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Excess Free Energies and Entropies at 45°C for Ternary System Acetonitrile-Benzene-Carbon Tetrachloride

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Excess free energies are determined from measurements of liquid-vapor equilibrium over the whole range of composition at 45°C for the ternary system acetonitrile(1)-benzene(2)-carbon tetrachloride(3), and excess entropies are calculated from these excess free energies and excess enthalpies obtained previously. The excess free energies can be represented simply in terms of binary contributions and are positive at all compositions; there is no ternary azeotrope. The excess entropies are negative except for solutions very dilute in acetonitrile. Constants are given for the calculation of these properties and the corresponding excess partial molar quantities.

Excess enthalpies for the ternary system acetonitrile-benzene-carbon tetrachloride at 45°C have been reported previously (*6*). This is a system in which one component (acetonitrile) is highly polar and in which there is a pair of components (acetonitrile-carbon tetrachloride) which may serve as a cosolvent system in facilitating separations of hydrocarbons (*5*). In spite of the moderate complexity of the system, the excess enthalpy for the ternary system could be predicted from binary contributions without the need of ternary constants.

In this paper the excess free energy of the system at 45°C is similarly investigated, and the results are used together with those for the excess enthalpy to determine the excess entropy of the system.

Experimental

Purification of the materials used was mainly by distillation, as described previously (*6*). BDH "Analar" acetonitrile was first dried and then fractionated twice over phosphorus pentoxide. BDH "Analar" carbon tetrachloride was first dried over the pentoxide. Fisher "Certified Reagent" benzene was first washed with concentrated sulfuric acid and then neutralized, dried, and fractionated over the pentoxide. The relative densities ($d^{25}{}_4$) and refractive indices ($n^{25}{}_D$) of the purified components are given in Table I. The values of these properties all lie within the ranges given by Timmermans (*14*), with the exception of the value of $n^{25}{}_D$ for benzene, for which the range given is 1.4979-1.4981. Also given in the table are the vapor pressures (p^*) measured at 45°C with the equilibrium apparatus described below, and the second virial coefficients (B) at 45°C (*1, 2*).

The excess free energies were calculated from liquid-vapor equilibrium measurements made in a condensate-recirculation equilibrium still of the Gillespie type used previously (*8*). Measurements were made at 45°C for the three binary systems and the ternary system. For the ternary system, a series of solutions with fixed ratios of benzene and carbon tetrachloride was used and acetonitrile added to make a pseudobinary system.

The liquid and vapor (condensate) samples removed from the equilibrium still were analyzed by gas-liquid chromatography by use of a Burrell K-1 chromatograph, together with a thermal conductivity cell as detector and a column utilizing Carbowax 400. The precision of the method was determined by analyzing a number of binary and ternary solutions of known composition. The standard deviation in the mole fractions of all components determined in this way was 0.002.

Results and Discussion

The liquid-vapor equilibrium measurements for the binary systems and the values of the excess free energies calculated from them are not reported in detail, since the latter agree with the equations given by Brown and Smith (*1, 2*) and by Scatchard and Ticknor (*12*) as follows (with g^E the excess free energy in cal/g mol and x mole fraction): acetonitrile(1)-benzene(2) system (*2*):

$$g_{12}{}^E = x_1x_2[643.3 - 8.1\ (x_1 - x_2) + 70.1\ (x_1 - x_2)^2] \quad (1)$$

benzene(2)-carbon tetrachloride(3) system (*12*):

$$g_{23}{}^E = x_2x_3[75.9 - 0.85\ (x_3 - x_2)] \quad (2)$$

carbon tetrachloride(3)-acetonitrile(1) system (*1*):

$$g_{31}{}^E = x_3x_1[1134.3 + 118.9\ (x_3 - x_1) + 162.2\ (x_3 - x_1)^2 + 99.5\ (x_3 - x_1)^3] \quad (3)$$

The standard deviations of the fits of the experimental data obtained here to these equations were 0.7, 0.1, and 1.1 cal/g mol, respectively. These values are within or close to the values given in the work leading to Equations 1-3. We conclude that these equations may be used to represent binary data for comparison with the measured ternary data, and that the chromatographic method of analysis is suitable.

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The liquid-vapor equilibrium measurements for the ternary system at 45°C and the experimental values of excess free energy (g_{123}^E) obtained from them are given in Table II. Here, x is mole fraction in the liquid phase, y is mole fraction in the vapor phase, P is total pressure, and δ_g is the difference between observed and calculated values of g_{123}^E as described below.

