Thermodynamic Properties of the Systems Benzene–Chloroethanes

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Data on heats of mixing at 35 °C and vapor–liquid equilibrium for the systems benzene–1,2-dichloroethane, benzene–1,1,1-trichloroethane, and benzene–1,1,2,2-tetrachloroethane are presented.

Introduction

This paper presents the experimental data on vapor–liquid equilibrium and heats of mixing of mixtures of benzene with 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane. A literature survey revealed that the heats of mixing of benzene–1,2-dichloroethane have been studied and Table I shows the extent of study on this system.

Table I. Literature Survey on the Heats of Mixing of Benzene-1,2-Dichloroethane

authors	temp, °C	ref
Cheesman and Whitaker	24.7, 41.8	5
Korveze et al.	24.7, 41.8	14
Ruiter	7.6, 25, 41.8	23
Otterstedt and Missen	25	19
Brown and Fock	25	4

Materials Used and Purification

"Proanalysi" grade benzene supplied by Sarabhai Merck, Bombay, laboratory grade 1,2-dichloroethane supplied by British Drug House, Bombay, 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane supplied by BDH Chemicals, England, were purified by the methods described by Weissberger (*35*) and Riddick and Bunger (*24*). The purities were checked against refractive index and density and are reported in Table II. Vapor-phase chromatographs were obtained for the liquids using a Willy Giede Type GCHF 18.2 chromatograph using elastometer for benzene and tricresyl phosphate as column material for the chloroethanes. Single peaks were obtained for all the liquids. Infrared spectra were taken on a Carl-Zeiss UR10 spectrometer. The characteristic peaks were identified and compared with those available in literature for benzene (*27*), 1,1,1-trichloroethane (*8*), 1,2-dichloroethane (*27*), and 1,1,2,2-tetrachloroethane (*30*) and were found to have a 1:1 correspondence.

Table II. Properties of Benzene and the Chloroethanes

material	$\eta^{30}{}_D$ present work	$\eta^{30}{}_D$ lit. (*6*)	density, 30 °C present work	density, 30 °C lit. (*6*)
benzene	1.4947	1.4946	0.8664	0.8681
1,2-dichloroethane	1.4388	1.4392	1.2386	1.2390
1,1,1-trichloroethane	1.4317	1.4320	1.3206	1.3209
1,1,2,2-tetrachloroethane	1.4889	1.4884	1.5783	1.5786

Vapor Pressure Data

Vapor pressures of benzene and the chloroethanes were obtained in a Brown still (*3*) up to the laboratory pressure of 685 mmHg and at higher pressures in a Swiestosalwski type still. Figure 1 shows the excellent agreement between the present data and the data available in literature (*2*, *13*, *15*, *25*, *26*, *28*, *32*). The vapor pressure data of benzene when compared with those calculated from eq 1 taken from ref 28 gave a maximum deviation of 0.53% and average absolute deviation of 0.26%. The experimental vapor pressures of the chloroethanes obtained in the present work were fitted by least-squares technique to obtain eq 2–4. The first and the second values in parentheses indicate the percentage maximum and average absolute deviations, respectively. The values in the second set of parentheses indicate the temperature range in °C. The experimental vapor pressure data of 1,2-dichloroethane and 1,1,1-trichloroethane when compared with the data calculated from the Antoine equations, the constants for which were obtained from TRC tables (*28*), gave average absolute deviations of 0.44 and 0.62%, respectively. The deviations in the case of 1,1,-2,2-tetrachloroethane, however, were higher and of the order of 1.5%. The experimental observations are shown in Figure 1 and Table III.

$$\log P_B{}^\circ = 6.90565 - \frac{1211.03}{220.79 + t} \quad (0.53, 0.26)\ (67\text{–}77) \tag{1}$$

$$\log P_D{}^\circ = 7.03993 - \frac{1274.078}{223 + t} \quad (0.54, 0.22)\ (70\text{–}109) \tag{2}$$

$$\log P_{TR}{}^\circ = 6.87645 - \frac{1195.649}{225 + t} \quad (0.54, 0.19)\ (70\text{–}105) \tag{3}$$

$$\log P_{TE}{}^\circ = 7.88347 - \frac{2096.8606}{273.16 + t} \quad (0.8, 0.25)\ (104\text{–}146) \tag{4}$$

