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PREDICTION OF TERNARY EXCESS ENTHALPIES FROM BINARY DATA

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ABSTRACT

Excess enthalpy data at 298.15 K were measured with a continuous dilution calorimeter for binary mixtures of methanol–*p*-xylene, ethanol-*p*-xylene, 1-propanol–*p*-xylene, 2-propanol–*p*-xylene, and *p*-xylene–cyclohexane, and for ternary mixtures of ethanol–*p*-xylene–cyclohexane, 1-propanol–*p*-xylene–cyclohexane, and 2-propanol–*p*-xylene–cyclohexane. The data for the present ternary systems and three others obtained from the literature were well predicted using the UNIQUAC associated solution theory, which incorporates two equilibrium constants of the self-association of alcohols, with only binary parameters

NOTATION

C_{A_i}	Concentration of alcohol imer defined as number of moles divided by segment number of one true mole of solution, n_{A_i}/V
C_{A_iB}	Concentration of chemical complex A_iB defined as number of moles divided by segment number of one true mole of solution, n_{A_iB}/V
C_{A_iC}	Concentration of chemical complex A_iC defined as number of moles divided by segment number of one true mole of solution, n_{A_iC}/V
C_i, D_i	Constants in eqn (15)
H_f	Total enthalpy of chemical complex formation
h_2	Enthalpy of formation of alcohol-dimer
h_A	Enthalpy of formation of a hydrogen bond in alcohol-imer
h_{AB}	Enthalpy of formation of an alcohol–unsaturated hydrocarbon bond
h^E	Excess enthalpy
K_2	Chemical equilibrium constant of alcohol-dimer.
K_A	Chemical equilibrium constant of alcohol-imer.
K_{AB}	Chemical equilibrium constant of complex formation between an alcohol-imer and an unsaturated hydrocarbon (=component B)
l_i	Bulk factor of component i
n	Number of moles of a particular species
q_i	Surface parameter of component i
r_i	Segment parameter of component i.
R	Gas constant
T	Absolute temperature
u_{ji}	Binary interaction parameter

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V	Segment number of one true mole of solution in which alcohol complexes and alcohol–unsaturated hydrocarbon component complexes are considered as chemical species.
x_i	Liquid phase mole fraction of component i
Z	Lattice coordination number, a constant here set equal to 10

Greek letters

θ_i	Surface fraction of component i.
ρ_{AB}	r_B/r_A.
ρ_{AC}	r_C/r_A.
τ_{ji}	$\exp[-(u_{ji}-u_{ii})/RT]$
ϕ_i	Volume fraction of component i

Superscript

^{c}	Pure alcohol

Subscripts

A	Alcohol or component A
A_1, A_i	Alcohol monomer and $i$mer
AB	Complex formation between alcohol and component B
A_iB	Alcohol-$i$mer–unsaturated hydrocarbon B complex
AC	Complex formation between alcohol and component C
A_iC	Alcohol-$i$mer–unsaturated hydrocarbon C complex
B	Component B in a solution
C	Component C in a solution
chem	Chemical
f	Formation of complex
i,j,k	Components
phys	Physical
OB	Free component B unattached to alcohol
OC	Free component C unattached to alcohol.
1,2,3	Components (alcohol and unsaturated hydrocarbons, respectively)

INTRODUCTION

Several methods for predicting ternary excess enthalpies from binary data have been proposed and were tested for different types of solutions. The UNIQUAC associated solution theory has been applied to correlate the excess thermodynamic properties of alcohol–unassociated component solutions over the whole concentration range [1–3]. These approaches assumed that the association of alcohols in saturated hydrocarbons is described by successive chemical equilibria $A_i + A_1 = A_{i+1}$ ($i \geq 1$) and that all equilibrium constants of these equilibria are the same. The purpose of this work is to examine whether improved representation of excess enthalpy data for alcohol–unsaturated hydrocarbon solutions may be possible where only the dimerization constant is different from the other remaining equilibrium constants.