The observed values of g_{123}^E were obtained from

$$g_{123}^E = \Sigma x_i \mu_i^E \tag{4}$$

where μ_i^E is the excess chemical potential of component i given by (*12*)

$$\mu_i^E = RT \ln (y_iP/x_ip_i^*) + (B_{ii} - v_i^*)(P - p_i^*) + P[\Sigma_j \delta_{ij}y_j(1 - y_i) - \Sigma_{jk} \delta_{jk}y_iy_k/2] \tag{5}$$

where $i \neq j \neq k$, and

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \tag{6}$$

The B's are the second virial coefficients corresponding to the interactions indicated by the subscripts, R is the gas constant, T is temperature, and v_i^* is the molar volume of pure liquid i. (The values of g^E for the binary systems used for comparison with Equations 1-3 were obtained from the two-component forms of Equations 4-6.)

Table I. Properties of Purified Components

Component	d^{25}_4	$n^{25}D$	p^*,[a] mm Hg	B,[a] l./g mol
CH_3CN	0.7769	1.3416	208.6	−4.50
C_6H_6	0.8739	1.4978	223.6	−1.24
CCl_4	1.5845	1.4572	258.8	−1.24

[a] $t = 45°C$.

The values of B_{ij} and of δ_{ij} were taken from the work of Brown and Smith (*1, 2*) and that of Scatchard and Ticknor (*12*) for the sake of internal consistency in comparing the binary and ternary data. The values used are given in Table III. The values used for v_i^* in Equation 5 were obtained from the density data in Table I.

The observed values of g_{123}^E for the ternary system given in Table II were compared with values calculated from the binary equations, 1-3, through the quantity δ_g given in the table and defined by

$$\delta_g = g_{123,\text{obsd}}^E - g_{123,\text{calcd}}^E \tag{7}$$

where $g_{123,\text{calcd}}^E$ is given by

$$g_{123,\text{calcd}}^E = x_1x_2[643.3 - 8.1(x_1 - x_2) + 70.1(x_1 - x_2)^2] + x_2x_3[75.9 - 0.85(x_3 - x_2)] + x_3x_1[1134.3 + 118.9(x_3 - x_1) + 162.2(x_3 - x_1)^2 + 99.5(x_3 - x_1)^3] \tag{8}$$

and the mole fractions refer to the ternary compositions.

The mean value of δ_g is 4 cal/g mol, and the algebraic mean is +1 cal/g mol. The former is close to the estimated error in g^E, ±3 cal/g mol, obtained by varying the mole fractions and P by amounts corresponding to the precision of their determination. From this we conclude that there is no significant ternary effect, and that the ternary data can be predicted from the binary constants according to Equation 8, as was found similarly for h_{123}^E for this system (*6*).

Table II. Excess Free Energies (g^E) and Liquid-Vapor Equilibrium for Ternary System $CH_3CN(1)-C_6H_6(2)-CCl_4(3)$ at 45°C