Vapor–Liquid Equilibrium Data

A Brown still (*3*) was used to determine the isobaric equilibrium data. The still required 230 cm^3 of feed and took about 3 h to attain equilibrium. The data taken at 685 mmHg are shown in Tables IV–VI and as a typical set the data for benzene–1,1,2,2-tetrachloroethane are also shown in Figure 2. The temperature was measured to an accuracy of 0.1 °C and pressure to an accuracy of 0.1 mmHg.

The analysis of each mixture of benzene–1,2-dichloroethane and benzene–1,1,1-trichloroethane was done using the refractive index at 30 °C determined in a Pulfrich refractometer with an accuracy of ±0.0001. The calibration chart prepared in terms of mole fraction of benzene was fitted to eq 5 and 6.

$$\eta_{B\text{-}D} = 1.43915 + 0.052281x_1 \quad (0.02, 0.01) \tag{5}$$

$$\eta_{B\text{-}TR} = 1.49480 - 0.07131x_1 + 0.00851x_1{}^2 \quad (-0.01, 0.01) \tag{6}$$

For benzene–1,1,2,2-tetrachloroethane as the pure component, refractive indices were very close to each other, the analysis of each mixture was done by density measurements at 30 °C using a pycnometer. The calibration was fitted to eq 7.

$$\rho_{B\text{-}TE} = 1.57753 - 0.058238x_1 - 0.12668x_1{}^2 \quad (-0.06, 0.03) \tag{7}$$

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Table III. Vapor Pressure

Benzene		1,2-dichloroethane		1,1,1-trichloroethane		1,1,2,2-tetrachloroethane	
t, °C	pressure, mmHg	*t*, °C	pressure, mmHg	*t*, °C	pressure, mmHg	*t*, °C	pressure, mmHg
67.1	500						
68.3	520	70.5	500.0	70.9	686.2	142.3	681.0
69.5	540	71.1	507.5	69.8	664.1	140.2	646.5
70.4	560	71.9	523.5	68.4	633.5	137.9	605.5
71.5	580	74.4	571.0	66.9	604.3	135.5	566.5
72.7	600	76.1	605.5	66.0	586.0	131.3	501.5
73.8	620	78.1	645.0	63.5	537.0	126.1	430.3
74.6	640	80.2	687.0	62.2	514.9	119.6	350.8
75.7	660	79.6	678.5	70.7	682.5	111.8	272.5
76.5	680	84.2	782.5	70.8	679.5	109.1	250.0
76.7	684	88.2	880.5	74.9	779.5	104.2	212.0
		90.3	942.5	78.9	880.0	115.9	313.0
		95.1	1082.5	82.6	977.0		
		99.1	1215.0	85.7	1067.0		
		102.3	1335.5	89.7	1195.5		
		105.6	1453.5	93.9	1339.0		
		108.3	1559.0	97.6	1475.5		
				100.6	1601.5		
				102.6	1687.5		
				104.3	1761.0		

Table IV. *t-x-y* Data at 685 mmHg for Benzene-1,2-Dichloroethane

t/°C	x_B	y_B	*t*/°C	x_B	y_B
79.85	0.0526	0.0620	78.25	0.4730	0.4985
79.65	0.1048	0.1196	77.95	0.5492	0.5730
79.50	0.1304	0.1476	77.70	0.6366	0.6564
79.35	0.1754	0.1956	77.50	0.7058	0.7221
79.10	0.2310	0.2540	77.25	0.7797	0.7925
78.90	0.2786	0.3037	77.15	0.8127	0.8234
78.55	0.3778	0.4042	77.10	0.8371	0.8464