EXPERIMENTAL

Reagent grade chemicals were purchased for experimental work. Alcohols were fractionally distilled after storage over drying materials: methanol (anhydrous calcium sulfate), ethanol (calcium oxide), propanols (anhydrous copper sulfate). Cyclohexane was used directly. *p*-Xylene was purified by fractional crystallization. Densities and refractive indices of the compounds used for this work are compared with the acceptable literature values in Table 1.

TABLE 1

Densities and refractive indices of compounds at 298.15 K

Compound	Density ($g\,cm^{-3}$)		Refractive index	
	Exptl	Ref 4	Exptl	Ref 4
Methanol	0.7866	0.7866	1.3265	1.3265
Ethanol	0.7857	0.7850	1.3594	1.3594
1-Propanol	0.7998	0.7998	1.3837	1.3837
2-Propanol	0.7813	0.7813	1.3751	1.3752
p-Xylene	0.8567	0.8567	1.4932	1.4933
Cyclohexane	0.7738	0.7739	1.4237	1.4235

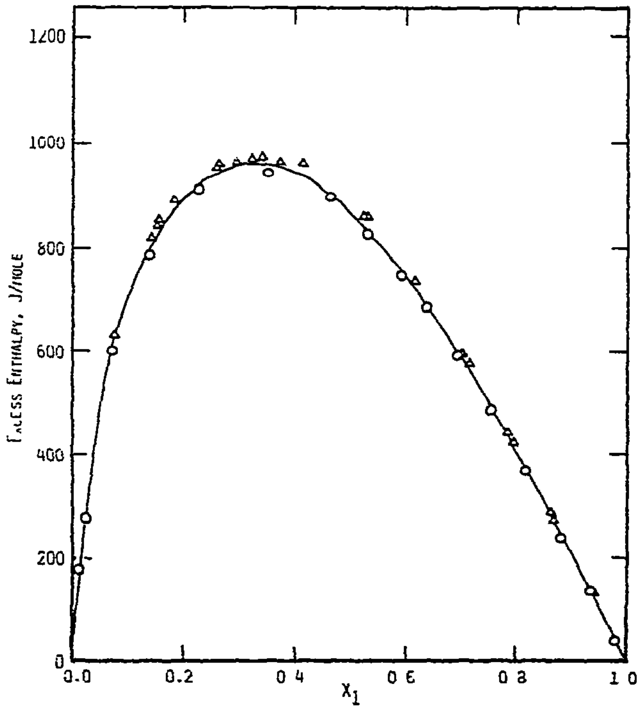

Fig 1 Excess enthalpies for the 1-propanol (1)–*p*-xylene (2) system at 298.15 K. Experimental △, Christensen et al. [6]; ○, this work Calculated, ————.

TABLE 2

Experimental excess enthalpies for binary systems at 298.15 K

x_1	h^E (J mole^{-1})	x_1	h^E (J mole^{-1})	x_1	h^E (J mole^{-1})
Methanol(1)–*p*-xylene(2)					
0.0462	433.1	0.4826	665.8	0.8030	356.7
0.0991	587.3	0.6069	574.7	0.8498	286.5
0.1601	671.9	0.6756	508.0	0.8938	213.7
0.2228	710.6	0.7186	465.8	0.9413	126.1
0.2797	723.5	0.7434	430.6	0.9796	46.4
0.3671	714.2	0.7605	414.3		
Ethanol(1)–*p*-xylene(2)					
0.0112	156.6	0.4651	753.6	0.7641	401.8
0.0434	433.1	0.5440	684.5	0.8184	314.9
0.0603	511.3	0.6380	577.4	0.8724	224.4
0.1466	724.9	0.6509	563.3	0.9216	139.1
0.2325	803.4	0.7089	484.5	0.9712	51.1
0.3491	814.1				
1-Propanol(1)–*p*-xylene(2)					
0.0115	177.5	0.4562	895.4	0.7535	489.4
0.0207	274.6	0.5288	826.2	0.8141	372.5
0.0714	602.6	0.5913	748.5	0.8819	238.5
0.1387	789.8	0.6375	689.2	0.9340	132.9
0.2273	913.1	0.6949	594.2	0.9776	43.7
0.3490	947.6				
2-Propanol(1)–*p*-xylene(2)					
0.0195	270.8	0.3903	1187.4	0.7487	770.5
0.0462	507.1	0.4773	1163.0	0.8102	616.7
0.0923	738.1	0.5454	1107.5	0.8797	415.1
0.1583	936.7	0.5715	1081.7	0.9330	242.0
0.2418	1090.5	0.6245	1008.8	0.9700	113.6
0.3249	1168.8	0.6936	887.7		
p-Xylene(1)–cyclohexane(2)					
0.0238	66.6	0.3935	551.1	0.7486	376.7
0.0954	235.1	0.4547	557.3	0.7956	319.6
0.1507	335.6	0.5099	548.5	0.8412	258.6
0.2128	422.7	0.5687	526.0	0.8858	193.2
0.2934	501.4	0.6291	488.2	0.9252	130.3
0.3664	541.4	0.6907	436.9	0.9644	64.5