x_1	x_2	y_1	y_2	P, mm Hg	g_{123}^E, cal/g mol	δ_g, cal/g mol
0.151	0.598	0.225	0.501	286.0	125	+10
0.156	0.767	0.256	0.650	272.0	103	+4
0.169	0.179	0.303	0.126	336.3	173	+8
0.176	0.511	0.269	0.396	300.1	144	+9
0.279	0.657	0.352	0.564	282.5	145	+1
0.289	0.506	0.354	0.403	300.9	169	−1
0.303	0.436	0.360	0.338	312.0	187	+4
0.304	0.154	0.374	0.107	347.8	231	+2
0.310	0.248	0.365	0.180	337.2	222	+6
0.372	0.356	0.391	0.280	323.4	215	+8
0.395	0.555	0.422	0.499	287.1	166	0
0.396	0.434	0.402	0.364	303.8	186	−5
0.401	0.070	0.402	0.050	363.2	271	+6
0.404	0.379	0.408	0.308	315.3	205	+2
0.422	0.128	0.393	0.103	350.1	254	−1
0.423	0.208	0.412	0.159	339.7	240	+2
0.479	0.379	0.439	0.345	303.9	191	−6
0.491	0.114	0.422	0.087	350.1	254	−4
0.494	0.325	0.441	0.286	315.0	206	−1
0.497	0.056	0.427	0.043	364.6	277	+7
0.505	0.453	0.478	0.452	287.8	174	+2
0.510	0.183	0.444	0.150	339.6	243	+3
0.518	0.279	0.452	0.242	323.8	220	+5
0.553	0.328	0.472	0.320	302.3	185	−8
0.563	0.099	0.443	0.084	347.9	246	−5
0.570	0.396	0.515	0.421	286.0	170	+2
0.575	0.276	0.481	0.265	311.6	198	−2
0.578	0.159	0.468	0.140	337.0	234	+2
0.593	0.048	0.457	0.039	363.2	268	+10
0.604	0.233	0.455	0.228	318.9	205	+2
0.629	0.276	0.512	0.298	298.2	173	−8
0.640	0.083	0.471	0.080	342.3	226	−7
0.640	0.333	0.557	0.385	281.6	158	+1
0.642	0.237	0.514	0.249	307.4	185	−2
0.646	0.133	0.490	0.132	331.9	215	−1
0.659	0.204	0.512	0.216	314.4	191	+1
0.662	0.041	0.477	0.038	357.1	245	+8
0.673	0.244	0.547	0.278	294.0	164	−6
0.705	0.275	0.600	0.349	277.3	146	+3
0.706	0.198	0.548	0.235	300.5	164	−4
0.709	0.113	0.526	0.124	324.4	189	−5
0.712	0.175	0.541	0.203	306.8	173	0
0.721	0.210	0.569	0.268	289.0	148	−7
0.731	0.036	0.505	0.035	347.8	212	+6
0.750	0.064	0.525	0.073	328.2	180	−7
0.753	0.169	0.584	0.220	293.4	147	−3
0.756	0.097	0.545	0.121	317.4	170	−3
0.757	0.227	0.633	0.322	271.4	128	+1
0.763	0.181	0.596	0.252	282.5	128	−11
0.770	0.143	0.589	0.188	299.4	152	+4
0.782	0.027	0.533	0.034	339.2	187	+8
0.791	0.057	0.548	0.069	319.5	153	−10
0.791	0.147	0.610	0.209	286.4	127	−5
0.799	0.084	0.586	0.115	307.1	149	+1
0.800	0.188	0.665	0.296	265.5	110	0
0.814	0.120	0.625	0.173	288.2	125	0
0.817	0.025	0.568	0.033	329.3	167	+11
0.829	0.075	0.615	0.112	297.5	129	−1
0.835	0.154	0.703	0.263	259.9	98	+2
0.856	0.020	0.596	0.029	316.0	133	+5
0.878	0.019	0.622	0.028	304.2	110	−1
0.903	0.015	0.673	0.027	291.6	98	+8

Table III. Values of B_{ij} and δ_{ij} for Equation 5

Component			
i	j	B_{ij}, l./g mol	δ_{ij}, l./g mol
1	2	−1.173	3.39
2	3	−1.220	0
3	1	−1.174	3.40

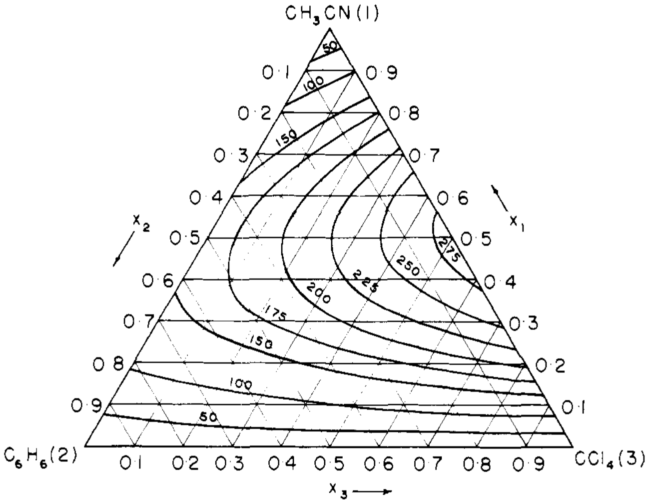

Figure 1. $g_{123}{}^E$ contours for system CH$_3$CN-C$_6$H$_6$-CCl$_4$ at 45°C in cal/g mol

