Excess Gibbs Free Energies for Binary Systems Isopropanol with Benzene, Cyclohexane, Methylcyclohexane

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Isothermal vapor-liquid equilibrium data were determined using a Jones still for the systems isopropanol-benzene at 50°, 60°, and 70°C, isopropanol-cyclohexane at 50° and 60°C, and isopropanol-methylcyclohexane at 50° and 60°C. The Kretschmer and Wiebe equation was used for the isopropanol-cyclohexane and isopropanol-methylcyclohexane systems. Equilibrium data for the isopropanol-benzene mixtures were analyzed by using an extension of the Kretschmer and Wiebe equation suggested by Nagata. Calculated results for the three systems are generally in good agreement with the experimental values. The experimental data for all systems were also correlated with the Wilson, Heil, and NRTL equations.

Vapor-liquid equilibrium data for the isopropanol-benzene systems have been reported by two investigations (*2*, *14*). We have studied the isopropanol-hydrocarbon systems in a long-range program to supply isothermal equilibrium data for highly nonideal hydrogen bonding solutions.

Experimental

Materials. Reagent grade cyclohexane and methylcyclohexane were used for experimental work without further purification. Chemically pure benzene was recrystallized several times. Isopropanol was distilled twice in a glass column packed with McMahon packings after storage over copper anhydride overnight. The physical constants of materials used are listed with the literature values in Table I.

Apparatus. Equilibrium data were obtained using a Jones vapor-recirculation still (*3*). Temperature measurements were made using a Yokogawa P-7B potentiometer and a copper-constantan thermocouple calibrated against a mercury thermometer certified by the National Research Laboratory of Metrology, Tokyo, with an accuracy of ±0.05°C. A mercury manometer and a cathetometer were used to read off the pressure in the still. The accuracy of pressure measurements was within ±0.1 mm Hg. Barometric pressure and room temperature were recorded for each experimental run and necessary corrections were made on the observed pressure values (*3*).

Analytical method. The refractive indices of vapor and liquid samples of mixture under investigation were observed by using a Shimadzu Pulfrich refractometer controlled at 25° ± 0.1°C and a sodium lamp, and the compositions of the samples were determined on a refractive index-composition chart prepared previously for mixtures of known composition.

Data Reduction

The equilibrium equation of a component *i* in the vapor and liquid phases is

$$\psi_i y_i P = \gamma_i x_i P_i^s \psi_i^s \exp\left[-V_i^L(P - P_i^s)/RT\right] \qquad (1)$$

The vapor phase fugacity coefficients were obtained from the virial equation, truncated after the second term:

$$\ln \psi_i = \frac{2}{V^V}\sum_j^N y_j B_{ij} - \ln Z \qquad (2)$$

where the compressibility factor, *Z*, and the molar volume of vapor mixture, V^V, are related by

$$Z = PV^V/RT = 1 + \sum_i^N\sum_j^N y_i y_j B_{ij}/V^V \qquad (3)$$

Second virial coefficients for pure components and cross coefficients were calculated with the O'Connell and Prausnitz correlation developed from the Curl and Pitzer method (*8*). The pure vapor pressure data were obtained using the Antoine equation (*1*). Liquid molar volumes available at three temperatures were fitted to a quadratic equation and the resultant equation was used to extrapolate the liquid volume to a specified temperature (*10*).

The excess Gibbs free energy was calculated from the activity coefficients

$$G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \qquad (4)$$

The association theory derived by Kretschmer and Wiebe (*5*) has been successfully applied to several alcohol-saturated hydrocarbon mixtures by Renon and Prausnitz (*12*). Recently Nagata extended the original theory of the Kretschmer and Wiebe equation to cover alcohol-unsaturated hydrocarbon systems (*7*).