Table V. *t-x-y* Data at 685 mmHg for Benzene-1,1,1-Trichloroethane

t/°C	x_B	y_B	*t*/°C	x_B	y_B
76.30	0.9244	0.9059	73.70	0.5136	0.4661
76.05	0.8857	0.8603	73.40	0.4534	0.4084
75.95	0.8549	0.8359	73.05	0.3926	0.3511
75.60	0.8165	0.7810	72.80	0.3583	0.3195
75.40	0.7842	0.7447	72.55	0.3127	0.2775
75.00	0.7250	0.6805	72.15	0.2399	0.2119
74.60	0.6566	0.6091	71.80	0.1798	0.1584
74.15	0.5837	0.5356	71.50	0.1232	0.1080
			71.25	0.0800	0.0698

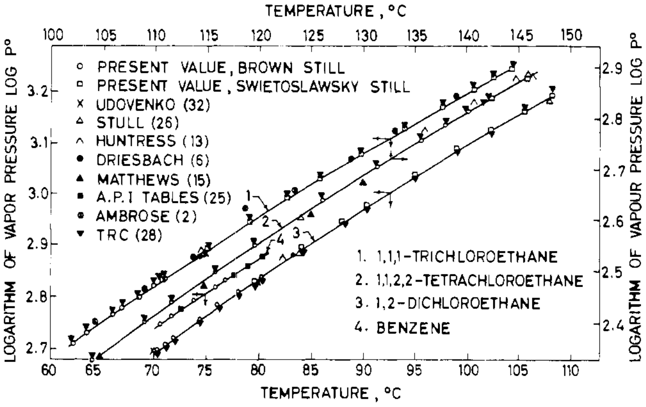

Figure 1. Vapor pressure data for benzene and chloroethanes.

Table VI. *t-x-y* Data at 685 mmHg for Benzene-1,1,2,2-Tetrachloroethane

t/°C	x_B	y_B	*t*/°C	x_B	y_B
135.3	0.0703	0.2304	97.5	0.5147	0.8880
129.5	0.1346	0.3946	92.1	0.6065	0.9300
124.0	0.1938	0.5136	88.5	0.6750	0.9522
119.0	0.2517	0.6137	85.3	0.7405	0.9685
113.5	0.3181	0.7031	81.9	0.8290	0.9832
104.8	0.4207	0.8182	80.0	0.8834	0.9899
			78.0	0.9420	0.9955

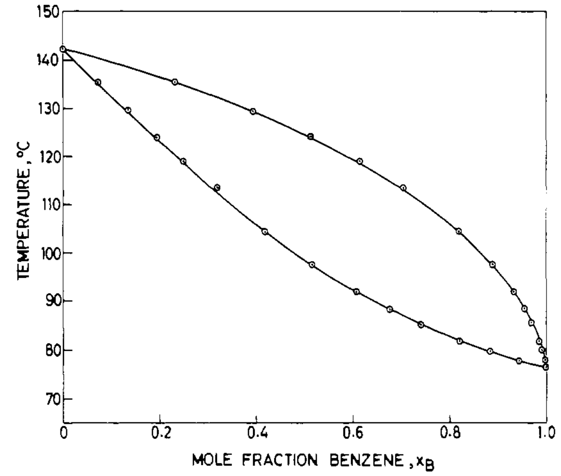

Figure 2. *t-x-y* data for benzene-1,1,2,2-tetrachloroethane.

Heats of Mixing

The calorimeter used in the present study was similar to those used by Vold (*34*), Tsao and Smith (*31*), and Ruiter (*23*) in that all these calorimeters have vapor space. The calorimeter consisted of a cylindrical Dewar flask of 7 cm height and 4.5 cm internal diameter. The total volume of the calorimeter was 145 cm^3. The space between the walls was evacuated to 10^{-3} mmHg. The calorimeter had four inlets at the top, two for feeding the pure liquids through jacketed burets, one for introducing the heater and a thermistor, and the fourth for a stirrer. A thermistor of 10K resistance was used in conjunction with a Wheatstone bridge manufactured by Bajaj Electricals, Bombay, and a spot galvanometer to measure the changes in temperature on mixing. The heater of resistance 0.5 Ω was made of fine nichrome wire. The power supply for the heater was from a 2-V battery. The electrical power was measured with a voltmeter and ammeter manufactured by Bajaj Electricals, Bombay, and with a standard 1-Ω resistance. The meters were calibrated in the electrical engineering department of this institute. The jacketed burets were of 50 cm^3 capacity, graduated in steps of 0.1 cm^3.

