{12}'/(x_2 + x_1G_{12})] + \\ & px_1x_2\tau_{21}'G_{21}/(x_1 + x_2G_{21}) + x_1\tau_{21}G_{21}'/(x_1 + x_2G_{21})^2 + \\ & \tau_{12}'G_{12}/(x_2 + x_1G_{12}) + x_2\tau_{12}G_{12}'/(x_2 + x_1G_{12})^2] \end{aligned} \tag{3}$$

where $\rho_{ij}' = (1/\rho_{ij})[d\rho_{ij}/d(1/T)]$ ($\rho_{ij}' = 0$, if $\rho_{ij} = 1$), $\rho_{ij}' = -\rho_{ji}'$, $\tau_{ij}' = d\tau_{ij}/d(1/T)$, $\alpha_{ij}' = d\alpha_{ij}/d(1/T)$, and $G_{ij}' = dG_{ij}/d(1/T) = G_{ij}(\rho_{ij}' - \alpha_{ij}'\tau_{ij} - \alpha_{ij}\tau_{ij}')$.

Calculation Procedure

In this work the parameters of the semitheoretical equations are assumed to change with temperature as follows:

$$g_{21} - g_{11} = C_1 + D_1(T - 273.15) + E_1(T - 273.15)^2 \tag{4}$$

$$g_{12} - g_{22} = C_2 + D_2(T - 273.15) + E_2(T - 273.15)^2 \tag{5}$$

$$\alpha_{12} = C_3 + D_3(T - 273.15) \tag{6}$$

The constants, C, D, and E, are evaluated by fitting Equations 2 and 3 to experimental excess free energy and heat of mixing data. A nonlinear fitting program was used which minimized the sum of absolute arithmetic mean deviations in experimental and calculated g^E and h^E values for all data points, an objective function as defined by Q:

$$Q = \frac{\sum_1^M \frac{\sum_{i=1}^m |g_{\text{calcd}}{}^E - g_{\text{exptl}}{}^E|_i}{m}}{M} + \frac{\sum_1^N \frac{\sum_{j=1}^n |h_{\text{calcd}}{}^E \quad h_{\text{exptl}}{}^E|_j}{n}}{N} \tag{7}$$

Equation 7 means that first the absolute arithmetic mean deviations for g^E and h^E were obtained at a specified tem-

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Table I. Parameters of Wilson, Heil, and NRTL Equations

		Wilson			Heil			NRTL			
System		C_1 C_2	D_1 D_2	$E_1 \times 100$ $E_2 \times 100$	C_1 C_2	D_1 D_2	$E_1 \times 100$ $E_2 \times 100$	C_1 C_2	D_1 D_2	$E_1 \times 100$ $E_2 \times 100$	C_3 $D_3 \times 1000$
Ethanol (1)-	I[a]	2910.6	−9.0921	0.0000	1134.0	−0.8978	0.0000	1901.4	−6.3337	0.0000	0.46001
n-heptane (2)		422.5	−1.6455	0.0000	−0.6	−1.0062	0.0000	1124.4	−1.5268	0.0000	0.4216
	II[b]	2626.4	−3.5856	−3.1590	987.0	3.5661	−3.4773	1463.7	5.8230	−7.7072	0.38718
		422.2	−1.2224	−0.5300	50.7	−1.5153	0.4970	797.8	1.0522	−0.8853	0.2414
2-Propanol (1)-	I	2614.8	−9.0331	0.0000	943.6	−1.0981	0.0000	1470.3	−4.7054	0.0000	0.48164
n-heptane (2)		162.1	−2.4068	0.0000	23.2	−1.0026	0.0000	699.3	−2.0514	0.0000	−0.4193
	II	2089.0	−2.9689	−2.5358	1030.1	−2.0350	2.0079	1259.2	5.7212	−9.0164	0.43295
		193.2	−1.0412	−1.1754	−74.8	−0.1655	−1.6163	581.2	1.6410	−2.0679	0.9395
Ethanol (1)-	I	1934.3	−6.2534	0.0000	942.2	−1.6713	0.0000	1362.3	−4.3280	0.0000	0.46261
toluene (2)		115.5	−0.2298	0.0000	−76.0	−0.4344	0.0000	505.0	−1.0947	0.0000	−0.9508
	II	1913.2	−5.5479	−0.2641	1071.7	−2.0677	1.0602	1410.9	−5.2404	0.6123	0.47298
		108.4	0.1894	−0.7125	−104.1	−0.4843	−0.7278	519.3	−0.3766	−0.5590	−0.4858