According to the association model theory, the excess Gibbs free energy, activity coefficients, and heats of mixing are expressed by:

$$\begin{aligned} G^E = RT\{&x_A \ln(\phi_1/\phi_1^o x_A) + x_B \ln(\phi_{OB}/x_B) - \\ &[(x_A V_A + x_B V_B)/V] + x_B + (x_A V_A/V^o)\} + \\ &\beta\phi_A\phi_B(x_A V_A + x_B V_B) \end{aligned} \qquad (5)$$

$$\ln \gamma_A = \ln(\phi_1/\phi_1^o x_A) - (V_A/V) + (V_A/V^o) + (\beta/RT)V_A\phi_B^2 \qquad (6)$$

Table I. Physical Constants of Compounds

Compound	Bp,°C	Density, 25°C	Refractive index n_D^{25}
Benzene	80.1	0.8735	1.4979
	80.1 (*13*)	0.87364 (*13*)	1.49792 (*13*)
Cyclohexane	80.8	0.7739	1.4237
	80.72 (*13*)	0.7737 (*13*)	1.42354 (*15*)
Methyl-	100.9	0.7653	1.4208
cyclohexane	100.934 (*15*)	0.7651 (*15*)	1.42058 (*15*)
Isopropanol	82.3	0.7808	1.3748
	82.4 (*15*)	0.78083 (*15*)	1.3747 (*15*)

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$$\ln \gamma_B = \ln(\phi_{OB}/x_B) + 1 - (V_B/V) + (\beta/RT)V_B\phi_A^2 \quad (7)$$

$$H^E = h_A K_A x_A(\phi_1 - \phi_1^{\circ}) + h_{AB}(x_A/\rho)\{K_{AB}\phi_{OB}(1 - K_A\phi_1)/[1 + K_{AB}(\phi_{OB}/\rho)]\} + \beta'\phi_A\phi_B(x_AV_A + x_BV_B) \quad (8)$$

$$\beta' = \beta - T(d\beta/dT) \quad (9)$$

where the subscripts *A* and *B*, respectively, represent alcohol and unsaturated hydrocarbon; ρ is the ratio of V_B to V_A. The overall volume fractions, ϕ_A, and ϕ_B, and the molar volume of a liquid mixture, *V*, are given as follows:

$$\phi_A = [\phi_1/(1 - K_A\phi_1)^2][(1 + K_{AB}(\phi_{OB}/\rho)] \quad (10)$$

$$\phi_B = \phi_{OB}[1 - (K_A - K_{AB})\phi_1]/(1 - K_A\phi_1) \quad (11)$$

$$1/V = [1/V_A(1 - K_A\phi_1)] + (\phi_{OB}/V_B)[1 - (K_A - K_{AB})\phi_1]/(1 - K_A\phi_1) \quad (12)$$

For pure alcohol

$$1/V^{\circ} = (1 - K_A\phi_1^{\circ})/V_A \quad (13)$$

ϕ_1° is the volume fraction of alcohol monomer in pure alcohol and may be obtained by:

$$\phi_1^{\circ} = [(2K_A + 1) - (1 + 4K_A)^{1/2}]/2K_A^2 \quad (14)$$

If ϕ_A, ϕ_B, and the equilibrium constants, K_A and K_{AB}, are given, ϕ_1°, ϕ_1, ϕ_{OB}, V°, and *V* may be calculated in the prescribed equations.

The temperature dependence of *K* is given by the van't Hoff relationship:

$$[d \ln K/d(1/T)] = -(h/R) \quad (15)$$

where *h* is the molar enthalpy of formation of a hydrogen bond. Renon and Prausnitz (*12*) set the value of K_A for isopropanol to be 60 at 50°C, and h_A is to be −6 kcal/mol. In this investigation K_{AB} was chosen to be 6.5 at 25°C, and h_{AB} to be −2200 cal/mol. Least-square fitting programs were used to obtain β and β'. The values of β and β', respectively, were obtained by fitting experimental G^E with Equation 5 and experimental H^E with Equation 8.

The Wilson, Heil, and NRTL equations (*4*, *10*, *11*), derived from the concept of local composition, are given by

$$\ln \gamma_1 = q[x_2G_{21}/(x_1 + x_2G_{21}) - x_2G_{12}/(x_2 + x_1G_{12}) - \ln(x_1 + x_2G_{21})] + px_2^2[\tau_{21}G_{21}^2/(x_1 + x_2G_{21})^2 + \tau_{12}G_{12}/(x_2 + x_1G_{12})^2] \quad (16)$$

$$\ln \gamma_2 = q[x_1G_{12}/(x_2 + x_1G_{12}) - x_1G_{21}/(x_1 + x_2G_{21}) - \ln(x_2 + x_1G_{12})] + px_1^2[\tau_{12}G_{12}^2/(x_2 + x_1G_{12})^2 + \tau_{21}G_{21}/(x_1 + x_2G_{21})^2] \quad (17)$$

where $G_{12} = \rho_{12} \exp(-\alpha_{12}\tau_{12})$, $G_{21} = \rho_{21} \exp(-\alpha_{12} \cdot \tau_{21})$, $\tau_{12} = (g_{12} - g_{22})/RT$, $\tau_{21} = (g_{21} - g_{11})/RT$. *p*, *q*, ρ_{12}, and α_{12} are defined for each equation as follows:

Equation	ρ	q	ρ_{12}[a]	α_{12}
Wilson	0	1	V_1/V_2	1
Heil	1	1	V_1/V_2	1
NRTL	1	0	1	α_{12}

[a] $\rho_{12} = 1/\rho_{21}$

The nonrandomness constant of the NRTL equation, α_{12}, was taken to be 0.47 for the present systems. The parameters, $(g_{21} - g_{11})$ and $(g_{12} - g_{22})$, are determined using a nonlinear regression method which minimizes the sum of the squared deviations in vapor phase mole fraction plus the sum of the squared relative deviations in pressure.

Results

Isothermal vapor-liquid equilibrium data for the isopropanol-benzene system have been published by Brown et al. (*2*) at 45°C and by Udovenko and Mazanko (*14*) at 30°, 45°, and 60°C. We present here equilibrium data for the same system at 50°, 60°, and 70°C. There is no isothermal equilibrium data for mixtures of isopropanol with cyclohexane and methylcyclohexane. We obtained equilibrium data for these systems at 50° and 60°C. Table II shows experimental data for three binary systems. Conventional thermodynamic consistency test was applied to the present systems. It is the well-known area test that a thermodynamically consistent isothermal binary data should satisfy the following equation.

$$\int_0^1 \ln(\gamma_1/\gamma_2)dx_1 = 0 \quad (18)$$

However, some experimental error is inevitably involved in observed data. Practically it may be acceptable that a given set of data are consistent (*9*) if

$$0.02 > D = |(\text{Area above } x\text{-axis} - \text{Area below } x\text{-axis})/(\text{Area above } x\text{-axis} + \text{Area below } x\text{-axis})| \quad (19)$$

The test shows that 0.02 > *D* for the present systems:

System	*D*
Isopropanol-benzene	0.005(50°C) 0.003(60°C) 0.003(70°C)
Isopropanol-cyclohexane	0.003(50°C) 0.003(60°C)
Isopropanol-methylcyclohexane	0.005(50°C) 0.003(60°C)

The magnitude of deviations between calculated and experimental results is a direct indication of the quality of experimental data taken from different data source. Table III indicates the physical constants used for calculations and the deviations of calculated from observed values for three systems obtained by using the association model theory. The experimental data of Udovenko and Mazanko for the isopropanol-benzene system at 30°C are not good, especially in the lower concentration region of isopropanol. Their data at 45°C are less accurate than those of Brown et al. Their data at 60°C are also less accurate than the present data. Both *x*-*y* data are compared in Figure 1.

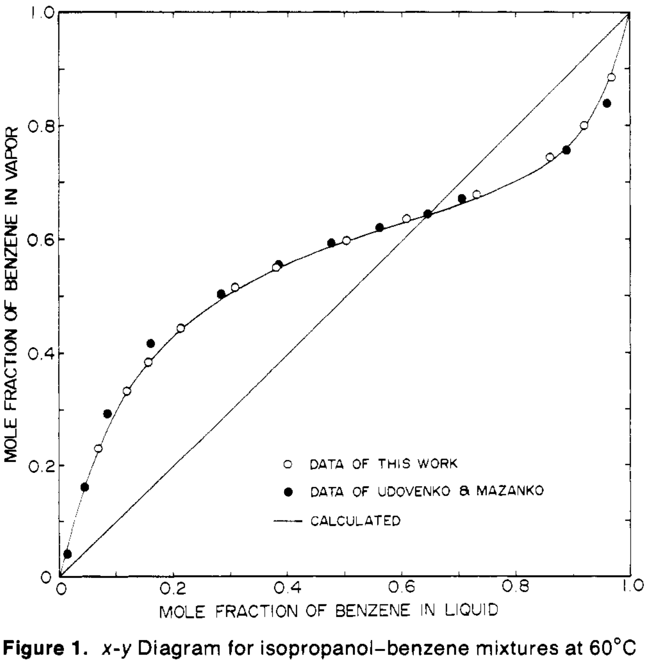

Figure 1. *x*-*y* Diagram for isopropanol-benzene mixtures at 60°C

Table II. Experimental Isothermal Vapor-Liquid Equilibrium Data for Binary Systems