Table VII. Heats of Mixing of Systems Used for Calibration of the Apparatus

system	% max deviation	% min deviation	% av abs deviation
benzene-methanol	2.6	0.3	1.4
benzene-2-propanol	4.0	0.0	2.1
toluene-2-propanol	2.7	0.2	1.6
toluene-1-butanol	3.1	0.0	1.8

The calorimeter was immersed in a constant-temperature bath of water whose temperature was controlled by two heaters of 65 W each and an auxiliary heater of 25 W. The two 65-W heaters were controlled by a Hg regulator. The 25-W heater was controlled by a special relay circuit. The sensing device for this control system was a glass probe thermistor with 60 K resistance at 20 °C which formed one of the arms of a Wheatstone bridge. The unbalances due to temperature changes in the bath were amplified and were used to actuate a relay which controlled the power to the 25-W heater. This arrangement permitted control of temperature within ±0.005 °C of the set value. The water from this bath was circulated through the two burets.

The liquids whose heats of mixing were measured were charged to the jacketed burets. When the temperature was 35 °C a known amount of the first liquid was fed to the calorimeter. About 5 cm^3 of the second liquid was added and the maximum deflection in the galvanometer noted. For endothermic systems, the heater and the stop watch were simultaneously switched on as soon as the maximum deflection was attained. The time taken to bring the system back to its original temperature was recorded. For exothermic systems, the systems were allowed to cool down to the initial temperature and then reheated back to the maximum deflection noted earlier, simultaneously recording the time. The process was repeated for successive additions of the second liquid. The heats of mixing for the whole range of composition were determined by taking the second liquid in the calorimeter and adding the first.

The heat of mixing was calculated by eq 8 and the composition by eq 9.

$$\Delta H_m = \frac{EIt'}{(V_1\rho_1/M_1) + (V_2\rho_2/M_2)} \qquad (8)$$

$$x_1 = \frac{(V_1\rho_1/M_1)}{(V_1\rho_1/M_1) + (V_2\rho_2/M_2)} \qquad (9)$$

The calorimeter was checked with systems reported in the literature (*17*). Table VII shows the systems studied and their deviations from literature values after making the vapor space correction suggested by McGlashan (*16*).

Figure 3 shows the heats of mixing data for benzene-1,2-dichloroethane after correcting for the vapor space at 35 °C and the data of Ruiter (*23*) at 24.7 and 41.8 °C. Figures 4 and 5 present the experimental data for the systems of benzene with 1,1,1-trichloroethane and 1,1,2,2-tetrachloroethane at 35 °C. The heats of mixing data were fitted to an equation of the form

$$\Delta H_m = x_1x_2\Big[A_0 + \sum_{i=1}^{3} A_i(2x_i - 1)^i\Big] \qquad (10)$$

by the least-squares technique. The constants and the deviations of the fit are shown in Table VIII. The experimental data are also given in Table IX.

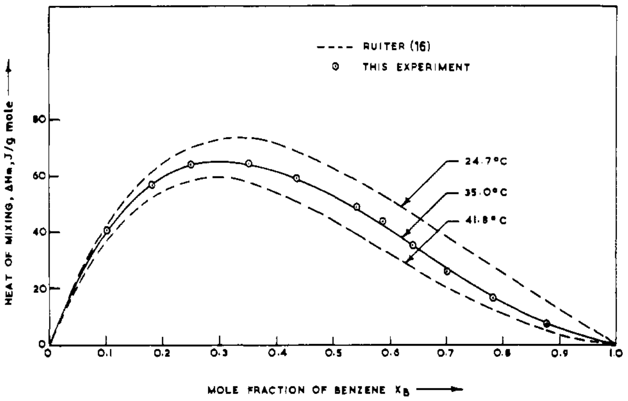

Figure 3. Heats of mixing at 35 °C for benzene-1,2-dichloroethane.