The continuous dilution calorimeter used for the measurements and the experimental procedure were the same as described previously [5]. The errors of the results obtained with this calorimeter were of the order of ±0.5%. Table 2 lists the results at 298.15 K for five binary systems: methanol–*p*-xylene, ethanol–*p*-xylene, 1-propanol–*p*-xylene, 2-propanol–*p*-xylene, and *p*-xylene–cyclohexane. Our results for the alcohol–*p*-xylene systems are uniformly lower than those of Christensen et al. [6]

TABLE 3

Experimental excess enthalpies for ternary systems[a] at 298.15 K

Ethanol(1)–*p*-xylene(2)–cyclohexane(3)

$x_2'=0.2493$			$x_2'=0.4999$			$x_2'=0.7494$		
x_1	x_2	h^E (J mole^{-1})	x_1	x_2	h^E (J mole^{-1})	x_1	x_2	h^E (J mole^{-1})
0.0048	0.2481	553.9	0.0035	0.4982	591.7	0.0173	0.7367	589.1
0.0248	0.2431	709.6	0.0127	0.4936	732.6	0.0448	0.7161	766.4
0.0593	0.2345	806.8	0.0513	0.4742	932.7	0.0945	0.6788	902.7
0.1058	0.2229	876.3	0.1103	0.4448	1035.9	0.1533	0.6347	968.1
0.1449	0.2132	909.8	0.1580	0.4209	1068.9	0.2173	0.5867	999.3
0.1835	0.2035	929.3	0.2299	0.3850	1079.0	0.2703	0.5405	999.3
0.2365	0.1903	939.9	0.2942	0.3528	1062.2	0.3278	0.5039	981.5
0.2924	0.1764	935.8	0.3399	0.3300	1036.6	0.3750	0.4686	954.5
0.3607	0.1594	910.4	0.4298	0.2850	962.3	0.4446	0.4164	898.0
0.4490	0.1373	855.2	0.5024	0.2487	883.6	0.5100	0.3673	829.3
0.5249	0.1182	791.1	0.5873	0.2063	773.9	0.5644	0.3266	763.8
0.5302	0.1171	783.4	0.6521	0.1739	678.0	0.6300	0.2774	672.6
0.5963	0.1006	714.2	0.6565	0.1717	670.9	0.6909	0.2317	578.2
0.5984	0.1001	710.5	0.7150	0.1425	576.9	0.7363	0.1977	502.7
0.6414	0.0894	659.4	0.7490	0.1255	517.7	0.7789	0.1658	428.7
0.6649	0.0835	618.1	0.7881	0.1060	446.3	0.8233	0.1325	348.1
0.6825	0.0792	605.0	0.7939	0.1030	405.9	0.8535	0.1099	291.5
0.7165	0.0707	556.2	0.8198	0.0901	386.1	0.8737	0.0947	252.5
0.7508	0.0621	503.8	0.8354	0.0823	331.7			
0.7841	0.0538	449.8	0.8642	0.0679	278.1			
			0.8837	0.0581	240.7			

TABLE 3 (continued)

1-Propanol(1)-*p*-xylene(2)–cyclohexane(3)

