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Excess Enthalpies at 45°C for Ternary System Acetonitrile–Benzene–Carbon Tetrachloride

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Excess enthalpies are measured calorimetrically over the whole range of composition at 45°C for the ternary (single liquid-phase) system acetonitrile(1)–benzene(2)–carbon tetrachloride(3), and for the three constituent binary systems. The excess enthalpy is positive for all these systems (endothermic mixing). For the ternary system the excess enthalpy can be represented simply in terms of binary contributions and reaches its greatest value of 218 cal/g mol in the binary acetonitrile–carbon tetrachloride region at a mole fraction of acetonitrile of about 0.4. Constants are given for the calculation of the excess enthalpies and the excess partial molar enthalpies.

As part of an investigation of three-component behavior in which one component (acetonitrile) is highly polar, excess enthalpies or heats of mixing have been measured at 45°C for the system acetonitrile–benzene–carbon tetrachloride. Although this system is not of commercial importance in itself, acetonitrile is used as a third component in separation processes (*1*), and carbon tetrachloride is a possible cosolvent with it in preventing isopycnics (*5*). The system involving these two components with benzene was chosen for study at 45°C, since information is available on excess enthalpies at this temperature for the three binary systems (*3, 4, 10, 11*) for comparison. All these systems, binary and ternary, form only one liquid phase at 45°C.

Experimental

Purification of the materials used was mainly by fractional distillation in a packed column, with the purified components being removed over a range of less than 0.1°C at a high reflux ratio. Fisher "Spectranalyzed" carbon tetrachloride was first dried over phosphorus pentoxide, and the same grade of benzene was first dried with metallic sodium. BDH "Analar" acetonitrile (methyl cyanide) was first dried over phosphorus pentoxide. Values of the relative densities ($d^{25}{}_4$) and refractive indices ($n^{25}{}_{\mathrm{D}}$) of the purified components are given in Table I. These values all lie within the ranges given by Timmermans (*14*), with the exception of the value of $d^{25}{}_4$ for benzene, for which the range given is 0.8736–0.8739.

Excess enthalpies were measured with the same apparatus used previously (*2, 8*) with only a few minor modifications, as noted below. Measurements were made on the three binary systems at 45°C for comparison with other work and for internal consistency with the measurements on the ternary system at various compositions at the same temperature.

The apparatus used consists essentially of a brass calorimeter divided initially into two compartments by a thin metal disc; a Dewar flask containing a calorimetric fluid, in which the calorimeter is immersed, a thermistor for measuring temperature effects, and a calibrating heater; a thermostat in which the Dewar flask is placed; a recording potentiometer for continuously tracing the temperature changes inside the Dewar flask sensed by the thermistor; and a guarded Wheatstone bridge, one arm of which is the thermistor. The head of the Dewar assembly, which acts as a mounting for the thermistor and heater, was rebuilt, and the calorimetric fluid used was water instead of ethylene glycol. There is a small vapor space in the calorimeter, about 1 or 2% of the total volume.

For the binary systems the procedure involved placing a pure liquid in each compartment, with mixing being effected on continued inversion of the Dewar together with the breaking of the thin metal disc by a steel pellet. For the ternary system, mixtures of benzene and carbon tetrachloride, the binary system with the smallest excess enthalpy, were placed in one compartment and acetonitrile in the other, with allowance being made in each case for the binary system in determining the excess enthalpy for the resulting ternary system.

Results and Discussion

The measured values of excess enthalpies, $h_{ij}{}^E$, in cal/g mol for the three binary systems at 45°C and various compositions are given in Table II, in which x is the mole fraction of the component indicated by the subscript used. The data were fitted to equations of the Scatchard (*12*)–Guggenheim (*6*) type:

$$h_{ij}{}^E = x_i x_j[h_{ij}{}^{(0)} + h_{ij}{}^{(1)}(x_i - x_j) + h_{ij}{}^{(2)}(x_i - x_j)^2 + \dots] \quad (1)$$

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where $h_{ij}^{(0)}$, $h_{ij}^{(1)}$, and $h_{ij}^{(2)}$ are constants which depend on the components i and j of the system. The values of the constants for each system are given in Table III, together with the standard deviation of the fit, σ, defined by

$$\sigma = [\Sigma(h_{ij,\mathrm{obsd}}^E - h_{ij,\mathrm{calcd}}^E)^2/(n - m)]^{1/2} \qquad (2)$$

where $h_{ij,\mathrm{obsd}}^E$ is the observed value of h_{ij}^E (Table II), $h_{ij,\mathrm{calcd}}^E$ is the value calculated from Equation 1, n is the number of observed points, and m is the number of constants used.