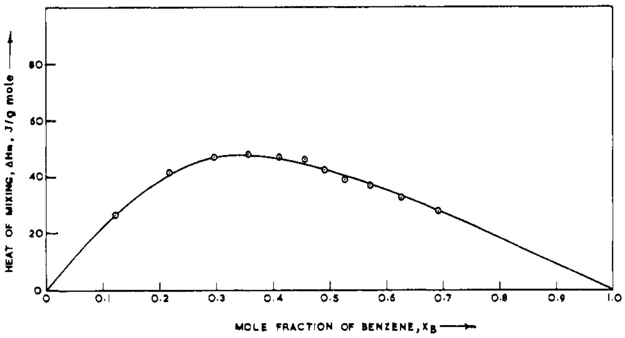

Figure 4. Heats of mixing at 35 °C for benzene-1,1,1-trichloroethane.

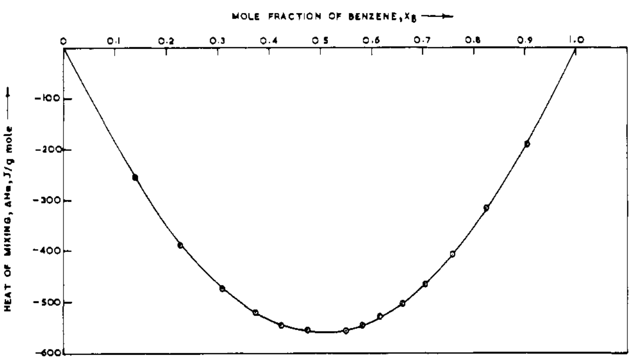

Figure 5. Heats of mixing at 35 °C for benzene-1,1,2,2-tetrachloroethane.

Consistency Checks

The rigorous equation for checking the thermodynamic consistency of isobaric vapor-liquid equilibrium data has been derived (*29*, *33*) and is

$$\int_0^1 \log\frac{\gamma_1}{\gamma_2}\,dx_1 + \int_0^1 -\frac{\Delta H_m}{2.3RT^2}\frac{dT}{dx_1}\,dx_1 = 0 \qquad (11)$$

where

$$\log \gamma_1/\gamma_2 = \log\left[(y_1P/x_1P_1^0)/(y_2P/x_2P_2^0)\right] + 0.4342[(B_{11} - V_1^L)(P - P_1^0) - (B_{22} - V_2^L)(P - P_2^0)]/RT + 0.4342[P\delta_{12}(y_2^2 - y_1^2)/RT] \qquad (12)$$

$$\log \gamma_1/\gamma_2 = A' - 0.4342B' - 0.4342C' + 0.4342D' \qquad (13)$$

Table VIII. Constants for Equation 10

system	A_0	A_1	A_2	A_3	% max deviation	% av abs deviation
benzene-1,2-dichloroethane	211.4	−220.8	72.5	−39.3	5.3	2.3
benzene-1,1,1-trichloroethane	170.4	138.3	47.3	−120.4	2.0	1.0
benzene-1,1,2,2-tetrachloroethane	−2256.2	−110.1	143.7	−49.0	−1.0	0.9

Table IX. Heats of Mixing Data at 35 °C for Benzene-Chloroethane Systems

system B-D		system B-TR		system B-TE	
x_B	ΔH_m, J/mol	x_B	ΔH_m, J/mol	x_B	ΔH_m, J/mol
0.100	41.4	0.123	26.7	0.132	−237.9
0.182	57.2	0.219	41.6	0.232	−384.9
0.250	64.1	0.296	47.2	0.312	−471.2
0.357	65.4	0.359	48.4	0.377	−518.8
0.437	59.4	0.412	47.5	0.431	−544.3
0.542	48.5	0.457	46.0	0.476	−555.8
0.587	43.9	0.490	42.6	0.548	−555.7
0.640	35.0	0.528	39.7	0.580	−584.4
0.703	26.6	0.573	36.9	0.617	−532.2
0.781	16.8	0.627	33.5	0.660	−507.7
0.877	7.9	0.691	28.5	0.708	−468.2
		0.771	22.4	0.765	−408.6
				0.829	−322.3
				0.906	−195.0