x_1	y_1	P, mm Hg	γ_1	γ_2	ψ_1	ψ_2	g^E, cal/mol
Isopropanol (1)-Benzene (2) at 50°C							
0.920	0.700	239.3	1.003	3.349	0.985	0.989	64.16
0.861	0.595	263.8	1.004	2.862	0.983	0.986	95.83
0.819	0.544	280.8	1.026	2.631	0.983	0.985	125.88
0.693	0.447	313.1	1.109	2.092	0.982	0.982	191.68
0.634	0.418	321.2	1.163	1.893	0.981	0.982	211.46
0.540	0.382	328.5	1.276	1.634	0.981	0.981	229.68
0.394	0.336	333.9	1.564	1.354	0.982	0.981	231.12
0.341	0.325	334.9	1.753	1.269	0.982	0.981	223.92
0.283	0.305	336.1	1.990	1.205	0.982	0.981	211.08
0.253	0.291	334.2	2.112	1.174	0.982	0.981	198.33
0.193	0.271	332.1	2.563	1.110	0.982	0.981	170.81
0.136	0.239	327.5	3.166	1.068	0.983	0.981	136.93
0.102	0.215	321.6	3.731	1.041	0.984	0.981	109.29
0.038	0.127	300.6	5.543	1.011	0.986	0.982	48.56
0.022	0.085	291.5	6.220	1.011	0.987	0.982	32.88
Isopropanol (1)-Benzene (2) at 60°C							
0.932	0.769	359.7	1.006	3.163	0.980	0.985	55.31
0.881	0.668	390.8	1.003	2.814	0.978	0.982	83.03
0.845	0.617	416.4	1.027	2.651	0.977	0.981	115.21
0.788	0.557	441.2	1.053	2.371	0.976	0.979	148.01
0.693	0.486	464.7	1.099	1.997	0.976	0.977	184.03
0.621	0.451	477.3	1.169	1.773	0.975	0.976	207.83
0.498	0.403	490.8	1.339	1.495	0.975	0.975	229.86
0.391	0.365	493.9	1.555	1.318	0.976	0.975	225.65
0.353	0.352	495.4	1.666	1.270	0.976	0.975	221.61
0.269	0.323	494.9	2.005	1.173	0.976	0.974	201.01
0.143	0.258	482.6	2.943	1.069	0.978	0.975	140.26
0.081	0.201	458.3	3.852	1.021	0.980	0.976	84.96
0.034	0.117	426.1	4.981	1.000	0.982	0.977	35.93

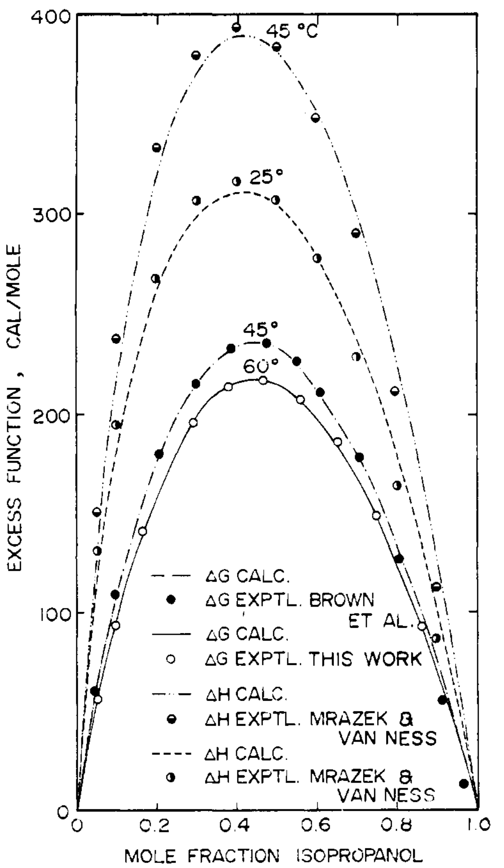

Figure 2. Excess functions for isopropanol–benzene mixtures

Figure 2 shows good agreement between the experimental data and the results calculated with the association model theory for the isopropanol-benzene system. The degree of fitting the present experimental data with the association model theory is comparable to that obtained by Renon and Prausnitz (*12*) for 11 alcohol-saturated hydrocarbon systems. Table IV shows the numerical values of the parameters of three local-composition equations and the deviations of calculated values from experimental data. Again this table demonstrates that the data of Udovenko and Mazanko for the isopropanol-benzene systems are less accurate than those of Brown et al. and the present investigation. The magnitudes of deviations are the same as those obtained by Renon and Prausnitz (*11*) for nine alcohol-hydrocarbon systems as a comparative study concerning the ability of the Wilson, Heil, and NRTL equations.