For the systems acetonitrile-benzene and carbon tetrachloride-acetonitrile, three constants were required in each case, but only one was used for the system benzene-carbon tetrachloride. The indicated precision for the two acetonitrile systems is about the same as obtained by Brown and Fock (*3*) for these systems, but the measurements of Ewing et al. (*4*) for the benzene-carbon tetrachloride system are of higher precision. The data of Brown and Fock for the acetonitrile systems generally agree with the data of Tables II and III for $x_1 > 0.5$, the agreement for the carbon tetrachloride-acetonitrile system being virtually perfect, but their data are several cal/g mol higher in the region $x_1 < 0.5$. The data of Palmer and Smith (*10*) for the acetonitrile-benzene system at 45°C are uniformly higher than the results given here by about 2 cal/g mol; the fragmentary data of Prausnitz and Anderson (*11*) are higher by about 1 cal/g mol. For the benzene-carbon tetrachloride system, h_{23}^E is better defined by Ewing et al. (*4*) than here, but the agreement is within 1 cal/g mol, which is within the precision indicated for the ternary system representation described below; hence, the data of Tables II and III for this system are suitable for the purpose here.

The measured excess enthalpies for the ternary system, h_{123}^E, are given in Table IV, with the composition defined by the mole fractions of acetonitrile (x_1) and benzene (x_2). The deviation quantity δ_h in Table IV is defined by

$$\delta_h = h_{123;\mathrm{obsd}}^E - h_{123,\mathrm{calcd}}^E \qquad (3)$$

where $h_{123,\mathrm{obsd}}^E$ is from Table IV, and $h_{123,\mathrm{calcd}}^E$ is obtained from binary contributions using Equation 1 and the constants of Table III, together with the ternary compositions of Table IV, according to

$$h_{123,\mathrm{calcd}}^E = x_1x_2[h_{12}^{(0)} + h_{12}^{(1)}(x_1 - x_2) + h_{12}^{(2)}(x_1 - x_2)^2] + x_2x_3h_{23}^{(0)} + x_3x_1[h_{31}^{(0)} + h_{31}^{(1)}(x_3 - x_1) + h_{31}^{(2)}(x_3 - x_1)^2] \qquad (4)$$

From the data in Table IV, the mean deviation in δ_h is 3.5, from which it is concluded that there is no significant ternary effect, and that h_{123}^E may be written in terms of binary contributions only, as in Equation 4.

The ternary excess enthalpies smoothed from Equation 4 are shown in Figure 1 as lines of constant h_{123}^E. As indicated by the binary data, the values of h_{123}^E are everywhere positive. The maximum value is 218 cal/g mol for the binary system acetonitrile-carbon tetrachloride with $x_1 \simeq 0.4$. The addition of benzene as a third component lowers the excess enthalpy, and in particular, the lowest values of h_{123}^E generally occur in the vicinity of the binary system benzene-carbon tetrachloride.

Although not provided explicitly here, the excess partial molar enthalpies can be readily obtained from Equation 4. For component 1, in symmetrical form with independent mole fractions x_2 and x_3 (*15*),

$$\bar{h}_1^E = h_{123}^E - x_2(\partial h_{123}^E/\partial x_2)_{x_3} - x_3(\partial h_{123}^E/\partial x_3)_{x_2} \qquad (5)$$

Corresponding expressions for h_2^E and h_3^E can be writ-

Table I. Properties of Purified Components

Component	d^{25}_4	$n^{25}D$
CH_3CN	0.7765	1.3415
C_6H_6	0.8735	1.4979
CCl_4	1.5845	1.4573

Table II. Excess Enthalpies (h_{ij}^E) for Binary Systems at 45°C in cal/g mol

$CH_3CN(1)-C_6H_6(2)$		$C_6H_6(2)-CCl_4(3)$		$CCl_4(3)-CH_3CN(1)$	
x_1	h_{12}^E	x_2	h_{23}^E	x_1	h_{31}^E
0.189	58	0.204	21.2	0.136	140
0.190	61.5	0.485	30.3	0.218	183
0.217	67	0.566	32.1	0.241	194
0.259	76	0.585	28.5	0.246	191
0.369	100	0.774	22.0	0.252	193
0.427	108			0.255	196
0.540	114			0.264	196
0.546	116			0.353	213
0.721	104			0.361	212
0.834	77.5			0.380	214
0.899	54.5			0.385	219
				0.399	215
				0.446	225
				0.450	220
				0.697	176
				0.835	126
				0.845	112

Table III. Values of Constants in Equation 1 for Binary Systems (h_{ij}^E in cal/g mol at 45°C)