$x'_2 = 0.2510$			$x'_2 = 0.4988$			$x'_2 = 0.7466$		
x_1	x_2	h^E (J mole^{-1})	x_1	x_2	h^E (J mole^{-1})	x_1	x_2	h^E (J mole^{-1})
0.0063	0.2494	566.3	0.0268	0.4855	842.2	0.0135	0.7365	553.9
0.0344	0.2423	763.3	0.0774	0.4602	1008.1	0.0372	0.7188	753.7
0.0832	0.2301	877.5	0.1366	0.4307	1089.2	0.0755	0.6902	906.3
0.1610	0.2106	951.9	0.2394	0.3794	1121.5	0.1249	0.6534	1008.7
0.2423	0.1902	972.1	0.3289	0.3348	1088.3	0.1759	0.6153	1065.6
0.3253	0.1693	948.5	0.4072	0.2957	1020.2	0.2569	0.5549	1096.4
0.4007	0.1504	896.8	0.4679	0.2654	947.9	0.3388	0.4937	1074.2
0.4832	0.1297	814.0	0.5249	0.2370	867.9	0.3973	0.4500	1032.7
0.5444	0.1143	739.0	0.5718	0.2136	794.7	0.4768	0.3906	949.3
0.6007	0.1002	662.1	0.6280	0.1856	699.7	0.5450	0.3397	857.0
0.6595	0.0855	574.5	0.6536	0.1728	655.7	0.6092	0.2918	755.4
0.7163	0.0712	485.3	0.7085	0.1454	555.9	0.6488	0.2622	686.7
0.7646	0.0591	406.4	0.7611	0.1192	456.8	0.6909	0.2308	610.8
0.7921	0.0522	360.4				0.7576	0.1811	483.2
0.8192	0.0454	314.2						

TABLE 3 (continued)

2-Propanol(1)–*p*-xylene(2)–cyclohexane(3)

$x_2'=0.2477$			$x_2'=0.5002$			$x_2'=0.7494$		
x_1	x_2	h^E (J mole^{-1})	x_1	x_2	h^E (J mole^{-1})	x_1	x_2	h^E (J mole^{-1})
0.0404	0.2377	825.2	0.0102	0.4951	697.7	0.0229	0.7323	662.6
0.1000	0.2229	986.5	0.0388	0.4808	936.2	0.1193	0.6601	1075.1
0.1627	0.2074	1080.0	0.1191	0.4406	1168.1	0.1856	0.6104	1195.5
0.2386	0.1886	1144.1	0.2007	0.3999	1270.0	0.2368	0.5720	1251.0
0.3108	0.1707	1164.7	0.2797	0.3603	1309.8	0.3062	0.5200	1287.2
0.3816	0.1532	1149.7	0.3474	0.3265	1305.0	0.3839	0.4617	1284.7
0.4631	0.1330	1093.7	0.4417	0.2793	1244.5	0.4689	0.3980	1232.5
0.5257	0.1175	1025.4	0.5176	0.2413	1156.6	0.5479	0.3388	1142.8
0.5717	0.1061	962.0	0.5831	0.2085	1055.5	0.6029	0.2976	1058.6
0.6120	0.0961	899.5	0.6499	0.1751	931.2	0.6537	0.2595	964.2
0.6547	0.0855	825.6	0.6887	0.1557	849.2	0.7048	0.2212	857.5
0.7002	0.0743	739.3	0.7156	0.1423	789.9	0.7423	0.1931	771.1
0.7300	0.0669	678.5	0.7478	0.1261	714.8	0.7768	0.1673	685.3
0.7633	0.0586	607.1	0.7899	0.1051	610.5	0.8027	0.1479	617.5
0.7956	0.0506	534.7	0.8195	0.0903	533.2	0.8294	0.1279	544.2
0.8185	0.0450	482.4				0.8468	0.1148	495.7
0.8557	0.0357	390.8				0.8562	0.1079	467.3
0.8846	0.0286	317.3				0.8845	0.0866	382.0
0.8910	0.0270	300.9				0.9051	0.0712	318.3
						0.9194	0.0604	272.7
						0.9302	0.0523	237.8