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Nomenclature

B_{ij} = second virial coefficient, ml/mol
D = area test constant
G^E = excess Gibbs free energy, cal/mol
G_{ij} = coefficient as defined by $G_{ij} = \rho_{ij} \exp(-\alpha_{ij}\tau_{ij})$
g_{ij} = energies of interaction between an i-j pair of molecules, cal/mol
H^E = excess enthalpy of mixing, cal/mol
h = enthalpy of formation of a hydrogen bond, cal/mol

Table II. *Continued*

x_1	y_1	P, mm Hg	γ_1	γ_2	ϕ_1	ϕ_2	g^E, cal/mol
			Isopropanol (1)-Benzene (2) at 70°C				
0.860	0.678	596.1	1.009	2.509	0.971	0.976	92.97
0.751	0.565	652.5	1.052	2.077	0.969	0.972	149.90
0.647	0.500	682.3	1.129	1.757	0.969	0.970	189.06
0.559	0.456	696.1	1.215	1.559	0.968	0.968	207.90
0.465	0.417	704.1	1.351	1.392	0.969	0.968	216.21
0.382	0.386	707.1	1.530	1.274	0.969	0.967	212.83
0.291	0.350	705.1	1.817	1.172	0.970	0.967	195.27
0.164	0.283	685.5	2.539	1.067	0.971	0.968	140.97
0.095	0.222	655.9	3.298	1.024	0.974	0.969	92.06
0.053	0.149	619.8	3.761	1.013	0.976	0.970	56.43
			Isopropanol (1)-Cyclohexane (2) at 50°C				
0.911	0.626	263.9	0.998	4.123	0.984	0.985	79.88
0.874	0.567	282.7	1.009	3.606	0.983	0.983	108.56
0.733	0.443	337.5	1.119	2.601	0.980	0.978	216.76
0.549	0.375	357.1	1.337	1.824	0.980	0.977	276.63
0.366	0.344	364.6	1.879	1.390	0.980	0.976	282.19
0.252	0.315	363.3	2.491	1.225	0.980	0.976	245.34
0.167	0.286	361.7	3.399	1.142	0.981	0.976	202.18
0.071	0.238	347.6	6.404	1.051	0.982	0.977	114.30
0.054	0.219	342.6	7.641	1.043	0.983	0.977	96.01
			Isopropanol (1)-Cyclohexane (2) at 60°C				
0.874	0.602	431.5	1.004	3.526	0.977	0.977	107.24
0.815	0.533	462.8	1.021	3.014	0.976	0.974	146.24
0.754	0.490	491.7	1.076	2.624	0.974	0.972	193.86
0.700	0.464	507.9	1.133	2.336	0.974	0.971	226.02
0.569	0.417	532.0	1.312	1.846	0.973	0.969	277.10
0.381	0.366	541.8	1.751	1.422	0.974	0.968	285.59
0.279	0.346	539.9	2.254	1.255	0.974	0.968	258.43
0.149	0.305	528.9	3.649	1.107	0.975	0.968	185.04
0.101	0.279	512.6	4.779	1.055	0.976	0.969	136.30
0.040	0.199	473.5	7.976	1.016	0.979	0.971	64.99
			Isopropanol (1)-Methylcyclohexane (2) at 50°C				
0.043	0.319	197.8	8.132	1.019	0.990	0.982	69.15
0.105	0.425	221.1	4.948	1.026	0.988	0.980	122.63
0.216	0.469	239.0	2.865	1.168	0.986	0.979	224.05
0.317	0.497	240.0	2.077	1.275	0.986	0.979	255.39
0.432	0.521	247.0	1.643	1.502	0.986	0.979	286.16
0.541	0.545	247.6	1.376	1.770	0.985	0.979	279.11
0.615	0.567	247.8	1.260	2.010	0.985	0.979	263.83
0.680	0.588	247.9	1.182	2.303	0.985	0.979	244.34
0.783	0.633	241.3	1.076	2.948	0.985	0.980	187.27
0.879	0.716	222.6	1.001	3.783	0.986	0.983	103.72
0.937	0.789	211.3	0.982	5.133	0.986	0.984	55.46
			Isopropanol (1)-Methylcyclohexane (2) at 60°C				
0.042	0.342	305.5	8.486	1.032	0.986	0.975	79.60
0.104	0.437	336.8	4.815	1.039	0.984	0.973	130.86
0.225	0.494	357.0	2.662	1.143	0.982	0.972	214.36
0.363	0.530	376.5	1.864	1.360	0.981	0.971	279.47
0.495	0.561	380.1	1.460	1.618	0.980	0.971	284.98
0.548	0.576	381.0	1.357	1.750	0.980	0.971	278.35
0.576	0.583	383.1	1.314	1.845	0.980	0.971	276.06
0.651	0.602	379.7	1.190	2.122	0.980	0.972	248.70
0.766	0.656	376.9	1.094	2.717	0.980	0.973	200.19
0.865	0.719	360.4	1.015	3.686	0.980	0.975	125.40
0.936	0.820	336.3	1.000	4.665	0.981	0.978	65.05
0.962	0.880	320.0	0.994	4.994	0.982	0.980	36.68