[a] $E_1 = E_2 = 0$ in Equations 4 and 5. [b] $E_1 \neq 0$, $E_2 \neq 0$ in Equations 4 and 5.

Table II. Deviations of Calculated Excess Free Energy and Enthalpy of Mixing Data from Experimental Results

				Absolute arithmetic mean dev, cal/mol						
				I[a]			II[b]			
System	h^E or g^E	Temp, °C	Data points	Wilson	Heil	NRTL	Wilson	Heil	NRTL	Ref.
Ethanol (1)-	h^E	10	21	6.6	41.2	24.8	4.4	18.6	15.6	(*11*)
n-heptane (2)	h^E	30	19	7.3	39.7	25.5	5.9	15.6	14.1	(*11*)
	h^E	45	19	6.8	30.4	21.8	6.1	20.8	16.5	(*11*)
	h^E	60	22	7.6	28.5	16.1	7.3	28.1	19.4	(*11*)
	h^E	75	17	8.3	39.2	19.2	5.8	31.9	17.1	(*11*)
	g^E	30	10	3.8	9.1	2.8	2.6	9.0	6.3	(*4*)
2-Propanol (1)-	h^E	30	26	10.7	28.0	14.6	6.6	18.9	13.0	(*12*)
n-heptane (2)	h^E	45	25	6.5	19.9	12.6	7.1	12.7	8.9	(*12*)
	h^E	60	25	9.9	28.4	12.6	6.7	16.2	12.5	(*12*)
	g^E	30	18	6.2	6.7	4.6	3.8	8.3	4.9	(*12*)
	g^E	45	18	6.4	6.4	4.7	3.9	7.9	4.8	(*12*)
	g^E	60	18	7.0	5.7	4.3	3.8	7.7	4.3	(*12*)
Ethanol (1)-	h^E	25	29	8.3	17.1	9.3	3.5	11.5	9.5	(*12*)
toluene (2)	h^E	45	25	4.0	15.6	9.2	3.0	10.0	8.7	(*12*)
	h^E	60	30	5.8	16.2	8.5	2.8	8.6	7.8	(*12*)
	g^E	30	19	1.5	3.7	2.1	1.5	8.9	2.0	(*12*)
	g^E	45	19	1.7	3.2	1.9	1.7	8.9	1.8	(*12*)
	g^E	60	19	1.9	3.0	2.6	1.8	8.1	2.3	(*12*)

[a] $E_1 = E_2 = 0$ in Equations 4 and 5. [b] $E_1 \neq 0$, $E_2 \neq 0$ in Equations 4 and 5.