---

[a] Ternary mixtures were obtained by mixing pure alcohol with $\{x_2'\,p\text{-xylene}+(1-x_2')\text{cyclohexane}\}$

by about 20 J mole^{-1} as shown in Fig. 1. The data of Hsu and Clever [7] for the *p*-xylene–cyclohexane system is about 14 J mole^{-1} higher than the results given here. Ternary mixtures were prepared by adding pure alcohol to the binary mixtures of *p*-xylene–cyclohexane of known composition. Table 3 presents the results at 298.15 K for three ternary systems: ethanol–*p*-xylene–cyclohexane, 1-propanol–*p*-xylene–cyclohexane, and 2-propanol–*p*-xylene–cyclohexane.

THEORY

We assume that the dimerization constant is different from polymerization constants and that there is no size change of mixing. The chemical equilibrium constants of alcohol association are defined as suggested by Kretschmer and Wiebe [8].

$$A_1 + A_1 = A_2 \qquad K_2 = \frac{C_{A_2}}{C_{A_1}C_{A_1}r_A} = \frac{\phi_{A_2}}{2\phi_{A_1}\phi_{A_1}} \tag{1}$$

$$A_i + A_1 = A_{i+1} (i > 2) \qquad K_A = \frac{C_{A_{i+1}}}{C_{A_i}C_{A_1}r_A} = \frac{\phi_{A_{i+1}}}{\phi_{A_i}\phi_{A_1}}\frac{i}{i+1} \tag{2}$$

The equilibrium constants of complex formation between alcohol and unsaturated hydrocarbons B and C are given as

$$A_i + B = A_iB\ (i \geq 1) \qquad K_{AB} = \frac{C_{A_iB}}{C_{A_i}C_{OB}r_A} = \frac{\phi_{A_iB}}{\phi_{A_i}\phi_{OB}}\frac{i\rho_{AB}}{i+\rho_{AB}} \tag{3}$$

$$A_i + C = A_iC\ (i \geq 1) \qquad K_{AC} = \frac{C_{A_iC}}{C_{A_i}C_{OB}r_A} = \frac{\phi_{A_iC}}{\phi_{A_i}\phi_{OC}}\frac{i\rho_{AC}}{i+\rho_{AC}} \tag{4}$$

where C_{A_iB} and ϕ_{A_iB} are the molar concentration and the segment fraction of chemical species A_iB, respectively, and ρ_{AB} is the ratio of r_B of component B to r_A of the alcohol. C_{A_iC} and ϕ_{A_iC} are similarly defined. ϕ_{A_1}, ϕ_{OB} and ϕ_{OC} are the segment fractions of monomers of the alcohol and components B and C.

We assume that the total excess enthalpy of a ternary alcohol–hydrocarbon mixture is expressed as the sum of chemical and physical contributions and the latter contribution is obtainable from the residual term of the UNIQUAC equation [9].

$$h^E = h^E_{chem} + h^E_{phys} \tag{5}$$

The enthalpy of complex formation in the mixture is

$$H_f = h_2 n_{A_2} + h_A\left\{\sum_{i=3}^{\infty}(i-1)n_{A_i} + \sum_{i=2}^{\infty}(i-1)n_{A_iB} + \sum_{i=2}^{\infty}(i-1)n_{A_iC}\right\} + h_{AB}\sum_{i=1}^{\infty}n_{A_iB} + h_{AC}\sum_{i=1}^{\infty}n_{A_iC} \tag{6}$$

The chemical term of the excess enthalpy of the mixture is defined by

$$h^E_{chem} = H_f - x_1 H_f^0 \tag{7}$$

where H_f^0 is the value of H_f at pure alcohol state and x_1 is the nominal mole fraction of the alcohol (= component 1). Performing the sums in eqn. (6) and substituting the final expressions for H_f and H_f^0 into eqn. (7) give