K = association constant
P = total pressure, atm
P_i^s = vapor pressure of pure component i at system temperature, atm
p = coefficient (0 or 1) of Equations 16 and 17
q = coefficient (0 or 1) of Equations 16 and 17
R = gas constant, 1.987 cal/mol K
T = absolute temperature, K
V = molar volume, cc/mol
x_i = liquid phase mole fraction of component i
y_i = vapor phase mole fraction of component i
Z = compressibility factor

Greek Letters

α_{12} = nonrandomness constant for binary 1-2 interaction
β,β' = physical interaction parameters, cal/cc
ρ = ratio of molar volume defined as $\rho = V_B/V_A$

Table III. Calculated Results Using Association Model Theory

System	Temp, °C	K_A	K_{AB}	β, cal/cc	Absolute arithmetic dev		Temp, °C	Abs arithmetic dev heats of mixing, cal/mol	K_A	K_{AB}	β', cal/cc	Ref.	
					Vapor mole fraction × 100	Pressure, mm Hg						Vapor-liquid equilibria	Heats of mixing
Isopropanol (1)–benzene (2)	45	69.49	5.15	4.78	0.95	1.1	25	9.1	131.34	6.50	3.02	(*2*)	(*6*)
	30	111.14	6.11	4.56	2.69	2.6	35	11.6	94.56	5.76	4.13	(*14*)	(*6*)
	45	69.49	5.15	4.68	1.72	2.9	45	12.2	69.49	5.15	5.01	(*14*)	(*6*)
	60	45.33	4.40	4.67	1.72	4.5						(*14*)	
	50	60.00	4.88	4.90	0.78	1.4						This work	
	60	45.33	4.40	4.86	0.94	2.8						This work	
	70	34.81	3.99	4.33	1.36	3.2						This work	
Isopropanol (1)–cyclohexane (2)	50	60.00	0.00	2.35	0.86	2.1						This work	
	60	45.33	0.00	2.15	0.77	3.5						This work	
Isopropanol (1)–methylcyclohexane (2)	50	50.00	0.00	1.48	1.40	2.9						This work	
	60	45.33	0.00	1.52	1.02	3.0						This work	

Table IV. Parameters of Wilson, Heil, and NRTL Equations and Root-Mean-Square Deviations for Binary Systems