The vapor pressures $P_1°$ and $P_2°$ at various temperatures were calculated from eq 1 to 4. The liquid densities of benzene were obtained from Francis (*9*) and those of chloroethanes from Gallant (*10*). The second virial coefficients of benzene and 1,1,1-trichloroethane were taken from Dymond and Smith (*7*) and those of 1,2-dichloroethane from Bohmhammel and Mannchen (*1*). The principle of corresponding states was applied to calculate the second virial coefficients of 1,1,2,2-tetrachloroethane from the literature values of the second virial coefficients of 1,2-dichloroethane, 1,1,1-trichloroethane, and chloroethane (*7*). To calculate the cross coefficients a new three-term potential energy function (*20*) of the form

$$\phi(r) = \frac{a}{r^{18}} + \frac{b}{r^{12}} + \frac{c}{r^6} \tag{14}$$

was used. O'Connell and Prausnitz (*18*) and Hirschfelder (*12*) have suggested that more than two variable parameters are required for better representation of experimental second virial coefficients.

The three constants a, b, and c can be evaluated using the relations

$$\phi(\sigma) = 0$$

$$\phi(r_m) = -\epsilon$$

and

$$\partial\phi(r)/\partial r|_{r=r_m} = 0$$

where σ is the intermolecular distance at which the potential energy is zero, ϵ is the minimum value of potential energy function, and r_m is the intermolecular distance at which $\phi(r) = -\epsilon$. Further it is assumed that $r_m = K\sigma$ and it can be shown that for $K = 1.12$, the potential energy function ϕ degenerates to the Lennard-Jones form. Using the above conditions and for $K = 1.1$, the constants take the following values: $a/\epsilon\sigma^{18} = 2.1336$; $b/\epsilon\sigma^{12} = 0.7296$; $c/\epsilon\sigma^6 = -2.8632$.

The force constants obtained with the new potential energy function were benzene (590, 5.32), 1,2-dichloroethane (350, 7.221), 1,1,1-trichloroethane (500, 5.671) and 1,1,2,2-tetrachloroethane (550, 6.984) where the first value in parentheses is ϵ/k, K, and the second is σ, Å. To calculate the force constants for the mixture an arithmetic average of the pure components was used for σ and the geometric mean for ϵ.

Herington's (11, 21) Consistency Test. This test requires that D, given by

$$D = \frac{A1 - B1}{A1 + B1} \times 100$$

be less than J or at least $J + 10$, where J is given by

$$J = \frac{150\Theta}{T_{\min}}$$

The areas $A1$ and $B1$ were obtained using a planimeter from a plot of $\log \gamma_1/\gamma_2$ vs. x_1. Table X gives the values for $A1$, $B1$, D, and J which show that $(D - J) < 10$ for benzene with 1,2-dichloroethane and 1,1,1-trichloroethane while $D < J$ for benzene-1,1,2,2-tetrachloroethane.

Rigorous Test for Consistency. To evaluate rigorously the second integral (I_2) of eq 11, the heats of mixing were assumed independent of temperature and calculated values using eq 10 along with the constants given in Table VIII were used. The bubble point curve of the isobaric vapor-liquid equilibrium data of the three systems fitted the following equations:

$$T_{\text{B-D}} = 353.26 - 4.773x_1 + 2.05x_1^2 - 0.781x_1^3 \quad (0.007,\ 0.004) \tag{15}$$

$$T_{\text{B-TR}} = 349.98 - 6.883x_1 + 1.238x_1^2 - 0.373x_1^3 \quad (0.01,\ 0.003) \tag{16}$$

$$T_{\text{B-TE}} = 415.51 - 98.522x_1 + 14.791x_1^2 + 18.775x_1^3 \quad (-0.17,\ 0.06) \tag{17}$$

The first integral I_1 of eq 11 was evaluated from a plot of $\log \gamma_1/\gamma_2$ vs. x_1 using a planimeter. The second integral I_2 of eq 11 was calculated using Simpson's rule with 20 points. The values of I_1 and I_2 given in Table X show that the data are consistent. The values of I_2 are likely to be much smaller if the heats of mixing at the boiling points were used.