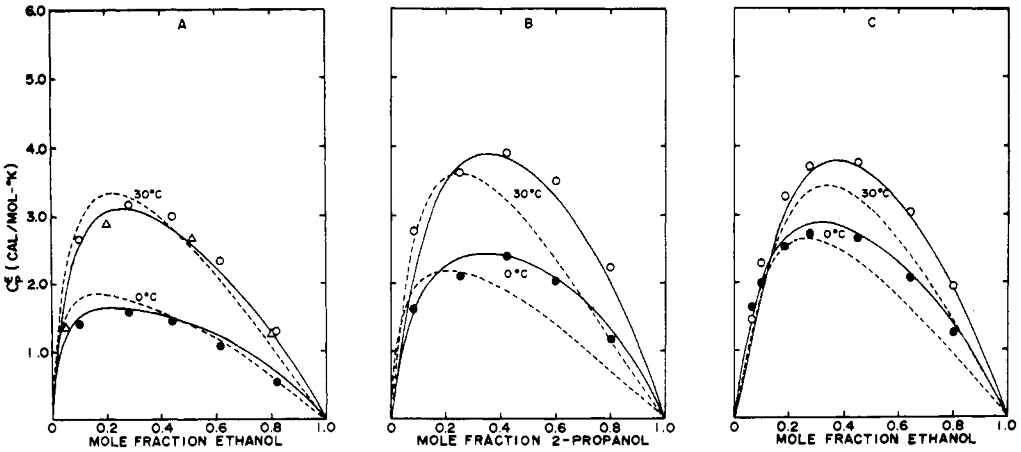

Figure 1. Comparison of predicted and experimental excess heat capacity data for three alcohol–hydrocarbon mixtures

Pred. ---------------------------------- ($E_1 = E_2 = 0$ in Equations 4 and 5) ——————($E_1 \neq 0$, $E_2 \neq 0$ in Equations 4 and 5)

A. ethanol (1)-*n*-heptane (2)	*B*. 2-propanol (1)-*n*-heptane (2)	*C*. ethanol (1)-toluene (2)
Exptl ● 0°C Ref. 2	Exptl ● 0°C Ref. 2	Exptl ● 0°C Ref. *6*
○ 30°C Ref. 2	○ 30°C Ref. *2*	○ 30°C Ref. *6*
△ 30°C Ref. *7*		

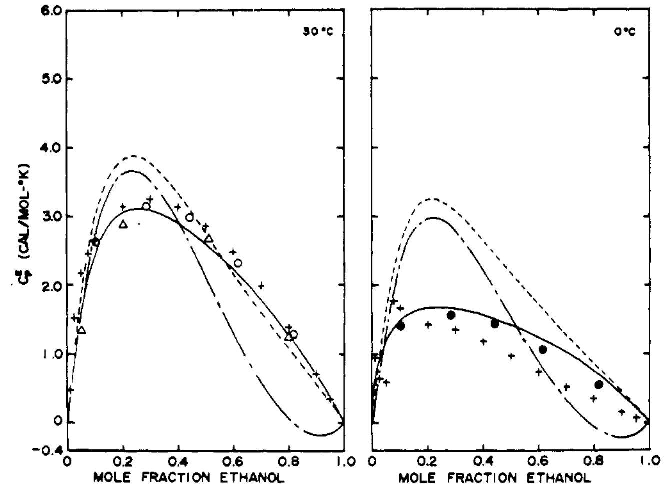

Figure 2. Comparison of predicted and experimental excess heat capacity data for ethanol-*n*-heptane system using Wilson, Heil, and NRTL equations and the method of Van Ness et al.
Exptl: ● 0°C, ○ 30°C Ref. 2, Δ 30°C Ref. 7
Pred.: + Van Ness et al. Ref. 11 ——Wilson, — — —Heil, -----NRTL

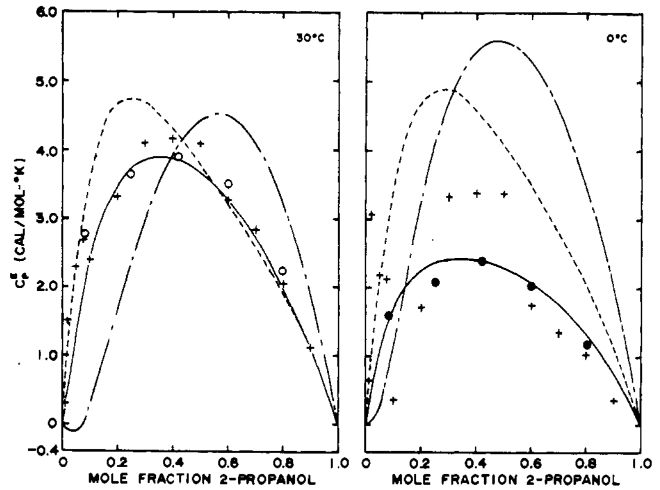

Figure 3. Comparison of predicted and experimental excess heat capacity data for 2-propanol-*n*-heptane system using Wilson, Heil, and NRTL equations and the method of Van Ness et al.
Exptl: ● 0°C, ○ 30°C Ref. 2
Pred.: + Van Ness et al. Ref. 12 ——Wilson, — — —Heil, -----NRTL