System	Temp, °C	No. of data points	Parameters, cal/mol				Rel dev in press. × 10³			Dev in vapor mol fraction × 10³			Abs dev in press., mm Hg			Ref.
			Wilson	Heil	NRTL											
			$(g_{12}-g_{22})$ $(g_{21}-g_{11})$	$(g_{12}-g_{22})$ $(g_{21}-g_{11})$	$(g_{12}-g_{22})$ $(g_{21}-g_{11})$	α_{12}	Wilson	Heil	NRTL	Wilson	Heil	NRTL	Wilson	Heil	NRTL	
Isopropanol (1)–benzene (2)	45	12	215 1205	49 590	350 1001	0.47	5	7	6	7	10	8	1	2	1	(*2*)
	30	12	160 1546	−5 805	300 1300	0.47	31	31	30	39	39	39	2	3	2	(*14*)
	45	14	226 1255	48 623	358 1061	0.47	9	12	10	15	16	15	2	3	2	(*14*)
	60	12	175 1225	38 588	300 1040	0.47	15	15	15	17	18	18	6	6	6	(*14*)
	50	15	280 1060	102 501	400 900	0.47	6	9	7	8	12	10	2	3	2	This work
	60	13	250 1030	121 449	403 822	0.47	5	10	6	5	11	7	2	5	3	This work
	70	10	210 950	30 520	313 828	0.47	4	4	4	5	5	5	3	3	3	This work
Isopropanol (1)–cyclohexane (2)	50	9	301 1580	39 777	553 1250	0.47	11	15	11	8	15	11	4	5	4	This work
	60	10	240 1580	60 700	513 1231	0.47	5	15	5	7	13	10	2	7	3	This work
Isopropanol (1)–methylcyclohexane (2)	50	11	155 1721	−43 828	570 1170	0.47	12	19	14	12	18	12	3	4	3	This work
	60	12	110 1810	−45 837	500 1300	0.47	15	26	20	13	18	15	5	9	7	This work

ρ_{ij} = coefficient as defined by $G_{ij} = \rho_{ij} \exp (-\alpha_{ij} \tau_{ij})$
τ_{ij} = coefficient as defined by $\tau_{ij} = (g_{ij} - g_{jj})/RT$
ϕ_1 = volume fraction of alcohol monomer
ϕ_{OB} = volume fraction of hydrocarbon at free state
ϕ = volume fraction
ψ_i = vapor phase fugacity coefficient of component *i*
ψ_i^s = vapor phase fugacity coefficient of pure component *i* at system temperature and P_i^s

Subscripts

A = alcohol
AB = alcohol-hydrocarbon complex formation
B = hydrocarbon
i = component

Superscripts

o = properties of a pure substance in its particular reference state
E = excess property
L = liquid
V = vapor

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Liquid-Phase Diffusion Coefficients for Dissolved Gases: Systems Chlorine–Carbon Tetrachloride and Hydrogen Chloride–Ethylene Glycol

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A steady-state diaphragm cell method has been used to measure the liquid-phase diffusion coefficients of chlorine in carbon tetrachloride and hydrogen chloride in ethylene glycol. In the chlorine–carbon tetrachloride system, it is shown that the Wilke-Chang equation correlates the experimental values very closely.

Experimental data on the liquid-phase diffusion coefficients of dissolved gases are sparse, especially for systems in which the gas solubility is high. The theoretical interpretation of gas absorption rates in such cases has therefore often had to rely on diffusivity values predicted by one of the many correlations available in the literature. This paper reports measured values for two such high-solubility systems which have not been previously investigated.

Experimental

The technique employed is a steady-state diaphragm cell method first described by Tham et al. *(4)*. In brief, the apparatus consists of two chambers, each of volume 500 cm^3, separated by a vertical sintered-glass diaphragm of 9-cm diam and mean pore size 5 μ. In one chamber, the liquid solvent is kept saturated by a continuous stream of solute gas, while diffused solute is continually stripped from solvent in the other chamber by a stream of nitrogen. When steady state is attained, a direct measure of the diffusion rate is obtained by determining the total amount of solute gas in the nitrogen stream in a known time. Hydrogen chloride and chlorine are absorbed in $N/10$ sodium hydroxide and 10 wt % potassium iodide solutions, respectively. Subsequent titrations are reproducible to ±0.05 ml. The diffusion coefficient may then be calculated by applying a cell constant found from experiments using $N/10$ potassium chloride solution, a substance whose diffusion coefficient is well established *(2)*. The diffusion cell is completely immersed in a water bath which is thermostatically controlled to ±0.05°C. Measurements were taken at 5°C intervals in the range 25–45°C.

Flow rates of approximately 30 ml/min of presaturated gas ensure that good liquid mixing is obtained in the cell compartments, effectively eliminating the possibility of density-induced streaming through the vertical diaphragm. Careful balancing of the pressure drop in the gas exit lines ensures that pumping effects are also negligible. This technique, which has been shown to produce results equivalent to those from the usual diaphragm cell *(4)*, has several advantages. It does not require handling of liquids containing dissolved gas, and an experiment may be completed in about 2 hr. Also, since measurement is not made until steady state is reached, adsorp-

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