$$
\begin{aligned}
h^{E}_{\text{chem}} = {} & x_1 h_2 K_2\left(\frac{\phi_{A_1}^2}{\phi_1} - \phi_{A1}^{02}\right) + x_1 h_A K_A\left\{\left(\phi_{A_1} - \phi_{A_1}^0\right) - \left(\frac{\phi_{A_1}^2}{\phi_1} - \phi_{A_1}^{02}\right)\right\} \\
& + \frac{x_1 h_A \phi_{A_1}^2 (K_2 - K_A)}{\phi_1}\left(\frac{K_{AB}\phi_{OB}}{\rho_{AB}} + \frac{K_{AC}\phi_{OC}}{\rho_{AC}}\right) \\
& + \left(\frac{x_1 h_{AB} K_{AB}\phi_{A_1}\phi_{OB}}{\rho_{AB}\phi_1} + \frac{x_1 h_{AC} K_{AC}\phi_{A_1}\phi_{OC}}{\rho_{AC}\phi_1}\right)\left(1 + \frac{K_2\phi_{A_1}}{1 - K_A\phi_{A_1}}\right) \qquad (8)
\end{aligned}
$$

where h_2 is the enthalpy of hydrogen bond formation for dimerization, h_A is that for linear polymerization ($i \geqslant 3$), and h_{AB} and h_{AC} are the enthalpy of complex formation of an alcohol–component B bond and that of an alcohol–component C bond, respectively.

The nominal size fractions of three components are related to the size fractions of the chemical species.

$$
\begin{aligned}
\phi_1 & = \phi_{A_1} + \sum_{i=2}^{\infty}\phi_{A_i} + \sum_{i=1}^{\infty}\phi_{A_iB}\frac{r_{A_i}}{r_{A_iB}} + \sum_{i=1}^{\infty}\phi_{A_iC}\frac{r_{A_i}}{r_{A_iC}} \\
& = \phi_{A_1} - \frac{K_2}{K_A}\phi_{A_1}\left[1 - \frac{1}{\left(1 - K_A\phi_{A_1}\right)^2}\right] \\
& \quad + \left[\frac{K_{AB}\phi_{OB}\phi_{A_1}}{K_A\rho_{AB}} + \frac{K_{AC}\phi_{OC}\phi_{A_1}}{K_A\rho_{AC}}\right]\left[K_A - K_2 + \frac{K_2}{\left(1 - K_A\phi_{A_1}\right)^2}\right] \qquad (9)
\end{aligned}
$$

$$
\phi_2 = \sum_{i=0}^{\infty}\frac{\phi_{A_iB}}{r_{A_iB}}r_2 = \frac{\phi_{OB}}{K_A}\left\{K_A + K_{AB}(K_A - K_2)\phi_{A_1} + \frac{K_2K_{AB}\phi_{A_1}}{1 - K_A\phi_{A_1}}\right\} \qquad (10)
$$

TABLE 4

Values of the pure component structural parameters

Component	r	q	l[a]
Methanol	1.15	1.12	0
Ethanol	1.69	1.55	0
1-Propanol	2.23	1.98	0
2-Propanol	2.23	1.98	0
Benzene	2.56	2.05	1
Toluene	3.10	2.48	1
p-Xylene	3.65	2.92	1
Cyclohexane	3.18	2.55	1
Methylcyclohexane	3.72	2.98	1

[a] $l=(Z/2)(r-q)-(r-1)$ and $Z=10$.

$$\phi_3 = \sum_{i=0}^{\infty} \frac{\phi_{A_iC}}{r_{A_iC}} r_3 = \frac{\phi_{OC}}{K_C} \left\{ K_A + K_{AC}(K_A - K_2)\phi_{A_1} + \frac{K_2 K_{AC} \phi_{A_1}}{1 - K_A \phi_{A_1}} \right\} \tag{11}$$

The monomer size fractions, ϕ_{A_1}, ϕ_{OB}, and ϕ_{OC}, are obtained by solving eqns. (9)–(11) if the equilibrium constants are known. The pure alcohol monomer size fraction $\phi^0_{A_1}$ is calculated from the equation

$$1 = \phi^0_{A_1} - \frac{K_2}{K_A}\phi^0_{A_1} + \frac{K_2}{K_A} \frac{\phi^0_{A_1}}{\left(1 - K_A \phi^0_{A_1}\right)^2} \tag{12}$$

The two-constant model equations ($K_2 \neq K_A$) described here reduce to the one-constant model equations, which were given previously [5], if $K_2 = K_A$.