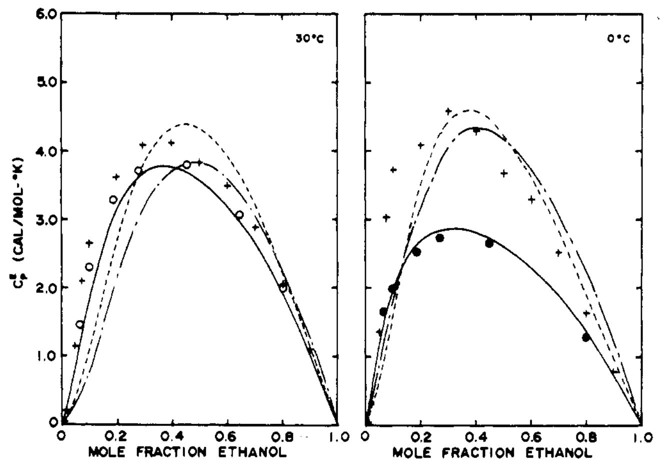

Figure 4. Comparison of predicted and experimental excess heat capacity data for ethanol-toluene system using Wilson, Heil, and NRTL equations and the method of Van Ness et al.
Exptl: ● 0°C, ○ 30°C Ref. 6
Pred.: + Van Ness et al. Ref. 12 ——Wilson, — — —Heil, -----NRTL

perature, then the sum of these deviations was divided by the number of temperature, and finally Q is given by the mean deviation of g^E plus that of h^E. A computer program was used for calculating the parameters using the Simplex method described by Nelder and Mead (*9*). The parameters so obtained were then used to compute excess heat capacity c_p^E:

$$c_p^E = (\partial h^E/\partial T)_{P,x} \qquad (8)$$

These computations were carried out using a FACOM 230-35 computer.

Results and Discussions

Table I gives the values of the parameters obtained by fitting g^E with Equation 2 and h^E with Equation 3 for three highly nonideal alcohol-hydrocarbon systems. The systems presented here met the requirements that for a binary system both isothermal vapor-liquid equilibrium data and excess enthalpy of mixing data must have been measured at more than two different temperatures and presented a suitable test to the present method. The magnitudes of the absolute arithmetic mean deviations reported on Table II indicate directly a measure of the fit of the experimental data by Equations 2 and 3.

To express the energy parameters as a quadratic function of temperature seems to improve the fit of experimental data obtained by using the parameters given as a linear function of temperature. The Wilson equation does a better job in fitting g^E and h^E than the other two equations. How correctly the used semitheoretical equation represents the temperature dependence of the excess enthalpies of mixing is indicated by a comparison of calculated and experimental excess heat capacity data. The existing data sources for the excess heat capacity are limited in number. Figure 1 shows graphical representations of experimental values and calculated results obtained using the Wilson equation for the excess heat capacity data for the three systems, ethanol-*n*-heptane, 2-propanol-*n*-heptane, and ethanol-toluene, which are presently available to us. The figure indicates clearly that the predicted values are in good agreement with the experimental data when the energy parameters are expressed by the quadratic functions of temperature. Prediction is successful at 0°C which is extrapolated from the temperature range of experimental h^E data. However, this is not the case for the Heil and NRTL equations whose energy parameters are expressed by a quadratic function of temperature as shown in Figures 2-4. These figures, respectively, compare the experimental c_p^E data and predicted results obtained by using the Wilson, Heil, and NRTL equations and the method of Van Ness and co-workers (*11*, *12*) for the ethanol-*n*-heptane, 2-propanol-*n*-heptane, and ethanol-toluene systems. Van Ness et al. have assumed that h^E for a mixture of given composition is represented by a quadratic function of absolute temperature, and subsequent differentiation of the h^E data yields a linear function for c_p^E. Hence, their calculated values are not continuous with respect to liquid composition. The figures demonstrate definitely that the Wilson equation is the best on the basis of the three binary systems studied.