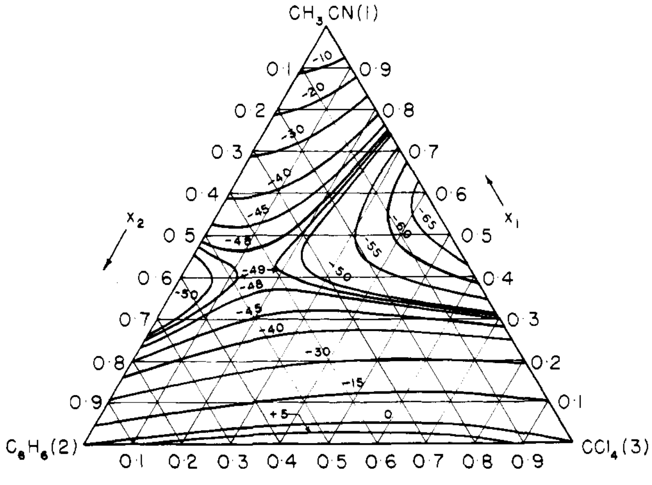

Figure 2. $Ts_{123}{}^E$ contours for system CH$_3$CN-C$_6$H$_6$-CCl$_4$ at 45°C in cal/g mol

The ternary data were also examined by grouping the nonpolar compounds as suggested by Scatchard et al. (*11, 12*). In this approach $x_1 - x_2$ in Equation 8 is replaced by $2x_1 - 1$ and $x_3 - x_1$ by $1 - 2x_1$. Scatchard et al. found that this improved the representation considerably for both h^E and g^E for the methanol-benzene-carbon tetrachloride system. The same result was found by Posa et al. (*9*) for h^E for the system 1-pentanol-*n*-hexane-cyclohexane at 25°C. However, in the acetonitrile-benzene-carbon tetrachloride system, there is no significant difference: the mean value of the quantity corresponding to δ_g is still 4 cal/g mol, although the algebraic mean is changed from +1 to −1 cal/g mol. We prefer the use of Equation 8 because of the greater symmetry involved. It is perhaps to be expected that the more complex systems involving an alcohol require special treatment.

The excess entropy at 45°C obtained from Equation 8 and the corresponding equation for $h_{123}{}^E$ (*6*) is

$$Ts_{123}{}^E = g_{123}{}^E - h_{123}{}^E = x_1x_2[-188.6 + 137.6\,(x_1 - x_2) - 28.8\,(x_1 - x_2)^2] + x_2x_3[49.1 + 0.85\,(x_3 - x_2)] + x_3x_1[-276.4 + 66.0\,(x_3 - x_1) + 171.2\,(x_3 - x_1)^2 - 99.5\,(x_3 - x_1)^3] \quad (9)$$

The ternary plot for $h_{123}{}^E$ has been given before (*6*), and similar plots for $g_{123}{}^E$ and $Ts_{123}{}^E$ are given in Figures 1 and 2, in which the values are calculated from Equations 8 and 9.

Figure 1 is similar to the corresponding plot for h^E (*6*). The values are everywhere positive, and the largest values occur in the vicinity of the CH$_3$CN-CCl$_4$ binary system, and the smallest values in the vicinity of the C$_6$H$_6$-CCl$_4$ system. The maximum for the former system is 285 cal/g mol. Although not shown directly in Figure 1, the binary systems involving acetonitrile are both azeotropic (*1, 2*), but there is no ternary azeotrope. The third binary system is not sufficiently nonideal for this latter to appear (*13*).

The values of $g_{123}{}^E$ are generally higher than those of $h_{123}{}^E$, and this is reflected in the negative values of $Ts_{123}{}^E$ shown in Figure 2, except for the region in the vicinity of the binary system C$_6$H$_6$-CCl$_4$, where they become slightly positive. For the binary systems involving acetonitrile, the values of Ts^E given here agree well with those given by Brown and Fock (*4*) for $x_1 > 0.5$ but are several cal/g mol more negative for $x_1 < 0.5$. This is due to the (similar difference in) excess enthalpies (*6*) and not to the excess free energies, which are the same. The excess enthalpies used here are in better agreement with more recent data (*7*) for $x_1 < 0.5$, the difference being about 2 cal/g mol, which would be reflected directly in Ts^E.

For the ternary system generally, the negative values of Ts^E probably indicate a certain amount of ordering in the solutions relative to the pure components. This means that the ternary system, like the binary systems, particularly the two involving acetonitrile, is significantly nonregular. The excess volumes for the binary systems (*3, 7, 10*) are too small to indicate that a volume correction would lead to near-zero excess entropies.