The physical term of the excess enthalpy is expressed by differentiating the residual term of the UNIQUAC equation with respect to temperature.

$$h^E_{\text{phys}} = \frac{\partial\left(g^E_{\text{residual}}/T\right)}{\partial(1/T)} = -R \sum_{i=1}^{m} q_i x_i \frac{\sum_{j=1}^{m} \theta_j \frac{\partial \tau_{ji}}{\partial(1/T)}}{\sum_{j=1}^{m} \theta_j \tau_{ji}} \tag{13}$$

where

$$\tau_{ji} = \exp\left[-\left(u_{ji} - u_{ii}\right)/RT\right] \tag{14}$$

TABLE 5

Values of chemical equilibrium constants and enthalpies of hydrogen bond formation of alcohols at 298.15 K

Alcohol	h_2 (kJ mole^{-1})	h_A (kJ mole^{-1})	K_2	K_A^a
Methanol	−36.7	−23.2	50	280
Ethanol	−36.7	−23.2	60	180
1-Propanol	−36.7	−23.2	40	120
2-Propanol	−36.7	−23.2	40	90

[a] 323.15 K

TABLE 6

Values of h_{AB} and K_{AB} at 298.15 K

System(1–2)	h_{AB} (kJ mole^{-1})	K_{AB}
Methanol-*p*-xylene	−11.0	6
Ethanol-benzene	−9.2	5
Ethanol-toluene	−10.0	5
Ethanol-*p*-xylene	−11.0	5
1-Propanol-*p*-xylene	−11.0	5
2-Propanol-benzene	−9.2	4
2-Propanol-toluene	−10.0	4
2-Propanol-*p*-xylene	−11.0	4

TABLE 7

Calculated results based on two constant models at 298.15 K

System(1-2)	No of data points	Abs arith mean dev (J mole^{-1})		C_1/RT	C_2/RT	D_1/RT (K^{-1}) $\times 10^{-3}$	D_2/RT (K^{-1}) $\times 10^{-3}$	Ref
		I[a]	II[b]					
Methanol-*p*-xylene	17	11.7	10.3	0.9667	−0.5840	2.9725	−2.2473	This work
Ethanol-*p*-xylene	16	5.1	2.0	2.3569	−0.2010	7.1057	0.8046	This work
1-Propanol-*p*-xylene	16	17.8	4.6	0.8451	−0.6519	−0.3697	−1.2339	This work
2-Propanol-*p*-xylene	17	7.6	5.5	0.0727	0.0852	−0.5966	0.0053	This work
Ethanol-benzene	10	8.4[c]	1.7	1.3501	1.3480	3.2111	5.4545	12
2-Propanol-benzene	17	7.1[c]	4.0	−0.0033	0.0824	0.8766	0.5149	13
Ethanol-toluene	10	2.5[c]	2.0	1.4347	0.7216	3.9624	2.9018	12
2-Propanol-toluene	10	20.3[c]	4.4	−0.1395	0.5050	−2.3677	2.9144	12
Ethanol-cyclohexane	21	4.9	2.7	−0.5090	0.1223	−2.5195	0.4652	5
1-Propanol-cyclohexane	18	4.7	3.1	1.3299	−0.6971	5.8361	−3.2056	5
2-Propanol-cyclohexane	18	12.2	10.3	−0.7298	0.8772	−5.3431	8.9686	14
2-Propanol-methylcyclohexane	19	12.6	9.9	−0.3987	0.6932	−2.3446	3.4477	13
p-Xylene-cyclohexane	19	3.3		0.0988	0.0606	−3.1659	2.6535	This work
Methylcyclohexane-benzene	17	0.7		0.2662	0.3839	−0.1154	0.2262	13
Toluene-cyclohexane	12	3.2		0.2904	0.0770	−0.2704	−0.0072	7

[a] One-constant model

[b] Two-constant model

[c] Taken from the literature

TABLE 8

Values of chemical equilibrium constants and enthalpies of hydrogen bond formation of alcohols based on one constant model