Nomenclature

C_1, C_2 = values of $(g_{21} - g_{11})$ and $(g_{12} - g_{22})$ at 0°C, cal/mol
C_3 = value of α_{12} at 0°C
c_p^E = excess heat capacity, cal/mol K

D_1, D_2 = coefficients of temperature change of $(g_{21} - g_{11})$ and $(g_{12} - g_{22})$, cal/mol K
D_3 = coefficient of temperature change of α_{12}, K^{-1}
E_1, E_2 = coefficients of temperature change of $(g_{21} - g_{11})$ and $(g_{12} - g_{22})$, cal/mol $(K)^2$
g^E = excess Gibbs free energy, cal/mol
g_{ij} = energies of interaction between an i-j pair of molecules, cal/mol
G_{ij} = coefficient as defined by $G_{ij} = \rho_{ij} \exp(-\alpha_{ij} \cdot \tau_{ij})$
h^E = excess enthalpy of mixing, cal/mol
p = coefficient (0 or 1) of Equations 2 and 3
q = coefficient (0 or 1) or Equations 2 and 3
Q = objective function as defined by Equation 7, cal/mol
R = gas constant, 1.98726 cal/mol K
T = absolute temperature, K
x_i = liquid-phase mole fraction of component i

Greek Letters

α_{ij} = nonrandomness constant for binary i-j interaction
ρ_{ij} = coefficient as defined by $G_{ij} = \rho_{ij} \exp(-\alpha_{ij}\tau_{ij})$
τ_{ij} = coefficient as defined by $\tau_{ij} = (g_{ij} - g_{jj})/RT$

Subscript

i = component

Superscript

E = excess

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Received for review April 26, 1972. Accepted August 18, 1972.

Thermodynamic Properties of Liquid Gallium Alloys. I. Gallium-Lead

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Vapor pressure measurements have been made on liquid lead and gallium-lead alloys by use of the torsion effusion technique. From the resulting lead activities, the values for the gallium component have been calculated by the Gibbs-Duhem integration at 1143K. Wide deviations from ideal behavior have been observed. By use of previous calorimetric enthalpies, entropy values for the alloys and for their components have been derived.

Activities of the elements of Ga-Pb alloys are not well known. These parameters can be calculated using the partial free energies of formation obtained by Predel and Stein *(10)* at 923K on the basis of solubility equilibria and using calorimetric mixing enthalpies measurements. When this procedure is followed, the resulting activity values could be affected by considerable uncertainties. Therefore it has been deemed useful to determine them directly with vapor pressure measurements.

The torsion effusion method is particularly suitable for this study for the most rapid, precise reading of experimental data.

Torsion effusion measurements of lead vapor pressure, reported here, were made as an essential preliminary to the alloy studies.

Experimental

The principle of the torsion effusion technique and the apparatus details have been described elsewhere *(2, 8)*.

The relationship between the cell deflection, α, and the pressure, P, is given by:

$$P = 2K\alpha/(a_1 d_1 f_1 + a_2 d_2 f_2) \tag{1}$$

where K is the torsion constant of the suspension; a_1, a_2, d_1, and d_2 the orifice areas and distances from the axis of rotation; and f_1 and f_2 the Freeman and Searcy *(3)* correction factors for orifice geometry. Vapor pressure

Table I. Constants of Orifice Cells

	Cell 1	Cell 2
Orifice area		
a_1, 10^{-3} cm^2	9.71 ± 0.05	10.70 ± 0.05
a_2, 10^{-3} cm^2	10.25 ± 0.05	11.45 ± 0.05
Moment arm		
d_1, cm	0.648 ± 0.005	0.653 ± 0.005
d_2, cm	0.574 ± 0.005	0.641 ± 0.005
Force correction factor *(3)*		
f_1	0.570	0.601
f_2	0.578	0.621

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