Activity coefficients of the three species and smoothed liquid-vapor equilibrium data can be calculated by use of Equation 8 as a basis. For component 1, the activity coefficient may be obtained from (*15*)

$$RT \ln \gamma_1 = \mu_i{}^E = g_{123}{}^E - x_2\,(\partial g_{123}{}^E/\partial x_2)_{x_3} - x_3\,(\partial g_{123}{}^E/\partial x_3)_{x_2} \quad (10)$$

Similar expressions for γ_2 and γ_3 can be written by cyclic advancement of the subscripts (1 → 2 → 3 → 1). The effect of temperature on the activity coefficients and liquid-vapor equilibrium can be estimated by use of excess partial molar enthalpies similarly obtained from the excess enthalpies for the ternary system (*6*).

Nomenclature

B = second virial coefficient
$d^{25}{}_4$ = density at 25°C relative to water at 4°C
g^E = excess Gibbs free energy, molar
h^E = excess enthalpy, molar
$n^{25}{}_D$ = refractive index at 25°C relative to sodium D line
p^* = vapor pressure
P = (total) pressure
R = gas constant

s^E = excess entropy
v^* = molar volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase

Greek Letters

γ = activity coefficient
δ_{ij} = deviation quantity defined in Equation 6
δ_g = deviation quantity in Equation 7
μ^E = excess chemical potential

Subscripts

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

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Molecular Associations in 2-Butanone

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Association in solutions of 2-butanone with the solutes 4-hydroxy benzaldehyde, 4-hydroxy-3-methoxy benzaldehyde, 4-hydroxy benzoic acid, and 4-hydroxy-3-methoxy benzoic acid was studied by ebulliometric measurements to about 1*m* concentration. Association numbers for solutes and observed equilibrium constants for solute dimerization reactions at 79.5°C + ΔT_b at 1-atm pressure were calculated.

The solvent 2-butanone is particularly useful for polar solutes which may not be appreciably soluble in nonpolar solvents. Most previous studies of nonaqueous solution association have been with inert solvents to minimize solute-solvent association (*1, 2, 8*). However, one object of this present work has been to study the effect of solute-solvent interaction on solute-solute association as a function of concentration in 2-butanone, as well as to investigate the effect of intramolecular hydrogen bonding on solute-solute and solute-solvent association.

The association of the hydroxy compound solutes with the ketone solvent 2-butanone described in this study is of especial interest because both the solute-solute and solute-solvent interactions may be assumed to be primarily owing to hydrogen bonding (*8–12*). In dilute solution the solute-solute equilibrium reactions which predominate in these systems may be assumed to be dimerization (*1, 18*). In this study the effect of solute intramolecular hydrogen bonding on the dimerization reactions and the concentration dependence of dimerization have been studied by ebulliometric measurements of association numbers and by determination of the observed equilibrium constants for the solute dimerization reactions.

Experimental

Chemicals. All chemicals used were reagent grade. The 2-butanone was obtained from Aldrich Chemical Co. and was dried with $CaCl_2$, decanted, and fractionally distilled twice, by use of a Todd distillation column following standard procedures (*17*). The 4-hydroxy-3-methoxy benzaldehyde was obtained from Matheson Coleman & Bell; 4-hydroxy benzaldehyde, 4-hydroxy benzoic acid, and 4-hydroxy-3-methoxy benzoic acid were obtained from Aldrich Chemical Co. Solid reagents were desiccator-dried and stored and were used soon after their receipt without further purification. Table I compares determined solute melting points with literature values.

Apparatus and procedures. An improved Washburn-Read (*16*) modification of the Cottrell ebullioscope (*3*) was used for measurements. A platinum wire heating coil was sealed into the bottom of the apparatus, and a constant current was maintained. Temperatures were corrected for pressure fluctuations by use of a barometer and applying the temperature coefficient of pressure (*17*) and also by use of a second apparatus with solvent only. A minimum of 2 hr was allowed for all temperature equilibrations.

The apparatus was carefully shielded from drafts and was assembled with standard tapers and protected from moisture with a drying-agent tube; standard measurement procedures (*5, 14*) were followed. Apparatus reliability was determined by measuring the true molecular weight of benzoic acid in methanol where single molecules are stabilized by the solvent. The overall reliability of data has been determined to be no more uncertain than ±1 molecular-weight unit. Uncertainty in calculated values of *Kx* (obs) is ±0.05.

Table I. Solute Melting-Point Data

Solute	Mp, °C	
	Exp	Lit
4-Hydroxy benzaldehyde	116	116 (*15*)
4-Hydroxy-3-methoxy benzaldehyde	81	81.5 (*15*)
4-Hydroxy benzoic acid	214	214–215 (*15*)
4-Hydroxy-3-methoxy benzoic acid	212	213–215 (*6*)