Heats of Vaporization

The experimental and calculated heats of vaporization have been reported earlier (*22*).

Glossary

A_1	area above the x axis from a plot of $\log \gamma_1/\gamma_2$ vs. x_1
B_1	area below the x axis from a plot of $\log \gamma_1/\gamma_2$ vs. x_1
B_{12}	cross coefficient, cm^3 mol^{-1}
B_{ii}	second virial coefficient, cm^3 mol^{-1}
E	voltage, V
I	current, A
M	molecular weight
$P°$	vapor pressure, mmHg
P	total pressure, mmHg
r	intermolecular distance, Å
t	temperature, °C
t'	time, s
T	absolute temperature, (t + 273.15) K
$T_{\min}$	smaller boiling point of the two components
V	volume, cm^3

Table X. Consistency Test

system	10^3A_1	10^3B_1	Θ, K	J	D	10^5I_1	10^5I_2	$10^5(I_1 + I_2)$
benzene-1,2-dichloroethane	6.89	6.535	3.2	1.37	2.64	35.5	−5.7	29.8
benzene-1,1,1-trichloroethane	7.62	7.235	5.8	2.52	2.53	38.5	−7.6	30.9
benzene-1,1,2,2-tetrachloroethane	55.02	40.44	65.6	28.13	15.2	1458	904	2363

V_L	liquid specific volume, cm^3 mol^{-1}
x	mole fraction in liquid phase
y	mole fraction in vapor phase
γ	activity coefficient
δ_{12}	$2B_{12} - B_1 - B_2$
ρ	liquid density, g cm^{-3}
ΔH_m	heats of mixing, J mol^{-1}
η	refractive index at 30 °C, using sodium D line
Θ	difference between the pure component boiling points
ϕ	intermolecular potential energy

Subscripts

1	component 1, benzene
2	component 2
B	benzene
D	1,2-dichloroethane
TR	1,1,1-trichloroethane
TE	1,1,2,2-tetrachoroethane
B-D	mixture of benzene–1,2-dichoroethane
B-TR	mixture of benzene–1,1,1-trichloroethane
B-TE	mixture of benzene–1,1,2,2-tetrachloroethane

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Corn Syrup Composition–Refractive Index–Dry Substance Relation: Development of a General Equation

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A general equation relating refractive index–dry substance–composition of corn syrups was developed from data published by the Corn Refiners Association. The composition information used was dextrose equivalents and saccharide distribution through DP7+. Using the equation, refractive index–dry substance tables for the reference syrups were computed which agreed well with the reference tables. The equation can be used to generate refractive index tables for new syrups or blends without extensive laboratory work.

Introduction

Wartman et al.[1] reported a study (sponsored by the Corn Refiners Association) of the relation between refractive index and dry substance for a variety of commercial corn syrups. The saccharide compositions and dextrose equivalents (DE) also were reported. Examination of the data suggested a functional relation between refractive index, dry substance, and composition.

Other investigators using previously reported syrup refractive index–dry substance tables have shown the effect of composition on the relation between refractive index and dry substance. Malinsky,[2] and Cakebread[3] expressed the dry substance determined by refractive index as a function of dextrose equivalent.

With the introduction of enzyme technology in the manufacture of corn syrup, a variety of syrup compositions have been produced, which differ from compositions obtained by simple acid hydrolysis of starch. Syrups of the same dextrose equivalent sometimes differ significantly in their saccharide composition. See, for example, the pairs of syrups 2 and 5, 3 and 6, and 9 and 10 in Wartman Table II.[1] It is apparent that the dextrose equivalent dependence of refractive index is not sufficient to explain all of the variation in the relationship with dry substance and that saccharide composition also must be

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