Alcohol	h_A (kJ mole^{-1})	K_A^a
Methanol	−23 2	280
Ethanol	−23 2	170
1-Propanol	−23 2	90
2-Propanol	−23 2	60

[a] 323 15 K

We assume that the energy parameters could change linearly with temperature.

$$u_{ji} - u_{ii} = C_i + D_i(T - 273.15) \tag{15}$$

CALCULATED RESULTS

The pure component structural parameters, r and q, for the coordination number of 10 were estimated by the method of Vera et al. [10]. Table 4 lists the values of r and q of the pure components. Table 5 shows chemical equilibrium constants and enthalpies of hydrogen bond formation for alcohols. The values of h_2 and h_A, enthalpies of dimer and higher polymer formation, are the same as determined by Haskell et al. [11]. The temperature dependence of the equilibrium constants must satisfy the van't Hoff relation.

$$\frac{\partial \ln K}{\partial (1/T)} = -\frac{h}{R} \tag{16}$$

Table 6 shows the values of h_{AB} and K_{AB} for several alcohol–unsaturated hydrocarbon mixtures. The two-constant model generally reduces the deviations between calculated and experimental values derived from the one-constant model as shown in Table 7. The simplex method of Nelder and Mead [15] was used to

TABLE 9

Values of h_{AB} and K_{AB} based on one-constant model

System(1–2)	h_{AB} (kJ mole^{-1})	K_{AB}^a
Methanol-p-xylene	−11 0	9
Ethanol-p-xylene	−11 0	8
1-Propanol-p-xylene	−11 0	7
2-Propanol-p-xylene	−11 0	7

[a] 298 15 K

TABLE 10

Calculated results based on one constant model at 298.15 K

System(1–2)	No. of data points	Abs. arith mean dev. (J mole^{-1})	C_1/RT	C_2/RT	D_1/RT (K^{-1}) $\times 10^{-3}$	D_2/RT (K^{-1}) $\times 10^{-3}$	Ref
Methanol–*p*-xylene	17	11.7	4.0619	−2.9392	−4.9336	10.5467	This work
Ethanol–*p*-xylene	16	5.1	3.7581	0.6941	6.9803	2.6303	This work
1-Propanol–*p*-xylene	16	4.7	0.6862	−0.9254	13.4840	−7.4901	This work
2-Propanol–*p*-xylene	17	7.3	3.7303	0.8680	8.8561	1.9767	This work
Ethanol–cyclohexane	21	4.9	0.2702	0.1757	1.7380	−0.8841	5
1-Propanol–cyclohexane	18	4.7	0.2985	−0.2785	0.0654	0.5964	5
2-Propanol–cyclohexane	18	12.2	0.2902	0.1860	1.2729	0.3113	14

TABLE 11

Predicted results for ternary systems at 298 15 K

System(1-2-3)	No of data points	Abs arith. mean dev. (J mole^{-1})		Ref.
		I^a	II^b	
Ethanol-p-xylene-cyclohexane	59	35 3	25.8	This work
1-Propanol-p-xylene-cyclohexane	42	22 3	12 9	This work
2-Propanol-p-xylene-cyclohexane	55	31 3	13.6	This work
2-Propanol-benzene-methylcyclohexane	61	17 4	14 4	13
Ethanol-toluene-cyclohexane	8	23 8	18 1	16
2-Propanol-toluene-cyclohexane	56	22 5	9 8	17

[a] One-constant model

[b] Two-constant model

determine the constants, C_i and D_i, for each system by minimizing

$$\sum_{i=1}^{n} \left[h_i^E(\text{calculated}) - h_i^E(\text{experimental})\right]^2 \qquad (17)$$

The values of h_A, K_A, h_{AB}, K_{AB}, and the constants of the energy parameters used by the one-constant model are listed in Tables 8-10. h_A and h_{AB} were assumed independent of temperature.

Ternary prediction of excess enthalpies from binary data was made for six systems. Table 11 indicates that the two-constant model gives better predicted results than the one-constant model.

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