System, (i) + (j)	$h_{ij}^{(0)}$	$h_{ij}^{(1)}$	$h_{ij}^{(2)}$	σ
$CH_3CN(1)-C_6H_6(2)$	454.7	129.5	41.3	1.5
$C_6H_6(2)-CCl_4(3)$	125	. . .	. . .	1.3
$CCl_4(3)-CH_3CN(1)$	857.9	184.9	333.4	3.4

Table IV. Excess Enthalpies (h_{123}^E) for Ternary System $CH_3CN(1)-C_6H_6(2)-CCl_4(3)$ at 45°C in cal/g mol

x_1	x_2	h_{123}^E	δ_h
0.158	0.669	85	−1
0.162	0.663	80	−8
0.177	0.249	149	+1
0.225	0.119	178	+1
0.225	0.614	108	+2
0.226	0.382	142	−5
0.415	0.465	135	0
0.418	0.461	138	+2
0.420	0.459	129	−7
0.424	0.458	137	+1
0.433	0.280	173	−1
0.441	0.086	207	+1
0.455	0.165	191	−1
0.505	0.076	203	0
0.553	0.135	187	+1
0.706	0.232	116	−7
0.707	0.145	140	−3
0.708	0.232	124	+2
0.709	0.231	125	+3
0.722	0.043	150	−10
0.722	0.221	119	−1
0.725	0.042	148	−10
0.729	0.042	146	−12
0.826	0.138	88	−2
0.840	0.025	105	−8
0.845	0.024	112	+2

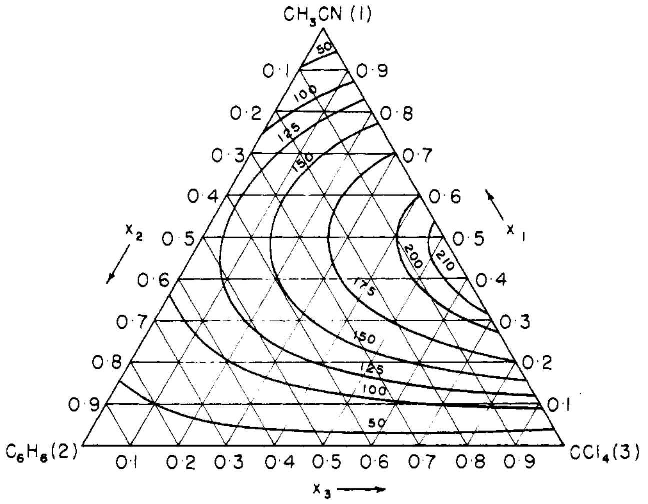

Figure 1. h_{123}^E Contours for system $CH_3CN-C_6H_6-CCl_4$ at 45°C in cal/g mol

ten by cyclic advancement of the subscripts (1 → 2 → 3 → 1).

The smaller magnitude of the (positive) excess enthalpy in the acetonitrile-benzene binary region compared with the acetonitrile-carbon tetrachloride region presumably results from the relatively strong interaction between the dipole of acetonitrile and the π electrons in benzene. According to Schneider's interpretation of the nmr spectra for this system (*13*), this results in a rather weak complex, the formation of which, however, is not such as to lead to negative values of excess enthalpy, as in the case of chloroform or methylene dichloride interacting with benzene (*9*). Thus, the excess enthalpy-composition surface for the ternary system (Figure 1) slopes downward away from the highest value (218 cal/g mol) near the midpoint on the acetonitrile-carbon tetrachloride axis as benzene is added, the drop-off being more rapid in the direction of the benzene-carbon tetrachloride axis, along which it is relatively small, not exceeding 32 cal/g mol. Along the acetonitrile-benzene axis, the largest value is about 116 cal/g mol at x_1 = 0.575. The implications for phase equilibrium in such a system (hydrocarbon+acetonitrile-carbon tetrachloride cosolvent) would be through the temperature effect on liquid-phase activity coefficients, as reflected in the excess partial molar enthalpies (*7*).

Nomenclature

$d^{25}{}_4$ = density at 25°C relative to water at 4°C
$h^{(0)}, h^{(1)}, h^{(2)}$ = constants in Equation 1
h^E = excess enthalpy, cal/g mol
$\bar{h}^E$ = excess partial molar enthalpy
m = number of constants in Equation 1
n = number of experimental points
$n^{25}{}_D$ = refractive index at 25°C relative to sodium-D line
x = mole fraction

Greek Letters

δ_h = deviation quantity in Equation 3
σ = standard deviation (Equation 2)

Subscripts

1 = acetonitrile
2 = benzene
3 = carbon tetrachloride
i = component i
j = component j

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